## Mesoscale modeling of magnetic elastomers and gels – theory and simulations

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## Abstract

Magnetic elastomers and gels are a class of smart materials that are manufactured by embedding magnetic colloidal particles into a cross-linked polymer matrix. The composite becomes magneto-responsive, allowing its elastic properties to be noninvasively and reversibly controlled by applying external magnetic fields. For instance, the magneto-rheological effect allows to dynamically tune the elastic response of the material to mechanical forces, enabling applications as dampers or vibration absorbers. As another example, large-scale shape changes that can be triggered by applying magnetic fields qualify magnetic elastomers as magneto-mechanical actuators.

The theoretical description of these materials is challenging, because of the different length scales that have to be addressed. To be able to engineer the magnetic elastomers for practical purposes, one is typically interested in their bulk properties. However, the macroscopically observed magneto-elastic effects are largely influenced by the structure of the composite on the mesoscopic length scale. Therefore, a groundwork for accurate macroscopic material models has to be laid by concentrating on the mesoscale first. This cumulative Ph.D. thesis is a contribution to this effort and concentrates on three main topics.

The first topic of this thesis concerns how the mesoscopic structure influences the responsiveness of the composite to magnetic fields. One important structural aspect is the particle distribution within the composite. It can be controlled to some degree during the chemical cross-linking process that permanently embeds the particles into the polymer matrix. Applying a magnetic field before and during the synthesis, when the particles are still relatively mobile, incentivizes the formation of parallel chain-like particle aggregates. A magnetic elastomer with a uniaxial anisotropy arises as the cross-linking reaction locks these structures permanently into the emerging polymer matrix. Another structural aspect is the magneto-elastic coupling between particles and matrix. If the surrounding polymer chains are covalently connected to the surfaces of the magnetic particles, the latter can transfer magnetic torques to the elastic environment. A relatively loose connection on the contrary allows the particles to rotate freely without deforming the elastic matrix in the long term.

Three different studies are performed on this first topic. Using a minimal dipolespring representation for a magnetic elastomer, it is tested for which particle distributions coarse-grained material descriptions that are restricted to affine sample deformations are a feasible approach. It is demonstrated that the assumption of affine deformations is still valid for particle arrangements on slightly distorted regular lattices, but leads to qualitatively erroneous results for realistic particle distributions. Additionally, the tunability of the elastic behavior depends on the type of assumed structure for affine as well as non-affine deformations. Second, it is investigated how the dynamical relaxation behavior of a magnetic elastomer depends on the particle distribution and the magneto-elastic coupling. Here it is also shown that the appearance of the dominant relaxation modes as well as the corresponding relaxation rates can be controlled by external magnetic fields. Third, the experimentally observed buckling behavior of a chain of superparamagnetic particles embedded in a soft gel when a homogeneous magnetic field is applied perpendicular to the chain axis is modeled. Within a phenomenological model, it is identified how the chain length, the elastic modulus of the polymer matrix, and the strength of the applied field influence the morphology of the buckling behavior.

The second topic of this thesis is the non-linear stress-strain behavior of magnetic elastomers. It represents the main focus area of this thesis as it concerns the majority of the research conducted. Here, using particle-resolved numerical simulations, it is revealed that anisotropic magnetic elastomers featuring chain-like aggregates can display a superelastic stress-strain behavior under uniaxial tensile load. Superelasticity is a fascinating phenomenon that is known from shape-memory alloys and some other smart materials. It appears in the form of a plateau-like regime in the stressstrain curve, where the sample can be reversibly further elongated, basically without increasing the load. In magnetic elastomers, as an additional benefit, the superelastic stress-strain behavior can be reversibly tailored on-demand by applying external magnetic fields. How the superelastic plateau reacts to these stimuli depends on the type of magneto-elastic coupling between polymer matrix and magnetic particles. In any case, a strong enough magnetic field applied perpendicular to the chain-like aggregates can switch the superelastic stress-strain behavior off. Since the mesoscopic mechanisms generating this fascinating behavior are also identified, it can properly be accounted for in future models for the macroscale.

The final topic of this thesis is the description of magnetic elastomers using density functional theory and other statistical methods. Density functional theory is a well established statistical mechanical approach for ensembles of indistinguishable particles. It cannot be applied directly to magnetic elastomers though, because the embedded magnetic particles can be clearly labeled according to their position within the polymer matrix. The elastic interactions in the systems depend on these reference positions and therefore render the particles distinguishable. However, it is shown that they can reasonably be mapped to effective pairwise interactions that treat the particles as indistinguishable. In this way, a density functional description for these materials is enabled. The obtained results are also benchmarked with Monte-Carlo simulations and good agreement can be found. As a further contribution to this topic, a detailed statistical characterization of structural data obtained from X-ray tomography measurements on real experimental samples is performed. In the future, such experimentally realistic particle distribution functions could provide a valuable input to statistical theories.

# Zusammenfassung

Magnetische Elastomere und Gele sind eine Klasse von intelligenten Werkstoffen, die durch die Einbettung magnetischer kolloidaler Teilchen in eine quervernetzte Polymermatrix hergestellt werden. Der Verbundwerkstoff ist magnetisch beeinflussbar, so dass seine elastischen Eigenschaften durch Anwendung eines magnetischen Feldes nicht-invasiv und reversibel kontrolliert werden können. Beispielsweise erlaubt es der magnetorheologische Effekt, die elastische Reaktion des Materials auf Deformationen dynamisch zu justieren, was Anwendungen als schaltbare Schwingungsdämpfer und -absorber ermöglicht. Ein weiteres Beispiel sind starke Formänderungen, die durch das Anlegen magnetischer Felder ausgelöst werden können und magnetische Elastomere für den Einsatz als magnetomechanische Aktoren qualifizieren.

Die theoretische Beschreibung dieser Materialien stellt aufgrund der unterschiedlichen Längenskalen, die berücksichtigt werden müssen, eine Herausforderung dar. Für die Entwicklung von magnetichen Elastomeren hin zu praktischen Anwendungen beschäftigt man sich typischerweise mit den Bulk-Materialeigenschaften. Allerdings werden die makroskopisch zu beobachtenden magnetoelastischen Effekte zum großen Teil durch die Struktur des Werkstoffs auf der mesoskopischen Längenskala beeinflusst. Als Grundlage für ein akkurates makroskopisches Materialmodell muss daher zunächst ein Fokus auf die Mesoskala gelegt werden. Diese kumulative Dissertation ist ein Beitrag hierzu und befasst sich hauptsächlich mit den folgenden drei Themen.

Als erstes Thema beschäftigt sich diese Arbeit damit, wie die mesoskopische Struktur die Reaktion des Werkstoffs auf das Anlegen eines magnetischen Feldes beeinflusst. Ein wichtiger struktureller Aspekt ist die Teilchenverteilung innerhalb des Werkstoffs. Diese kann zu einem gewissen Grad während des chemischen Quervernetzungsprozesses, der die Teilchen permanent in die Polymermatrix einbettet, kontrolliert werden. Durch Anlegen eines magnetischen Feldes vor und während der Synthese, wenn die Teilchen noch in relativ mobil sind, wird die Bildung von parallelen, kettenartigen Aggregaten aus Teilchen angeregt. Ein magnetisches Elastomer mit uniaxialer Anisotropie entsteht, wenn die quervernetzende Reaktion diese Strukturen permanent in der entstehenden Polymermatrix fixiert. Ein weiterer struktureller Aspekt ist die magnetoelastische Kopplung zwischen Teilchen und Matrix. Wenn die Polymerketten mit den Oberflächen der magnetischen Teilchen kovalent verbunden sind, können sie magnetische Drehmomente auf die sie umgebende elastische Matrix übertragen. Im Gegensatz dazu erlaubt eine relativ lose Verbindung den Partikeln auf langen Zeitskalen eine freie Rotation ohne Verformung der umgebenden Matrix.

Zu diesem ersten Thema werden drei verschiedene Studien durchgeführt. Zuerst wird

mithilfe einer minimalistischen Dipol-Feder Darstellung eines magnetisches Elastomers getestet, für welche Teilchenverteilungen vergröberte Materialbeschreibungen, die auf affine Probendeformationen beschränkt sind, ein sinnvoller Ansatz sind. Es wird gezeigt, dass die Annahme von affinen Deformationen auch noch für Partikelanordnungen auf leicht gestörten regelmäßigen Gittern berechtigt ist, aber zu qualitativ fehlerhaften Ergebnissen für realistische Teilchenverteilungen führt. Zusätzlich ist die Anpassbarkeit des elastischen Verhaltens abhängig vom Typ der zugrunde liegenden Struktur, sowohl für affine als auch für nicht-affine Deformationen. Als zweites wird untersucht, wie das dynamische Ralaxationsverhalten eines magnetischen Elastomers von der Teilchenverteilung und der magnetoelastischen Kopplung abhängt. Hierbei zeigt sich auch, dass sowohl das Auftreten der dominanten Relaxationsmoden als auch die zugehörige Relaxationsrate durch externe magnetische Felder kontrolliert werden kann. Als drittes wird das experimentell beobachtete wellenförmige Deformationsverhalten einer Kette von superparamagnetischen Teilchen, eingebettet in einem weichen Gel, bei Anlegen eines homogenen magnetischen Feldes senkrecht zur Kettenachse modelliert. Innerhalb eines phänomenologischen Modells wird identifiziert, wie die Kettenlänge, der elastische Modul der Polymermatrix und die Stärke des angelegten Feldes die Morphologie der wellenartigen Deformationen beeinflussen.

Das zweite Thema dieser Dissertation ist das nicht-lineare Zugdehnungsverhalten von magnetischen Elastomeren. Dabei handelt es sich um das Hauptthema dieser Arbeit, das den Großteil der durchgeführten Forschung beinhaltet. Hier wird unter Anwendung teilchenaufgelöster numerischer Simulationen gezeigt, dass anisotrope magnetische Elastomere, die kettenähnliche Aggregate aufweisen, ein superelastisches Zugdehnungsverhalten unter uniaxialer Zugbeanspruchung zeigen. Superelastizität ist ein faszinierendes Phänomen, das von Formgedächtnislegierungen und anderen intelligenten Werkstoffen bekannt ist. In der Zugdehnungskurve tritt es in Form eines plateauartiges Regimes auf, in dem die Probe reversibel weiter gestreckt werden kann, praktisch ohne die Last zu erhöhen. Das Besondere bei magnetischen Elastomeren ist, dass das superelastische Zugdehnungsverhalten durch Anlegen externer magnetischer Felder reversibel und maßgerecht angepasst werden kann. Wie das superelastische Plateau auf diese Stimuli reagiert hängt dabei vom Typ der magnetoelastischen Kopplung zwischen der Polymermatrix und den magnetischen Teilchen ab. In jedem Fall kann durch ein ausreichend starkes Feld, das senkrecht zu den kettenartigen Aggregaten angelegt wird, das superelastische Zugdehnungsverhalten abgeschaltet werden. Da die mesoskopischen Mechanismen, die dieses faszinierende Verhalten verursachen, identifiziert werden können, kann es in zukünftigen Modellen für die Makroskala angemessen berücksichtigt werden.

Beim letzen Thema dieser Arbeit handelt es sich um die Beschreibung von magnetischen Elastomeren unter Nutzung der Dichtefunktionaltheorie und anderer statistischer Methoden. Die Dichtefunktionaltheorie ist ein gut etablierter Ansatz der statistischen Mechanik für Ensembles von ununterscheidbaren Teilchen. Sie kann jedoch nicht direkt auf magnetische Elastomere angewendet werden, da die eingebetteten magnetischen Teilchen klar anhand ihrer Positionen innerhalb der Polymermatrix gekennzeichnet werden können. Die elastischen Wechselwirkungen im System hängen von diesen Referenzpositionen ab und machen die Teilchen dadurch unterscheidbar. Es wird jedoch gezeigt, dass diese Wechselwirkungen sinnvoll auf effektive Paarwechselwirkungen abgebildet werden können, welche die Teilchen als ununterscheidbar behandeln. Auf diese Weise wird eine Beschreibung mittels Dichtefunktionaltheorie für diese Materialien ermöglicht. Beim Vergleich der erhaltenen Ergebnisse mit Monte-Carlo Simulationen kann eine gute Übereinstimmung erzielt werden. Einen zusätzlichen Beitrag zu diesem Thema stellt eine detaillierte statistische Charakterisierung von Strukturdaten dar, die durch röntgentomografische Messungen an realen experimentellen Proben ermittelt wurden. In zukünftigen statistischen Theorien könnten solche experimentell realistischen Teilchenverteilungsfunktionen einen wertvollen Beitrag liefern.

# **Eidesstattliche Versicherung**

Ich versichere an Eides Statt, dass die Dissertation von mir selbständig und ohne unzulässige fremde Hilfe unter Beachtung der "Grundsätze zur Sicherung guter wissenschaftlicher Praxis an der Heinrich-Heine-Universität Düsseldorf" erstellt worden ist.

Düsseldorf, \_\_\_\_\_

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xii

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## Preface

This cumulative thesis is the result of my work at the *Institut für Theoretische Physik II: Weiche Materie* of the *Heinrich-Heine Universität Düsseldorf* since July 2013. My progress was supervised by Priv.-Doz. Dr. Andreas M. Menzel and Prof. Dr. Hartmut Löwen.

During this time, I contributed to seven scientific papers that have been published in various peer-reviewed journals. The detailed bibliographic information is given below.

- I. G. Pessot, P. Cremer, D. Y. Borin, S. Odenbach, H. Löwen, and A. M. Menzel, Structural control of elastic moduli in ferrogels and the importance of non-affine deformations, J. Chem. Phys. 141, 124904 (2014).
- II. M. Tarama, P. Cremer, D. Y. Borin, S. Odenbach, H. Löwen, and A. M. Menzel, *Tunable dynamic response of magnetic gels: Impact of structural properties and magnetic fields*, Phys. Rev. E 90, 042311 (2014).
- III. S. Huang, G. Pessot, P. Cremer, R. Weeber, C. Holm, J. Nowak, S. Odenbach, A. M. Menzel, and G. K. Auernhammer, *Buckling of paramagnetic chains in* soft gels, Soft Matter 12, 228-237 (2016).
- IV. P. Cremer, H. Löwen, and A. M. Menzel, *Tailoring superelasticity of soft magnetic materials*, Appl. Phys. Lett. **107**, 171903 (2015).
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# Contents

1.	Introduction		1
	1.1.	Composition and structure of magnetic elastomers	6
		1.1.1. Elastomers $\ldots$	6
		1.1.2. Magnetic particles	8
		1.1.3. Coupling between matrix and filler	10
		1.1.4. Particle distribution	11
	1.2.	Magneto-elastic effects	12
		1.2.1. The magneto-rheological effect	12
		1.2.2. Field-induced shape changes	13
	1.3.	Structural control of magneto-elastic behavior	14
		1.3.1. Affine models and their limitations	14
		1.3.2. Tunable dynamic relaxation	16
		1.3.3. Buckling of paramagnetic chains	18
	1.4.	Non-linear stress-strain behavior	20
		1.4.1. Superelasticity $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	20
		1.4.2. Shape-memory effects	27
	1.5.	Statistical description	29
		1.5.1. Characterization of experimental particle distributions .	29
		1.5.2. Density functional theory	32
2.	Peer-reviewed publications		<b>37</b>
	Paper I.	Structural control of elastic moduli in ferrogels and the impor- tance of non-affine deformations	37
	Paper II.	Tunable dynamic response of magnetic gels: Impact of structural	0.
		properties and magnetic fields	49
	Paper III.	Buckling of paramagnetic chains in soft gels	65
	Paper IV.	Tailoring superelasticity of soft magnetic materials	97
	Paper V.	Superelastic stress-strain behavior in ferrogels with different	
	Ĩ	types of magneto-elastic coupling	109
	Paper VI.	A density functional approach to ferrogels	133
	Paper VII.	Statistical analysis of magnetically soft particles in magnetorhe-	
	-	ological elastomers	151

## 3. Concluding remarks

## Bibliography

173

# Chapter 1. Introduction

Smart materials possess capabilities to sense environmental changes or stimuli, to adapt their physical properties in response to external stimuli, and to react back on the environment [1]. They do so in a reversible way, finding back to their original state after the stimulus is removed, allowing cyclic operation and reuse [2]. Due to these inherent properties, they can single-handedly fulfill tasks that would otherwise require a possibly more complex and bulky multicomponent system.

Nowadays, smart materials are present in many applications. Liquid crystals have revolutionized the industry of display devices due to their optical switching capabilities in reaction to electric fields [3]. Smart gels [4–7] can sense changes in temperature or pH-concentration. Piezoelectric materials [8,9] are used to transform a mechanical deformation into an electrical voltage and vice versa. Shape-memory alloys [10–12] are known for their shape-recovery upon heating, which has established them as thermally controlled actuators [13]. Their superelastic properties [14] further allow them to recover even from large deformations. As soft actuators, dielectric elastomers [15–19] have received much attention as they respond to electric fields with large-scale shape changes. Finally, magnetic liquids are used in many applications that require damping or vibration absorption applications [20–22].

This thesis revolves around magnetic elastomers and gels [1,23-26], a relatively new class of smart materials with equally fascinating properties. As some of the smart or stimuli-responsive materials mentioned above, it can be classified as soft matter [27], which comprises systems such as colloidal suspensions, polymers, elastomers, gels, and even biological cells and tissue [28]. The common ground of these systems is the mesoscopic size of their building blocks, ranging from a few nanometers to often around a hundred micrometers. This is much larger than an atom, such that quantum effects are negligible, but at the same time it is small enough to make thermal fluctuation an important factor [29,30]. In colloidal suspensions for example, the mesoscopic particles undergo Brownian motion due to the constant bombardment by the thermally agitated molecules of the surrounding medium [31,32].

The defining "softness" [28] is an appealing property for smart materials, as it means a typically strong response to stimuli and environmental changes [27]. But where does it come from? On the one hand, a system built of mesoscopic blocks has necessarily a much lower number of bonds per unit volume than an atomic solid [29]. Consequently, the response of such a system to deformation should be "soft". On that account, the elastic modulus of a crystal built of colloidal particles [33] is many orders of magnitude lower than that of a "hard" atomic solid like iron.

Polymers, on the other hand, have an elastic response that can be connected to thermal fluctuations, or more precisely to configurational entropy. They are, for instance, given by large chain-like molecules assembled by chemically linking molecular repeat units, the so-called monomers, in a process called polymerization [34]. A simple model for a single polymer considers it as a chain of jointed segments that perform a random walk [29]. Since there are more configurations corresponding to a compact, curled-up state than to a stretched-out one, the former state is favored by the chain on average. Mechanical stretching of a polymer chain away from this favored curled-up state entails a restoring force. Thus, the elastic response of polymers can be attributed to entropic interactions, and is therefore "soft". Since these interactions scale with temperature, already a single polymer chain has inherent smart capabilities.

When many polymer chains are cross-linked to form a network, a three-dimensional structure with the characteristics of a solid is obtained. At temperatures and densities away from the glass or crystallization transition of the polymer, these networks remain flexible and are called *elastomers* [28, 35, 36]. The stereotypical example is rubber, which we all know from practical experience to be both solid and also soft and reversibly deformable [35, 36]. These soft elastic properties can again be related to entropic interactions of the constituting polymer chains. Elastomers can be stretched by hundreds of percent without incurring a plastic deformation [37], as even strong strains mostly impart only configurational changes of the polymer network.

Polymeric gels are a sub-group of elastomers that are not "dry" like natural rubber, silicone, or polyurethane. Instead, they can additionally contain large amounts of solvent, which is trapped in the network due to hydrophilic interactions with the polymer. They can be obtained by performing the cross-linking or polymerization process in solution [29]. Alternatively, an already formed polymer network can be swollen in a good solvent. The temperature and chemical composition of the solvent has a significant influence on the swelling behavior of the gel and, therefore, controls its shape and elastic properties. Smart gels [4–7] are extremely versatile materials that are specifically optimized to exploit these and many additional stimuli.

Magnetic liquids [26, 38–45] are an example of a *colloidal suspension* with smart properties. They consist of ferromagnetic colloidal particles suspended in a liquid medium, stabilized to prevent coagulation [46, 47]. In *ferrofluids*, for instance, single domain nanoparticles of a size of up to 15 nanometers are employed. A magnetic field aligns the magnetic moments and leads to an overall magnetization of the fluid. When the field is switched off, the magnetization quickly dissipates by thermal fluctuation, either due to rotational Brownian motion of the particles [48, 49] or by Néel relaxation of their internal magnetic moments [48, 50, 51]. Thus, a ferrofluid has overall superparamagnetic properties. Suspending larger multidomain particles instead results in *magneto-rheological fluids*. They display magneto-viscous effects in external magnetic fields, allowing to tune the viscosity dynamically and reversibly over a wide range [40,52–58]. The main origin of these effects is the formation of chain-like particle aggregates in the direction of the applied field, which lead to a viscous friction against a shearing of the surrounding fluid [59–63]. Due to their tunable properties, both ferrofluids and magneto-rheological fluids have found applications in flow control and as tunable dampers [20–22].

Now, we come back to magnetic elastomers. Per definition, they are soft composite materials [64–66] manufactured by embedding ferromagnetic colloidal particles into a cross-linked polymer matrix [64, 65, 67–71]. Basically, they combine the merits of magnetic liquids with those of elastomers. Magnetic elastomers are highly deformable like rubber [72] and at the same time magneto-responsive. Furthermore, due to the coupling of elastic and magnetic interactions, a wide range of unique effects arises. Consequently, they offer great potential for technical applications [24, 73–75].

Magnetic elastomers appear under many different names in the literature [25]. When the polymer network is swollen with a solvent, the material is rather gellike and often referred to as a *ferrogel* [76]. By using smart gel matrices that are by themselves already stimuli-responsive [4–7], ferrogels can have an even wider range of possible interplays to choose from [1]. Another term often used is *magnetorheological elastomer*. It directly refers to the characteristic magneto-rheological effect that allows to reversibly adjust the elastic constants of the composite by applying an external magnetic field [1, 72, 77–89], not unlike the magneto-viscous effect in magnetic liquids. This magnetically tunable stiffness can be utilized, e.g., to construct tunable dampers [24, 90–92] and vibration absorbers [73, 75, 78, 93]. Due to their magneto-responsiveness, these elastomers and gels can also be operated as magnetic field sensors [94], or conversely translate a mechanical deformation into a magnetic signal [95, 96].

Another characteristic feature of magnetic elastomers are the large-scale shape changes that can be accessed by applying magnetic fields [1,97–102]. Using homogeneous magnetic fields, sample elongations in the range of tens of percent are easily reached [101], while in inhomogeneous magnetic fields, this can be further extended up to deformation amplitudes in the range of 100% [23]. Other shape-changes like deflections [103] are possible as well, even almost arbitrary deformation patterns in some samples [104].

With these capabilities, magnetic elastomers make excellent magneto-mechanical soft actuators [23, 102, 105]. Those devices transfer magnetic energy into mechanical work on their environment and single-handedly perform tasks for which more complex devices, such as motors, would be too bulky or unpractical. For example, soft magnetic actuators provide a closing mechanism for valves [83] or can be used as locomotion systems [104, 106–109] to propel soft robots [110, 111] or magnetic microswimmers [112]. Employed as magnetically controlled artificial muscles, they have similar characteristics as their natural, biochemical counterparts [23, 105].

Finally, one should mention the remarkably non-linear stress-strain behavior of magnetic elastomers. Magnetic shape-memory effects [2] have been observed in several experiments on magnetic elastomers [79, 113–116]. While exposed to a magnetic field, the material deforms seemingly plastically under load. As soon as the field is switched off, however, the sample can recover its initial state. Recent findings in theoretical models and simulations [117–119] hint towards the possibility of a plateau-like "superelastic" regime [14, 120–126] in the tensile stress-strain curve, similar to the phenomenology observed in shape-memory alloys. In this regime, the material is very susceptible to deformations, allowing large-scale reversible length changes while barely altering the load. Moreover, the non-linear stress-strain behavior can be tuned, tailored, and switched-off by external magnetic fields.

All of these capabilities can be transferred to a biomedical environment as well [127]. A concern in these applications is, of course, that the employed materials must not be harmful to the organism [74, 127–130]. However, as polymer-based composites, magnetic elastomers may already possess a high degree of biocompatibility [131–134]. On top of that, the magnetic field as a stimulus is tolerable by living organisms up to high field strengths [135] and does not rely on environmental properties like thermal or electrical conductivity [136]. This allows to control the material non-invasively from outside of the organism.

This non-invasive control makes smart implants based on magnetic elastomers very promising. For example, the mechanical stimulation of damaged muscle tissue by an implanted soft magnetic actuator was found to be beneficial to its regeneration. [129, 130]. In tissue engineering, porous ferrogel scaffolds can act as tunable templates for cell growth [127].

Finally, magnetic particles that are embedded into biological cells and tissue can be regarded as a magnetic gel, too. This point of view is relevant, e.g., to model the processes during hypothermal cancer treatment using magnetic nanoparticles [127,137]. Here, magnetic particles are injected into the organism and subsequently enriched in the degenerated tissue by external magnetic fields. Once accumulated and embedded in there, they are heated by alternating magnetic fields to destroy the tumor cells [138–140]. To make this selective treatment as effective as possible, accurate models of the heat distribution around the magnetic nanoparticles and for the effect on the surrounding tissue are required [128,141,142]. It is also important to understand the mechanical interaction between magnetic particles and cells [143], i.e. their ability to reach their destination by penetrating cell layers [144]. Related to this topic, microgel drug carriers with embedded magnetic particles [51,74,135,136,145–148] are an elegant method for directed transport and release of therapeutic substances. The ultimate goal of these localized non-invasive therapies are less side effects for the patient than conventional treatments.

While magnetic elastomers are certainly very promising, in most prospective applications [23, 24, 75, 110, 111] they are at the current stage still overshadowed by the more established smart materials mentioned in the beginning. Although there

has been significant progress in recent years in enhancing the magnitude of the key magneto-deformational effects, such as stiffness and shape changes in applied magnetic fields, there is still much room for improvement.

With a profound theoretical understanding of the underlying mechanisms, one could systematically engineer the materials towards a specific purpose. It is quite challenging, however, to devise an accurate macroscopic model for such a composite material because of the different length scales that have to be addressed. Many aspects of the bulk magneto-deformational behavior actually originate from processes occurring on the mesoscale. Simplifying macroscopic material models can easily miss those mesoscopic details and draw conclusions that are in disagreement with experimental observations [99, 149, 150].

Aware of this fact, recent modeling attempts increasingly concentrate on those smaller length scales. One can roughly distinguish between microscopic, mesoscopic, and macroscopic approaches for both the representation of the polymer matrix and the influence of the embedded particles. For the elastic matrix in microscopic approaches, the polymer network is resolved on the level of the individual polymer chains [151– 154]. Mesoscopic viewpoints coarse-grain the polymer matrix while still resolving deformations on the length scale of the embedded particles. This can either be a continuum mechanical formulation [149, 155–159] for the elastic medium between the particles or a representation by a network of springs connecting them [114, 150, 160–163]. Macroscopically, only the large-scale shape changes of the sample are considered [164–166].

Similarly, the magnetization can be microscopically resolved within each embedded particle [149, 155–157, 167] or mesoscopically approximated by multipolar [168, 169] or dipolar magnetic moments [117, 118, 150, 161–163, 170–174] of the particles.

Finally, on the macroscale, only the bulk magnetization is considered, not resolving the individual particles anymore [164–166, 175].

The different scales can be connected via scale-bridging approaches [154, 176–179]. First, a profound understanding on one length scale has to be developed. Then, a coarse-grained model is devised that captures the essential properties on that scale. Finally, this model can be used as an input to an approach that addresses a larger scale. Ultimately, a macroscale description is desired that takes all essential aspects of the smaller scopes into account.

This thesis is an effort to provide the required insight on the effects on the mesoscale, paving the way for future macroscopic descriptions. As methods, we have used particle-resolved models, computer simulations, and statistical theories. We have also collaborated with research groups that are capable of tracking individual particles in experiments [62, 180, 181]. These live insights into ongoing mesoscopic processes are exceptionally valuable for the characterization of magnetic elastomers.

In the further course of this introduction, I will first point out the basic properties of magnetic elastomers and how the different considered materials can be modeled. Following that, I will elaborate on some selected aspects qualifying magnetic elastomers as smart materials, as well as the challenges in modeling them, while putting a strong focus on my own research.

# 1.1. Composition and structure of magnetic elastomers

In magnetic elastomers, quite different materials are brought together. It is worthwhile to describe their properties separately before explaining how they couple and interact in the composite.

#### 1.1.1. Elastomers

The building blocks of an elastomer are polymer chains. An individual polymer chain responds elastically to deformations, as a simple qualitative model demonstrates [29]: The polymer is regarded as a freely jointed chain of N straight segments with end-toend vectors  $\mathbf{b}_1, \ldots, \mathbf{b}_N$ . They are of length b and linked together at their ends. The segments do not interact and their orientations are independent of each other.

If we take a look at a random configuration of the chain, the segments perform an ideal random walk of N uncorrelated steps of length b. For large N, the statistics of such a random walk produces a Gaussian probability distribution  $P(\mathbf{L}, N)$  for the vector  $\mathbf{L} = \sum_{i=1}^{N} \mathbf{b}_{i}$  pointing from the start of the chain to its end,

$$P(\mathbf{L}, N) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{L}^2}{2N b^2}\right).$$
(1.1)

It has a zero mean and variance  $\langle \mathbf{L}^2 \rangle = Nb^2$ . We see that the end-to-end separation  $|\mathbf{L}|$  is likely to be small. The chain prefers a coiled up state over a stretched-out one.

When we actively stretch the chain, we increase  $|\mathbf{L}|$  and force the chain to assume a less likely configuration. In other words, we decrease the configurational entropy

$$S(\mathbf{L}, N) = k_B \ln \left( P(\mathbf{L}, N) \right) = -k_B \frac{3\mathbf{L}^2}{2Nb^2} + \frac{3}{2} k_B \ln \left( \frac{3}{2\pi Nb^2} \right)$$
(1.2)

and end up with a state of larger free energy

$$F(\mathbf{L}, N) = -TS(\mathbf{L}, N) = \frac{3k_B T}{2Nb^2} \mathbf{L}^2 + \text{const}, \qquad (1.3)$$

i.e., the freely jointed chain essentially behaves like a harmonic spring of spring constant  $(3k_BT)/(Nb^2)$ . This surprising result justifies representing a polymer matrix by a coarse-grained network of springs, which is a common approach in models and simulations of magnetic elastomers [114, 150, 160, 161, 163, 174].

By cross-linking many polymer chains to a three-dimensional network, an elastomer is obtained. Elastomers behave like usual solids in the sense that they have an elastic resistance to deformation. In fact, we can calculate this elastic response via scale-bridging. For this purpose, we switch the point of view from individual polymer chains to that of a larger, coarse-grained piece of material.

Consider a volume element containing a statistical amount of cross-links and polymer strands connecting them, expressed by a cross-link density n. First, we assume that the distribution  $P(\mathbf{L}, N)$  for the end-to-end vector of each polymer strand of N segments still holds after the cross-linking. Second, we assume an arbitrary distribution  $\Phi(N)$ satisfying  $\int_0^{\infty} \Phi(N) dN = 1$  for the number of segments N of the polymer strands in the network. Finally, Eq. (1.3) provides us with the deformational energy for a polymer chain of N segments and end-to-end distance  $\mathbf{L}$ . In total, we can express the free energy density of the undeformed reference state of the polymer network as [28]

$$f_{\rm r} = n \int_0^\infty dN \int d\mathbf{L} \frac{3k_B T}{2Nb^2} \mathbf{L}^2 P(\mathbf{L}, N) \Phi(N)$$
  
=  $\frac{3nk_B T}{2b^2} \int_0^\infty dN \frac{\Phi(N)}{N} \underbrace{\int d\mathbf{L} \, \mathbf{L}^2 P(\mathbf{L}, N)}_{=Nb^2} = \frac{3nk_B T}{2}.$  (1.4)

Now, we deform the volume element to obtain the energy of the strained polymer network. We restrict ourselves to an overall affine deformation. This means that each material point  $\mathbf{X}$  is related to its deformed state counterpart  $\mathbf{x} = \mathbf{F} \cdot \mathbf{X}$  via a constant deformation gradient tensor  $\mathbf{F}$  [182]. In particular, this also applies to the end-to-end vectors  $\mathbf{L}$  so that the free energy density in the deformed state is given by [28]

$$f_{\rm d}(\mathbf{F}) = n \int_0^\infty dN \int d\mathbf{L} \frac{3k_B T}{2Nb^2} \left[ \mathbf{F} \cdot \mathbf{L} \right]^2 P(\mathbf{L}, N) \Phi(N) = \frac{3nk_B T}{2b^2} F_{\alpha\beta} F_{\alpha\gamma} \int_0^\infty dN \frac{\Phi(N)}{N} \underbrace{\int d\mathbf{L} L_\beta L_\gamma P(\mathbf{L}, N)}_{=(Nb^2/3)\delta_{\beta\gamma}} = \frac{nk_B T}{2} F_{\alpha\beta} F_{\alpha\beta} .$$
(1.5)

In total, the free energy density associated with the deformation is given by

$$f(\mathbf{F}) = f_{\rm d}(\mathbf{F}) - f_{\rm r} = \frac{nk_BT}{2} \left( \operatorname{Tr}(\mathbf{F}^T \mathbf{F}) - 3 \right) \,. \tag{1.6}$$

Remarkably, the prefactor only depends on the temperature  $k_B T$  and the cross-link density n.

This expression defines the stress-strain behavior [182] of the idealized elastomer. We can, therefore, identify the elastic constants by performing a volume-conserving tensile deformation. We apply a diagonal deformation gradient tensor with entries  $F_{xx} = \lambda$ 

and  $F_{yy} = F_{zz} = 1/\sqrt{\lambda}$ . Inserting it into Eq. (1.6) yields  $f(\lambda) = \frac{nk_BT}{2} (\lambda^2 + 2/\lambda - 3)$  and the elastic Young's modulus

$$E := \lim_{\lambda \to 1} \frac{\partial^2 f(\lambda)}{\partial \lambda^2} = 3nk_B T.$$
(1.7)

Because of the typical incompressibility of elastomers, we can further identify  $G = E/3 = nk_BT$  as the shear modulus of the polymer network [29, 182], obtained, e.g., in analogy by setting  $F_{xz} = \lambda$  and all other  $F_{\alpha\beta}$  to zero, and finally obtain

$$f(\mathbf{F}) = \frac{G}{2} \left( \operatorname{Tr}(\mathbf{F}^T \mathbf{F}) - 3 \right) \,. \tag{1.8}$$

This expression is known as the neo-Hookean hyperelastic model for rubber [28, 35, 36, 183]. Technically, Eq. (1.8) only holds for a strictly incompressible elastomers. However, variants with a finite compressibility exist [184]. Because of its simplicity, the neo-Hookean material model is often used to represent the polymer matrix in magnetic elastomers in a coarse-grained way [117, 118, 149, 155–157, 164, 166].

#### 1.1.2. Magnetic particles

Elastomers can be equipped with magneto-responsive properties by embedding colloidal ferromagnetic particles into the polymer matrix. The magnetic properties of these filler particles depend on the employed magnetic material as well as on their size.

Above a size of around 100 nanometers, ferromagnetic particles consist of multiple magnetic domains [167, 185, 186]. A domain is a localized region of spontaneous magnetization where the atomic dipole moments are on average aligned along a common direction [187]. Normally, different domains are oriented in different directions so that the overall magnetization vanishes.

However, multidomain particles can receive a net magnetization  $\mathbf{M}$  in an applied magnetic field that aligns the domains. When the field strength is tuned up, the aligned domains grow at the expense of the misaligned ones until finally the saturation magnetization  $M_{\rm s}$  is reached. Typically, these domain processes are not reversible and show hysteresis. Defects and impurities as well as crystalline anisotropy can pin the domain boundaries, keeping the domains partially aligned after the field is removed. In this way, the material retains a remanent magnetization  $M_{\rm r}$ . The required coercive field strength to remove this remanent magnetization determines the resistance of the material to demagnetization [188].

Multidomain particles can be categorized as magnetically hard or magnetically soft. Magnetically hard particles have a high remanent magnetization and coercivity and can be turned permanently magnetic. Neodymium-iron-boron (NdFeB) is often employed as a filler material [85, 104, 189–191] for its high remanent magnetization of  $M_{\rm r} \simeq 800 \,\text{kA/m}$  [192]. Elastomers with such magnetically hard fillers [108, 193] can essentially represent flexible permanent magnets. Hence, they have a pronounced magnetic hysteresis themselves [190].

Elastomers with magnetically soft fillers, on the contrary, possess the advantage that the magnetization of the embedded particles can be quickly tuned on demand by an applied magnetic field [26]. For this purpose, the ferromagnetic filler material must feature a narrow hysteresis loop with a low remanence and coercivity, but high saturation magnetization  $M_{\rm s}$  [170]. Mostly, commercially available carbonyl-iron powders [78,86,92] with  $M_{\rm s} \simeq 1600 \,\text{kA/m}$  [171,194,195] are used in this respect. These powders typically display a large variation in particle sizes and shapes [62,181,196,197]. Rubbery materials filled with carbonyl-iron are often called magneto-rheological elastomers [26,72].

The properties of ferromagnetic particles change drastically below a size of about 100 nanometers when they finally become small enough to consist of a single domain [167, 185, 186]. Such monodomain particles possess a permanent magnetic moment, typically oriented along a favored crystalline axis. Temporary rotations out of this favored axis are possible, but subject to an energetic penalty [198–201]. For a permanent reorientation of the magnetic moments to the opposite direction of the anisotropy axis, strong magnetic fields are required. This high resistance to remagnetization is expressed by calling these particles *magnetically blocked*.

Yet another size threshold is at around 10–15 nanometers. There, the Néel relaxation mechanism [48,50] becomes relevant. The strong thermal fluctuations at this size cause the permanent magnetic moments to constantly rotate and flip away from the favored axes. These nanoparticles become magnetically unblocked and have superparamagnetic properties [202,203]. Isolated superparamagnetic particles appear to be unmagnetic as the time average of the fluctuating magnetization vanishes. A magnetic field can incentivize a net alignment and, therewith, an effective magnetization that saturates at high field strength. Therefore, isolated superparamagnetic particles effectively have a magnetically soft response. However, in an ensemble, the aligning magnetic fields are momentarily provided by other particles so that collective effects can arise [204, 205]. In magnetic elastomers, mostly nanoparticulate magnetite with a saturation magnetization  $M_s \simeq 450 \text{ kA/m}$  [202] is employed [82,147]. These composites possess superparamagnetic properties also on the macroscopic scale [202, 203].

In models and simulations of magnetic elastomers, the magnetization is represented in various ways. Numerically sophisticated methods can resolve microscopic magnetization effects within each particle [167]. In this way, the magnetic interactions can be accurately captured even if the magnetic particles are very close to each other [168]. This is restricted, however, to small numbers of particles.

To treat larger numbers of particles, the magnetic interactions have to be represented more coarsely. A popular approximation is to assign magnetic dipole moments to the particles [117, 118, 150, 161–163, 170–174]. This becomes accurate when the particle separation reaches a few particle diameters [168]. However, it is also often used at smaller particle distances for its simplicity. The interaction energy of such an ensemble of dipolar magnetic particles is given by [187]

$$U_m = \frac{\mu_0}{4\pi} \sum_i \sum_{j < i} \frac{\mathbf{m}_i \cdot \mathbf{m}_j - 3\left(\mathbf{m}_i \cdot \mathbf{r}_{ij}\right) \left(\mathbf{m}_j \cdot \mathbf{r}_{ij}\right) / (r_{ij})^2}{(r_{ij})^3} - \sum_i \mathbf{m}_i \cdot \mathbf{B}_{\text{ext}} \,. \tag{1.9}$$

Here  $\mu_0$  is the vacuum permeability,  $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$  the vector separating two particles i, j, and  $\mathbf{B}_{\text{ext}}$  an externally applied magnetic field. The dipole moments  $\mathbf{m}_i$  of the particles can be assigned in different ways.

- A field-dependent magnetization  $\mathbf{M}(\mathbf{B})$  of magnetically soft or superparamagnetic particles can be treated by setting  $\mathbf{m}_i = V_i \mathbf{M}(\mathbf{B}(\mathbf{r}_i))$  at each instant, where  $V_i$  is the volume of the particle and  $\mathbf{B}(\mathbf{r}_i)$  is the local magnetic field at its position.
- In a magnetically hard particle, the magnetic moment  $\mathbf{m}_i = M_r V_i \hat{\mathbf{u}}_i$  is rigidly coupled to an axis  $\hat{\mathbf{u}}_i$  within the particle frame of reference. In a magnetic field, the magnetic moment can, therefore, transfer a magnetic torque  $\boldsymbol{\tau}_i = \mathbf{m}_i \times \mathbf{B}$  to the particle.
- The collective dynamics of superparamagnetic particles can be simulated by keeping only the magnitudes  $|\mathbf{m}_i|$  of the permanent magnetic moments fixed and their orientations unconstrained [206, 207].
- The permanent magnetic moments of magnetically blocked monodomain particles can be treated in the same way if an energetic penalty for the rotation of the moment away from the easy magnetization axis is introduced [198–201].

In conclusion, the dipolar approximation is quite versatile as all types of filler particles discussed above can be represented in a simple way in many practical situations.

#### 1.1.3. Coupling between matrix and filler

Let us now discuss how the magnetic particles interact with the polymer matrix into which they are embedded.

First of all, there is a *translational* magneto-elastic coupling between the components. Activating magnetic interactions between the particles leads to their displacement against the polymer network. The surrounding elastic matrix elastomer deforms and exerts restoring forces on the particles that attempt to drive them back [159]. In this way, the particles mediate their magnetic interactions to the surrounding polymer matrix and, e.g., shape-changes can be induced [101, 208, 209]. When the magnetic interactions are switched off, the matrix drives the particles back to their original positions [79, 86, 114, 180].

Recently, a new class of magnetic elastomers has been developed, which also features a strong *rotational* magneto-elastic coupling. In these composites, the polymer matrix is directly anchored to the particle surfaces [25, 210]. This can be achieved by a chemical surface-functionalization of the particles, such that they become covalent cross-linkers of the polymer network themselves [67, 68, 70, 71, 211]. The particles possess a permanently imprinted *orientational memory* [154, 160, 161]. A particle rotation in these materials twists the surrounding polymer matrix and is met with restoring torques. If particles of blocked permanent magnetic moments are employed, they can mediate the torques on their magnetic moments to the surrounding matrix in this way [118, 151, 152]. Additionally, this covalent embedding is associated with improved mechanical properties like decreased brittleness and overall higher recoverable deformations [211].

In more conventional magnetic elastomers, where the polymer matrix is not firmly attached to the particles, the rotational coupling may be more of a frictional kind. The matrix deforms elastically under small torques, but may start to slip when the rotational distortions become too high [191]. When the rotational friction is low, the particles can reorient quite freely without deforming the surrounding matrix. This can go so far that some magnetic gels may display pseudo-superparamagnetic properties. In such gels, the permanent magnetic particles undergo rotational Brownian relaxation processes similar to those in magnetic liquids [68, 69, 202].

A different aspect of the coupling between matrix and filler is that the filler particles represent rigid inclusions within the polymeric composite material [64–66,212] already in the absence of any magnetic interactions. The particles are much less deformable than the polymer matrix. Thus, the composite has an overall stiffer response to deformations with the particles included than the pure elastomer. [212–215]. As a rough estimate, the reinforced elastic modulus of an elastomer composite with a volume fraction  $\phi$  of rigid inclusions is given by [216]

$$E' = E(1 + 2.5\phi + 14.1\phi^2) \tag{1.10}$$

in terms of the modulus E of the pure elastomer.

This filler reinforcement becomes important when trying to optimize magnetic elastomers for strong *relative* magneto-elastic effects [82, 217]. A high fraction of filler particles leads to enhanced magnetic interactions due to the decreased average distance between particles, see Eq. (1.9). On the other hand, the deformational response to these magnetic interactions roughly scales inverse with the elastic constants and decreases by adding more filler. Model predictions suggest that an optimal filler fraction is reached at around 27% [90, 171]. However, a high filling fraction also increases the brittleness of the material [211, 218], which limits the recoverable deformation. Most experiments, therefore, aim for filler volume fractions of about 10% [26, 80, 85, 87, 189], although considerably higher values of up to 40% have been explored as well [93, 170, 209].

#### 1.1.4. Particle distribution

Finally, magnetic elastomers can be characterized by the distribution of the magnetic particles in the polymer matrix [181]. As we will see, the particle distribution can have a large impact on the magneto-deformational response of the composite [25, 99, 149, 150, 156, 157, 170, 172, 219, 220].

The structure can be influenced during the synthesis of the composite. Two major types of structures are experimentally accessible: isotropic and uniaxially anisotropic [1, 77].

Anisotropic samples are manufactured by applying a homogeneous magnetic field before and during the chemical cross-linking process [221, 222]. In this state, the magnetic particles are still mobile. Therefore, similarly to the processes observed in magnetic liquids [53, 54, 60, 61, 63], they can form chain-like aggregates aligned in the direction of the field. When the polymer matrix forms, it arrests the chain-like aggregates and they persist even after the magnetic field has been turned off. The chains can have various morphologies, depending on the strength of the applied field as well as the particle content in the precursor mixture [53, 181]. They can be relatively short [180, 196, 223, 224] or percolate the whole sample [62, 181, 197, 225].

Isotropic samples, on the contrary, are simply manufactured in the absence of a magnetic field. Consequently, the particles in these samples are more or less randomly dispersed [181].

## 1.2. Magneto-elastic effects

In the following, we describe in more detail the experimental observations made for the magneto-rheological effect and shape changes in external magnetic fields.

#### 1.2.1. The magneto-rheological effect

The magneto-rheological effect, as one of the key features of magnetic elastomers, allows to actively tune the deformational response of the material on-demand by applying a magnetic field [1, 26, 77, 84, 170, 219, 226]. It is of high relevance for industrial applications [73, 75] because it can be exploited to construct actively controlled dampers [24, 90–92] and vibration absorbers [73, 75, 78, 93]. The term is actually borrowed from magneto-rheological fluids [40, 52–58], which display a similar dynamic tunability of the viscosity and are a strong competitor for the same applications [20–22]. Magnetic elastomers possess some advantages though. They are self-contained, i.e., do not require a container, and have no issues with particle sedimentation [73].

The origin of the stiffness changes is ultimately the magnetic interaction between the filler particles [77,84,170,219,226]. They give a contribution to the free energy cost for sample deformation and, therefore, alter the elastic constants. In permanently magnetic elastomers, these interactions are always present, such that they display a *passive* magneto-rheological effect [26]. The stiffness of these composites can be altered by remagnetizing the sample [85]. In contrast, the magnetization of magnetically soft elastomers can be *actively* tuned on demand with an applied magnetic field [1,81,87,227], which is more appealing for applications. By mixing both kinds of fillers, the passive and active effects can be combined [189,228].

The magneto-rheological effects of highest relative magnitude have been reported for shear deformations [72, 77, 78, 80, 81, 84, 86–89]. There, a reinforcement, e.g., an increase of the shear modulus, has been observed in homogeneous magnetic fields for both isotropic and anisotropic samples. It has been found that the relative range of tunable shear stiffness can be extended by softening the polymer matrix [80, 87]. In this way, a field-induced increase of the shear modulus by a factor of more than 10.000 has been reached in Ref. [87]. Of course, the matrix cannot be made arbitrarily soft as mechanical stability of the composite is still a concern [75].

In tension and compression tests [79,82,227,229,230], the achieved relative changes of the tensile elastic modulus are admittedly smaller, but still remarkable. Increases of the tensile modulus in a typical range of 20–100% have been observed in isotropic samples [227,229,230]. For anisotropic magnetic elastomers, it has been demonstrated that the reinforcing effect depends on the relative orientation of imposed deformations, the applied magnetic field, and the axes of the chain-like structures [1]. The largest effect seems to occur when these three directions coincide [1,231]. In Ref. [232], an increase of the tensile modulus as high as 280% was reached for such a set-up.

#### 1.2.2. Field-induced shape changes

The shape-changes in an applied magnetic field are another signature effect of magnetic elastomers. This capability enables the operation as magneto-mechanical soft actuators, devices that transform magnetic field energy into mechanical work.

Inhomogeneous fields [103, 208] seem to be particularly suited for this purpose as high actuation strains of the order of 100% can be achieved [23]. The sample deforms towards the regions of higher magnetic field strength to minimize its magnetic interaction energy [98]. Turning up the overall magnetic field strength, at first the sample still finds a balance between the magnetic stretching forces and the elastic restoring forces, keeping the strain limited. However, a discontinuous elongation may occur when the magnetic interactions begin to dominate and the sample is suddenly drawn into the field [1,94,98,208,233]. The sudden elongation is only stopped because the incompressible sample exposes a smaller cross-section to the inhomogeneous field at high elongations, which favors the elastic interactions again.

Other shape deformations, like deflections [103, 108], are available as well. In this context, the extremely versatile soft magnetic actuator presented in Ref. [104, 109] should be highlighted. There, an elastomer bar filled with magnetically hard particles was magnetized inhomogeneously and therewith "programmed" for future shape-

changes. A time-dependent control field further allowed to induce virtually arbitrary deformation patterns of the bar by locally exerting forces and torques on the embedded permanent magnetic particles. These shape-programmable magnetic elastomer bars were then used as fins for fish-like robots that propel themselves with swimming strokes. A number of other locomotion systems have been proposed as well, see Refs. [106–109, 112].

In homogeneous fields, mostly contractions or elongations are observed. Experiments on samples with an isotropic particle distribution predominantly display an elongation [97,100,209,234,235]. For anisotropic samples with a homogeneous field applied parallel to the chain-like aggregates, some experiments have reported a sample elongation [101], others a contraction [224, 234, 236]. The authors of Refs. [236] and [224] pointed out that their chain structures are remarkably ordered. Thus, the contraction could be explained by simple magneto-dipolar attraction between the neighboring particles [117, 118, 219, 237]. Elongation in anisotropic samples on the other hand might be associated with a certain randomness of the chain structure [149, 163]. We further elaborate on this topic in the next section.

### 1.3. Structural control of magneto-elastic behavior

In this section we address the question how the mesoscopic structure of magnetic elastomers influences their response to external magnetic fields in the context of our three studies on this topic.

#### 1.3.1. Affine models and their limitations

To describe the behavior of a mesoscopic [77, 170, 177, 179] or macroscopic [165, 166, 175, 238] piece of material, it is a common approach to assume affine deformations. This means that an overall deformation of a considered piece of material is uniformly mapped to all positions of the particles embedded within. There are two great advantages connected to such a simplifying approach. First, the elastic part of the deformational energy can be expressed in a simple form, for example using a rubber elasticity model like the neo-Hookean solid, see Eq. (1.8). Second, an affine deformation changes the distribution of magnetic particles in the elastomer in a clearly defined manner, which also sets the contribution of magnetic interactions to the deformational energy [166, 219, 220, 239]. Affine models are, therefore, powerful tools for scale-bridging, yet they contain a major simplification.

Using such models, the qualitative impact of the particle distribution inside the elastomer on the magneto-rheological effect has been investigated [25]. For typical regular lattices with a magnetic field applied parallel to the imposed axis of deformation, a decrease of the tensile modulus was predicted for *simple-cubic* and *bcc* structures [176, 219, 220]. For particles on an *fcc* lattice, reinforcement was found instead.

In models addressing the chain-like aggregates in anisotropic magnetic elastomers, the particle distribution is an important factor as well. Here it was found that the behavior qualitatively changes when a different chain morphology is assumed. Using simple affine models as well as well as non-affine finite element simulations, it was demonstrated in Ref. [149] that an increasing degree of waviness of the chains can change the behavior when the external magnetic field is applied parallel to the chain axes. Perfectly straight chains lead to reinforcement under perpendicular shear [77, 170, 219] in qualitative agreement with experiments, but show a decrease of the tensile modulus under uniaxial load. In contrast, slightly wavy chains produce the experimentally expected reinforcement effect for both shear and tensile deformation. In fact, the chains observed in experiments are often at least slightly wavy [223, 224, 236]. The authors reported good qualitative agreement between model and simulation, which suggests that affine models perform well in describing anisotropic magnetic elastomers.

For isotropic particle distributions, it is overall much harder to obtain agreement between experiments and affine models. It has been pointed out that the effects of particle clusters have to be taken into account to achieve agreement with experiments [99,100,163]. These clusters arise naturally in these samples when groups of randomly dispersed particles are close to each other by chance. If magnetic interactions are activated by an external field, the close particles attract each other and form clusters, which then rotate in the direction of the applied field. In this way, these clusters can contribute to an overall sample elongation in homogeneous fields. However, such an elongation is not not consistently reproduced in affine models [166, 219, 220, 238]. Of course, the local deformations involved in these clustering processes are clearly non-affine.

Still, affine models are quite important for the theoretical progress of the field. Therefore, it is important to understand for which particle distributions they are a valid approximation.

This was the motivation for **Paper I**, where we systematically tested the approximation of affine deformations. In order to test affine as well as non-affine deformations within the same model, we considered point-dipolar particles connected by a network of springs. Such a minimal dipole-spring model provides a simple description of the magnetic and elastic energy of the system, which enables the treatment of relatively large overall particle numbers. Using this set-up, we numerically tested the magnitude and sign of the magneto-rheological effect for various two-dimensional particle distributions with an in-plane magnetic field.

For simplicity, we assumed the magnetic moments to be of equal magnitude and aligned along the same direction parallel to a homogeneous magnetizing field. For each particle distribution, we first let the system relax to a state of minimum energy. Then we clamped the sample at the ends and extracted the elastic modulus by applying a small tensile deformation and measuring the change in overall system energy. This was done either by constraining the dipole-spring network to affine deformations or by numerical energy relaxation with all its local degrees of freedom considered. Afterwards, we compared the elastic moduli measured under affine deformations with those under non-affine deformations.

We first considered different regular lattices: rectangular, honeycomb, and hexagonal. To benchmark the accuracy of affine deformations, we randomly rearranged the initially regular lattices by a certain degree. Thereby, we found that an increasing degree of randomization of the initial lattice leads to increasing deviations between the elastic moduli measured under affine and non-affine deformations.

Overall, our results indicated that affine deformations perform relatively well as an approximation for distorted regular lattice structures, producing the same qualitative behavior of the magneto-rheological effect as the non-affine deformations. The best agreement is achieved for the rectangular lattice, the worst for honeycomb, and hexagonal resides in between.

As other studies before, we observed the qualitative behavior of the magnetorheological effect to be greatly affected by the structure of the sample. We found it particularly important in this context whether the connecting vector between nearest-neighboring particles is parallel to their magnetic moments, so that they feel a magneto-dipolar attraction towards each other. In the considered lattices where this was the case, we obtained a negative contribution of the magnetic interactions to the overall elastic modulus. For nearest neighbors in a repulsive configuration, we found reinforcement instead. This means that the qualitative behavior of the material can often be changed by simply rotating the lattice, for instance a hexagonal one by  $60^{\circ}$ .

As a final test to the feasibility of affine deformations, we tested them on an experimentally realistic, more disordered particle distribution. It was extracted from an X-ray tomographic image of a uniaxially anisotropic experimental sample [62]. We made a cross-sectional cut perpendicular to the anisotropy direction to obtain the two-dimensional positions of the particle chains within the cross-sectional plane. On each position, we placed one point-dipolar particle. This time, we applied the magnetic field perpendicular to the plane, such that the dipole-dipole interaction within the plane was always repulsive. We generated the initial network of springs connecting the particles via Delaunay triangulation [181, 196, 240], treating the particles as vertices of the triangular mesh and setting the springs at its edges. Upon activating the magnetic field we found a stiffening effect for shear and tensile non-affine deformations. Under the constraint of affine deformations, however, the behavior was qualitatively different: we saw a slight decrease of the shear and Young's moduli. For these experimentally realistic irregular distributions, it therefore becomes mandatory to resolve non-affine deformations.

Overall, our work provided more evidence that the structure of the composite has a big impact on the observed magneto-deformational effects. It could also act as a guideline to when affine deformations are a justifiable approximation.

#### 1.3.2. Tunable dynamic relaxation

No matter if we are talking about tunable dampers, vibration absorbers, soft actuators, or hypothermal cancer treatment, in all these applications the dynamic relaxation processes within the material play a role [165, 241]. In **Paper II** [161], we therefore investigated how the structure of the composite controls its dynamic response. Not only the particle arrangement, but also the magneto-elastic rotational coupling is an aspect of the structure, as discussed in Sec. 1.1.3. We implemented it as part of a dipole-spring model as an orientational memory of the magnetic moments of the particles with respect to the surrounding spring network [160]. In addition to the contributions to the harmonic spring energy for a change of the bond length between a pair of particles, we also energetically penalized torsions of the bond as well as rotations of the magnetic moments away from their memorized orientations relative to the bond. We controlled the impact of each energetic contribution by a different prefactor. In this way, we represented different types of couplings of the orientations of the magnetic moments to the surrounding polymer network.

To describe the dynamics, we formulated the overdamped equations of motions [47] for the positions and orientations of the magnetic moments of all particles in the system. We linearized these equations with respect to small deviations from the energetic ground state and solved the resulting coupled system of equations. This approach is, to some degree, similar to the calculation of phonon spectra in classical solids [242]. However, here the governing equations of motion are overdamped [47] instead of oscillatory, and the arrangement of particles is not necessarily regular. As a result, we obtained the dominant relaxation modes and corresponding relaxation rates. Each relaxatory mode prescribes a characteristic pattern of positional and orientational displacements of all particles in the system.

As an example to demonstrate the influence of different types of orientational memory, we considered a linear chain of particles with magnetic moments of equal magnitude and initially identical orientation. Our analysis of the relaxation spectra revealed that the relative strength of the different rotational couplings has a qualitative impact on the appearance of the characteristic modes, especially on those representing mainly rotations of the magnetic moments. We observed that rotations associated with a strong coupling in the dipole-spring models relax particularly fast. Generally, in our analysis, the rotational modes had a slower relaxation compared to positional compressions and dilations along the chain axis though. The fastest relaxing modes were high-wavenumber displacements involving small groups of particles.

Next, we concentrated on the influence of the spatial distribution of particles in the absence of orientational memory. We considered quadratic, rectangular, and hexagonal two-dimensional arrangements of the particles. We kept their magnetic moments fixed in the same direction perpendicular to the plane. Again, we observed an influence of the type of structure on the qualitative appearance of the characteristic modes.

Finally, we probed the tunability of the dynamical relaxation behavior by an

external magnetic field for magnetizable particles. For this purpose, we utilized the two-dimensional distribution of chain-like aggregates that we had already extracted from an anisotropic experimental sample for our previous approach in Paper I. As before, we generated the two-dimensional spring-network via Delaunay triangulation. To represent a homogeneous magnetizing field of varying field strength, we set all magnetic moments to an equal but controllable magnitude m and oriented them perpendicular to the plane. In the resulting relaxation spectra, lower modes with a slow relaxation are typically related to global shape-changes of the sample, whereas faster modes show a localized character and involve fewer particles. Interestingly, the relaxation spectra and, therewith, the overall relaxation rate are tunable. By increasing m (possibly by increasing the strength of the magnetizing field), the density of modes here can be shifted significantly towards an overall faster relaxation.

In conclusion, we showed that dynamic properties of magnetic elastomers can be tuned by several factors: mesoscopic structure, orientational memory, and external magnetic field. The latter in particular allows to tune the relaxation rate on demand during application.

#### 1.3.3. Buckling of paramagnetic chains

In Sec. 1.2.2, we discussed what kind of bulk magneto-deformational behavior can be observed in anisotropic uniaxial magnetic elastomers. In an appropriate set-up, however, also the mesoscopic shape changes of individual chains can be experimentally observed and studied. In **Paper III**, we used a laser-scanning confocal-microscopy set-up [243], which allowed us to trace individual particles during experiments on chains of superparamagnetic particles embedded in a soft gel. Upon application of a homogeneous external magnetic field perpendicular to the chain axes, we observed a rich variety of deformational responses, see Fig. 1.1. Shorter chains rotated towards the field, chains of intermediate length bent at their ends, and long chains buckled into a sinusoidal-like deformation pattern. The longer the chain, the more half-wave oscillations were typically observed. It was possible to increase the buckling amplitude by increasing the strength of the applied magnetic field strength or by employing a softer gel matrix.

We were able to explain this behavior within a phenomenological model for the overall energy of a certain deformational pattern of the chain. For this purpose, we assumed the chain to carry dipolar magnetic moments along its contour that are perfectly aligned with the magnetizing external field. This describes the changes in magnetic energy of the chain when reorienting in the external magnetic field.

For the elastic energy of the deformation, we found a bending contribution scaling with the curvature of the chain to be relevant. This was based on two observations. First, we had experimental evidence of an inherent bending rigidity of the chains, possibly due to a layer of stiffer polymer in the vicinity of the particles. Second, we could reveal the dominating deformational modes of the surrounding gel matrix during the buckling to be of an oscillatory kind. Furthermore, we also introduced a displacement contribution to describe the deformational energy cost for displacing segments of the chain within the elastic gel environment. This term penalized rotations of the chains within the elastic gel environment, especially discouraging overall rotations of longer chains in accordance to the experimental observation that these chains tend to buckle instead. We then made an ansatz for the chain shape and fitted it to our experimental contours to assess the relative weight for each of the three energy contributions. With the completed phenomenological model, we were able to predict the energetically optimal number of half-waves and buckling amplitude for chains of various lengths with good agreement with the experimental results.



Figure 1.1.: Under the influence of an applied perpendicular magnetic field, superparamagnetic chains embedded in a soft gel display intriguing deformational patterns. Short chains are rotated towards the field, while longer chains buckle and bend. The longer the chain, the more half-wave oscillations are typically observed. The amplitude of the buckling can be tuned by the field strength and the elastic modulus of the gel matrix. Reproduced from Ref. [180] (Online graphical abstract) – Published by The Royal Society of Chemistry under a Creative Commons Attribution 3.0 Unported Licence (CC BY 3.0).

Finally, we simulated the shape change of the paramagnetic particle chain within two-dimensional particle-resolved molecular dynamics simulations. We represented the polymer network by a fine hexagonal mesh of finite extensible non-linear elastic springs [154, 244]. Into this mesh, we embedded rigid spherical particles arranged in a linear chain, each carrying a dipolar magnetic moment aligned parallel to an external magnetic field perpendicular to the chain axis. Here, the bending rigidity of the chain actually proved to be a crucial ingredient. We had to assume the mesh to be stiffer in the vicinity of the particles to observe the buckling morphology of the chains as in the experiment. Without this contribution, the chain broke up into smaller clusters oriented in the field direction instead. This again supported our conjecture that a stiff polymer layer connects the particles and stabilizes the chains in the experiment.

Our modeling and simulation approaches used the mesoscopic information from a particle-resolving experiment. Hence, it provided valuable theoretical insights about the magneto-deformational coupling between chains and polymer matrix on this length scale.

### 1.4. Non-linear stress-strain behavior

The stress-strain behavior of an elastic material defines its response to deformation and load [182]. In a deformed sample, restoring forces attempt to drive the sample back to its initial state. Conversely, the material deforms under an external stress until the counteracting internal stresses balance the load. In the small-strain regime, there is typically a linear relation  $\sigma = E\varepsilon$  between stress  $\sigma$  and strain  $\varepsilon$ , for which the elastic modulus E provides the corresponding proportionality constant.

In Sec. 1.2.1, we have seen that the magneto-rheological effect provides an ondemand tunability of the linear stress-strain behavior. This capability also extends to the non-linear stress-strain regime, allowing to tune the deformational behavior at greater deformations as several experiments have demonstrated [1,227,231,232]. These insights about the change of the deformational behavior in applied magnetic fields are quite valuable, e.g., for the design of magneto-mechanical actuators that perform work under loaded conditions [23,101,102,104–106]. Still, surprisingly few theoretical simulation or modeling attempts have explored the non-linear stress-strain regime so far.

#### 1.4.1. Superelasticity

In **Paper IV** and **Paper V**, using particle-resolved numerical simulations, we revealed that anisotropic magnetic elastomers can feature a pronounced non-linear "superelastic" stress-strain behavior under uniaxial deformation. This behavior can be reversibly tailored from outside by applying magnetic fields.

"Superelasticity" expresses the fascinating capability of some smart materials [14,120–126] to perform large-scale reversible deformations at a basically constant load. It typically occurs in the form of a plateau-like regime in the stress-strain behavior, see Fig. 1.2 for an illustration. The term originates from shape-memory alloys, which display this behavior due to a stress-induced phase transition. Typically, on the superelastic plateau, a high-symmetry crystal structure changes into an elongated low-symmetry lattice that can accommodate the applied deformation [14]. Since the elongated phase is in principle only stable under stress, the material can perform the reverse transition back to the high-symmetry crystal when the load is removed.
Because of these transitions, shape-memory alloys can reversibly recover from much higher strains than conventional metallic materials.

Also in other materials, the superelastic behavior can be associated with some kind of stress-induced restructuring. In our anisotropic magnetic elastomers, we identified two



Figure 1.2.: Schematic of a typical stress-strain cycle for a superelastic material. After the stress  $\sigma$  initially increases with the strain  $\varepsilon$ , a flat plateau is reached. There, stress-induced restructuring processes within the material allow further deformations under basically constant load. The newly acquired structure is only stable under loaded conditions. Upon unloading, the material can therefore transition back while crossing a reverse plateau, possibly showing hysteretic behavior.

such deformation-induced restructuring mechanisms. One is a *detachment* mechanism of embedded chain-like particle aggregates gradually breaking up into smaller segments, the other is a *flipping* mechanism of magnetic moments. Both mechanism respond to external magnetic fields. Otherwise, a magnetically controlled superelastic stress-strain behavior is known from ferromagnetic shape-memory alloys [2, 245–248], however, restricted to impractically low operation temperatures in these materials.

We used the following set-up to perform numerical stress-strain tests on a magnetic elastomer. To describe the polymer matrix around the embedded magnetic particles, we treated it as an elastic continuum and tessellated it into a fine mesh of deformable tetrahedra [249]. We assumed a nearly-incompressible neo-Hookean elastic material model [184] for the elastic energy of deformation of this mesh. Restricting each tetrahedron to deform affinely allowed us to obtain simple expressions for the restoring forces on the tetrahedral nodes. Using this approach, the collective deformation of the mesh of many connected tetrahedra can still be distinctly non-affine as each tetrahedron may deform in a different way.

Then, we embedded rigid spherical magnetic particles into the mesh. We approximated their surfaces as polyhedra with triangular faces to rigidly connect them to the faces of the surrounding tetrahedra. This creates a no-slip coupling between embedded particles and the surrounding matrix, see Sec. 1.1.3. Therefore, particle rotations can deform the surrounding mesh, while likewise a mesh deformation can induce particle rotations.

Our numerical samples were supposed to mimic the anisotropic structure of percolating chain-like particle aggregates observed in some experiments [62, 181, 197, 225]. Accordingly, we arranged the particles into parallel straight chains spanning the long edge of an initially rectangular box of elastic material. Within each chain, the particles were equally spaced and initially separated by a finite gap filled by elastic material. We positioned the chains in a random non-overlapping way in the box and created 20 distinct numerical samples in this way.

To represent the magnetic interactions, we finally equipped the particles with permanent dipolar magnetic moments of equal magnitude. Here we distinguished between two major types of rotational magneto-elastic coupling, which we will call *covalent* and *free* here. Our *covalent* systems model samples of particles carrying permanent magnetic moments that are rigidly fixed to the particle axes, hence, each dipole moment can transfer a magnetic-field-induced torque to the corresponding particle. In contrast to that, we also considered *free* systems, where we allowed the dipole moments to freely reorient with respect to their carrying particles. Let us first discuss the *covalent* system.

We initially magnetized these *covalent* samples uniaxially by setting all magnetic moments to the same orientation parallel to the chains. This activates strong attractive magneto-dipolar forces between neighboring particles in a chain, compressing the elastic gap material in between and leading to an overall sample contraction. This state, illustrated in Fig. 1.3 (bottom left), was the starting point for our uniaxial stress-strain measurements. We clamped the sample at the ends and quasi-statically stretched it in the direction parallel to the chains, performing an energetic relaxation after each step [250–252]. Meanwhile, we kept track of the force required to keep the sample in the prescribed elongated state. After averaging the stress-strain curves of our 20 different numerical samples, we obtained the markedly non-linear superelastic behavior shown as the black curve in Fig. 1.3 (right). It displays the characteristic plateau, along which the sample can be deformed without significantly increasing the applied load.

We were able to relate this behavior to the following strain-induced *detachment* mechanism of the individual chain-like aggregates. After the initial contraction of the sample, the distance between nearest-neighboring particles in a chain is small so that their magneto-dipolar attraction along the chain axis is quite strong. At the same time, the compressed gap material between them stores deformational elastic energy. In the initial stiff regime of the stress-strain curve in Fig. 1.3 (right), the chains are first held together by these strong magnetic bonding forces and can resist an extension. As the imposed strain is further increased, however, the stretching forces eventually become strong enough to detach a part of a chain from the remainder. Once the corresponding magnetic energy barrier is overcome, the two parts suddenly become easily separable as their mutual magnetic attraction is severely weakened



Figure 1.3.: Left: Illustrations of a *covalent* sample at different states of elongation. The magnetic moments of the particles are depicted as bar magnets. Right: The stress-strain curves obtained by averaging the behavior of 20 of such samples. Solid lines signify the behavior under loading while the dotted lines depict unloading. The particles are initially arranged in chain-like aggregates with a finite gap between them and magnetized along the chain axes. Thus, there is an overall initial contraction of the sample, compressing the elastic gap material between the particles. The chains are initially held together by strong magneto-dipolar bonding forces, but when the sample is stretched, particles can gradually be detached from the chains. These processes lead to the superelastic plateau in the stress-strain curve. A magnetic field applied parallel to the field (green curve) leaves the superelastic plateau untouched but stiffens the material at larger strains. Under a strong perpendicular magnetic field (orange curve), there are no magnetic bonding forces along the chains in the first place and the superelastic behavior is turned off.

with increased separation. On top of that, the elastic energy initially stored in the inter-particle gap between the two parts is released.

Momentarily, one such detachment event means a stress release, which appears as a sudden drop in the stress-strain curve. Further stretching of the sample leads to further detachment events involving the remaining parts of the chain. In the stress-strain curve of an individual chain, this results in a spiky plateau, see Paper IV for a more detailed discussion. A recent study [119] has likewise confirmed the superelastic stress-strain behavior of individual chain-like aggregates. After averaging over the multitude of chains within different samples, the discrete drops occurring at various strains combine to a smooth superelastic plateau-like regime in the stress-strain curve as shown in Fig. 1.3 (right). When all particles have been detached from all chain parts, the restructuring is complete, see the illustration in Fig. 1.3 (top left). This marks the end of the plateau, where the response of the sample to further elongation becomes stiff again. Upon unloading, the particles simply reattach to their respective chains, the magnetic bonding forces between nearest neighbors are restored and the elastic gap material is compressed, once again storing elastic energy. Thus, the initial state, depicted in Fig. 1.3 (bottom left), can be recovered at the end of the stress-strain cycle.

Applying external magnetic fields further allows to exert control over the non-linear stress-strain behavior, see the colored curves in Fig. 1.3 (right). A field applied in the direction of the imposed uniaxial strain, i.e., parallel to the chain-like aggregates and their initial magnetization, has no significant effect on the superelasticity as it does not interfere with the detachment mechanism. It stiffens the response of the material in the regime following the superelastic plateau though. Thorough analysis suggested the following explanation for this effect. When the chains are in the detached state, the particles tend to rotate away from the chain axes due to shear stresses in the inhomogeneous sample. This situation is depicted in Fig. 1.3 (top left). A parallel applied field, however, can stabilize the particle orientations and keep their magnetic moments aligned parallel to the chain axes. Thus, even at high strains they repel in the direction perpendicular to the stretching direction and, thereby, work against a further elongation. A further cause for the stiffening is that the emerging local shear stresses within the system are kept from relaxing via the favored channel which is the rotation of particles.

A field applied perpendicular to the imposed strain incentivizes the covalently embedded particles to rotate away from the initial chain axes. With a strong enough field, the particles can be rotated far enough to prevent their magneto-dipolar attraction along the stretching direction. Then, there are no magnetic bonding forces in the chain-like aggregates in the first place. This deactivates the detachment mechanism and the superelastic behavior, see the orange curve in Fig. 1.3 (right).

Let us now move to the aforementioned *free* systems, where the magnetic moments can freely reorient with respect to their carrying particles. As an experimental realization for this type, we think, for instance, of magnetically unblocked nanoparticles. Core-shell particles with a rotatable magnetic core [253, 254] should have a similar behavior. Finally, we also suppose that particles embedded into a matrix environment under slip surface conditions with little rotational friction [68, 69, 197, 202] are adequately modeled by our *free* systems.

In the *free* system, the unconstrained magnetic moment of each particle tends to align as set by the magnetic field, imposed by its nearest neighbors, to assume the energetically most favorable configuration. Thus, we observed a slightly different initial state than in the *covalent* system, see Fig. 1.4 (bottom left). Within each individual chain, the particles can find their nearest neighbors along the chain axis, causing their magnetic moments to align parallel to the stretching direction. However, separate chains can show an opposing alignment of their magnetic moments. Still, the prerequisites for the detachment mechanism, i.e., strong magneto-dipolar attractions between chain segments along the axis of the imposed strain, are met. We evaluated the uniaxial stress-strain behavior analogously to above. The superelastic plateau that we observed in the *free* system in the absence of an external magnetic field, see the black curve in Fig. 1.4 (right), had a different appearance than the one in the *covalent* system though.

We could relate this to the strain-induced *flipping* mechanism of the unconstrained magnetic moments. When an increasing imposed strain pulls the chains apart, the distance between nearest-neighboring particles within the chains increases. At the same time, the approximate incompressibility of the sample brings separate chainlike aggregates closer to each other in the direction perpendicular to the stretching direction. For some particles, the direction in which they can find their nearest neighbor eventually changes from parallel to the stretching direction to perpendicular to it. At this point, it becomes energetically favorable for their magnetic moments to likewise flip from parallel to the chain axes to perpendicular. During such flip events, a magneto-dipolar attraction between the involved particles in the stretching direction is turned into an attraction perpendicular to it. The former impedes an overall sample elongation, while the latter supports it. Thus, flip events are associated with drops in the stress-strain curve and contribute to the superelastic behavior. Actually, we found that flip events and detachment events mostly occur simultaneously in the *free* system. Note how in the strained state, depicted in Fig. 1.4 (top left), the regions, where the material is both flipped and detached and those, where no transition has occurred yet, can be clearly distinguished.

The strain-induced reorientation of the magnetic moments also leads to a pronounced hysteresis. At high strains, the particles with flipped magnetic moments brought together from different chains strongly attract each other in the direction perpendicular to the imposed strain. When unloading the sample, magnetic energy barriers have to be overcome to detach them from this state so that the loading and unloading curves differ. In any case, the flipped state is completely unstable without an applied load so that the initial state is recovered at the end of the stress-strain cycle.

Due to the easy reorientation of magnetic moments, the *free* system is quite



Figure 1.4.: As Fig. 1.3, but for the *free* system. The magnetic moments prefer a head-to-tail alignment to each nearest neighbor of the carrying particle. Therefore, in the initial state (bottom left), the magnetic moments are mainly aligned with the chain axes. However, different chains can have opposite alignment. When the sample is stretched, the particles are gradually detached from the chains and their magnetic moments flip from parallel to the chain axes to perpendicular (top left). The additional flipping mechanism in the *free* system leads to a different appearance of the superelastic stress-strain behavior (black curve) than in the *covalent* system. There is also a much more pronounced hysteresis. With a magnetic field applied parallel to the stretching direction (green curve), the reorientation mechanism can be deactivated. With a field perpendicular to the chains (orange curve), superelasticity can be switched off completely. Reproduced from Ref. [118] (Online graphical abstract) with permission from the PCCP Owner Societies.

susceptible to applied magnetic fields, see the colored curves in Fig. 1.4 (right). An applied magnetic field parallel to the chain axes creates a state of uniform magnetization in this direction and deactivates the flipping mechanism. The stress-strain behavior then resembles the one of the *covalent* system without an external field. Applied perpendicular to the chain-like aggregates, the external magnetic field can relatively easily rotate the magnetic moments away from the chain axes and, thereby, also deactivate the detachment mechanism. Switching the superelasticity off in this way requires a much lower field strength than in the *covalent* system, see the different scales in Fig. 1.3 and Fig. 1.4.

In conclusion, we demonstrated with our numerical studies in Paper IV and Paper V that the non-linear stress-strain behavior of magnetic elastomers is not only strongly tunable by magnetic fields, but also shows exceptional features known from other smart materials. We performed our numerical simulations with permanent magnetic particles. However, our results should also hold for magnetically soft particles. In a strong applied magnetic field that magnetizes them up to saturation, the behavior should be similar to our *free* system. This would additionally open up the opportunity to tune the overall magnitude of magnetization from outside and control the superelasticity in this way.

To experimentally realize our systems, relatively strong magnetic interaction compared to the elastic interactions are required. This means that the volume magnetization M of the particles should be preferably high while the elastic modulus E of the embedding polymer matrix should be low. For the parameters we assumed in Paper IV and Paper V and a given M, this implies a polymer matrix fulfilling  $E \leq \mu_0 \pi M^2/225$ . Filling in the typical volume magnetizations achievable by the commonly used ferromagnetic filler materials mentioned in Sec. 1.1.2, we obtain  $E \leq 3.5$  kPa for superparamagnetic magnetite,  $E \leq 11$  kPa for magnetically hard neodynium-iron-boron, and  $E \leq 45$  kPa for magnetically soft carbonyl-iron, respectively. Many existing experimental realizations meet these requirements [80, 87, 114, 180].

### 1.4.2. Shape-memory effects

In fact, experiments on isotropic magnetically soft elastomers have already demonstrated a different, but perhaps related, exceptional stress-strain characteristic [113– 116]. There magnetically controlled shape-memory effects have been observed. Shapememory [11] can provide a material with the fascinating ability to recover from a plastic deformation when a suitable stimulus is applied, see Fig. 1.5 for an illustration of a typical stress-strain cycle. The proposed mechanism [116] shows quite some analogies to the detachment mechanism we have described above in the context of superelasticity.

When a magnetic field is applied to a sample, the magnetic particles begin to attract each other and form small clusters and chains oriented in the direction of the magnetic field [114, 163, 181]. These clusters remain stable under small imposed loads due to their strong magnetic interactions at close distances [160, 168, 173], see the initial regime in Fig. 1.5. Under an enhanced load, however, the magnetic energy barriers holding the clusters together can be overcome. Then, they rearrange into larger, more elongated clusters that are still oriented in the direction of the applied field. This restructuring process characterizes the plateau in Fig. 1.5.

After the load is removed, the larger, elongated clusters still remain mostly stable. The strong magnetic bonding forces between the close particles dominate the elastic restoring forces exerted by the strained polymer matrix [160, 168, 173]. Thus, the composite retains an overall strain in the direction of the clusters even after the load is removed. However, deactivating the magnetizing field switches off the magnetic interactions. In this way, the strain can be recovered as the elastic memory of the polymer matrix drives the particles back to their initial positions. Finally, reactivation of the magnetic field restores the initial state of small magnetic particle clusters.



Figure 1.5.: Typical stress-strain cycle for shape-memory alloys as well as for the shape-memory effect observed for some isotropic magnetic elastomers. For small loads, there is an initial elastic regime  $(1 \rightarrow 2)$  of recoverable deformation. Increasing the load further leads to an internal restructuring of the material  $(2 \rightarrow 3)$ , which remains as a plastic deformation when the load is removed  $(3 \rightarrow 4)$ . A suitable stimulus, however, renders the acquired structure unstable and allows to recover the initial state  $(4 \rightarrow 1)$ . In shape-memory alloys, this stimulus corresponds to heating and subsequent cooling. In magnetic elastomers, a deactivation and subsequent reactivation of the magnetizing field restores the initial structure.

These processes are to some degree similar to the transitions that enable the shape recovery in several shape-memory alloys [11, 12, 14]. At lower temperatures, these metallic compounds possess a heterogeneous structure characterized by differently oriented domains of the low-symmetry elongated lattice phase. Put under stress, the different elongated crystalline domains align irreversibly and accommodate a plastic deformation. Heating, however, induces a phase transition to the high-symmetry parent phase and renders the elongated structure unstable, reversing the plastic strain. After subsequent cooling, the low-symmetry phase forms again in differently oriented domains, which completes the cycle, see again Fig 1.5.

## 1.5. Statistical description

As discussed in Sec. 1.3.1, the particle distribution within real samples is typically not regular, which can qualitatively impact the material bulk behavior [99, 114, 149, 150]. To obtain accurate results, some mesoscopic particle-resolved modeling and simulation approaches, therefore, included experimentally realistic distributions from real samples as an input [150, 158, 161, 180] or generated them from a simulation of a magnetic liquid [163, 172, 255].

However, in macroscopic material models it is clearly not feasible to resolve individual particles. Still, there are ways to introduce the mesoscopic interactions into such models, such as treating them within a mean-field approximation [166, 176, 179].

There, the influence of the embedded particles on a piece of the bulk material is obtained by performing a statistical average of their mesoscopic contributions. The input into these models is given by the distribution functions, that statistically characterize the particle arrangement, as well as the form of the particle interactions. The output are bulk material properties, which are key when designing materials for specific applications.

### 1.5.1. Characterization of experimental particle distributions

This was in part the motivation for the statistical characterization of experimental samples which we performed in **Paper VII**. The samples were typical magneto-rheological elastomers of polydisperse carbonyl-iron particles (average diameter ~  $45 \,\mu\text{m}$ ) embedded in a silicone elastic matrix. An X-ray tomographic set-up [62,196,225] allowed imaging of the magnetic particles that were embedded within cylindrical samples with filler contents of 2–15 wt% (0.27–2.32 vol%).

We analyzed both anisotropic and isotropic samples. The anisotropic samples were cured within a homogeneous external magnetic field of amplitude B = 270 mT applied along the cylinder axis. Using an image processing software, we extracted the particle positions, shapes, and sizes from the X-ray tomograms of the finalized samples. It was also possible to create tomograms of samples while placed into a homogeneous magnetic field of strength B = 270 mT, applied parallel to the cylinder axis. This allowed us to characterize the field-induced changes in the particle distributions as well.

We presumed that the particle distributions of the isotropic samples in the absence of an external magnetic field have a radial symmetry. Thus, it was feasible to statistically



Figure 1.6.: Results for an isotropic sample with a filler content of 15 wt%, subject to an external magnetic field of magnitude B = 270 mT applied along the axial direction of the overall cylindrical shape. (a) The cylindrical distribution function  $g(r_{\parallel}, r_{\perp})$  shows a pronounced peak at an axial distance  $r_{\parallel}$  from the origin, indicating mainly the formation of clusters containing small particle numbers oriented in that direction. (b) Visualization of individual particles moving in the sample and forming chains when the magnetic field is activated. Reproduced from Ref. [181]. ©2017 IOP Publishing Ltd.

characterize them by the radial distribution function [256, 257]

$$g(r) = \frac{V}{4\pi r^2 N^2} \left\langle \sum_{i} \sum_{j \neq i} \delta(r - |\mathbf{r}_j - \mathbf{r}_i|) \right\rangle, \qquad (1.11)$$

which is proportional to the probability density of finding any two particles i, j in the sample at a separation r. Here  $\mathbf{r}_i = (x_i, y_i, z_i)$  and  $\mathbf{r}_j = (x_j, y_j, z_j)$  denote their respective positions, N is the total number of particles in the sample of volume V,  $\delta$  is the Dirac delta function, and  $\langle \cdot \rangle$  the ensemble average. The radial distribution function g(r) is normalized with the probability density of finding two particles at a separation r in the ideal gas. Therefore, g(r) = 1 for large distances, as the correlation between two particles eventually gets lost. Without a magnetizing external field, we expect the particles to be essentially randomly distributed within the isotropic samples. We were able to confirm this suspicion by comparing the radial distribution functions of the measured samples with those of ensembles of randomly distributed polydisperse hard spheres, finding good agreement.

Upon activating the external magnetic field along the cylinder axis, small chain-like

clusters oriented along the direction of the field formed inside the composite. Hence, the particle distributions changed from radially symmetric to cylindrically symmetric. We afterwards had to distinguish the directions  $r_{\parallel}$  parallel to the cylinder axis (the z-axis) and  $r_{\perp}$  perpendicular to it and characterized the probability to find two particles at such distances by a cylindrical distribution function [163]

$$g(r_{\parallel}, r_{\perp}) = \frac{V}{4\pi r_{\perp} N^2} \left\langle \sum_{i} \sum_{j \neq i} \delta(r_{\parallel} - |z_j - z_i|) \delta(r_{\perp} - \sqrt{(x_j - x_i)^2 + (y_j - y_i)^2}) \right\rangle.$$
(1.12)

In analogy to the radial distribution function, it provides the probability to find two particles at a distance  $r_{\parallel}$  and  $r_{\perp}$  parallel and perpendicular to the cylinder axis, respectively, normalized by this probability in the ideal gas. Figure 1.6 shows this distribution function for an initially isotropic sample (15 wt%) as well as a visualization of the chain formation upon application of the magnetic field. The cylindrical distribution function shows a pronounced peak at a distance of around one particle diameter in the axial direction. This mainly indicates that small groups of particles cluster and align in that direction to minimize their magnetic interaction energy. Further analysis revealed that the fraction of clustered particles and the size of these small chain-like clusters increased with the total particle fraction [54]. With these results, we provided direct evidence for the cluster formation in isotropic magnetic elastomers under the action of a magnetic field.

The anisotropic samples displayed characteristic percolating chain-like aggregates aligned with the cylinder axes. We observed that the chain morphologies strongly varied for different filling fractions of the samples [62, 223]. At low filling fractions, slender and straight chain-like aggregates formed. The corresponding samples showed a slow decay of  $g(r_{\parallel}, r_{\perp})$  in the axial direction  $r_{\parallel}$  and a fast decay in the perpendicular direction  $r_{\perp}$ . With increasing particle content, the chain-like aggregates grew thicker and less ordered, with more of a clustered and branched structure. For the distribution function  $g(r_{\parallel}, r_{\perp})$ , this means a faster decay in the axial direction  $r_{\parallel}$  and a slower one in the perpendicular direction  $r_{\perp}$ . Since the particles were concentrated in the chains, there were large voids in-between where practically no particles resided.

The overall number of chain-like aggregates in the anisotropic samples was a nonmonotonous function of the particle content. With increasing filler concentration, the slender chains first became more numerous, but then combined to a smaller number of broader, branched chain-like aggregates.

In total, we have developed a combined tool to characterize the particle distributions in experimental samples, using X-ray tomography and statistical analysis. In this way, we showed how the formation of chains in magnetic elastomers influences the appearance of the particle distribution functions. This might serve as an input for future statistical theories, or as a reference for other experiments.

## 1.5.2. Density functional theory

Finally, in **Paper VI**, we actually pursued a statistical mechanical description [258, 259] of magnetic elastomers. More precisely, we developed a framework to apply density functional theory (DFT) [260] to these materials and benchmarked our approach using particle-resolved Monte-Carlo simulations. Usually, density functional theory is employed to describe phenomena in ensembles of indistinguishable particles [260–262]. In these systems, the particles interact via a pair potential  $u(\mathbf{r})$  with an interaction strength that depends only on the separation  $\mathbf{r}$  between the two respective particles. In magnetic elastomers, on the contrary, the particles are typically firmly embedded into the elastic network. Their mutual elastic interactions are dictated by their reference positions within the embedding matrix environment, which makes them distinguishable.

We demonstrated that a statistical mechanical description can still be made feasible for these systems by mapping them to ensembles of indistinguishable particles. To this end, we considered a one-dimensional dipole-spring model for a magnetic elastomer [160], as sketched and described in detail in Fig. 1.7. In short, the particle interaction



Figure 1.7.: Simple one-dimensional dipole-spring model for a magnetic elastomer. The system is bounded by two outer particles (blue) at a fixed separation L, while all other particles in between (dark gray) are mobile. All particles have hard cores of diameter d, carry magnetic dipole moments  $\mathbf{m} = m\hat{\mathbf{x}}$  aligned with the system axis  $\hat{\mathbf{x}}$ , and, finally, are connected to their immediate neighbors by harmonic springs of spring constant k and equilibrium length  $\ell$ . Reproduced from Ref. [174]. ©2017 IOP Publishing Ltd.

energies have three sources: the hard cores of the particles, the magnetic dipolar moments aligned with the system axis, and, finally, the harmonic springs connecting each particle with its immediate neighbors. The hard core and magnetic interactions are expressible as sums over pairwise interactions  $u_h(x)$  and  $u_m(x)$ , respectively, and, therefore, treat the particles as interchangeable. In contrast, the harmonic springs specifically connect certain pairs of particles and, as a result, render the particles distinguishable.

We mapped this system by replacing the spring connectivity between immediate neighbors with the approximative "pseudo-spring" pair interaction  $\tilde{u}_{e}(x)$ , illustrated in Fig. 1.8. The basic idea is to use a harmonic well to mimic the springs between pairs of immediate neighbors. In one spatial dimension under hard-core repulsions, it



Figure 1.8.: Pseudo-spring pair interaction as approximation for the real-spring connectivity between immediate neighbors. The spring is mimicked by a harmonic well of spring constant  $k = 40 k_B T/d^2$ , centered around a pair distance  $x = \ell = 1.5d$ . The well is cut off and shifted to zero at a distance x = 2d to restrict the interaction to pairs of immediate neighbors. In the configuration sketched on the left, the pseudo-spring interaction between a particle (blue) and its immediate neighbor (red) is active since both are at a distance x < 2d (red). On the right, the distance is too large ( $x \ge 2d$ ) so that the interaction is inactive and the pseudo-spring effectively "breaks". Particle pairs that are not immediate neighbors can never interact because they are always at a distance  $x \ge 2d$ . Reproduced from Ref. [174]. ©2017 IOP Publishing Ltd.

is guaranteed that two particles at a distance x < 2d are immediate neighbors, with d the hard-core diameter. In a spring model, they would be connected by elastic springs. Thus, the harmonic interactions can be restricted to nearest neighbors by cutting and shifting the well to zero potential strength at  $x \ge 2d$ . The difference to the "real" springs in Fig. 1.7 is that the "pseudo-springs" can break at a separation  $x \ge 2d$ . Accordingly, we expect good agreement between the real-spring and the pseudo-spring systems at a sufficiently high density and strong elastic particle–particle interactions when the breaking of pseudo-springs is unlikely. The comparison with Monte-Carlo (MC) computer simulations for both systems confirmed our expectation.

The above mapping allowed us to develop a mean-field DFT for the pseudo-spring system. We numerically minimized the grand canonical free energy functional

$$\Omega[\rho] = \mathcal{F}[\rho] + \int_0^L \rho(x) \left( U_{\text{ext}}(x) - \mu \right) dx \qquad (1.13)$$

with respect to the one-body density profile  $\rho(x)$ . Here  $U_{\text{ext}}(x)$  is an external potential and  $\mu$  the chemical potential of a particle reservoir to which the system is in contact. As a free energy functional  $\mathcal{F}[\rho]$  we used the combination

$$\mathcal{F}[\rho] = \mathcal{F}_{id}[\rho] + \mathcal{F}_{ex}^{P}[\rho] + \mathcal{F}_{ex}^{MF}[\rho]. \qquad (1.14)$$

Here the first term is the ideal gas functional. The second one is the Percus excess functional [263] which exactly accounts for the hard-core interactions. Finally, the mean-field contribution

$$\mathcal{F}_{\rm ex}^{\rm MF}[\rho] = \int_0^L \int_0^L \left( \tilde{u}_{\rm e}(|x-x'|) + u_{\rm m}(|x-x'|) \right) g(|x-x'|) \rho(x) \rho(x') \, dx' \, dx \,, \quad (1.15)$$

includes the pairwise pseudo-spring and dipolar magnetic interactions. For the distribution function, we used the simple approximation that g(x) = 0 for x < d and g(x) = 1 for  $x \ge d$ . The minimization yielded the equilibrium density profile and grand canonical free energy. This allowed us to calculate the pressure and the compression modulus as key thermodynamic quantities of our magnetic elastomer model.

Thermal fluctuations have a particularly strong impact in one spatial dimension. They can escalate into long-ranged fluctuations and drive the well-known Landau-Peierls instability [264–266], which can destroy periodic ordering in lower dimensions. However, these thermal fluctuations are only incompletely represented in our mean-field DFT. This resulted in an artificial crystallization in the density profile at low temperatures [267–270] that could not be observed in our MC simulations. Considering higher temperatures allowed us to obtain at least qualitative agreement with the pseudo-spring MC simulations. Substantial agreement with real-spring MC simulations could not be achieved though, due to the frequent breaking of pseudo-springs under these conditions.

Within an extended dipole-spring model, we achieved much better agreement between DFT and MC simulations. This model is sketched and described in Fig. 1.9 and represents a chain of magnetic particles embedded into a three-dimensional elastic matrix. For each particle, there is a pinning spring representing the restoring force that the matrix exerts when the particle is displaced against it [158, 159, 271, 272]. Between each pair of particles, there are connecting springs with a spring constant that decays with the initial distance between the pair. Those springs can be motivated by considering the matrix-mediated force that two embedded particles feel when they are symmetrically displaced against each other, see Paper VI for details.

To treat this extended model using DFT, we again replaced the real springs with pseudo-springs. Instead of the pinning springs, we used a series of harmonic wells as an external potential  $U_{\text{ext}}(x)$ . To represent the effect of the connecting springs with decaying spring constants by a pair potential  $\tilde{u}_{e}(x)$ , we mapped them to a series of harmonic wells that reflect the springs of strength decaying with the spring length.

The Landau-Peierls instability can be counteracted by such a stronger coupling [273] and periodic structures become a physically valid result also in one spatial dimension [267–270]. Consequently, we achieved good agreement between DFT and MC simulations, even when using the real spring connectivity for the latter. Figure 1.10 demonstrates this for the density profiles for vanishing magnetic moment m. But also for thermodynamic quantities like the pressure and the compression



Figure 1.9.: Extended dipole-spring model for a chain of magnetic particles embedded into a three-dimensional elastic matrix. The initial spacing between the embedded particles is  $\ell$ . Springs of spring constant  $k_{\rm mp}$  represent the embedding into the elastic matrix and pin the particles to their initial positions. The matrix also mediates elastic particle-particle interactions. This is represented by harmonic springs with a spring constant that decays with the initial distance between the particles. The springs connecting nearest neighbors have an equilibrium length of  $\ell$  and a spring constant  $k_{\rm pp} = \frac{3d}{8\ell}k_{\rm mp}$ . For next-nearest neighbors at initial separation  $2\ell$ , the spring constant is  $k_{\rm pp}/2$ . Thereafter, the equilibrium length is  $3\ell$  and the spring constant  $k_{\rm pp}/3$ , and so forth. As in Fig. 1.7, all particles have hard cores of diameter d and carry magnetic dipole moments of magnitude m aligned with the chain axis. Reproduced from Ref. [174]. ©2017 IOP Publishing Ltd.



Figure 1.10.: Density profiles obtained for the extended dipole-spring model for the case of zero magnetic moments. The density peaks are sharply peaked around the pinning positions of the particles. Good agreement between DFT, pseudo-spring MC simulations, and real-spring MC simulations can be achieved. Reproduced from Ref. [174]. ©2017 IOP Publishing Ltd.

modulus as a function of the magnetic moment we found good quantitative agreement between DFT and MC.

In conclusion, we have shown that the mapping of distinguishable bead-spring models to ensembles of indistinguishable particles and subsequent description by tools of statistical mechanics works reasonably well. This also opens the possibility for other statistical mechanical treatments of magnetic elastomers, see the supplemental material of Paper VI for an approach using liquid integral theory [258].

# Chapter 2.

# **Peer-reviewed publications**

In the following, the peer-reviewed papers that constitute the scientific content of this cumulative thesis are provided as a reference. As a supplement to each paper, I give a detailed breakdown of my individual contribution to the scientific work.

## Paper I. Structural control of elastic moduli in ferrogels and the importance of non-affine deformations

G. Pessot, P. Cremer, D. Y. Borin, S. Odenbach, H. Löwen, and A. M. Menzel, Structural control of elastic moduli in ferrogels and the importance of non-affine deformations, I. Chem. Phys. 141, 124004 (2014)

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## Statement of contribution

AMM, HL, and SO supervised the work. GP performed the numerical calculations and evaluation of the results. DYB and SO provided the experimental input data. I extracted input for the model calculations from these experimental data using Delaunay triangulation. I estimate my overall contribution to this work to be around 10%.

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THE JOURNAL OF CHEMICAL PHYSICS 141, 124904 (2014)

### Structural control of elastic moduli in ferrogels and the importance of non-affine deformations

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One of the central appealing properties of magnetic gels and elastomers is that their elastic moduli can reversibly be adjusted from outside by applying magnetic fields. The impact of the internal magnetic particle distribution on this effect has been outlined and analyzed theoretically. In most cases, however, affine sample deformations are studied and often regular particle arrangements are considered. Here we challenge these two major simplifications by a systematic approach using a minimal dipole-spring model. Starting from different regular lattices, we take into account increasingly randomized structures, until we finally investigate an irregular texture taken from a real experimental sample. On the one hand, we find that the elastic tunability qualitatively depends on the structural properties, here in two spatial dimensions. On the other hand, we demonstrate that the assumption of affine deformations leads to increasingly erroneous results the more realistic the particle distribution becomes. Understanding the consequences of the assumptions made in the modeling process is important on our way to support an improved design of these fascinating materials. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4896147]

#### I. INTRODUCTION

In the search of new materials of outstanding novel properties, one route is to combine the features of different compounds into one composite substance.<sup>1–5</sup> Ferrogels and magnetic elastomers provide an excellent example for this approach. They consist of superparamagnetic or ferromagnetic particles of nano- or micrometer size embedded in a crosslinked polymer matrix.<sup>6</sup> In this way, they combine the properties of ferrofluids and magnetorheological fluids<sup>7–16</sup> with those of conventional polymers and rubbers:<sup>17</sup> we obtain elastic solids, the shape and mechanical properties of which can be changed reversibly from outside by applying external magnetic fields.<sup>6,18–25</sup>

This magneto-mechanical coupling opens the door to a multitude of applications. Deformations induced by external magnetic fields suggest a use of the materials as soft actuators<sup>26</sup> or as sensors to detect magnetic fields and field gradients.<sup>27,28</sup> The non-invasive tunability of the mechanical properties by external magnetic fields makes them candidates for the development of novel damping devices<sup>29</sup> and vibration absorbers<sup>19</sup> that adjust to changed environmental conditions. Finally, local heating due to hysteretic remagnetization losses in an alternating external magnetic field can be achieved. This effect can be exploited in hyperthermal cancer treatment.<sup>30,31</sup>

In recent years, several theoretical studies were performed to elucidate the role of the spatial magnetic particle distribution on these phenomena.<sup>23,32–42</sup> It turns out that the particle arrangement has an even qualitative impact on the effect that external magnetic fields have on ferrogels. That

is, the particle distribution within the samples determines whether the systems elongate or shrink along an external magnetic field, or whether an elastic modulus increases or decreases when a magnetic field is applied. As a first step, many of the theoretical investigations focused on regular lattice structures of the magnetic particle arrangement. 32, 36, 42 Meanwhile, it has been pointed out that a touching or clustering of the magnetic particles and spatial inhomogeneities in the particle distributions can have a major influence.<sup>23,35,39–41,43</sup> More randomized or "frozen-in" gas-like distributions were investigated.<sup>23,33–35,38,40</sup> Yet, typically in these studies an affine deformation of the whole sample is assumed, i.e., the overall macroscopic deformation of the sample is mapped uniformly to all distances in the system. An exception is given by microscopic<sup>37</sup> and finite-element studies,<sup>23,35,41</sup> but the possible implication of the assumption of an affine deformation for non-aggregated particles remains unclear from these investigations.

Here, we systematically challenge these issues using the example of the compressive elastic modulus under varying external magnetic fields. We start from regular lattice structures that are more and more randomized. In each case, the results for affine and non-affine deformations are compared. Finally, we consider a particle distribution that has been extracted from the investigation of a real experimental sample. It turns out that the assumption of affine deformations growingly leads to erroneous results with increasingly randomized particle arrangements and is highly problematic for realistic particle distributions.

In the following, we first introduce our minimal dipolespring model used for our investigations. We then consider

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#### 124904-2 Pessot et al.

different lattice structures: rectangular, hexagonal, and honeycomb, all of them with increasing randomization. Different directions of magnetization are taken into account. Finally, an irregular particle distribution extracted from a real experimental sample is considered, before we summarize our conclusions.

#### **II. DIPOLE-SPRING MINIMAL MODEL**

For reasons of illustration and computational economics, we will work with point-like particles confined in a twodimensional plane with open boundary conditions. On the one hand, we will study regular lattices, for which simple analytical arguments can be given to predict whether the elastic modulus will increase or decrease with increasing magnetic interaction. These lattices will also be investigated after randomly introducing positional irregularities. Such structures could reflect the properties of more realistic systems, for example, those of thin regularly patterned magnetic block-copolymer films.<sup>44,45</sup>

On the other hand, irregular particle distributions in a plane to some extent reflect the situation in three dimensional anisotropic magnetic gels and elastomers.<sup>47–52</sup> In fact, our example of irregular particle distribution is extracted from a real anisotropic experimental sample. These anisotropic materials are manufactured under the presence of a strong homogeneous external magnetic field. It can lead to the formation of chain-like particle aggregates that are then "locked-in" during the final crosslinking procedure. These chains lie parallel to each other along the field direction and can span the whole sample.<sup>50</sup> To some extent, the properties in the plane perpendicular to the anisotropy direction may be represented by considering the two-dimensional cross-sectional layers on which, in this work, we will focus our attention.

Our system is made of  $N = N_x \times N_y$  point-like particles with positions  $\mathbf{R}_i$ , i = 1...N, each carrying an identical magnetic moment m. That is, we consider an equal magnetic moment induced for instance by an external magnetic field in the case of paramagnetic particles, or an equal magnetic moment of ferromagnetic particles aligned along one common direction. We assume materials in which the magnetic particles are confined in pockets of the polymer mesh. They cannot be displaced with respect to the enclosing polymer matrix, i.e., out of their pocket locations. Neighboring particles are coupled by springs of different unstrained length  $l_{ii}^0$  according to the selected initial particle distribution. All springs have the same elastic constant k. The polymer matrix, represented by the springs, is assumed to have a vanishing magnetic susceptibility. Therefore, it does not directly interact with magnetic fields. (The reaction of composite bilayered elastomers of non-vanishing magnetic susceptibility to external magnetic fields was investigated recently in a different study<sup>46</sup>).

The total energy U of the system is the sum of elastic and magnetic energies<sup>43,53,54</sup>  $U_{el}$  and  $U_m$  defined by

$$U_{el} = \frac{k}{2} \sum_{\langle ij \rangle} \left( r_{ij} - l_{ij}^0 \right)^2, \tag{1}$$

J. Chem. Phys. 141, 124904 (2014)

where  $\langle ij \rangle$  means sum over all the couples connected by springs,  $\mathbf{r}_{ii} = \mathbf{R}_i - \mathbf{R}_i$ ,  $r_{ii} = |\mathbf{r}_{ii}|$  and

$$U_m = \frac{\mu_0 m^2}{4\pi} \sum_{i < j} \frac{r_{ij}^2 - 3(\hat{\boldsymbol{m}} \cdot \boldsymbol{r}_{ij})^2}{r_{ij}^5},$$
 (2)

where i < j means sum over all different couples of particles, and  $\widehat{\boldsymbol{m}} = \boldsymbol{m}/\boldsymbol{m}$  is the unit vector along the direction of  $\boldsymbol{m}$ . In our reduced units, we measure lengths in multiples of  $l_0$  and energies in multiples of  $kl_0^2$ ; here we define  $l_0 = 1/\sqrt{\rho}$ , where  $\rho$  is the particle area density. To allow a comparison between the different lattices we choose the initial density always the same in each case. Furthermore, our magnetic moment is measured in multiples of  $m_0 = \sqrt{4\pi k^2 l_0^{-5}/\mu_0}$ .

Estimative calculations show that the magnetic moments obtainable in real systems are 4–5 orders of magnitude smaller than our reduced unit for the magnetic moment, so only the behavior for the rescaled  $|\mathbf{m}|/m_0 = m/m_0 \ll 1$  would need to be considered. Here, we run our calculations for *m* as big as possible, until the magnetic forces become so strong as to cause the lattice to collapse, which typically occurs beyond realistic values of *m*. After rescaling, the magnetic moment *m* is the only remaining parameter in our equations which can be used to tune the system for a given particle distribution.

#### III. ELASTIC MODULUS FROM AFFINE AND NON-AFFINE TRANSFORMATIONS

We are interested in the elastic modulus E for dilative and compressive deformations of the system, as a function of varying magnetic moment and lattices of different orientations and particle arrangements. For a fixed geometry and magnetic moment m, once we have found the equilibrium state of minimum energy of the system, we calculate E as the second derivative of total energy with respect to a small expansion/shrinking of the system, here in x-direction:

$$E = \frac{d^2 U}{d\delta_x^2} \simeq \frac{U(-\delta_x) + U(\delta_x) - 2U(0)}{\delta_x^2}.$$
 (3)

 $\delta_x$  is a small imposed variation of the sample length along  $\hat{x}$ . In order to remain in the linear elasticity regime,  $\delta_x$  must imply an elongation of every single spring by a quantity small compared to its unstrained length. In our calculations, we chose a total length change of the sample of  $\delta_x = L_x/100\sqrt{N} \simeq l_0/100$  throughout, where  $L_x$  is the equilibrium length of the sample along  $\hat{x}$ . Thus, on average, each spring is strained along  $\hat{x}$  by less than 1%. To indicate the direction of the induced strain, we use the letter  $\varepsilon$  in the figures below. The magnitude of the strain follows as  $|\varepsilon| = \delta_x/L_x \simeq 10^{-4} - 10^{-3}$ . Strains of such magnitude were for example applied experimentally using a piezo-rheometer.<sup>47</sup> A natural unit to measure the elastic modulus *E* in Eq. (3) is given by the elastic spring constant *k*.

There are different ways of deforming the lattices in order to find the equilibrium configuration of the system and calculate the elastic modulus. We will demonstrate that considering non-affine instead of affine transformations can lead

40

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#### 124904-3 Pessot et al.

to serious differences in the results, especially for randomized and realistic particle distributions.

An affine transformation (AT) conserves parallelism between lines and in each direction modifies all distances by a certain ratio. In our case of a given strain in *x*-direction, in AT we obtain the equilibrium state by minimizing the energy over the ratio of compression/expansion in *y*-direction.

In a non-affine transformation (NAT), instead, most of the particles are free to adjust their positions independently of each other in 2D. Only the particles on the two opposing edges of the sample are "clamped" and forced to move in a prescribed way along *x*-direction, but they are free to adjust in *y*-direction. All clamped particles in the NAT are forced to be expanded in the *x*-direction in the same way as in the corresponding AT to allow better comparison (see Fig. 1 for an illustration of the two kinds of deformation). To perform NAT minimization, we have implemented the conjugated gradients algorithm<sup>55,56</sup> using analytical expressions of the gradient and Hessian of the total energy. Numerical thresholds were set such that the resulting error bars in the figures below are significantly smaller than the symbol size.



FIG. 1. An initial square lattice undergoing the same total amount of horizontal strain at vanishing magnetic moment and relaxed through NAT (top) and AT (bottom). Clamped particles are colored in black in the NAT case. The depicted deformations are much larger than the ones used in the following to determine the elastic moduli (here the sample was expanded in *x*-direction by a factor of 2.5).

#### J. Chem. Phys. 141, 124904 (2014)

As a consequence, NAT minimizes energy over  $\simeq 2N$  degrees of freedom. Since the NAT has many more degrees of freedom for the minimization than AT, we expect the former to always find a lower energetic minimum compared to the latter. Thus, for the elastic modulus, we obtain  $E^{\text{AT}} \ge E^{\text{NAT}}$ . Figure 1 shows how NAT and AT minimizations yield different ground states for the same total amount of strain along  $\hat{x}$ .

To compute the elastic modulus, we first find the equilibrium state through NAT for prescribed m. Next, using AT, we impose a small shrinking/expansion and after the described AT minimization obtain  $E^{\text{AT}}$  via Eq. (3). Then, starting from the NAT ground state again, we perform the same procedure using the NAT minimization and thus determine  $E^{\text{NAT}}$ .

#### **IV. RESULTS**

In the following, we will briefly discuss the behavior of the elastic modulus in the limit of large systems. Then, on the one hand, we will demonstrate that introducing a randomization in the lattices dramatically affects the performance of affine calculations. On the other hand, we will investigate how in each case structure and relative orientation of the nearest neighbors determine the trend of E(m).

#### A. Elastic modulus for large systems

We run our simulations for lattices of  $N_x = N_y$ . It is known that the total elastic modulus of two identical springs in series halves, whereas, if they are in parallel doubles, compared to the elastic modulus of a single spring. In our case of determining the elastic modulus in x-direction, the total elastic modulus E will be proportional to  $N_y/N_x$ . Thus, with our choice of  $N_x = N_y$ , it should not depend on N. We will investigate the exemplary case of a rectangular or square lattice for m = 0 to estimate the impact of finite size effects on our results, since a simple analytical model can be used to predict the value of E.

Our rectangular lattice is made of vertical and horizontal springs coupling nearest neighbors and diagonal springs connecting next-nearest neighbors. The diagonal springs are necessary to avoid an unphysical soft-mode shear instability of the bulk rectangular crystal. In the large-N limit, there are on average one horizontal, one vertical, and two diagonal springs per particle. The deformation of a corresponding "unit spring cell" is depicted in Fig. 2.  $b_0$  and  $h_0$  are, respectively, the length of the horizontal and vertical spring of the unit cell in the undeformed state, whereas b and h are the respective



FIG. 2. Minimal rectangular model consisting of one x-oriented, one y-oriented, and two diagonal springs.  $b_0$  and  $h_0$  are the base and height of the rectangular cell in the unstrained state. Under strain,  $b_0 \rightarrow b$  and the height is free to adjust in order to minimize the elastic energy,  $h_0 \rightarrow h$ .

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J. Chem. Phys. 141, 124904 (2014)



FIG. 3.  $E^{\text{NAT}}(m = 0)/k$  for different rectangular lattices increasing the number of particles N. Fits with a power law of the form  $E_N/k = E_{\infty} + \alpha N^{\beta}$  show a convergence towards the finite values indicated in the figure, while the values predicted by Eq. (4) are, (bottom to top curve) 1.154, 1.500, and 2.351. The values of  $\beta$  resulting from the fit are (bottom to top curve) -0.56, -0.55, and -0.54.  $E^{\text{NAT}}(m \neq 0)/k$  show the same convergence behavior for any m.

quantities in the deformed state. *b* is fixed by the imposed strain, whereas *h* adjusts to minimize the energy,  $\partial U/\partial h = 0$ . This model describes, basically, the deformation of a cell in the bulk within an AT framework.

If magnetic effects are neglected, we find that the linear elastic modulus of such a system is

$$E(m=0) \simeq \left. \frac{d^2 U_{el}}{db^2} \right|_{b=b_0} = k \left( 1 + \frac{2r_0^2}{3 + r_0^2} \right).$$
(4)

Here  $r_0 = b_0/h_0$  is the base-height ratio of the unstrained lattice. Furthermore, we have linearized the h(b) deformation around  $b = b_0$ .

In the limit of large *N*, the elastic modulus determined by NAT should be dominated by bulk behavior. For regular rectangular lattices stretched along the outer edges of the lattice cell, the deformation in the bulk becomes indistinguishable from an affine deformation. We therefore can use our analytical calculation to test whether our systems are large enough to correctly reproduce the elastic modulus of the bulk. For this regular lattice structure, it should correspond to the modulus following from Eq. (4). We calculated numerically  $E^{\text{NAT}}(m = 0)$  for different rectangular lattices as a function of *N* and plot the results in Fig. 3. Indeed, for large *N*, we find the convergence as expected.

From Fig. 3, we observe that the modulus has mostly converged to its large-*N* limit at N = 400, therefore most of our calculations are performed for N = 400 particles. We have checked numerically that a similar convergence holds for any investigated choice of *m* and lattice structure. For any  $m \neq 0$  that we checked, we found a similar convergence behavior as the one depicted for m = 0 in Fig. 3.

#### B. Impact of lattice randomization on AT calculations

We have seen how, in the large-*N* limit, AT analytical models and NAT numerical calculations converge to the same result in the case of regular rectangular lattices. In fact, we expect AT to be a reasonable approximation in this regular lattice case, since it conserves the initial shape of the lattice. For symmetry reasons, this behavior may be expected also for NAT at small degrees of deformation. But how does AT perform in more realistic and disordered cases where the initial particle distribution can be irregular? To answer this question we will consider the difference  $E^{\text{AT}} - E^{\text{NAT}}$ , the elastic modulus numerically calculated with AT and NAT, at m = 0, for different and increasingly randomized lattices.

We have considered a rectangular lattice with diagonal springs, a hexagonal lattice with horizontal rows of nearest neighbor springs, one with vertical rows, and a honeycomb lattice with springs beyond nearest neighbors (as depicted in Fig. 4).

To obtain the randomized lattices, we start from their regular counterparts and randomly move each particle within a square box of edge length  $\overline{\eta}$  and centered in the regular lattice site. We call  $\overline{\eta}$  the randomization parameter used to quantify the degree of randomization. In our numerical calculations, we increased  $\overline{\eta}$  up to  $\overline{\eta} = 0.375l_0$ . This is an appreciable degree of randomization considering that at  $\overline{\eta} = l_0$  two nearest neighbors in a square lattice may end up at the same location. To average over different realizations of the randomized lattices, we have performed 100 numerical runs for every initial regular lattice and every chosen value of  $\overline{\eta}$ . In Fig. 4, we plot the relative difference between  $E^{\text{AT}}$  and  $E^{\text{NAT}}$ .

Already for the regular lattices of vanishing randomization  $\overline{\eta} = 0$ , we find a relative deviation of  $E^{\text{AT}}$  from  $E^{\text{NAT}}$  in

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#### 124904-5 Pessot et al.

J. Chem. Phys. 141, 124904 (2014)



FIG. 4. Different lattices for m = 0 with the initial unstrained state randomized by displacing each particle by  $(\eta_1, \eta_2)$ , where  $\eta_1, \eta_2$  are stochastic variables uniformly distributed in  $[-\overline{\eta}/2, \overline{\eta}/2]$ . Each point in this figure is obtained averaging over 100 different realizations of random distributions generated from the same starting regular lattice. Error bars were obtained from the resulting standard deviation. We indicate the direction of the applied strain by the double arrow marked by  $\varepsilon$ . The difference in E(m = 0) calculated on the one hand by AT and on the other hand by NAT is plotted in % of  $E^{NAT}(m = 0)$  as a function of an increasing randomization parameter  $\overline{\eta}$ .

the one-digit per-cent regime. This deviation is smallest for the regular rectangular lattice, where the principal stretching directions are parallel to the nearest-neighbor bond vectors. The deviation for  $\overline{\eta} = 0$  increases when we consider instead the hexagonal and honeycomb lattices. Obviously, and this is our main point here, the relative difference between  $E^{\text{AT}}$ and  $E^{\text{NAT}}$  increases for each lattice that we investigated with the degree of randomization  $\overline{\eta}$ . Therefore NAT finds much lower equilibrium states with increasing randomization, and AT leads to erroneous results. So far, however, we could not yet establish a simple rigid criterion that would quantitatively predict the observed differences between AT and NAT.

#### C. The case m // x

We will now consider a non-vanishing magnetic moment  $m // \hat{x}$ . This is parallel to the direction in which we apply the strain in order to measure the elastic modulus. As we will see below, the behavior of the elastic modulus as a function of the magnetic moment E(m) strongly depends on the orientation of m and on the lattice structure. The kind of magnetic interaction between nearest neighbors is fundamental for its impact on the elastic modulus. On the one hand, when the magnetic coupling between two particles in  $U_m$  [see Eq. (2)] is solely repulsive, i.e.,  $m \perp r_{ij}$ , its second derivative is positive and therefore gives a positive contribution to the elastic modulus. On the other hand, when  $m // r_{ij}$  the interaction is attractive and the second derivative of  $U_m$  gives a negative contribution to the elastic modulus.

When *m* is parallel to the strain direction  $\hat{x}$ , the magnetic interaction along  $\hat{x}$  is attractive and, for *m* large enough,

will cause the lattice to shrink and the elastic modulus to decrease. For some cases, though, E(m) shows an initial increasing trend. This happens when in the unstrained lattice the particles are much closer in  $\hat{y}$  than in  $\hat{x}$ . Then, for small deformations, magnetic repulsion is prevalent and the magnetic contribution to *E* is positive, as can be seen for the rectangular case from Fig. 5.

The total energy of the system is the sum of elastic and magnetic energies. Since the derivative is a linear operator, the elastic modulus can be decomposed in elastic and magnetic components:  $E = E_{el} + E_m$ . The analytical calculation for the minimal rectangular system described in Subsection IV A applied to this configuration and considering magnetic interaction up to nearest neighbors only predicts that

$$E_m \simeq \frac{d^2 U_m}{db^2} \bigg|_{b=b_0} = \frac{12m^2}{b_0^5} \left( -2 + \frac{4r_0^7}{(3+r_0^2)^2} \right)$$
(5)

in the rectangular case.

From Eq. (5), we expect a magnetic contribution to the total elastic modulus increasing with *m* for  $r_0 \ge 1.175$  and decreasing with *m* for  $r_0 \le 1.175$ . Qualitatively we observe this trend for  $m/m_0 \ll 1$  in Fig. 5. However, it seems that the initial trend for E(m), i.e., close to the unstrained state, switches from increasing to decreasing around  $r_0 \simeq 1.60$ , higher than we expected. Although the minimal analytical model can predict the existence of a threshold value for  $r_0$  it would need the magnetic contribution of more than only nearest neighbor particles to be more accurate, since the magnetic interaction is long ranged (whereas the elastic interaction acts only on nearest neighbors).

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J. Chem. Phys. 141, 124904 (2014)



FIG. 5. Rectangular lattice with  $m / \hat{x}$ . Different trends of  $E^{\text{NAT}}(m/m_0)$  are shown for different unstrained lattice shapes using the undeformed base-height ratio  $r_0$  as shape parameter. We indicate the direction of the applied strain by  $\varepsilon$ . To compare and enhance the different trends,  $E^{\text{NAT}}(m/m_0)$  is rescaled by  $E^{\text{NAT}}(m = 0)$ .

#### D. The case $m \parallel \hat{y}$

In this orientation of the magnetic moment, the hexagonal lattice case is exemplary, because it shows very well the orientational structural dependence of E(m).

On the one hand, for the hexagonal lattice "horizontally" oriented (see the bottom inset in Fig. 6) there are no nearest neighbors in the attractive direction  $\hat{y}$ ; there are instead two along  $\hat{x}$  whose interaction is purely repulsive, therefore the

second derivative of their interaction  $U_m$  is positive. On the other hand, for the same lattice rotated by  $\pi/2$  (see the top inset in Fig. 6) there are two nearest neighbors in the direction of m and their interaction is strongly attractive; therefore, the second derivative of their interaction  $U_m$  is negative.

The result, as can be seen in Fig. 6, is that in the former case the elastic modulus is increasing and in the latter is decreasing.



FIG. 6. Hexagonal lattice with  $m \not \mid \hat{y}$  for a hexagonal lattice with horizontal rows (bottom inset, where two nearest neighbors are oriented along  $\hat{x}$ ) and for one with vertical rows (top inset, where two nearest neighbors are oriented along  $\hat{y}$ ). We indicate the direction of the applied strain by  $\varepsilon$ . It is remarkable how the magnetic interaction between nearest neighbors and the  $E^{\text{NAT}}(m)$  behavior change when the lattice is rotated by  $\pi/2$ .

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#### 124904-7 Pessot et al.

J. Chem. Phys. 141, 124904 (2014)



FIG. 7. Elastic modulus  $E(m/m_0)/k$  calculated with NAT for  $m / \hat{z}$  for the different lattices shown. We indicate the direction of the applied strain by  $\varepsilon$ . The magnetic interaction is purely repulsive and strengthens the elastic modulus in this configuration.

#### E. The case m // z

In this configuration, the magnetic interactions between our particles are all repulsive and have the form  $m^2/r_{ij}^3$ . The second derivative of the magnetic interparticle energy is always positive along the direction connecting the particles. Therefore, we expect the elastic modulus to be enhanced with increasing *m*, and *E*(*m*) to be a monotonically increasing function. As can be seen from Fig. 7, this is true for all the different lattices we have considered.

We have already seen in Fig. 4 how the randomization of the lattice seriously affects the difference between AT and NAT. For the  $m // \hat{z}$  case, we have also considered a real particle distribution taken from an experimental sample.<sup>50</sup> The real sample was of cylindrical shape with a diameter of about 3 cm. It had the magnetic particles arranged in chain-like aggregates parallel to the cylinder axis and spanning the whole sample. The positions of the particles were obtained through X-ray micro-tomography and subsequent image analysis. We extracted the data from a circular cross-section taken approximately at half height of the cylinder and shown in Fig 8. In this way we consider by our model the physics of one crosssectional plane of the cylindrical sample.

The extracted lattice was used as an input for our dipolespring model. We placed a magnetic particle at the center of each identified spot in the tomographic image, see Fig 8. Guided by the situation in the real sample, the magnetic moments of the particles are chosen perpendicular to the plane (i.e., "along the cylinder axis"). The springs in the resulting lattice are set using Delaunay triangulation<sup>51,57,58</sup> with the particles at the vertices of the triangles and the springs placed at their edges. Then, we cut a square block from the center of the sample containing the desired number of particles. The clamped particles are chosen in such a way that they cover about 10% of the total area (see left inset in Fig. 9).



FIG. 8. Realistic lattice used to determine the elastic modulus as a function of the magnetic interactions in the case  $m / \hat{z}$ . The lattice was determined from an X-ray micro-tomographic image of a real experimental sample<sup>50</sup> in the following way. The sample was of cylindrical shape with a diameter of approximately 3 cm. We show a cross-sectional cut through the sample at intermediate height. Inside the sample, the magnetic particles formed chains parallel to the cylinder axis, i.e., perpendicular to the depicted plane. The average size of the particles was around 35  $\mu$ m. Gray areas correspond to the tomographic spots generated by the magnetic particles in the sample and were identified by image analysis. In our model, we then used the centers of these spots, marked by the black boxes, as lattice sites. One magnetic particle was placed on each lattice site. Then the whole plane was tessellated by Delaunay triangulation with the particle positions at the vertices of the resulting triangles. Elastic springs were set along the edges of the triangles. The micro-tomography data (see Fig. 5 (H=3 mm) in Ref. 50) are reproduced with permission from Gunther et al., Smart Mater. Struct. 21, 015005 (2012). Copyright 2012 by IOP Publishing.

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FIG. 9. Elastic modulus  $E(m/m_0)/k$  calculated for  $m / \hat{z}$  with NAT and AT techniques for the experimental lattice drawn in the left inset. Black dots represent clamped particles. Besides considerably overestimating the elastic modulus,  $E^{AT}(m/m_0)/k$  shows a flat/decreasing behavior, whereas  $E^{NAT}(m/m_0)/k$  is correctly increasing. In the right inset, we rescaled  $E(m/m_0)$  by E(m = 0) to better show the two different trends. The numerical error bars are much smaller than the symbol size.

Again we numerically investigate two-dimensional deformations within the resulting two-dimensional layer. If, in the future, this is to be compared to the case of a real sample, the deformations of this sample in the third direction, i.e., the anisotropy direction, have to be suppressed. For instance, the sample could be confined at the base and cover surfaces and compressed along one of the sides. Then it can only extend along the other side. Thus, within each cross-sectional plane, an overall two-dimensional deformation occurs, with macroscopic deformations suppressed in the anisotropy direction.

As we can see from Fig. 9, in our numerical calculations for this case, AT leads to a serious overestimation of the elastic modulus compared to the one obtained for NAT. Moreover, as can be seen in the right inset of Fig. 9, the former



FIG. 10. Zero-field elastic modulus  $E^{\text{NAT}}(m = 0)$  calculated with NAT for the experimental lattice drawn in the inset picture varying the rotation angle  $\theta$ . To illustrate the effective isotropy we plot the elastic modulus rescaled by the average of  $E^{\text{NAT}}(m = 0)$  over  $\theta$ . The black square in the inset contains the block of particles extracted from the experimental data after the rotation and used in our calculation.

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124904-8

#### 124904-9 Pessot et al.

J. Chem. Phys. 141, 124904 (2014)



FIG. 11. Shear modulus  $G(m/m_0)/k$  calculated for  $m //\hat{z}$  with NAT and AT techniques for the experimental lattice drawn in the left inset. Black dots represent clamped particles. Here again, besides considerably overestimating the elastic modulus,  $G^{\text{AT}}(m/m_0)/k$  shows a flat/decreasing behavior, whereas  $G^{\text{NAT}}(m/m_0)/k$  is correctly increasing. In the right inset, we rescaled  $G(m/m_0)$  by G(m = 0) to better show the two different trends. The numerical error bars are much smaller than the symbol size.

predicts an erroneous flat/decreasing trend for E(m), whereas the latter shows instead a correct increasing behavior. This result can be interpreted considering that in AT all the particles must move in a prescribed way along each direction. When the particle arrangement is irregular, some couples are very close and some are very distant. The erroneous trend in AT is mainly attributed to the very close particle pairs. AT can force them to still move closer together despite the magnetic repulsion, whereas NAT allows them to avoid such unphysical approaches. Therefore, in order to properly minimize the energy, each particle must be free to adjust position individually with respect to its local environment. As a consequence, for such realistic lattices AT provide erroneous results both quantitatively and qualitatively, making NAT mandatory in most practical cases.

Since within the analyzed two-dimensional crosssectional layer the particle distribution appears to be rather isotropic, we expect the elastic modulus to be approximately the same in any direction in the plane. To demonstrate this fact, we rotate the configuration in the plane with respect to the stretching direction by different angles  $\theta$  between 0 and  $\pi/2$ . As we can see from Fig. 10, the zero-field elastic modulus E(m = 0) shows only small deviations for the different orientations. The origin of such deviations is ascribed to the square-cutting procedure which, after a rotation by an angle  $\theta$ , produces samples containing different sets of particles, each with different local inhomogeneities in particle distribution and spring orientation. For samples large enough to significantly average over all these different local inhomogeneities, the angular dependence of E(m = 0) should further decrease. We found that for any rotation angle  $\theta$ , the behavior of E(m) is similar to the one in Fig. 9 corresponding to  $\theta = 0$ , supporting our statement about the erroneous AT result.

#### F. Shear modulus

For the set-up described in Subsection IV E (see the left inset of Fig. 9 with  $m //\hat{z}$ ), we have also calculated the shear modulus G(m) as a function of the magnetic moment, for both AT and NAT. The shear modulus is defined as the second derivative of the total energy U with respect to a small displacement  $\delta_v$  of the clamps in y-direction:

$$G = \frac{d^2 U}{d{\delta_y}^2} \simeq \frac{U(-\delta_y) + U(\delta_y) - 2U(0)}{{\delta_y}^2}.$$
 (6)

In this calculation, to allow for the comparison between the results from AT and NAT, all particles within the clamped regions are forced to move in a prescribed (affine) way.

It turns out that the behavior of the shear modulus is qualitatively the same as for the compressive and dilative elastic modulus (see Fig. 11). Again, an incorrect decreasing behavior for the AT calculation is obtained. In numbers, the relative difference between the AT and NAT results is larger than for the compressive and dilative elastic modulus. Here we set  $\delta_y$ as one percent of the dimension of the sample. In Fig. 11, this choice produces numerical error bars much smaller than the symbol size.

#### **V. CONCLUSIONS**

We have shown how the induction of aligned magnetic moments can weaken or strengthen the elastic modulus of a ferrogel or magnetic elastomer according to lattice structure and nearest-neighbor orientations. The orientation of nearest neighbors plays a central role. If the vector connecting two nearest neighbors lies parallel to the magnetic moment, they attract each other, the second derivative of their magnetic interaction is negative, and the corresponding contribution to

<sup>134.99.64.197</sup> On: Fri, 24 Oct 2014 08:32:24

#### 124904-10 Pessot et al.

the total elastic modulus is negative, too. If, instead, the nearest neighbors lie on a direction perpendicular to the magnetic moment, the second derivative of their magnetic interaction is positive and it tends to increase the total elastic modulus. This effect can be seen modifying the nearest-neighbor structure, for instance tuning the shape of a rectangular lattice or rotating a hexagonal lattice. We have also seen how the performance of affine transformations worsens for randomized and more realistic particle distributions, making non-affine transformation calculations mandatory when working with data extracted from experiments.

In the present case, we scaled out the typical particle separation and the elastic constant from the equations to keep the description general. Both quantities are available when real samples are considered. The mean particle distance follows from the average density, while the elastic constant could be connected to the elastic modulus of the polymer matrix.

The dipole-spring system we have considered is a minimal model. We look forward to improving it in different directions. First, we would like to go beyond linear elastic interactions using nonlinear springs, perhaps deriving a realistic interaction potential from experiments or more microscopic simulations. Second, the use of periodic boundary conditions may improve the efficiency of our calculations and give us new insight into the system behavior (although we demonstrated by our study of asymptotic behavior that border effects are negligible in the present set-up). Furthermore, we may include a constant volume constraint, since volume conservation is not rigidly enforced in the present model. To isolate the effects of different lattice structures and the assumption of affine deformations, we here assumed that all magnetic moments are rigidly anchored along one given direction. In a subsequent step, this constraint could be weakened by explicitly implementing the interaction with an external magnetic field or an orientational memory. Finally, to build the bridge to real system modeling, an extension of our calculations to three dimensions is mandatory in most practical cases.

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Chapter 2. Peer-reviewed publications

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## Paper II. Tunable dynamic response of magnetic gels: Impact of structural properties and magnetic fields

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## Statement of contribution

AMM, HL, and SO supervised the work. MT performed the numerical analysis involved in the paper. DYB and SO provided the experimental input data. I extracted input for the numerical model from these experimental data using Delaunay triangulation. I estimate my overall contribution to this work to be around 10%.

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#### PHYSICAL REVIEW E 90, 042311 (2014)

#### Tunable dynamic response of magnetic gels: Impact of structural properties and magnetic fields

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Ferrogels and magnetic elastomers feature mechanical properties that can be reversibly tuned from outside through magnetic fields. Here we concentrate on the question of how their dynamic response can be adjusted. The influence of three factors on the dynamic behavior is demonstrated using appropriate minimal models: first, the orientational memory imprinted into one class of the materials during their synthesis; second, the structural arrangement of the magnetic particles in the materials; and third, the strength of an external magnetic field. To illustrate the latter point, structural data are extracted from a real experimental sample and analyzed. Understanding how internal structural properties and external influences impact the dominant dynamical properties helps to design materials that optimize the requested behavior.

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#### I. INTRODUCTION

Often the internal dissipation in soft matter systems is sufficiently large so that their dynamics can be considered as overdamped. For instance the motion of dispersed colloidal particles is dominated by the friction with the surrounding liquid [1]. Another example is the dynamics of polymer chains in melt or solution, described in a first approach by the famous Rouse and Zimm models [2,3]. Apart from that, in polymeric systems the dynamic behavior is often dominated by relaxation processes. The reason is found in the large size of their building blocks. A long time is necessary for conformational rearrangements to adjust to changes in their environment [4]. Frequently, the slower processes are the ones that strongly influence the macroscopic behavior.

Here, we consider the combination of the two materials mentioned above in the form of ferrogels or magnetic elastomers [5]. In this case, magnetic colloidal particles are embedded into a crosslinked polymeric matrix. Qualitatively different kinds of this "embedding" can be achieved by different protocols of synthesis. On the one hand, the magnetic particles can simply be enclosed in mesh pockets of the polymer network [5]. This allows a certain degree of freedom for particle reorientations. On the other hand, via surface functionalization, the magnetic particles can serve as crosslinkers and thus become part of the polymer mesh [6–8]. Then, restoring torques hinder reorientations of the particles. We use the term "orientational memory" to refer to this situation [9].

From the internal architecture of these materials it is obvious that their magnetic and mechanical properties are strongly coupled to each other. This is what makes them interesting from both an academic and an application point of view. For example, the mechanical properties, such as the mechanical elastic modulus, can be tuned and adjusted reversibly from outside by applying external magnetic fields [5]. This may be exploited in constructing novel damping devices [10] and vibrational absorbers [11]. Several theoretical studies have shown that the internal spatial particle distribution plays a qualitative role in this effect [12–15].

Furthermore, applying time-dependent external magnetic fields can induce deformations, which makes the materials candidates for use as soft actuators [5,16,17]. Related to this feature, it has been demonstrated theoretically that the spatial particle arrangement in the materials has a qualitative impact on the magnetostrictive behavior [18–20].

Apart from that, quick remagnetizations of the magnetic particles by an alternating external magnetic field can lead to local heating. The effect is due to hysteretic losses in the dynamic magnetization processes. It can be used for hyperthermal cancer treatment when magnetic particles are embedded into tumor tissue [21,22]. Ferrogels, which likewise feature magnetic particles embedded in a gel-like matrix, can serve as model systems to investigate some of the aspects that become important during this form of medical treatment.

In all these processes, dynamic modes of the materials are excited. This happens via the time-dependence of the applied mechanical deformations and external magnetic fields. Different modes will dominate depending on the type of external stimulus. In the described situation there are two major differences when compared to the classical picture of phonon modes in conventional solids [23]: we expect the dynamics of the magnetic particles to be mainly of the relaxatory kind, and the particle arrangement is not that of a regular crystalline lattice.

A natural goal is to optimize the materials in view of their applications. For this purpose, it is important to understand if and how the dynamic modes are determined by internal structural properties and by external magnetic fields. So far, a macroscopic continuum theory for the dynamic response of magnetic gels has been developed using a hydrodynamic-like symmetry-based approach [16,24]. However, particle-resolved studies that connect the dynamic material behavior to structural properties on the magnetic particle level are missing. Our investigations in the following are a first step into this direction. In the next section, we review the simplified dipole-spring model that we recently introduced to investigate equilibrium

1539-3755/2014/90(4)/042311(9)

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#### MITSUSUKE TARAMA et al.

ground states of simple model systems [9]. We expand it by formulating the corresponding relaxation dynamics. Our approach contains memory terms to include a possible orientational coupling of the magnetic particles to the polymer network [9]. We then demonstrate and analyze the impact of three different factors on the dynamic relaxatory modes. First, the orientational memory can qualitatively impact the appearance of the materials, which also influences the dynamic modes. This is demonstrated for the illustrative example of a short linear magnetic chain in Sec. III. Second, the spatial distribution of the magnetic particles is important. We depict this fact using simple symmetric lattice cells in two spatial dimensions in Sec. IV. Third, the mode structure can be influenced by an external magnetic field. This is highlighted for a spatial particle distribution that was extracted from the cross section of a real experimental sample in Sec. V. The results are summarized in Sec. VI.

#### II. DYNAMIC DIPOLE-SPRING MODEL

Our ambition in this paper is to qualitatively demonstrate that the relaxation dynamics can be influenced by three different factors: orientational memory, spatial distribution of the magnetic particles, and external magnetic fields. For this purpose, we employ a minimal dipole-spring approach that includes all these ingredients.

We use the recently introduced model energy to describe the state of a ferrogel [9]:

$$E = \frac{\mu_0}{4\pi} \sum_{i,j=1,i(1)$$

Here, each of the *N* magnetic particles carries a magnetic dipolar moment  $\mathbf{m}_i$  and is located at position  $\mathbf{r}_i$  (i = 1, ..., N). The distance vectors are  $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ . For any vector  $\mathbf{x}$  we use the abbreviations  $x = \|\mathbf{x}\|$  and  $\hat{\mathbf{x}} = \mathbf{x}/x$ . All quantities with the superscript <sup>(0)</sup> refer to a memorized state imprinted into the material during its synthesis. We denote the sum over a limited number of close neighbors by angular brackets  $\langle i, j \rangle$ .

The first line of Eq. (1) contains the long-ranged dipolar interactions. Next, we model the elastic properties of the embedding polymer matrix by effective Hookean springs between the magnetic particles. *k* is the spring constant. Both remaining terms include a simple form of orientational memory of the dipolar orientations: the term with the coefficient *D* penalizes rotations of the dipole moments towards the connecting line between magnetic particles;  $\tau$  penalizes relative rotations of the dipolar moments around these connecting lines, typically involving torsional deformations. In the following we only

#### PHYSICAL REVIEW E 90, 042311 (2014)

consider situations and parameter values for which a collapse due to the dipolar attractions does not occur; we thus can neglect steric repulsion between the particles.

All magnetic particles are assumed to be identical. For ferrofluids [25–28] this simplifying picture could capture the experimentally observed effects correctly [29,30]. Particularly, in our case, an identical magnitude of the dipolar moments is assumed,  $m_i = m$  (i = 1, ..., N). Then, five degrees of freedom remain for each particle *i*, given by a five-dimensional vector  $\mathbf{y}_i \equiv (\mathbf{r}_i, \mathbf{\hat{m}}_i)$ . Thus the relaxation dynamics of the system follows as the 5*N*-dimensional coupled system of equations

$$\frac{\partial \mathbf{y}_i}{\partial t} = -\boldsymbol{\gamma} \cdot \frac{\partial E}{\partial \mathbf{y}_i}, \quad i = 1, \dots, N.$$
 (2)

Here, our final simplifying assumption is that the relaxation rate tensor  $\boldsymbol{\gamma}$  is diagonal and the same for all particles. Rescaling all lengths by an appropriate distance  $l_0$ , the positional relaxation rates can be adjusted to the angular ones, so that we obtain  $\boldsymbol{\gamma} = \boldsymbol{\gamma} \mathbf{I}$ , with  $\mathbf{I}$  the unity matrix. In all that follows, we measure time in units of  $(\boldsymbol{\gamma} k l_0^2)^{-1}$ , D and  $\tau$  in units of  $k l_0^2$ , as well as the magnetic moment m in units of  $[k l_0^5/\mu_0]^{1/2}$ .

We linearize Eqs. (2) with respect to small deviations  $\delta \mathbf{y}_i$  from the energetic ground state. The resulting system of linearized dynamic equations is rather lengthy and listed in the Appendix. We insert an ansatz  $\delta \mathbf{y}_i = \delta \mathbf{y}_{0,i} e^{\lambda t}$  into the resulting system of linearized dynamic equations. Denoting by  $\delta \mathbf{y}$  the vector composed of all  $\delta \mathbf{y}_i$ , the resulting system of equations can be written in the form  $\lambda \delta \mathbf{y} = \mathbf{M} \cdot \delta \mathbf{y}$ , with  $\mathbf{M}$ the force matrix. Therefore, the relaxation rates  $\lambda$  follow as the eigenvalues of this matrix, whereas its eigenvectors characterize the nature of the corresponding relaxatory dynamic modes. More precisely, the eigenvectors describe the spatial displacements and magnetic reorientations  $\delta \mathbf{y}_i = (\delta \mathbf{r}_i, \delta \mathbf{m}_i)$  of all particles i = 1, ..., N during the corresponding dynamic mode. These eigenvalues and eigenvectors are obtained by standard numerical methods [31]. In our overdamped system, the relaxation rates together with the relaxatory modes characterize the dynamic behavior.

#### **III. IMPACT OF ORIENTATIONAL MEMORY**

To demonstrate that the orientational memory has a qualitative impact, it is sufficient to consider a one-dimensional particle arrangement. For such a straight magnetic chain we had previously observed three qualitatively different energetic ground states [9]. They occur for a memorized direction  $\hat{\mathbf{m}}_i^{(0)}$ oblique to the chain axis and depend on the strength of the orientational memory  $(D, \tau)$ : we obtain a "ferromagnetic" state with all magnetic moments aligned along the chain (small *D*); an "antiferromagnetic" state with obliquely oriented magnetic moments rotated around the chain by  $\pi$  between neighboring particles (large *D*, small  $\tau$ ); and a "spiral"-like arrangement with the rotation angle smaller than  $\pi$  (large *D*, large  $\tau$ ).

For illustration, we here consider a finite straight chain of only N = 10 particles. It is characterized by an equal orientation of all memorized  $\mathbf{m}_i^{(0)}$  with an angle  $\triangleleft(\mathbf{m}_i^{(0)}, \mathbf{r}_{ij}^{(0)}) = \pi/4$ , the pairs  $\langle i, j \rangle$  in Eq. (1) denoting nearest neighbors. We consider three different strengths of orientational memory TUNABLE DYNAMIC RESPONSE OF MAGNETIC GELS: ...



FIG. 1. (Color online) Dynamic relaxatory behavior for three different linear elastic chains of N = 10 magnetic particles of m = 1.68. The chains differ by orientational memory  $(D, \tau)$  leading to qualitatively different energetic ground states: ferromagnetic "F"  $(D = 0.1, \tau = 0.04)$ , anti-ferromagnetic "AF"  $(D = 0.6, \tau = 0.0004)$ , and spiral-like "Sp"  $(D = 0.6, \tau = 0.04)$ . (a) Dynamic relaxation spectra, where *n* labels the modes. (b) Example of a characteristic eigenmode (n = 8) that appears very differently in the three cases due to the varying orientational memory. *i* labels the particles,  $\delta r$  denotes displacements along the chain axis,  $\delta m_{\theta}$  and  $\delta m_{\phi}$  mark the angular deviations of the magnetic moments in spherical coordinates. (c) Illustration of the three different energetic ground states (light gray) and the resulting different modes n = 8 as characterized in (b). In all cases the lengths of the unstrained linking springs between the particles are  $r_{ij}^{(0)} = 2$ .

 $(D, \tau)$  that lead to the three different ground states mentioned above; see Fig. 1 for further details.

We determined the corresponding relaxation spectra and depict them in Fig. 1(a). The more negative the eigenvalue  $\lambda$ , the quicker the corresponding mode relaxes. We order the modes by decreasing  $\lambda$ . First the zero-modes of global translation along and global rotation around the chain axis are obtained. The subsequent plateau of slowly decreasing relaxation rates mainly contains dynamic modes dominated by rotational relaxation; see Ref. [32] for details. At the end of this plateau, there is an obvious kink in the spectral curves and the relaxation rates start to significantly decrease. For these modes, the relaxation becomes significantly quicker. Those are the modes that are dominated by longitudinal compressive and dilative displacements along the chain with higher wave numbers; again see Ref. [32] for details. That is, these modes can quickly decay by repositioning within small localized groups of particles, implying that a collective rearrangement correlated along the whole chain is not necessary, which makes those processes faster. In the antiferromagnetic case, we find a specific step within the plateau region. It separates modes

#### PHYSICAL REVIEW E 90, 042311 (2014)

dominated by dipolar rotations first around and second towards the chain axis. As Figs. 1(b) and 1(c) show, the orientational memory can lead to qualitative differences in the nature of corresponding modes. The complete table illustrating all occurring modes is included in Ref. [32].

In the above considerations, our limitation to a relatively short chain of N = 10 particles is due to illustrative purposes only. The differences in the spectra in Fig. 1 and in Ref. [32] solely result from the varying orientational memory that lead to the ferromagnetic, anti-ferromagnetic, and spiral-like ground states. Analogous results follow for significantly longer chains. Likewise, there are no qualitative differences between chains of odd and even numbers of magnetic particles for  $N \ge 10$  and otherwise identical parameter values.

Summarizing, we have demonstrated the influence of the orientational memory on the dynamics for a one-dimensional spatial arrangement of the magnetic particles. Real threedimensional bulk samples can contain such chain-like aggregates [5,33-36]. If the distances between the chains are large enough so that the interaction between them can be neglected [37], the dynamic properties of the single chains will have a strong impact on the overall behavior. Nevertheless, the orientational memory should also become important in other cases of more isotropic particle distributions, a topic that shall be investigated further in the future. The orientational memory in our model is encoded by the parameters D and  $\tau$ . In reality, it can for example be tuned during synthesis by the way of embedding the magnetic particles in the polymer matrix. For instance, rotations of elongated magnetic particles [38] are hindered when compared to spheres, and magnetic particles that are actually part of the network due to chemical surface functionalization [6,7] experience permanent restoring torques under reorientation [8].

#### IV. EFFECT OF SPATIAL PARTICLE DISTRIBUTION

Next, we show that the spatial distribution of the magnetic particles has an obvious impact on the relaxation dynamics. For this purpose, it is sufficient to concentrate on a two-dimensional particle arrangement. We consider a system without orientational memory of the dipoles, i.e., D = 0 and  $\tau = 0$  in Eq. (1). Instead, we assume that a sufficiently strong external magnetic field orients all magnetic dipoles perpendicular to the two-dimensional layer. Due to the above rescaling, the only remaining system parameter is the rescaled magnitude *m* of the dipole moments. It characterizes the ratio between magnetic and elastic contributions to the system energy.

For illustration, we consider small regular arrangements of different lattice structures and only N = 9 particles. Of course much larger arrangements can be evaluated but not as easily be displayed. In our examples, the textures are of initially quadratic, rectangular, and hexagonal lattice structure.

We display the relaxation spectra for the three different lattice structures in Fig. 2(a). Since the orientations of the magnetic moments are fixed by the strong external magnetic field, all modes are solely determined by relaxations of the particle positions. In all cases, three zero modes are observed corresponding to global spatial translations and rotations. For the higher modes, the different lattice structures lead to

PHYSICAL REVIEW E 90, 042311 (2014)



MITSUSUKE TARAMA et al.

FIG. 2. (Color online) Dynamic relaxatory behavior of (from left to right) a small quadratic, rectangular (aspect ratio 2:3), and hexagonal lattice of N = 9 particles. Magnetic moments are oriented perpendicular to the plane and of magnitude m = 1. (a) Changes in the relaxation spectra for the three different particle distributions. (b) Different appearance of an example mode (n = 5) for the three lattices (undeformed energetic ground states indicated in light gray). In all cases the lengths of the unstrained linking springs between the particles are  $r_{ij}^{(0)} = 2$ , except for the long edges of the rectangular lattice, where they are  $r_{ij}^{(0)} = 3$ .

different magnitudes of corresponding relaxation rates. Also the nature of the relaxatory modes significantly depends on the spatial particle distribution. One example is illustrated by Fig. 2(b). A complete illustration of all relaxatory modes for each lattice is again included in Ref. [32].

#### V. INFLUENCE OF AN EXTERNAL MAGNETIC FIELD

Finally, we demonstrate that an external magnetic field can change the dynamic relaxatory behavior. This is particularly important from an application point of view because it allows us to tune the dynamic properties of the materials in a noninvasive way from outside.

We consider the same setup as above for the regular lattices. Now, however, there are N = 969 particles and their spatial distribution does not follow a regular lattice structure. In particular, to make the connection to real systems, we use a real experimental sample and extract the particle positions as an input for our study.

The experimental sample was extensively characterized in Ref. [36]. It is a two-component silicone elastomer of cylindrical shape with a diameter of 3 cm and a height of 1.5 cm. Furthermore, it contains 4.6 wt% of magnetically soft iron particles, the average size of which is around 35  $\mu$ m. During the synthesis of the elastomer, a strong homogeneous external magnetic field of 220 kA/m was applied parallel to the cylinder axis. This resulted in the formation of linear chains of the magnetic particles spanning the whole sample parallel to the cylinder axis. The chains were resolved by x-ray microtomography [36], the result of which is displayed in Fig. 3. Cross-sectional images in planes perpendicular to the cylinder axis are available—see the left column of Fig. 3—and contain information about the chain positions [36].

To first approximation, due to the linear chain-like aggregates that are all oriented in the same direction, the structure at intermediate height of the sample is translationally invariant along the cylinder axis. The exact positions and sizes of



FIG. 3. (Color online) Chain-like structures observed by x-ray microtomography in the experimental sample referred to in the main text [36]. On the left-hand side, three cross-sectional images at different heights H from the base of the sample are depicted. Bright spots label the positions of magnetic particles. On the right-hand side, a three-dimensional reconstruction of the chain-like structures formed by the magnetic particles in the sample is shown. For details of the data acquisition see Ref. [36]. Taken from Ref. [36], Fig. 5. ©IOP Publishing. Reproduced by permission of IOP Publishing. All rights reserved.

individual magnetic particles in the sample could not be resolved. We consider by our model the situation within one cross-sectional layer cut out from the sample at intermediate height H. In our example, we choose the cross-section at height H = 3 mm in Fig. 3.

Each spot in the cross-sectional tomography data identifies magnetic chain particles. We extracted by image analysis the centers of these spots; see Fig. 4(a). Then, in our model, we place one particle on each center, carrying a magnetic moment m oriented perpendicular to the plane. Finally, as shown in Fig. 4(a), the area between the particles is tessellated by Delaunay triangulation. We insert elastic springs along the edges of the resulting triangles, which here sets the pairs described by  $\langle i, j \rangle$  in Eq. (1). Magnetic interactions are still considered between all pairs of magnetic particles in the plane. In this way, we model the physics of one cross-sectional layer of the real system. Since the magnetic particles in the experimental sample are not covalently bound to the polymer matrix [6,7], and since the magnetic moments are perpendicular to the plane, the orientational memory terms in Eq. (1) do not play a role.

For large enough particle sizes, the magnetization of the particles and thus the magnitude of their magnetic moments can be tuned by the strength of an external magnetic field. We consider this external magnetic field perpendicular to the plane, i.e., along the linear chains formed by the magnetic particles in the real sample. This has two reasons. First, we know from the procedure of synthesis that such a magnetic field orients the magnetic moments perpendicular to the plane and maintains TUNABLE DYNAMIC RESPONSE OF MAGNETIC GELS: ...

#### PHYSICAL REVIEW E 90, 042311 (2014)



FIG. 4. (Color online) Tunability of the dynamic behavior by an external magnetic field oriented perpendicular to the plane and affecting the magnetic moments. (a) Positions of the magnetic moments are extracted from the x-ray microtomographic cross-sectional image of an anisotropic real experimental sample [36] displayed for H = 3 mm on the left-hand side of Fig. 3. Only a fraction of the image is shown for illustration. Gray areas correspond to the microtomographic spots. (b) Tunability of the spectrum by changing the magnetization. (c) The density of dynamic modes gets shifted in the frequency direction by adjusting the magnetization. Dynamic modes for  $\omega \approx 1.3$  and  $\omega \approx 2.5$  (m = 1) are illustrated in Figs. 5(b) and 5(c), respectively. [The tomography data in panel (a) are taken from Ref. [36], Fig. 5 (H = 3 mm), ©IOP Publishing. Reproduced by permission of IOP Publishing. All rights reserved.]

the axial symmetry of the sample. Second, in the static case, the largest degree of tunability of the compressive elastic modulus was achieved when the magnetic field was oriented parallel to the anisotropy direction [5]. A similar dependence may also hold in the dynamic case. To keep the description general and simple, we do not consider specific magnetization laws but study the relaxation dynamics directly as a function of the magnitude of the resulting dipolar magnetic moment m.

As is obvious from Fig. 4(b), the dynamic relaxation spectra can be tuned by adjusting m. We checked that the chosen values correspond to external magnetic field strengths that can be realized experimentally. In our geometry, the magnetic interactions within the plane are purely repulsive. Moreover, as can also be seen from Figs. 3 and 4(a), the sizes of the spots detected by x-ray microtomography in the cross-sectional layers are not homogeneous. In a variant of our approach, we varied the strengths of the magnetic moments proportionally to the area of the detected spots. However, this did not qualitatively influence our results.

Figure 5 displays several illustrative example modes from the spectrum for m = 1 in Fig. 4(b). Black dots mark the initial positions of the magnetic particles, whereas the overlayed lattice shows the deformed state. The directions and relative magnitudes of the displacements of the individual particles are obtained from the eigenvectors calculated as described at the end of Sec. II.

There are two major differences when compared to the classical phonon modes in crystalline solids [23]. First, our dynamics is overdamped [1]. Therefore, we here focus on the relaxational spectra determined from the corresponding relaxation rates  $\lambda_n$ . Second, our lattice is irregular. Nevertheless, the situation is typically discussed in terms of the mode density  $g(\omega)$  in frequency space following the notation of the classical phonon picture of nonoverdamped oscillations [23]. The frequencies  $\omega_n$  of these oscillations in the classical phonon picture would be determined from the same force matrix as the one that we find from the right-hand side of Eq. (2). However, on the left-hand side of Eq. (2), the phonon oscillations would imply a second time derivative. The two quantities that appear

on the left-hand side in these two different cases are related by  $\omega_n \sim \sqrt{|\lambda_n|}$ . Since it is common to plot the mode density  $g(\omega)$  in frequency space, we adhere to this convention.

At not too high frequencies that correspond to long-scale collective dynamics, the plane-wave picture should still apply. In fact, in this regime, a behavior of  $g(\omega)$  in accordance with the classical Debye picture [23] was obtained for disordered structures [39]. Likewise, we observe here for our two-dimensional disordered solid a "Debye plateau" of the function  $g(\omega)/\omega$  in Fig. 4(c) at not too high frequencies. Example modes at the low-frequency end of the spectrum indeed are related to long-scale collective dynamics, as demonstrated in Fig. 5(a).

However, instead of a pure drop of  $g(\omega)$  at higher frequencies, a typical "boson peak" can develop in disordered systems [39], the origin of which is still under debate [40]. In our example of a two-dimensional disordered solid, the curve for  $g(\omega)$  in Fig. 4(c), before it drops at the end of the plateau, shows a small hump. It is not possible to decide on the basis of our limited statistical data whether this is the signature of a "boson peak" in our non-glassy system. What does become obvious from Figs. 5(b) and 5(c) is that the higher-frequency modes are significantly more localized. This explains their higher relaxation rates: large-scale collective motion is not necessary to relax them.

Most significant for our present purposes is the observation in Fig. 4(c) that the spectral density  $g(\omega)$  can be shifted in frequency direction by adjusting *m* through an external magnetic field. This is an important ingredient from the application point of view. It allows to adjust the relaxation time reversibly in response to varying environmental conditions. We recall that the fraction of the magnetic component in our experimental sample was only 4.6 wt%. Significantly higher contents of magnetic particles can be realized. It turns out that already after halving all distances in our sample plane, switching *m* from 10 to  $10^3$  is sufficient to achieve a similar shift in the spectrum as the one occuring in Fig. 4(c) between m = 1 and  $m = 10^4$ . This underlines the potential of the magnetic interaction as an effective control parameter for the dynamic behavior. In combination with the established phononic properties of



MITSUSUKE TARAMA et al.

PHYSICAL REVIEW E 90, 042311 (2014)

sample. Colored illustrations of the deformed lattices for each mode are superposed to the black undistorted lattice corresponding to the energetic ground state. (a) Examples of lower modes show the expected global collective deformations, here of elliptic ( $\lambda_4$ ), triangular ( $\lambda_{10}$ ), quadratic ( $\lambda_{13}$ ), pentagonal ( $\lambda_{15}$ ), hexagonal ( $\lambda_{22}$ ), and heptagonal ( $\lambda_{24}$ ) shape. Selected eigenmodes (b) around the end of the "Debye plateau" ( $\omega \approx 1.3$ ) and (c) around the small hump that might be connected to a "boson peak" ( $\omega \approx 2.5$ ), cf. Fig. 4(c), show a much more localized character. The initial spring lengths  $r_{ij}^{(0)}$  were set according to the values extracted from the experimental sample, while the magnetic moment was chosen as m = 1.

FIG. 5. (Color online) Illustration of dynamic relaxational modes for the 969-particle planar irregular lattice extracted from the experimental

042311-6
TUNABLE DYNAMIC RESPONSE OF MAGNETIC GELS: ...

colloidal systems [41–43], this mechanism could provide a route to tunable sound absorbers.

#### VI. CONCLUSIONS

Summarizing, we have demonstrated that the dynamic behavior of ferrogels and magnetic elastomers can be tailored and adjusted by at least three factors: first, by the magnetoelastic coupling and orientational memory; second, by the particle distribution; and third, during application, by external magnetic fields. Thus we can forecast how microscopic details, e.g. the orientational coupling of the magnetic particles to their polymeric environment, affect aspects of the dynamic material properties. There are of course several further factors that determine our model parameters and in this way influence the relaxation behavior. For example, these could be the content of magnetic particles, the temperature during application, the degree of crosslinking, or the degree of swelling of the materials. The impact of these parameters should be analyzed both experimentally and theoretically in the future. On the experimental side, aspects of the dynamic relaxation properties can be inferred, for instance, from dielectric relaxation studies [44] or nanorheology [45]. Having all these tuning parameters at hand, it should be possible to adjust the dynamic properties to the requested applicational need.

To our knowledge, investigating aspects of the dynamic material behavior on the level of the magnetic particle distributions represents a new direction in the field. We hope that our study can stimulate further, more detailed, and more quantitative theoretical and simulation work in this context. Naturally, the extension to three spatial dimensions is an important next step. Our main goal here was to outline for simple one- and two-dimensional model cases the different factors that can influence the dynamics of the systems. To allow for quantitative predictions on the dynamic behavior of real samples, three-dimensional analyses will be mandatory in most situations. On the experimental side, for example the differences between isotropic and uniaxial ferrogels should be analyzed concerning dynamic properties. All of these questions are of high practical relevance in view of the dynamic applications. For instance, response and relaxation times determine the range of usability of ferrogels as the basis of the above-mentioned novel damping devices [10], vibrational absorbers [11], or soft actuators [5,17].

Our analysis represents a first step towards an optimization of the dynamic behavior of magnetic gels. Theory and simulations could assist this process by identifying particle properties and structural arrangements that lead to the requested characteristics. A further investigation to connect our

2

#### PHYSICAL REVIEW E 90, 042311 (2014)

approach to directly experimentally measured quantities such as the dynamical susceptibilities is currently underway [46]. We hope that our study can stimulate further investigations to support the design of these fascinating materials and optimize their tunable dynamic properties.

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#### APPENDIX: DYNAMIC EQUATIONS FOR THE RELAXATIONAL BEHAVIOR

Here we list the complete expressions for the linearized equations characterizing the relaxation dynamics and following from Eq. (2). In this way, the relaxation dynamics of small deviations  $\delta \mathbf{y}_i$  from the energetic ground state is obtained, where  $\mathbf{y}_i \equiv (\mathbf{r}_i, \hat{\mathbf{m}}_i)$  and i = 1, ..., N labels the particles:

$$\frac{\partial \delta \mathbf{y}_i}{\partial t} = -\gamma \sum_{j=1}^N \mathcal{L}_{ij} \delta \mathbf{y}_j. \tag{A1}$$

For simplicity, we only show the formulas for the onedimensional chain and for the two-dimensional planar particle arrangements considered in the main text. In the latter case, we assume that the orientation of the magnetic dipoles is fixed perpendicular to the plane. This can, for example, be achieved by a strong external magnetic field.

#### 1. Linear chain-like particle arrangement

First, for the one-dimensional chain-like aggregates, the vector  $\mathbf{y}_i$  reduces to a three-dimensional vector  $\mathbf{y}_i \equiv (r_i, \theta_i, \phi_i)$ . In our choice of coordinates,  $r_i$  marks the position of the *i*th particle along the chain, whereas the two angles  $\theta_i$  and  $\phi_i$  represent the azimuthal and polar angles of the dipolar orientation of the particle with respect to the chain direction. The linearized operator in the above Eq. (A1) is separated into four parts resulting from the four contributions to the energy *E* in Eq. (1) of the main text:

$$\mathcal{L}_{ij} = \mathcal{L}_{ij}^{\text{dip}} + \mathcal{L}_{ij}^{\text{el}} + \mathcal{L}_{ij}^{D} + \mathcal{L}_{ij}^{\tau}.$$
 (A2)

We start by calculating the contribution from the dipoledipole interaction energy. Its diagonal components are given by

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$$\mathcal{L}_{ii}^{dip} = \frac{3\mu_0}{4\pi} \sum_{k \neq i} |r_{ik}|^{-3} r_{ik}^{-1} m^2 \Big[ 4r_{ik}^{-1} \{\sin\theta_i \sin\theta_k \cos(\phi_k - \phi_i) - 2\cos\theta_i \cos\theta_k\} \hat{r} \hat{r} + \{\cos\theta_i \sin\theta_k \cos(\phi_k - \phi_i) + 2\sin\theta_i \cos\theta_k\} \hat{r} \hat{\theta}_i + \sin\theta_i \sin\theta_k \sin(\phi_k - \phi_i) \hat{r} \hat{\phi}_i \Big] + \frac{\mu_0}{4\pi} \sum_{k \neq i} |r_{ik}|^{-3} m \Big[ 3r_{ik}^{-1} \{\cos\theta_i \sin\theta_k \cos(\phi_k - \phi_i) + 2\sin\theta_i \cos\theta_k\} \hat{\theta}_i \hat{r} - \{\sin\theta_i \sin\theta_k \cos(\phi_k - \phi_i) - 2\cos\theta_i \cos\theta_k\} \hat{\theta}_i \hat{\theta}_i + 3r_{ik}^{-1} \sin\theta_k \sin(\phi_k - \phi_i) \hat{\phi}_i \hat{r} - \sin\theta_i \{\sin\theta_i \sin\phi_k \cos(\phi_k - \phi_i) - 2\cos\theta_i \cos\theta_k\} \hat{\phi}_i \hat{\phi}_i \Big]$$
(A3)

042311-7

#### MITSUSUKE TARAMA et al.

#### PHYSICAL REVIEW E 90, 042311 (2014)

and its off-diagonal components for  $j \neq i$  by

$$\mathcal{L}_{ij\neq i}^{\mathrm{dip}} = \frac{3\mu_0}{4\pi} |r_{ij}|^{-3} r_{ij}^{-1} m^2 \Big[ -4r_{ij}^{-1} \{\sin \theta_i \sin \theta_j \cos(\phi_j - \phi_i) - 2\cos \theta_i \cos \theta_j\} \hat{r} \hat{r} + \{\sin \theta_i \cos \theta_j \cos(\phi_j - \phi_i) + 2\cos \theta_i \sin \theta_j\} \hat{r} \hat{\theta}_j \\ - \sin \theta_i \sin \theta_j \sin(\phi_j - \phi_i) \hat{r} \hat{\phi}_j \Big] + \frac{\mu_0}{4\pi} |r_{ij}|^{-3} m \Big[ -3r_{ij}^{-1} \{\cos \theta_i \sin \theta_j \cos(\phi_j - \phi_i) + 2\sin \theta_i \cos \theta_j\} \hat{\theta}_i \hat{r} \\ + \{\cos \theta_i \cos \theta_j \cos(\phi_j - \phi_i) - 2\sin \theta_i \sin \theta_j\} \hat{\theta}_i \hat{\theta}_j - \cos \theta_i \sin \theta_j \sin(\phi_j - \phi_i) \hat{\theta}_i \hat{\phi}_j \\ - 3r_{ij}^{-1} \sin \theta_j \sin(\phi_j - \phi_i) \hat{\phi}_i \hat{r} + \cos \theta_j \sin(\phi_j - \phi_i) \hat{\phi}_i \hat{\theta}_j + \sin \theta_i \cos(\phi_j - \phi_i) \hat{\phi}_i \hat{\phi}_j \Big].$$
(A4)

Here  $r_{ij} = r_j - r_i$  and  $\hat{r}$  denotes the unit vector in the *r* direction, i.e., along the chain axis. Likewise,  $\hat{\theta}_i$  and  $\hat{\phi}_i$  represent the unit vectors in the  $\theta$  and  $\phi$  directions for the current orientation of the dipolar moment of the *i*th particle.

After straightforward calculation, the components of the operator containing the elastic part are obtained as

$$\mathcal{L}_{ij}^{\text{el}} = \begin{cases} k \sum_{\ell \in \delta\Omega_i} \hat{r} \hat{r} & \text{if } i = j, \\ -k\hat{r} \hat{r} & \text{if } j \in \delta\Omega_i, \\ 0 & \text{otherwise,} \end{cases}$$
(A5)

where  $\delta \Omega_i$  denotes the set of the (one or two) nearest neighbors of the *i*th particle.

In the same way, the first contribution from the orientational memory becomes

$$\mathcal{L}_{ii}^{D} = -2Dm^{-1} \Big[ \Big\{ -\sin^2\theta_i + \big(\cos\theta_i - \cos\theta_i^{(0)}\big)\cos\theta_i \Big\} \hat{\theta}_i \hat{\theta}_i + \big(\cos\theta_i - \cos\theta_i^{(0)}\big)\sin\theta_i\cos\theta_i \hat{\phi}_i \hat{\phi}_i \Big]$$
(A6)

and

$$\mathcal{L}^{D}_{ii\neq i} = 0. \tag{A7}$$

Finally, the diagonal components of the linearized operator resulting from the second part of the orientational memory are calculated as

$$\mathcal{L}_{ii}^{\tau} = 2\tau \sum_{k \in \delta \Omega_i} m^{-1} (\sin \theta_i)^{-1} \Big[ -\cos \theta_i \sin(\phi_k - \phi_i) \Big\{ \cos(\phi_k - \phi_i) - \cos \left(\phi_k^{(0)} - \phi_i^{(0)}\right) \Big\} \hat{\theta}_i \hat{\phi}_i - (\sin \theta_i)^{-1} \cos \theta_i \sin(\phi_k - \phi_i) \\ \times \Big\{ \cos(\phi_k - \phi_i) - \cos \left(\phi_k^{(0)} - \phi_i^{(0)}\right) \Big\} \hat{\phi}_i \hat{\theta}_i - \Big\{ -\cos(\phi_k - \phi_i) \cos \left(\phi_k^{(0)} - \phi_i^{(0)}\right) + \cos^2(\phi_k - \phi_i) - \sin^2(\phi_k - \phi_i) \Big\} \hat{\phi}_i \hat{\phi}_i \Big].$$
(A8)

The corresponding off-diagonal components are given by

$$\mathcal{L}_{ij\in\delta\Omega_i}^{\tau} = 2\tau m^{-1} (\sin\theta_i)^{-1} \left\{ -\cos(\phi_j - \phi_i)\cos\left(\phi_j^{(0)} - \phi_i^{(0)}\right) + \cos^2(\phi_j - \phi_i) - \sin^2(\phi_j - \phi_i) \right\} \hat{\phi}_i \hat{\phi}_j \tag{A9}$$

for pairs of nearest neighbors. Otherwise the off-diagonal components are zero,

$$\mathcal{L}_{ij\notin\Omega_i}^{\tau} = 0, \tag{A10}$$

with  $\Omega_i = \delta \Omega_i + \{i\}$  in this notation.

#### 2. Planar particle arrangement

Second, in the case of the two-dimensional plane, we assume that all dipole moments are aligned perpendicular to the plane. Then, since the degrees of freedom for the dipolar orientations drop out, the vector  $\mathbf{y}_i$  reduces to two dimensions, i.e.,  $\mathbf{y}_i \equiv (x_i, y_i)$ . Furthermore, the two terms of orientational memory characterized by the coefficients D and  $\tau$ , vanish. As a result, the linearized operator in Eq. (A1) above contains only two contributions resulting from the dipolar and from the elastic part of the energy Ein Eq. (1) of the main text:

$$\mathcal{L}_{ij} = \mathcal{L}_{ij}^{\rm dip} + \mathcal{L}_{ij}^{\rm el}.\tag{A11}$$

The operator characterizing the dipole-dipole interactions is linearized to

$$\mathcal{L}_{ii}^{\text{dip}} = \frac{3\mu_0}{4\pi} \sum_{k \in \delta\Omega_i} r_{ik}^{-7} m^2 \Big[ \{ 5(x_k - x_i)^2 - r_{ik}^2 \} \hat{x} \hat{x} + \{ 5(y_k - y_i)^2 - r_{ik}^2 \} \hat{y} \hat{y} + 5(x_k - x_i)(y_k - y_i)(\hat{x} \hat{y} + \hat{y} \hat{x}) \Big]$$
(A12)

for the diagonal components and to

$$\mathcal{L}_{ij\neq i}^{\text{dip}} = -\frac{3\mu_0}{4\pi} r_{ij}^{-7} m^2 \Big[ \{ 5(x_j - x_i)^2 - r_{ij}^2 \} \hat{x} \hat{x} + \{ 5(y_j - y_i)^2 - r_{ij}^2 \} \hat{y} \hat{y} + 5(x_j - x_i)(y_j - y_i)(\hat{x} \hat{y} + \hat{y} \hat{x}) \Big]$$
(A13)

for the off-diagonal components.

042311-8

TUNABLE DYNAMIC RESPONSE OF MAGNETIC GELS: ...

PHYSICAL REVIEW E 90, 042311 (2014)

For the linearized operator resulting from the elastic contribution, the diagonal components read

$$\mathcal{L}_{ii}^{\text{el}} = -k \sum_{\ell \in \delta\Omega_i} r_{i\ell}^{-1} \Big[ - \Big\{ L r_{i\ell}^{-2} (x_\ell - x_i)^2 + r_{i\ell} - L \Big\} \hat{x} \hat{x} - L r_{i\ell}^{-2} (x_\ell - x_i) (y_\ell - y_i) (\hat{x} \, \hat{y} + \hat{y} \hat{x}) - \Big\{ L r_{i\ell}^{-2} (y_\ell - y_i)^2 + r_{i\ell} - L \Big\} \hat{y} \hat{y} \Big].$$
(A14)

Its off-diagonal components are obtained as

 $\mathcal{L}_{ij\in\delta\Omega_i}^{\text{el}} = -kr_{ij}^{-1} \Big[ \Big\{ Lr_{ij}^{-2} (x_j - x_i)^2 + r_{ij} - L \Big\} \hat{x} \hat{x} + Lr_{ij}^{-2} (x_j - x_i) (y_j - y_i) (\hat{x}\hat{y} + \hat{y}\hat{x}) + \Big\{ Lr_{ij}^{-2} (y_j - y_i)^2 + r_{ij} - L \Big\} \hat{y}\hat{y} \Big] \text{ (A15)}$ for nearest neighbors and otherwise as

$$\mathcal{L}_{ij\notin\Omega_i}^{\rm el} = 0,\tag{A16}$$

where again  $\Omega_i = \delta \Omega_i + \{i\}.$ 

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042311-9

### Supplemental material for "Tunable dynamic response of magnetic gels: impact of structural properties and magnetic fields"

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In the following we include an illustration of the complete set of relaxational modes for a linear chain of N = 10 particles featuring a "ferromagnetic", "anti-ferromagnetic", and "spiral"-like ground state. After that, an illustration of the complete set of modes for the three small planar example lattices of N = 9 particles in a square-like, rectangular, and hexagonal arrangement is added.

#### I. COMPLETE SET OF RELAXATIONAL MODES FOR THE CHAIN-LIKE AGGREGATES

For illustration, we depict in Figs. 1–3 the complete set of relaxational modes obtained for the three linear chain-like aggregates considered in the main text. The different selected orientational memories lead to three qualitatively different energetic ground states, namely a "ferromagnetic", an "anti-ferromagnetic", and a "spiral"like one. Altogether, we chose these minimal examples to demonstrate that an orientational memory can have a qualitative impact on the relaxation dynamics of the materials, i.e. lead to a markedly different appearance of the dynamic modes. See for example the mode  $\lambda_8$ , which was picked for illustration in Fig. 1 of the main text.

#### **II. COMPLETE SET OF RELAXATIONAL** MODES FOR THE PLANAR LATTICES

Likewise, for illustration, we show in Fig. 4 the complete sets of modes obtained for the three small planar lattices introduced in the main text. Our central point here was to demonstrate that different spatial arrangements can lead to a pronouncedly different nature of the dynamic modes. Again, to keep the argument simple, only small particle arrangements were selected, and for simplicity the magnetic moments were fixed perpendicular to the plane. As we infer, the nature of the relaxatory modes strongly varies with the spatial particle distribution. See for example the mode  $\lambda_5$ , which we picked in this case for illustration in the main text.

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FIG. 1: Complete set of the dynamic relaxational modes for a 10-particle linear chain-like aggregate that shows a "ferromagnetic" energetic ground state (i.e. in the ground state all dipolar moments are oriented along the chain axis). The modes are ordered by increasing magnitude of the relaxation rate. Only one zero mode  $\lambda_1$  exists corresponding to uniform translations of the whole system along the chain axis. Effective parameter values in the numerical calculations were  $k = \mu_0 = \gamma = 1$ ,  $r_{ij}^{(0)} = 2$ , D = 0.1,  $\tau = 0.04$ , and m = 1.68.

2



FIG. 2: Complete set of the dynamic relaxational modes for a 10-particle linear chain-like aggregate that shows an "anti-ferromagnetic" energetic ground state (i.e. in the ground state the dipolar moments feature a finite angle with respect to the chain axis and are alternately rotated by 180 degrees around the chain axis). The modes are ordered by increasing magnitude of the relaxation rate. Here, two zero modes  $\lambda_1$  and  $\lambda_2$  exist corresponding to uniform translations and rotations of the whole system along and around the chain axis, respectively. Effective parameter values in the numerical calculations were  $k = \mu_0 = \gamma = 1$ ,  $r_{ij}^{(0)} = 2$ , D = 0.6,  $\tau = 0.0004$ , and m = 1.68.



FIG. 3: Complete set of the dynamic relaxational modes for a 10-particle linear chain-like aggregate that shows a "spiral"-like energetic ground state (i.e. in the ground state the dipolar moments feature a finite angle with respect to the chain axis and all nearest-neighboring dipoles are rotated by approximately the same finite angle around the chain axis with respect to each other). The modes are ordered by increasing magnitude of the relaxation rate. Here, two zero modes  $\lambda_1$  and  $\lambda_2$  exist corresponding to uniform translations and rotations of the whole system along and around the chain axis, respectively. Effective parameter values in the numerical calculations were  $k = \mu_0 = \gamma = 1$ ,  $r_{ij}^{(0)} = 2$ , D = 0.6,  $\tau = 0.04$ , and m = 1.68.

4



FIG. 4: Complete sets of the dynamic relaxational modes of the 9-particle planar (a) quadratic lattice, (b) rectangular lattice, and (c) hexagonal lattice. The illustrations of the deformed lattices for each mode are superposed to the initial lattice (displayed in gray) corresponding to the energetic ground state. The modes are ordered by increasing magnitude of the relaxation rate. Since the orientations of the magnetic moments are assumed to be fixed perpendicular to the plane, all modes are solely determined by relaxations of the particle positions. In each case, there are three zero modes corresponding to global uniform translations and rotations. Effective parameter values in the numerical calculations were  $k = \mu_0 = \gamma = 1$  and m = 1. We set  $r_{ij}^{(0)} = 2$  for the lengths of the unstrained springs in the square and hexagonal case as well as for the shorter springs in the rectangular case (the longer ones being initialized by  $r_{ij}^{(0)} = 3$ ).

# Paper III. Buckling of paramagnetic chains in soft gels

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# Statement of contribution

The work was supervised by GKA, AMM, SO, and CH. SH performed the main experiments using confocal microscopy under supervision of GKA. JN provided magnetization measurements under supervision of SO. GP did the bulk work associated with the modeling under guidance of AMM, I assisted in this part. I also assisted in the analysis of the experimental data by interpolating the data shown in Fig. 4b. RW performed the coarse-grained simulations shown in the paper under guidance of CH. I also performed simulations in the preliminary stages of the project. These preliminary results did not appear in the paper, but provided some initial insights. I estimate my overall contribution to the project to be around 10%.

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# Soft Matter

# PAPER



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Buckling of paramagnetic chains in soft gels†

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We study the magneto-elastic coupling behavior of paramagnetic chains in soft polymer gels exposed to external magnetic fields. To this end, a laser scanning confocal microscope is used to observe the morphology of the paramagnetic chains together with the deformation field of the surrounding gel network. The paramagnetic chains in soft polymer gels show rich morphological shape changes under oblique magnetic fields, in particular a pronounced buckling deformation. The details of the resulting morphological shapes depend on the length of the chain, the strength of the external magnetic field, and the modulus of the gel. Based on the observation that the magnetic chains are strongly coupled to the surrounding polymer network, a simplified model is developed to describe their buckling behavior. A coarse-grained molecular dynamics simulation model featuring an increased matrix stiffness on the surfaces of the particles leads to morphologies in agreement with the experimentally observed buckling effects.

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# 1 Introduction

Magneto-responsive hybrid gels (MRGs) have been attracting great attention due to their tunable elasticity, swelling properties and shape that can be remotely controlled by a magnetic field. They have potential applications as soft actuators, artificial muscles, as well as sensors<sup>1-3</sup> and can serve as model systems to study the heat transfer in hyperthermal cancer treatment.<sup>4</sup> Compared to other stimuli-responsive gels, MRGs have the advantage of fast response, controlled mechanical properties and reversible deformabilities.<sup>5-7</sup> A typical MRG consists of a chemically cross-linked polymer network, swollen in a good solvent, and embedded magnetic particles.<sup>5,8</sup> The size of the magnetic particles can range from ~10 nm to several  $\mu$ m.<sup>7</sup>

The origin of the magneto-responsive behavior of MRGs is the magnetic interaction between the magnetic filler particles as well as their interaction with external magnetic fields.<sup>9,10</sup> In a uniform magnetic field, paramagnetic particles can be polarized and act as approximate magnetic dipoles. Depending on their mutual azimuthal configuration, the dipolar interactions can be either attractive or repulsive. In a liquid carrier, the dipolar interaction drives the magnetic particles to form chains and columns<sup>11-14</sup> aligning in the direction of the magnetic field. However, in a polymer gel, the particles cannot change their position freely. Instead, relative displacements of the particles, induced e.g. by changes in the magnetic interactions, lead to opposing deformations of the polymer network. As a result, the magnetic interactions can induce changes in the modulus of the gel.7,15 This magneto-elastic effect is well known to be related to the spatial distribution of the magnetic particles.16-21 For example, the modulus of anisotropic materials that contain aligned chain-like aggregates of magnetic filler particles<sup>15,22-24</sup> can be significantly enhanced when an external magnetic field is applied along the chain direction.7 The anisotropic arrangement of particles also dominates the anisotropic magnetostriction effects.<sup>25-2</sup>

Different theoretical routes have been pursued to investigate the magneto-elastic effects of MRGs: macroscopic continuum mechanics approaches,<sup>28,29</sup> mesoscopic modeling,<sup>16–19</sup> and more microscopic approaches<sup>30–32</sup> that resolve individual polymer chains. Theoretical routes to connect and unify these different levels of description have recently been proposed.<sup>33–35</sup> The authors of ref. 34 show how the interplay between the mesoscopic particle distribution and the macroscopic shape of the sample affects the magneto-elastic effect. In addition to these factors, recent experiments and computer simulations also point out that a direct coupling between the magnetic particles and attached polymer chains can play another important role.<sup>1,30,31,36–39</sup>



67

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An experimental model system showing a well-defined particle distribution and a measurable magneto-elastic effect can help to understand the magneto-elastic behavior of MRGs at different length scales. Projected into a two-dimensional plane, the distribution of magnetic particles in thin diluted MRGs can be detected using optical microscopy or light scattering methods.<sup>15,40</sup> By combining these techniques with magnetic or mechanical devices, it is possible to observe the particle rearrangement when the MRG sample is exposed to a magnetic field or mechanical stimuli.15,41 For threedimensional (3D) characterization, X-ray micro-tomography has been used.23 Here we introduce another 3D imaging technique laser scanning confocal microscopy (LSCM). Compared to normal optical microscopy, LSCM is able to observe 3D structures and it has a better resolution.<sup>42</sup> Compared to X-ray micro-tomography, LSCM is faster in obtaining a 3D image and easier to combine with other techniques for real-time investigation.43,44

We use LSCM to study the magneto-elastic effects of paramagnetic chains in soft gels. As a result, we find that the paramagnetic chains in soft gels (elastic modulus <2 Pa) under an oblique magnetic field show rich morphologies. Depending on the length of the chain, modulus of the gel and strength of an external magnetic field, the chains can rotate, bend, and buckle. The deformation field in the polymer network around the deformed paramagnetic chains can also be tracked. The result confirms that the chains are strongly coupled to the polymer network. A simplified model is developed to understand the magnetically induced buckling behavior of the paramagnetic chains in soft gels. In addition to serving as a model experimental system for studying the magneto-elastic effect of MRGs, our approach may also provide a new microrheological technique to probe the mechanical property of a soft gel.45 Furthermore, our results may be interesting to biological scientists who study how magnetosome chains interact with the surrounding cytoskeletal network in magnetotactic bacteria.46

# 2 Materials and methods

The elastic network was obtained by hydrosilation of a difunctional vinyl-terminated polydimethylsiloxane (vinyl-terminated PDMS, DMS-V25, Gelest Inc.) prepolymer with a SiH-containing cross-linker (PDMS, HMS-151, Gelest Inc.). Platinum(0)-1,3divinyl-1,1,3,3-tetramethyldisiloxane complex (Alfa Aesar) was used as a catalyst. A low-molecular-weight trimethylsiloxyterminated PDMS (770 g mol<sup>-1</sup>, Alfa Aesar GmbH & Co. KG, in the following "PDMS 770") served as a solvent that carried the polymer network and the paramagnetic particles. The paramagnetic particles were purchased from microParticles GmbH. They were labeled with fluorophores (visible in LSCM). The materials consist of porous polystyrene spheres. Within the pores, nanoparticulate iron oxide was distributed rendering the particles superparamagnetic. To prevent iron oxide leaching, the particles had a polymeric sealing that also held the fluorophores. The particles had a diameter of 1.48  $\pm$  0.13  $\mu m$  (ESI,† Fig. S1a). We measured the magnetization curve (ESI,† Fig. S1b) of the paramagnetic particles by a vibrating sample magnetometer

(VSM, Lake Shore 7407). We found about 20% deviations in the magnetic properties of the magnetic particles (*e.g.*, magnetic moment, see ESI,† Fig. S2). In order to observe the deformation field in the polymer network, we used fluorescently labeled silica particles as tracers. They had a diameter of  $830 \pm 50$  nm and the surface was modified with *N*,*N*-dimethyl-*N*-octadel-3-amino-propyltrimethoxysilylchloride.

After drying under vacuum at room temperature overnight, the paramagnetic particles were dispersed into PDMS 770. In some samples, tracer particles (3 wt%) were also dispersed into PDMS 770 in this step. The prepolymer mixture was prepared with 9.1 wt% vinyl-terminated PDMS and 90.9 wt% SiH-containing cross-linker. The prepolymer mixture (2.86 wt%) was dissolved in PDMS 770, which contained the paramagnetic particles. Finally, by adding PDMS 770, which carried the catalyst, the concentration of the prepolymer mixture in the sol solution was carefully adjusted in the range from 2.74 wt% to 2.78 wt%. This concentration range guaranteed the formation of soft gels with an elastic modulus lower than 10 Pa (see ESI,† Fig. S3). In the sol solution, the catalyst concentration was 0.17 wt%, and the concentration of magnetic particles was 0.09 wt%. The sol solution was agitated at 2500 rpm with a Reax Control (Heidolph, Schwabach, Germany) for 2 min for homogenization, followed by ultrasonication (2 min, Transsonic 460/H, Elma) to disperse the magnetic particles. Then the sol solution was introduced into a thin sample cell ( $\sim 160 \ \mu m$  thick and  $\sim 1$  cm wide) by capillary forces. The sample cells consisted of two No. 1 standard coverslips, separated by  $\sim\!160\,\mu m$  spacers. After sealing with two-component glue, the cells that contained the sol were exposed to a 100.8  $\pm$  0.5 mT magnetic field. The paramagnetic particles aligned into chains along the direction of the applied magnetic field while the prepolymer was crosslinking. A visible reaction of the prepolymer occurred within 10 min, and the rheological measurements showed that it took about 40 min to form a gel. Due to the low concentration of magnetic particles, the magnetic chains in the gel were well separated (  $\!>\!30~\mu m$  ). The length of the chains varied from a single particle up to about 170 particles. We stored the samples at ambient temperature for at least two weeks before testing. The modulus of the gels in the sample cells was characterized using microrheological techniques (see ESI,† Fig. S4).47

A home-built LSCM setup was used to observe the chain structure in the gel.<sup>43,44</sup> We were able to analyze a sample of thickness of about 150  $\mu$ m. A homogeneous magnetic field was attained by building Halbach magnetic arrays near the sample stage of the LSCM.<sup>48</sup> A 32-magnet array (Fig. 1a) was used to change the field direction while keeping the field strength constant (216.4  $\pm$  1.1 mT, see ESI,<sup>†</sup> Fig. S5). Another 4-magnet Halbach array (see ESI,<sup>†</sup> Fig. S6) was used to change the field strength (up to 100.8  $\pm$  0.5 mT). The magnetic field was measured by a Lake Shore Model 425 Gaussmeter with a transverse probe.

To study the deformation of the PDMS gel around the magnetic chain, the magnetic field strength was increased from 0 mT to  $60.2 \pm 0.3$  mT in 8 steps (~30 min per step). 3D images of the sample with randomly distributed tracer particles were recorded in every step. One isolated magnetic chain was chosen for further analysis. Thus, from the 3D images we extracted a

Soft Matter



Fig. 1 (a) Laser scanning confocal microscopy (LSCM) was used to observe the morphologies of the paramagnetic chains in the soft gels. The Halbach magnetic array provided a homogeneous magnetic field (here  $B = 216.4 \pm 1.1$  mT). This array could be rotated to change the orientation of the magnetic field. (b) The orientation of the magnetic field **B** was successively increased from 0° to 180° in 36 steps (square points). A magnetic chain of 15 particles rotated to follow the magnetic field, but the rotation angle was smaller than the orientation angle of **B** (dashed line). (c) Morphologies of magnetic Arns scale bar is 10  $\mu$ m. The gel in (b) and (c) had an elastic modulus G' of 0.25  $\pm$  0.06 Pa.

time series of 2D images that focused on this magnetic chain. From these 2D images, the trajectories of the embedded tracer particles were determined using the particle tracker plug-in developed on ImageJ software.<sup>49</sup> The corresponding displacements of the tracers were deduced from the trajectories. Naturally, the tracer particles were stochastically distributed over the sample. We divided the images into a grid of small rectangles ( $7.0 \times 5.5 \ \mu m^2$ , containing, on average ~3.5 tracer particles) and determined the average displacement in each cell.

## 3 Results

In the absence of a magnetic field, the paramagnetic chains in a soft gel kept the aligned morphologies (ESI,† Section S1, Movie S1). When a magnetic field (216.4  $\pm$  1.1 mT) was applied in the direction parallel to the chains (Fig. 1c, images for  $0^{\circ}$ ), the paramagnetic chains still aligned with the original chain direction (horizontal). We changed the direction of the magnetic field step-by-step (5° steps) in the clockwise direction ( $\sim 1 \text{ min}$ between steps, quasi-static). We also define the orientation of the magnetic field B as the angle included between the magnetic field and the initial chain direction (see Fig. 1b). The left images of Fig. 1c show a short chain with 15 particles in a gel of elastic modulus G' of 0.25  $\pm$  0.06 Pa. The chain rotated to follow the magnetic field. However, the rotation angle of the chain was smaller than the orientation angle of the magnetic field (Fig. 1b). This difference increased until the orientation of *B* reached 135°, where the chain flipped backward and had a negative angle. The chain again became parallel to the field when the orientation of *B* increased to 180°. The morphology of the chain was the same at orientations of the magnetic field of 0° and 180° because of the superparamagnetic nature of the particles. Note that the chain was not straight at the intermediate angles (*e.g.*, images for 60°, 90° and 120°). Instead it bended.

The images on the right-hand side of Fig. 1c show a longer chain with 59 particles in the same gel. When the orientation of **B** was  $30^{\circ}$ , the chain rotated and bended, with its two ends tending to point in the direction of the magnetic field. When the orientation of B was 60°, the chain wrinkled and started to buckle. A sinusoidal-shape buckling morphology was observed when the magnetic field was perpendicular to the original chain (orientation of the magnetic field of 90°, see ESI,† Section S1, Movie S2). When the orientation of **B** increased from 90° to  $120^{\circ}$ , the left part of the chain flipped downward in order to follow the magnetic field. The right part flipped upward when the orientation of **B** increased from  $120^{\circ}$  to  $150^{\circ}$ . Finally, when the field direction was again parallel to the original chain direction (orientation of the magnetic field of 180°), the chain became straight. The same rotation/buckling morphologies as in Fig. 1c could be observed when increasing the orientation of B from  $180^{\circ}$  to  $360^{\circ}$ .

We also directly applied a perpendicular magnetic field to the paramagnetic chains in the soft gels. The paramagnetic chains showed different buckling morphologies (Fig. 2a) depending on the chain length. Fig. 2b gives frequency counts of the different morphologies in the same sample ( $G' = 0.25 \pm$ 0.06 Pa) under a magnetic field of 100.8  $\pm$  0.5 mT. In total 180 chains were observed. Longer chains tended to buckle with a higher number of half waves. Moreover, the distributions overlapped, implying that paramagnetic chains of identical length could have different morphologies under the perpendicular magnetic field.

These buckling morphologies are reminiscent of the buckling of paramagnetic chains in a liquid medium under a perpendicular magnetic field.<sup>50,51</sup> The most stable morphology in the latter system



Fig. 2 (a) Different morphologies of paramagnetic chains in a soft gel ( $G' = 0.25 \pm 0.06$  Pa) under a perpendicular magnetic field ( $100.8 \pm 0.5$  mT). The original chain direction was horizontal, and the applied magnetic field was vertical. The scale bar is 10  $\mu$ m. (b) Frequency count of different buckling morphologies in the same sample. *M* is the number of half waves.

Paper

69

230 | Soft Matter, 2016, 12, 228-237

View Article Online



Fig. 3 Influence of chain length, strength of magnetic field and elastic modulus of the gel matrix on the amplitude of the S-shaped chains, observed when the magnetic field is applied perpendicularly to the initial chain orientation. (a) The elastic modulus of the gel was  $0.25\pm0.06$  Pa, and the magnetic field strengths were  $216.4\pm1.1$  mT (black squares),  $80.5\pm0.4$  mT (red triangles), and  $18.7\pm0.1$  mT (blue circles), respectively. (b) The magnetic field strength was  $216.4\pm1.1$  mT and the elastic moduli of the gel were  $0.015\pm0.005$  Pa (black squares),  $0.25\pm0.06$  Pa (red triangles), and  $0.78\pm0.22$  Pa (blue circles), respectively. The solid lines are guides to the eye.

was a straight chain aligning along the magnetic field direction. However, in our system this morphology was not observed. Even the short chains showed a rotation angle smaller than the orientation of the magnetic field (*e.g.*, Fig. 1b). The major difference between our experiments and ref. 50 and 51 was the nature of the surrounding medium. In our system, the polymer network around the paramagnetic chains impeded the rotation of the chains into the magnetic field direction (a more detailed discussion will be given below).

We used ImageJ software (NIH<sup>52</sup>) to extract the skeletons of the chains that have 2 half waves (S-shaped). The amplitude of deflection or deformation of different chains was quantified by the square root of the mean square displacement, *i.e.* amplitude =  $(\langle y^2 \rangle - \langle y \rangle^2)^{1/2}$ , where y measures the particle displacement along the field direction. The results are shown in Fig. 3. The amplitude increased with increasing chain length. At the same chain length, the amplitude tends to increase with increasing magnetic field strength (Fig. 3a; an example is also given in Fig. 4a) or with decreasing gel modulus (Fig. 3b).

The modulus dependence of the amplitude demonstrated that the polymer network around the paramagnetic chains impeded the chain deformations. Therefore, the deformation field within the polymer network plays an important role to understand the buckling of the chains. We thus added tracer particles into the gel matrix, and used their trajectories to record the deformation field around the paramagnetic chains. As shown in Fig. 4a, a linear paramagnetic chain buckled and formed an S shape in a perpendicular magnetic field. The amplitude increased with increasing field strength, while the contour length of the chain remained constant. The chain extension decreased along the original chain direction (horizontal direction) and increased along the perpendicular direction. Simultaneously, the polymer network around the chain followed the deformation (Fig. 4b) of the paramagnetic chain, both in the transverse and longitudinal directions. This confirmed that the paramagnetic chain is strongly coupled to the polymer network. Within our experimental



Fig. 4 (a) Influence of the magnetic field strength on a buckling chain. From top to bottom, the magnetic field strengths were 0 mT,  $10.1 \pm 0.1$  mT,  $26.4 \pm 0.1$  mT,  $38.6 \pm 0.2$  mT and  $60.2 \pm 0.3$  mT, respectively. The modulus of this gel was about 0.01 Pa. (b) Tracer particles were inserted into the gel matrix of the sample. Tracking these embedded tracer particles, the deformation field in the gel matrix was determined. The red solid line represents the skeleton of the magnetic chain shown in (a) for a field strength of  $60.2 \pm 0.3$  mT, and the dashed blue line indicates the original chain shape. (c) We modeled the paramagnetic chain in the elastic gel as a continuous object uniformly carrying dipolar magnetic moments. Without the magnetic field, the straight chain was oriented along the *x*-axis. Under a perpendicular magnetic field **B** (oriented along the *y*-axis), the magnetic chain deformation.

resolution, the chain seemed to have a rigid non-slip contact to the surrounding network.

## 4 Modeling

We now turn to a qualitative description of the situation in the framework of a reduced minimal model. Theoretically capturing in its full breadth the problem of displacing rigid magnetic inclusions in an elastic matrix is a task of high complexity and enormous computational effort.<sup>53</sup> We do not pursue this route in the following. Instead, we reduce our characterization to a phenomenological description in terms of the shape of the magnetic chain only. This is possible if the dominant modes of deformation of the surrounding matrix are reflected by the deformational modes of the magnetic chain.

Below, we assume that the chain is composed of identical spherical particles. In its undeformed state, the straight chain is located on the *x*-axis of our coordinate frame. The contour line of the deformed chain running through the particle centers is parameterized as y(x), see Fig. 4c.

#### 4.1 Magnetic energy

First, concerning the magnetic energy along the chain, we assume dipolar magnetic interactions between the particles. In the perpendicular geometry (Fig. 4c), the external magnetic field approximately aligns all dipoles along the *y*-axis. For simplicity, we only include nearest-neighbor magnetic interactions. In an

#### Soft Matter

infinite straight chain, this would result in an error given by a factor of  $\zeta(3) \approx 1.2$ , where  $\zeta$  is the Riemann zeta function.<sup>33,54,55</sup> Within our qualitative approach this represents a tolerable error. Replacing the magnetic interaction energy between the discrete magnetic particles by a continuous line integral and shifting the path of integration from the contour line of the chain to the *x*-axis, we obtain the magnetic interaction energy (see ESI,† Section S3.1)

$$E_{\text{magn}} = W \int_{x_1}^{x_2} \frac{1}{\sqrt{1 + y'(x)^2}} dx, \qquad (1)$$

where  $x_1$  and  $x_2$  label the end points of the chain. The prefactor *W* has the dimension of energy per unit length and is given by (see ESI,<sup>†</sup> Section S3.1)

$$W \approx \frac{3\mu_0 m^2}{4\pi d^4},\tag{2}$$

where  $\mu_0$  is the vacuum magnetic permeability, *m* the magnetic moment of a single particle, and *d* its diameter.

#### 4.2 Elastic bending energy

Next, we need to include terms that provide a measure for the magnitude of the elastic deformation energy. To estimate the importance of different modes of the elastic matrix deformation, we analyze the experimentally determined displacement field around the distorted chain shown in Fig. 4b. For this purpose, we model the continuous matrix by a discretized spring network.<sup>19,56</sup> Network nodes are set at the positions where the displacement field was tracked experimentally. The nodes are then connected by elastic springs. After that, we determine the normal modes of deformation of this network.<sup>56</sup> Finally, we can decompose the experimentally observed deformation field in Fig. 4b into these normal modes. Occupation numbers  $\phi_n$  give the contribution of the *n*th mode to the overall deformation.

The four most occupied modes are shown in Fig. 5. We find a major contribution of "oscillatory" modes, *i.e.* alternating up and down displacements along the central horizontal axis. Such oscillatory displacements of the matrix are connected to corresponding oscillatory displacements of the chain, see Fig. 4b. A bending term of the form (see ESI,† Section S3.2)

$$E_{\text{bend}} = C_{\text{b}} \int_{x_1}^{x_2} \frac{[y''(x)]^2}{\left[1 + y'(x)^2\right]^{5/2}} \,\mathrm{d}x \tag{3}$$

becomes nonzero when such deformational modes occur and is therefore taken as a measure for their energetic contribution. In addition to that, we have experimental evidence that the chain itself shows a certain amount of bending rigidity (see ESI,† Fig. S7), possibly due to the adsorption of polymer chains on the surfaces of the magnetic particles. Similar indication follows from two-dimensional model simulations, see below.

#### 4.3 Elastic displacement energy

The bending term does not energetically penalize rotations of a straight chain, see Fig. 2a for M = 0. Yet, such rotations cost energy. Boundaries of the block of material are fixed, therefore any displacement of an inclusion induces a distortion of the



View Article Online

71

#### Paper



Fig. 5 The four most occupied normal modes of the deformation field in Fig. 5 The four most occupied normal modes of the deformation field in Fig. 4b after projection to an elastic spring network, ordered by decreasing magnitude of contribution to the overall deformation. The normal modes (a), (b) and (d) are of an "oscillatory" type, whereas mode (c) represents a longitudinal contraction. Corresponding relative weights of the modes are  $\phi_{(a)}^2 = 0.095$ ,  $\phi_{(b)}^2 = 0.057$ ,  $\phi_{(c)}^2 = 0.055$ , and  $\phi_{(d)}^2 = 0.051$ , where we normalized the sum of the weights over all modes to unity. For better visualization, the overall amplitudes are rescaled as against the actual weights. The matrix region in close vicinity of the chain is indicated by black arrows.

surrounding gel matrix. We model this effect by a contribution (see ESI,† Section S3.3)

$$E_{\rm displ} = C_{\rm d} \int_{x_1}^{x_2} [y(x)]^2 [1 + y'(x)^2]^{3/2} \, \mathrm{d}x. \tag{4}$$

This term increasingly disfavors the rotations of longer straight chains, which reflects the experimental observations (see ESI,† Fig. S9).

Moreover, in Fig. 5c the third dominating mode of the matrix deformation corresponds to a contraction along the chain direction and an expansion perpendicular to it. We conjecture that this should be the dominating mode in the deformational far-field, yet this hypothesis needs further investigation. It is induced by chain deflections in *y*-direction, which imply a matrix contraction in *x*-direction (experimentally we observe that the chain length is conserved under deformations and that the individual magnetic particles remain in close contact). We simultaneously use  $E_{displ}$  to represent the energetic contribution of this type of underlying matrix deformation.

#### 4.4 Energetic evaluation

We now consider the resulting phenomenological model energy  $E_{\text{tot}} = E_{\text{magn}} + E_{\text{bend}} + E_{\text{displ}}$ . A standard procedure would consist of minimizing  $E_{\text{tot}}$  with respect to the functional form of y(x). Corresponding calculations and results are listed in the ESI,† Section S3.4. There are, however, severe limitations to this route in the present case. In contrast to several previous approaches in different contexts, <sup>57–61</sup> our magnetic chains are of finite length and show significant displacements at their end points, see Fig. 2. Detailed knowledge of the boundary conditions of the deflection y(x) and its derivatives at the end points of the chain would be necessary to determine the chain shape.

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Soft Matter

Indeed the solutions become very sensitive to additional conditions (see ESI,† Section S3.4). In our case, the necessary additional boundary conditions depend on the interaction with the matrix. They are not accessible in the present reduced framework.

Therefore, we proceed in a different way. We use as an input for our calculations the experimental observations. The experimentally found chain shapes can to good approximation be represented by a polynomial form

$$y(x) = S \prod_{m=0}^{M-1} (x - mb) \text{ for } x_1 \le x \le x_2,$$
 (5)

where *M* is again the number of half-waves, the prefactor *S* sets the strength or amount of chain deformation and deflection, *b* is the spacing between the nodes, and the interval  $[x_1, x_2]$  follows from the experimental result of preserved chain length *L*,

$$\int_{x_1}^{x_2} \sqrt{1 + [y'(x)]^2} \, \mathrm{d}x = L. \tag{6}$$

We prefer the polynomial form of eqn (5) to, for instance, a sinusoidal ansatz because it better reproduces the deformations of our finite-sized chain objects. In particular, the pronounced displacements of the chain ends, see *e.g.* Fig. 2a, are well captured by polynomial forms. Likewise, an experimentally observed tendency to smaller oscillation amplitudes inside longer chains is covered. Furthermore, rotations of short straight chains are readily included in this way.

Next, we insert eqn (5) into the above expressions for the energy and minimize with respect to *S*,  $x_1$ , and  $x_2$  for a given *M*, with the constraint of constant length *L*, see eqn (6). The minimization was performed using Wolfram Mathematica minimization routines.<sup>62</sup> Parameter values of the coefficients  $C_{\rm b}$  and  $C_{\rm d}$  are found by matching the resulting shapes to the corresponding experimental profiles (chain deformations for G' = 0.25 Pa and magnetic field B = 100.8 mT as in Fig. 2a, M = 2, are used for this purpose). We obtain  $C_{\rm b} \approx 0.01 W b^2$  and  $C_{\rm d} \approx 2W/b^2$ .

To illustrate how the energetic contributions vary under increasing preset deformation, we plot in Fig. 6 the energies for increasing *S* for two fixed combinations of *M* and *L*. The total energy  $E_{\text{tot}}$  shows a global minimum in both panels, which we always observed for symmetric chain deformations. As expected, with increasing *S* the magnetic energy decreases, whereas the deformation energies increase.

Next, we determine the minimal total energy as a function of chain length L for different numbers of half-oscillations M, see Fig. 7. With increasing chain length L the shapes that minimize the energy show an increasing number of half-waves M in good agreement with the experimental data in Fig. 2b.

Moreover, we quantify the amplitude of the chain deflection or deformation by

Amplitude = 
$$\sqrt{\langle y^2 \rangle - \langle y \rangle^2}$$
,  $\langle \cdot \rangle = \frac{\int_{x_1}^{x_2} dx}{x_2 - x_1}$ . (7)

Resulting values are plotted in Fig. 8. As mentioned above, we optimized the model parameters with respect to the experimental



**Fig. 6** Contributions to the total energy as a function of the amount *S* of deformation and minimized with respect to  $x_1$  and  $x_2$  for a chain of the shape given by eqn (5). Here we show the cases (a) M = 2, L = 3b and (b) M = 4, L = 4.5b. The total energy  $E_{tot}$  has a global minimum as a function of *S*, which corresponds to the most stable chain shape. We always observed the global minimum for symmetric shapes.



Fig. 7 Energies  $E_{tot}$  of chain deformations of the shape given by eqn (5), minimized with respect to S,  $x_{1,}$  and  $x_{2}$  as a function of chain length L and number of half-oscillations M. Each curve describes a shape of M half-waves with a minimum total length of (M - 1)b. The resulting curves show crossing points from where the total energy for an increasing L is lowered by bending one extra time (jumping to a higher M) rather than conserving the same shape.

data for a magnetic field intensity of B = 100.8 mT. We demonstrate in Fig. 8 that moderate variations of the magnetic field intensity only slightly affect our results: the brighter curves are obtained when multiplying the magnetic energy scale *W* by a factor ~1.42, corresponding to an increased magnetic field intensity of approximately  $B \sim 216$  mT (see ESI,<sup>†</sup> Fig. S1b). This is in agreement with the experimental observations. We include in Fig. 8 the experimentally determined values for B = 80.5 mT and B = 216.4 mT. Only a slight trend of increasing deflection amplitudes is found for this increase of magnetic field intensity.

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3

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Soft Matter



Fig. 8 Resulting deflection amplitudes of the chain deformation, calculated according to eqn (7). Darker curves represent the model parameters optimized with respect to the experimental shapes for a magnetic field intensity B = 100.8 mT. Brighter curves were obtained by increasing the magnetic energy scale W by a factor  $\sim$ 1.42, which corresponds to an increased magnetic field intensity of B  $\sim$  216 mT (see ESI,† Fig. S1b), comparable with the triangular experimental data points. Both, model curves and included experimental data points, demonstrate that moderate variations of the magnetic field intensities only slightly affect the observed deflection and deformation amplitudes. The value of b necessary to perform the analysis was determined from the M = 2 experimental data as b = 12.6  $\mu$ m. For  $M \ge 2$ "kinks" appear in the curves, which arise from a change in the type of solution as illustrated by the insets: for each  $M \ge 2$  curve, left of the kink the chain deformation shows nodes at the end points of the chain, i.e.  $y(x_1) \simeq y(x_2) \simeq 0$  (lower left inset); right from the kink, these outer nodes are shifted to the inside of the chain (upper right inset). As seen from Fig. 7, the solutions left of the kinks are not energetically preferred.

Together, although the curves for M = 2 in Fig. 8 slightly overshoot the data points, Fig. 7 and 8 are in good agreement with the experimental results. The amplitude of deflection and deformation is not observed to unboundedly increase with chain length *L* in the experiments. Likewise, our model predicts that longer chains prefer to bend one extra time (switching to higher-*M* shape) rather than to show too large deflection amplitudes.

# 5 Coarse-grained molecular dynamics simulation

We also studied the buckling of the chain using two-dimensional coarse-grained molecular dynamics simulations by means of the ESPResSo software.<sup>63,64</sup> A simple model was developed that allowed us to analyze the influence of particular interactions and material properties on the buckling effect. Here, we focus on the elasticity of the polymer matrix in the immediate vicinity of the magnetic particles.

By choosing the coarse-grained scale for our model, we ignore any chemical details but rather describe the system in terms of the magnetic particles as well as small pieces of polymer gel. As the buckling effect appears to be two-dimensional, and as the ground states for systems of dipolar particles have also been found to be two-dimensional,<sup>55</sup> we use this dimensionality for our simulations. We study a chain of 100 magnetic particles with a significant amount of surrounding elastic matrix.

As in the analytical approach, the gel matrix is modeled by a network of springs. Here, however, we use a regular hexagonal mesh as a basis. To mimic the non-linear elastic behavior of

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#### Paper

73

polymers, we use a finitely extensible non-linear elastic spring potential (FENE-potential<sup>65</sup>) for the springs along the edges of the mesh. As a simple implementation of the finite compressibility, we introduce FENE-like angular potentials on the angles at the mesh points, with a divergence at  $0^{\circ}$  and  $180^{\circ}$  (see ESI,† Section S4.2). The magnetic particles are modeled as rigid spheres interacting by a truncated, purely repulsive Lennard-Jones potential, the so-called Weeks-Chandler-Andersen potential (see ESI,† Section S4.1).66 Their magnetic moment is assumed to be determined purely by the external magnetic field and to be constant throughout the simulation, *i.e.* we assume that the external field is significantly stronger than the field created by the particles. The magnetic moments are taken parallel to the external field and with a magnitude given by the experimentally observed magnetization curve. The coupling between the particles and the mesh is introduced in such a way, that under the volume occupied by a particle, the mesh does not deform, but rigidly follows the translational and rotational motion of the particle (see ESI,<sup>†</sup> Section S4.3). A local shear strain on the matrix can rotate a magnetic particle, but not its magnetic moment.

An important point is the elasticity of the polymer matrix in the immediate vicinity of the magnetic particles and, in particular, between two magnetic particles. We study two situations here, the first one including a stiffer region in the immediate vicinity of the particles, the second one without such a stiffer layer and directly jumping to the bulk elasticity. The stiffer layer, if imposed, is created using a spring constant larger by three orders of magnitude on those springs which originate from mesh sites within the particle volumes (see ESI,† Section S4.3). The angular potentials are unchanged.

A comparison between the cases with and without a stiffer layer of gel around the magnetic particles can be seen in Fig. 9. The images show a small part of the resulting configuration of magnetic particles and the surrounding mesh for a field applied perpendicular to the initial chain direction. Thus the magnetic moments of the particles are oriented perpendicular to the undistorted chain direction. This results in an energetically unfavorable parallel side-by-side configuration for the dipole moments. The energy can be reduced either by increasing the distance between the dipoles along the initial chain direction, or by moving dipoles perpendicularly to the initial chain direction so that they approach the energetically most favorable head-to-tail configuration. If the matrix is made stiffer immediately around the particles, and thus the contour length of the chain cannot change significantly, the re-positioning towards the head-to-tail configuration causes the buckling effect observed in the experiments (Fig. 9). When one assumes the matrix immediately around the magnetic particles to be as soft as in the bulk of the material, neighboring particles can move apart and the chain breaks up into individual particles or small columns perpendicular to the original chain direction. Additionally, a layer of increased stiffness also introduces a bending rigidity of the chain. In Fig. 10, the full chain and the surrounding matrix is shown for an external field of magnitude 216 mT, which from the experimental magnetization measurements corresponds to a magnetic moment of about 4.5  $\times$  10  $^{-14}$  A m  $^2$  (see ESI,† Fig. S1b). Due to the different

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Fig. 9 Detailed view of the local deformations in the polymer mesh around the magnetic particles with a layer of increased stiffness (top) and without one (bottom) in the immediate vicinity of the particle surfaces. The external magnetic field of strength 216 mT is applied in the vertical direction. When the boundary layer is assumed to be stiffer than the bulk (top), the buckling effect, as observed in the experiments, occurs. When the layer around the particles is soft (bottom), neighboring particles either form tight columns parallel to the field, or separate in the direction perpendicular to the field.

dimensionalities, the elastic modulus of the surrounding matrix could not be directly matched to the experimental system.

Actually, the amplitude of the chain oscillation increases when the external field is higher and induces larger dipole moments in the particles. This increases the tendency of the magnetic moments to approach the head-to-tail configuration, which in turn leads to a stronger deformation of the matrix. We note that the relative amplitude of the buckling along the chain is similar in the simulations (Fig. 9) and experiments (Fig. 2). The matrix surrounding the chain follows the chain oscillation with an amplitude that decreases over distance from the chain. Deviations may be expected from the deformational far-field in the experimental system due to the different dimensionalities of the systems.

In the ESI<sup>†</sup> (Fig. S7) we show an experimental evidence for the existence of a stiff polymer layer around the magnetic particles. The sample was prepared at a concentration of prepolymer mixture well below the percolation threshold, *i.e.*, some cross-linking of the polymer took place in the sample but no macroscopic gel was formed. When this cross-linking was done under an applied magnetic field, the particle chains stayed intact even after removal of the magnetic field (Fig. S7a, ESI†). Hairpin or "S"-shape morphologies were observed when these chains were exposed to a magnetic field (Fig. S7b, ESI†), indicating that they have a bending rigidity.<sup>50,51</sup> Our interpretation of this behavior is that a stiff gel layer connects the particles and stabilizes the particle chains, even though no bulk gel is formed. As the magnetic particles have a good affinity for PDMS (e.g., the magnetic particles can be easily dispersed into PDMS), we conjecture that there is an adsorbed layer of polymer (i.e., PDMS prepolymer or cross-linker) on the surface of the magnetic particles.<sup>67</sup> Therefore, the gel layer on the particles is denser and thus stiffer than in the bulk. Further study of the



Fig. 10 Buckling chain of magnetic particles and the surrounding polymer mesh for an external field of magnitude 216 mT pointing along the vertical direction. In this image, roughly one quarter of the full simulation area is shown. The surrounding matrix follows the chain oscillation with an amplitude that decreases over distance from the chain.

stiff polymer layer and its effect on the buckling behavior is under way.

Moreover, in Fig. S8 (ESI<sup>†</sup>) we show that the buckling behavior of the magnetic chains can still be observed in the gel when we increase the elastic modulus to 170 Pa (for this purpose, carbonyl iron particles are used as magnetic filler particles). Our studies on that stiffer sample provide further evidence that the interaction between the magnetic particles and the polymer matrix in their close vicinity can play an important role in the magneto-elastic response of soft MRGs.

# 6 Conclusions

We have shown that paramagnetic chains in a soft polymer gel can buckle in a perpendicular magnetic field. The buckling morphology depends on the length of the chain, the strength of the magnetic field and the modulus of the gel. Longer chains form buckling structures with a higher number of half waves. Higher strengths of the magnetic field and a lower modulus of the gel matrix can lead to higher deformation amplitudes. The deformation field in the surrounding gel matrix confirms that the embedding polymer network is strongly coupled to the paramagnetic chain. A minimal magneto-elastic coupling model is developed to describe the morphological behavior of the paramagnetic chains in the soft gel under a perpendicular magnetic field. It shows that the chains deform in order to decrease the magnetic energy. This is hindered by the simultaneous deformation of the gel matrix, which costs elastic energy. Additionally, we have introduced a coarse-grained molecular dynamics simulation model, which covers both, the magnetic particles and the surrounding polymer mesh. In this model, the buckling of the chains can only be observed when the surface layer around the particles is assumed to be stiffer than the bulk of the gel. This prevents the chains from breaking up into columns oriented perpendicular to the initial chain direction or into isolated particles. These findings support the picture that the embedded magnetic chains themselves feature a certain bending rigidity, possibly due to the existence of a stiff polymer layer on the particle surfaces.

Since the magneto-elastic effect demonstrated and analyzed in this paper is pronounced, reversible, and controllable, it may

#### Soft Matter

be useful for designing micro-devices, *e.g.* micro-valves and pumps for microfluidic control.<sup>68</sup> As the morphologies of the buckling paramagnetic chains are correlated with the modulus of the gel matrix, we may use them as mechanical probes for soft gels (similarly to active microrheology techniques).<sup>45</sup> Moreover, our study may help to understand the physical interactions between the magnetic chains and the surrounding cytoskeleton network in magnetotactic bacteria.<sup>46</sup> In our future study we will focus on how the interfacial coupling between the magnetic particles and the polymer network influences the local magneto-elastic coupling effect.

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236 | Soft Matter, 2016, 12, 228-237

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76

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# **Supplementary Information**

# Buckling of paramagnetic chains in soft gels

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# **1** Supplementary movies

Movie S1 Typical 3D morphology of paramagnetic chains in a soft gel in the absence of a magnetic field. The elastic modulus of the gel is  $0.78 \pm 0.22$  Pa and the scale bar is 300  $\mu$ m.

Movie S2 Typical 3D morphology of paramagnetic chains in a soft gel under a perpendicular magnetic field ( $B = 216.4 \pm 1.1$  mT). The elastic modulus of the gel is  $0.78 \pm 0.22$  Pa and the scale bar is 300  $\mu$ m.

# 2 Supplementary information for experiments

# 2.1 Paramagnetic particles

According to the manufacturer (microParticles GmbH), the paramagnetic particles were fabricated based on porous polystyrene particles. Within the pores of the polystyrene particles, nanoparticulate iron oxide was distributed, rendering the particles superparamagnetic. To prevent iron oxide leaching, the paramagnetic particles were covered with thin polymer layers which also held the fluorophores. The diameter of the paramagnetic particles from the scanning electron microscopy (SEM) images (see Fig. S1a) is  $1.4\pm0.2 \,\mu$ m. We also measured the length of linear particle chains in polydimethylsiloxane using laser scanning confocal microscopy (LSCM). Dividing the length of the chains by the number of particles in the chains we got a diameter of  $1.48\pm0.13 \,\mu$ m (average for 20 chains). We used the latter value for calibration and calculation in this paper.



**Figure S1** (a) Scanning electron microscopy (SEM) image of the paramagnetic particles. The scale bar is 5  $\mu$ m. (b) Magnetization curve of the paramagnetic particles. The magnetic field *H* was increased from 0 kA/m to 900 kA/m and then decreased to 0 kA/m, and the magnetization *M* showed no hysteresis, as indicated by the red arrows.

The magnetization curve of the paramagnetic particles was measured by a vibrating sample magnetometer (VSM, Lake Shore 7407). The magnetization of the particles showed no hysteresis when the external magnetic field was increased and decreased, demonstrating the superparamagnetic property (Fig. S1b).

# 2.2 Calibrating the magnetic properties of the paramagnetic particles

A spherical colloidal particle moving in a viscous fluid with a relative velocity  $\mathbf{v}$  is subject to a frictional force (Stokes' drag)

$$\mathbf{F}_d = -6\pi\eta R \mathbf{v},\tag{S1}$$

where *R* is the radius of the particle and  $\eta$  is the dynamic viscosity of the fluid.



**Figure S2** Histogram of velocity of paramagnetic particles moving in a viscous liquid. The viscosity of the liquid is  $0.61 \pm 0.02$  Pas. The magnetic field strength is  $32.7 \pm 0.2$  mT and the magnetic gradient is  $3.63 \pm 0.02 \times 10^{-5}$  mT/ $\mu$ m. Using a density of 1.7 g/cm<sup>3</sup>, the movement of the particles, the magnetic gradient, and the magnetization curve can be correlated. <sup>S1,S2</sup>

Under a magnetic field **B**, the magnetic particles move along the magnetic field gradient. The magnetic force  $\mathbf{F}_m$  acting on a paramagnetic particle is <sup>S1,S2</sup>

$$\mathbf{F}_m = \mathbf{m} \cdot \nabla \mathbf{B},\tag{S2}$$

where  $\mathbf{m}$  is the induced magnetic dipole moment of the paramagnetic particle. In the steady state, the magnetic force is balanced by Stokes' drag, thus

$$6\pi\eta R\mathbf{v} = \mathbf{m} \cdot \nabla \mathbf{B}.\tag{S3}$$

From experiments, the left-hand side of Eq. (S3) and  $\nabla \mathbf{B}$  can be measured directly. We dispersed the paramagnetic particles into a viscous liquid with a viscosity of 0.61  $\pm$  0.02 Pas. The dispersion was added into a sample cell with a thickness of 160  $\mu$ m. Then the sample cell was carefully sealed in order to avoid drift due to large-scale flow of the liquid. We used a magnetic field of  $32.7 \pm 0.2$  mT with a gradient of  $3.63 \pm 0.02 \times 10^{-5}$  mT/ $\mu$ m to induce flow of the paramagnetic particles. The magnetic field was measured by a Lake Shore Model 425 Gaussmeter with a transverse probe. The movement of the particles (far from the walls of the sample cell) was recorded using LSCM. The magnitude of the magnetic moment *m* can be calculated via  $m = 4\pi R^3 \rho M/3$ , where *M* can be obtained from the magnetization curve (Fig. S1b) and  $\rho$  is the density of the paramagnetic particles. Using  $\rho = 1.7$  g/cm<sup>3</sup>, we find that Eq. (S3) is satisfied. This density value is in agreement with the one provided by the manufacturer (1.5–2 g/cm<sup>3</sup>).

In our study the paramagnetic particles are not ideally monodispersed and the induced magnetic moment is not ideally identical for every particle. For example, the velocity of the paramagnetic particles moving in a viscous liquid under a magnetic gradient has a distribution with  $\sim 20\%$  deviation (Fig. S2). According to Eq. (S3), the magnetic moment of the particles should have a similar distribution. For simplification, we do not consider this distribution in the modeling and simulation.



# **2.3** Determining the elastic modulus of the soft gels

**Figure S3** (a) Shear elastic modulus (G') of the gels as a function of angular frequency. The gels were fabricated with different concentrations (c) of the prepolymer mixture as indicated for the different sets of data points. (b) The low-frequency G' of the gels plotted as a function of c. The solid curve is the best fit of Eq. (S4) to the experimental data.

The rheological experiments were performed in a strain-controlled rheometer (ARES-LS, Rheometric Scientific Inc., Piscataway, NJ, USA) equipped with a Couette cell at room temperature. The elastic modulus (G') shows a plateau at low frequencies for the soft gels (Fig. S3a), reflecting the formation of a percolating network. The plateau modulus increases with increasing concentration of the prepolymer mixture (c) following a power law<sup>S3</sup>

$$G' = G'_0 (c - c^*)^t,$$
(S4)

where  $G'_0$  is a prefactor, *t* is the critical exponent, and  $c^*$  is the percolation concentration. From this power law it is evident that the elastic modulus of the soft gels becomes very sensitive to the concentration of the prepolymer mixture when the concentration of the prepolymer mixture is close to  $c^*$ .

As a result, we cannot directly use the elastic modulus obtained from macroscopic rheological measurements to characterize our soft gels in the sample cells ( $\sim 160 \ \mu m$  thick), because a little change of the concentration of the prepolymer mixture during preparation of the gels can lead to a significant difference of the elastic modulus. In experiment, the concentration of the prepolymer mixture in the sample cells is difficult to control precisely, because the concentration can change slightly if some prepolymer molecules are adsorbed to the walls of the cell, to the pipette tips, or to the paramagnetic particles.

In order to solve this problem, we measured the elastic modulus of the soft gels directly in the sample cells (containing the paramagnetic chains) by passive microrheology (i.e., particle tracking). About 15 single particles were used as the mechanical probes, and a fast camera (Photron, FASTCAM SA1) and a microscope (Leica DMI6000B) were used to detect the thermal fluctuations of the particles.<sup>S4,S5</sup> Fig. S4a shows the mean-square displacement (MSD) of the particles in the gels as a function of lag time. At long lag times the MSD levels off, indicating that the particles are confined in a network. The moduli of the gels can be calculated from the MSD of the particles based on the generalized



**Figure S4** Probing the viscoelastic properties of the gels in the sample cells (containing the paramagnetic chains). (a) Mean-square displacement (MSD) of the particles in the gels as a function of lag time. The concentrations of the prepolymer mixture for the four samples A–D are 2.78 wt%, 2.77 wt%, 2.76 wt%, and 2.76 wt%, respectively. The slight changes of concentration can lead to significant differences in the MSD, because the concentration used here is close to the percolation threshold ( $c^* = 2.74\%$ , see Fig. S3b).<sup>S3</sup> It is the method of passive microrheology that makes it possible to measure the viscoelastic properties of the soft gels (containing the paramagnetic chains) directly within the sample cells. (b) Elastic modulus (G') calculated from the MSD. (c) Elastic modulus (G') and loss modulus (G'') plotted as functions of angular frequency ( $\omega$ ) for sample C. At low frequencies, the elastic character dominates.

Stokes-Einstein relation (GSER)<sup>S4,S6</sup>

$$G^*(\omega) = \frac{k_B T}{\pi R(i\omega)\mathscr{F}_u\{MSD(t)\}},\tag{S5}$$

where  $G^*(\omega)$  is the complex shear modulus and  $\mathscr{F}_u\{MSD(t)\}$  is the unilateral Fourier transform  $(\mathscr{F}\{f(t)\} = \int_0^\infty e^{-i\omega\tau} f(\tau) d\tau)$ . Using the algorithm from Crocker and Weeks, <sup>S4,S5</sup> we calculated the shear moduli (Fig. S4b). Fig. S4c shows that at low frequencies (corresponding to long time scales) the gel is mainly elastic. In the main article we use the elastic modulus of the gels obtained from passive microrheology to characterize the gels.

# 2.4 Magnetic field of the Halbach magnetic array

We used permanent magnets to provide a homogeneous magnetic field.<sup>S7</sup> The NdFeB permanent magnets were purchased from AR.ON GmbH. According to the manufacturer they have a remanence of 1.32 T. The magnets were arranged as shown in Fig. 1a. The magnets had dimensions of  $8 \times 8 \times 15 \text{ mm}^3$  and  $14 \times 14 \times 15 \text{ mm}^3$  for the inner and outer rings, respectively. The magnetic field at the center of this magnetic array was homogeneous (Fig. S5). This magnetic array was built around the objective of our home-built LSCM and it could be rotated by a motor. We put the samples in the middle of this array and used LSCM to observe the samples under the magnetic field. The typical observation area was in the central 2 mm<sup>2</sup>, where the homogeneity of the magnetic field was ~ 2000 ppm (Fig. S5b).



**Figure S5** Comparison of measured and simulated magnetic flux density in the Halbach magnetic array. The arrangement of the 32 permanent magnets is shown in Fig. 1a. (a) Magnitude *B* of the magnetic flux density along the x-axis. The red solid curve shows simulation results using Comsol software. The solid black points are experimental data (measured by a Lake Shore Model 425 Gaussmeter with a transverse probe). The data for x around 0 are shown in (b). The homogeneity in the central 2 mm<sup>2</sup> is ~ 2000 ppm. (c) Simulated magnetic field in the magnetic array. The magnetic flux density is shown by color map and the direction of the magnetic field is shown by red arrows.

The magnetic field of this magnetic array was simulated in Comsol Multiphysics (http://www.comsol.com). The parameters for the simulation were the same as in the experiments, such as the positions, the dimensions, and the remanence (1.32 T) of the magnets. The permanent magnets were modeled using Ampère's law. The influence of

the housing (made of Aluminum) of the magnets was not considered. A detailed description of the simulation can be found in the model library of Comsol Multiphysics, "Static Field Modeling of a Halbach Rotor".



**Figure S6** Magnetic field of the four-magnet Halbach array. (a) By changing the separation between the 4 magnets, the magnetic flux density at the center of the magnetic array can be changed. The red circle points are obtained from simulation using Comsol software, and the black square points are measured by a Lake Shore Model 425 Gaussmeter with a transverse probe. The homogeneity in the central 2 mm<sup>2</sup> is ~ 4000 ppm. (b) Simulated magnetic field in the four-magnet array. The magnetic flux density is shown by color map and the direction of the magnetic field is shown by red arrows.

In some experiments we needed to change the magnetic field strength. This was realized by using a four-magnet Halbach array (Fig. S6, the magnets had dimensions of  $14 \times 14 \times 15$  mm<sup>3</sup>). By changing the distance between the magnets, the magnetic flux density in the center of this array could be changed from 0 mT to 101 mT. The homogeneity of this array in the central 2 mm<sup>2</sup> was ~ 4000 ppm.

# 2.5 Bending rigidity of the paramagnetic particle chains

Here we provide experimental evidence that the paramagnetic particle chains already by themselves (i.e. without the embedding polymer matrix) feature a bending rigidity. For this purpose, instead of preparing a percolating polymer network (gel), we prepared a sol. We decreased the concentration of the prepolymer mixture to  $c^*/2$  ( $c^*$  is the critical concentration at which a percolating network can be formed, see Fig. S3b). The prepolymer mixture reacted and formed a sol after the catalyst was added. During the reaction a magnetic field of 100.8 mT was applied, thus the magnetic particles in the sol aligned into chains. If the particles had not been connected by the polymer, the linear particle chains would not have survived after the magnetic field was removed because of thermal agitation. However, we found that the linear particle chains were stable in the sol even for several days (Fig. S7a). Once more applying a magnetic field (18.7 mT) most of the permanent paramagnetic chains in the sol aligned along the magnetic field direction (Fig. S7b). However, some of the chains bent and showed hairpin or "S"-shape morphologies (marked by the red arrows in Fig. S7b), indicating that the chains had a bending rigidity.<sup>S8</sup>



**Figure S7** Typical chain morphologies in the sol (a) in the absence of a magnetic field and (b) under a magnetic field. The magnetic field of 18.7 mT was applied horizontally. Under the magnetic field most of the paramagnetic chains aligned along the magnetic field direction. Some of the chains bent and showed hairpin or "S"-shape morphologies (marked by the red arrows), indicating that they have a bending rigidity. <sup>S8</sup> The scale bars are 50  $\mu$ m.

We conjecture that some prepolymer molecules in the solution were adsorbed onto the surfaces of the paramagnetic particles. When the prepolymer cross-linked, a polymer layer on the surfaces of the particles was formed and connected the particles. This polymer layer contributed to the bending rigidity. Only when the concentration of the prepolymer mixture is higher than  $c^*$ , a gel can be formed in the bulk. Apparently, already below this concentration, a connecting polymer layer can be formed on the surfaces of the paramagnetic particles. This suggests that a thin layer of polymer with a higher modulus compared to the bulk should be considered to understand the buckling behavior of the paramagnetic chains in the soft gels.

# 2.6 Buckling of magnetic particles in a "stiff" gel

In the main article, very soft gels (<1.5 Pa) were used as a matrix. If a stiffer gel was used, the paramagnetic particle chains could not deform the gel significantly under the magnetic field of 216 mT (maximum field in our set-up). Here we used carbonyl iron (CI, CC grade, BASF, Germany, d50 value=3.8-5.3  $\mu$ m) as magnetic particles in order to increase the magnetic force between the magnetic particles. First, the saturation of magnetization of CI (~ 250 Am<sup>2</sup>/kg) is significantly larger than that of our otherwise used paramagnetic particles (~ 20 Am<sup>2</sup>/kg); second, the density of CI (~ 8 × 10<sup>3</sup> kg/m<sup>3</sup>) is higher than that of our paramagnetic particles (~ 1.7 × 10<sup>3</sup> kg/m<sup>3</sup>); last, the size of CI is about 3 times larger. According to  $m = 4\pi R^3 \rho M/3$  (see Section 2.2), the magnetic moment can be 10<sup>3</sup> times larger compared to our paramagnetic case in the main article. As a result, even in a relatively "stiff" gel, the CI magnetic chains can deform the gel significantly. As shown in Fig. S8, in the gel with an elastic modulus of 170 Pa, the CI chains can buckle when a magnetic field of 100.8 mT is applied.

However, promoted by the polydispersity of the CI particles, the CI chains are not as smooth as the chains formed by the monodisperse paramagnetic particles (see Figs. 1 and 2 in the main article for comparison). In addition, we also observed fractures in some CI chains (Fig. S8c) probably due to the polydispersity of the particles. However, the chains



**Figure S8** Magnetic chains formed by carbonyl iron particles in a gel with an elastic modulus of 170 Pa. (a) Without magnetic field, (b, c) under a magnetic field of 100.8 mT along the vertical direction. The inset in (c) shows an enlarged image of the fracture of the magnetic chain. The scale bars are 50  $\mu$ m. These images were obtained using a 10× objective (NA=0.28, M Plan Apo) which collected the reflection light from the carbonyl iron particles.

do not break up into structures as shown in Fig. 9 of the main article (lower image), suggesting that there is still a relatively stiff polymer layer around the CI particles.

# **3** Supplementary information concerning the modeling

## **3.1** Magnetic interactions within the chain

In the following, we derive Eqs. (1) and (2) of the main article. We start from two neighboring particles on the chain. According to the assumptions made in the main article, each of them carries a magnetic moment  $\mathbf{m}$  oriented in y-direction. They interact via the dipole-dipole magnetic interaction given by

$$V_{dd} = \frac{\mu_0}{4\pi} \left[ \frac{\mathbf{m} \cdot \mathbf{m}}{r^3} - \frac{3 \left( \mathbf{m} \cdot \mathbf{r} \right) \left( \mathbf{m} \cdot \mathbf{r} \right)}{r^5} \right],$$
(S6)

where **r** is the vector joining the centers of the particles,  $r = |\mathbf{r}|$ , and  $\mu_0$  is the vacuum magnetic permeability. Since the particles on the chain are experimentally observed to remain in contact, we have r = d, with d the particle diameter. Furthermore, we ignore the first term in the square brackets because it is constant under the given assumptions. Indicating by  $\alpha$  the angle between **r** and **m**, we obtain

$$V_{dd} \sim -\frac{3\mu_0 m^2}{4\pi d^3} \cos^2 \alpha. \tag{S7}$$

Since **m** is oriented in the y-direction,  $\psi = \pi/2 - \alpha$  is the angle between **r** and the x-axis. Skipping another constant term resulting from  $\cos^2 \alpha = 1 - \sin^2 \alpha$ , the non-constant part of the dipole-dipole interaction can thus be rewritten as

$$V_{dd} \sim \varepsilon_m \sin^2(\psi - \pi/2), \quad \text{with } \varepsilon_m = \frac{3\mu_0 m^2}{4\pi d^3}.$$
 (S8)

For an undeformed infinite straight chain oriented along the *x*-axis in the above set-up, the resulting expression for the total dipolar magnetic interaction energy per particle along the whole chain then reads

$$V_{dd}^{chain} \sim \varepsilon_m \sum_{n=1}^{\infty} \frac{1}{n^3} = \varepsilon_m \zeta(3), \tag{S9}$$

where  $\zeta$  is the Riemann Zeta function and  $\zeta(3) \simeq 1.202$ . Here,  $\varepsilon_m$  sets the scale of the nearest-neighbor dipolar interaction. In our minimal model the correction described by the factor  $\zeta(3) \simeq 1.202$  due to higher-order neighbors is negligible. Since the contour lines of the magnetic chains preserve a smooth shape under the observed deformations, without any kinks, and as the chains do not fold back onto themselves, we thus confine ourselves to nearest-neighbor interactions.

For a large number of particles, the quantity  $\varepsilon_m$  sets the magnetic interaction energy per particle. Moreover, the total magnetic interaction energy scales approximately linearly with the number of particles and chain length.

We now switch to a continuum picture by specifying the line energy density along the magnetic chain. In our coordinate system, the angle  $\psi$  that the connecting vector **r** between two neighboring particles forms with the *x*-axis is locally given by  $\psi \sim$  arctan [y'(x)], where y'(x) = dy/dx. To obtain the resulting magnetic energy of the whole magnetic chain, we need to integrate the energy line density along the contour line. For simplicity, we transform this line integral to an integration along the *x*-axis. If we parameterize the contour line by the parameter *s*, the line element *ds* along the chain can be expressed as  $ds = \sqrt{1 + y'(x)^2} dx$ . Therefore, the magnetic energy becomes

$$E_{magn}[y] = W \int_{x_1}^{x_2} \sin^2 \left\{ \arctan\left[y'(x)\right] - \frac{\pi}{2} \right\} \sqrt{1 + y'(x)^2} \, dx$$
  
=  $W \int_{x_1}^{x_2} \frac{1}{\sqrt{1 + y'(x)^2}} \, dx,$  (S10)

where

$$W = \frac{\varepsilon_m}{d} = \frac{3\mu_0 m^2}{4\pi d^4} \tag{S11}$$

is the magnetic energy per unit length and  $x_1, x_2$  are the *x*-coordinates of the end points of the chain.

## 3.2 Elastic bending energy

Next, we briefly sketch the derivation of the elastic bending energy in Eq. (3) of the main article. For this purpose, we consider a parameterization  $\mathbf{R}(s)$  of the contour line of the magnetic chain, where the positions  $\mathbf{R}$  mark the points on the contour line and  $s \in [s_1, s_2]$  with  $s_1$  and  $s_2$  labeling the end points of the chain. On this basis, the elastic bending energy is defined as<sup>S9</sup>

$$E_{bend} = C_b \int_{s_1}^{s_2} \left| \frac{d^2 \mathbf{R}(s)}{ds^2} \right|^2 ds.$$
(S12)

Using the parameterization  $\mathbf{R} = (x, y(x))$  and  $ds = \sqrt{1 + y'(x)^2} dx$ , we obtain

$$\frac{d\mathbf{R}}{ds} = \left(1 + y'(x)^2\right)^{-\frac{1}{2}} \left(\begin{array}{c}1\\y'(x)\end{array}\right)$$
(S13)

and

$$\frac{d^2\mathbf{R}}{ds^2} = y''(x)\left(1+y'(x)^2\right)^{-2} \begin{pmatrix} -y'(x)\\ 1 \end{pmatrix}.$$
 (S14)

From this last expression, we obtain Eq. (3) in the main article when we again transform the line element ds to Cartesian coordinates,  $ds = \sqrt{1 + y'(x)^2} dx$ .

# **3.3 Elastic displacement energy**

Finally, we motivate the expression for the elastic displacement energy in Eq. (4) of the main article. The part  $[y(x)]^2$  corresponds to a lowest order term in the displacement y(x). We weight each of the two displacement factors y(x) by the amount of chain material displaced per integration interval dx, given by the length of the chain per integration



**Figure S9** Experimentally observed rotation angles of magnetic chains in a gel of shear modulus G' = 0.25 Pa under a perpendicular magnetic field of magnitude B = 18.7 mT. To first approximation, a rigid rotation of straight chains occurs at small enough rotation angles. This is depicted, for instance, in Fig. 1c of the main article for small angles of the magnetic field.

interval dx, i.e.  $ds/dx = \sqrt{1 + y'(x)^2}$ . This leads to  $[y(x)]^2 [1 + y'(x)^2]$ . In addition to that, we have another factor  $\sqrt{1 + y'(x)^2}$ , again from transforming the line element ds of the integration to Cartesian coordinates,  $ds = \sqrt{1 + y'(x)^2} dx$ . In total, we obtain the expression in Eq. (4) of the main article.

We explain in the following why the experimental observations suggest this form as a lowest order term. In particular, we note that the experimental investigations suggest the form  $[y(x)]^2$  rather than one containing the first derivative  $[y'(x)]^2$ . For this purpose, we consider the case of straight chains (M = 0) undergoing small rotations in a perpendicular magnetic field. This situation can be simply parameterized by y(x) = Sx, where  $S = \tan \psi$  and  $\psi$  as introduced above giving the rotation angle. Furthermore  $E_{bend} = 0$ .

For y(x) = Sx,  $E_{magn}$  scales linearly with the chain length *L*. The same would apply for an energetic contribution  $\sim \int_{x_1}^{x_2} [y'(x)]^2 [1+y'(x)^2]^{3/2} dx$ . Therefore, the latter expression inevitably leads to a rotation angle  $\psi$  that is independent of the chain length *L*. However, this contradicts the experimental results. In Fig. S9 we plot the rotation angle  $\psi$  as a function of chain length *L* measured in a gel of shear modulus G' = 0.25 Pa exposed to a perpendicular magnetic field of magnitude B = 18.7 mT. There is a clear dependency of the rotation angle on the chain length *L*. The energetic expression  $E_{displ}$  in Eq. (4) of the main article for rotations of straight chains y(x) = Sx scales as  $E_{displ} \sim L^3$  and thus leads to disproportionally higher energetic penalties for longer chains, reflecting the experimentally observed smaller rotation angles.

## 3.4 Discussion of resulting chain shapes

Now that our total model energy  $E_{tot}$  is set as the sum of Eqs. (1), (3), and (4) in the main article, a standard route to determine the shape y(x) of the chain would be to find the extrema of the functional  $E_{tot}[y(x)]$  with respect to the function y(x). For this purpose,

one calculates the functional derivative of  $E_{tot}[y(x)]$  with respect to y(x) and equates it with zero. The procedure is well known from the famous brachistochrone problem.<sup>S10</sup> There one wishes to find the shape of a curve linking two end points such that a body moving between them under gravity passes the distance in the least possible amount of time.

However, there is a fundamental difference compared to the brachistochrone problem. While calculating the functional derivative, boundary terms appear that explicitly include contributions from the end points of the chain or trajectory y(x). Technically, they result from partial integration. In the brachistochrone problem, one has sufficient information to handle these boundary terms: by construction of the problem, one knows that the end points are fixed. Similarly, in other problems of infinitely extended elastic struts of periodic, periodically modulated, or localized deformations,  $S^{S11-S14}$  one can use the periodicity or localization to argue in favor of an evanescent influence of the boundary terms. This is very different from our present case, where the deflection encompasses the whole finite chain and in particular its end points. Unfortunately, acquiring sufficient knowledge of the associated boundary conditions would imply solving the whole complex three-dimensional nonlinear elasticity and magnetization problem, which is beyond the present scope and in fact was the reason to project to our reduced minimal model.

For completeness, however, we perform some additional variational analysis of our energy functional. We concentrate on possible solutions in the bulk that could be observed if boundary effects were absent (which is not the case for our experimentally investigated finitely-sized objects). Then, neglecting the boundary terms, the functional derivatives of Eqs. (1), (3), and (4) are calculated as follows (the dependencies of y(x) and its derivatives on x is omitted for brevity on the right-hand sides):

$$\frac{\delta E_{magn}}{\delta y(x)} = W y'' \left(1 - 2{y'}^2\right) \left(1 + {y'}^2\right)^{-\frac{3}{2}},$$
(S15)

$$\frac{\delta E_{bend}}{\delta y(x)} = C_b \left[ 5y''^3 \left( 6y'^2 - 1 \right) - 20y'y''y''' \left( 1 + {y'}^2 \right) + 2y'''' \left( 1 + {y'}^2 \right)^2 \right] \left( 1 + {y'}^2 \right)^{-\frac{9}{2}}, \tag{S16}$$

and

$$\frac{\delta E_{displ}}{\delta y(x)} = C_d \left[ 2y - 2yy'^2 - 4yy'^4 - 3y^2 y'' - 6y^2 y'^2 y'' \right] \left( 1 + {y'}^2 \right)^{-\frac{1}{2}}.$$
 (S17)

Together, we obtain a nonlinear fourth-order differential equation for y(x):

$$\frac{\delta E_{tot}}{\delta y(x)} = \left(1 + {y'}^2\right)^{-\frac{9}{2}} \left[ -\left(1 + {y'}^2\right) y'' \left(W\left(-1 + {y'}^2 + 2{y'}^4\right) + 20C_b y' y'''\right) - 3C_d y^2 \left(1 + {y'}^2\right)^4 \left(1 + 2{y'}^2\right) y'' + 5C_b \left(-1 + 6{y'}^2\right) y''^3 - 2C_d y \left(1 + {y'}^2\right)^5 \left(-1 + 2{y'}^2\right) + 2C_b \left(1 + {y'}^2\right)^2 y'''' \right] = 0.$$
(S18)

Eq. (S18) can in principle be solved numerically by integrating it outward from the center of the chain at x = 0. For this purpose, a sufficient amount of "initial conditions"



**Figure S10** Numerical solutions of Eq. (S18) for different imposed input conditions. In all cases we concentrate on uneven centro-symmetric solutions and thus prescribe y(0) = y''(0) = 0. As remaining necessary conditions, we specify the position of the first maximum: (a) y'(0.5) = 0, y(0.5) = 0.205; (b) y'(0.5) = 0, y(0.5) = 0.2; (c) y'(0.3) = 0, y(0.3) = 0.16; (d) y'(0.5) = 0, y(0.5) = 0.1.

(four in our case) for y(x) and its derivatives needs to be provided. We concentrate on uneven centro-symmetric solutions, which directly prescribes two conditions: y(0) = 0and y''(0) = 0. As was found before in a different context, <sup>S11</sup> the solution is extremely sensitive to the two remaining imposed conditions. For illustration, we depict four examples in Fig. S10. There, we provide slightly varying positions of the first maximum [y'(x) = 0] as the remaining two necessary conditions. Numerical integration shows that little variations in these conditions lead to qualitatively different oscillatory solutions. <sup>S15</sup>

Altogether, we may conclude that the solutions resulting from Eq. (S18) sensitively depend on the input conditions. As noted above, we do not have access to the appropriate conditions applying at the significantly displaced end points of the embedded chain. The strategy that we resorted to is therefore to use as an input directly the shapes of the chains suggested by the experiments. We found good representations of the experimental observations using the polynomial form suggested by Eq. (5) in the main article. In particular, with regard to the pronounced displacements of the chain ends, this choice is preferred to, for instance, a sinusoidal ansatz. Then, instead of solving Eq. (S18) explicitly, we minimize the energy functional  $E_{tot}[y(x)]$  with respect to the remaining degrees of freedom of the chain deformation (M, S,  $x_1$  and  $x_2$  in the main article). Thus, even if we have used an ansatz for the chain deformation, this remains a nonlinear approach as we evaluate the nonlinear contributions to the energy functional  $E_{tot}[y(x)]$ .

# 3.5 Oscillatory solutions in the linear regime

In the previous part, we have demonstrated that various complex solutions can result from the nonlinear nature of Eq. (S18). Here, we restrict ourselves to the situation in the inside of the magnetic chains for small amounts of deformation, i.e. at the onset of deformation. For this purpose, a linear stability analysis is performed by considering a linearized version of Eq. (S18). As a result, we obtain a condition describing the onset of a linear deformational instability

$$Wy''(x) + 2C_b y''''(x) + 2C_d y(x) = 0.$$
(S19)

This equation has solutions of the kind  $y(x) \sim \exp(\pm iqx)$ , with wavenumber

$$q^{2} = \frac{W \pm \sqrt{W^{2} - 16C_{b}C_{d}}}{4C_{b}}.$$
 (S20)

The condition for the solutions to be purely oscillatory is  $W^2/16C_bC_d > 1$  and defines an onset for this kind of deformation. It sets a threshold magnitude for the strength of the external magnetic field. Thus, for a perfectly oriented chain of identical particles in a spatially homogeneous elastic matrix, this linear stability analysis predicts a critical magnetic field amplitude above which an undulatory instability would arise in the inside of the chain. Our results are in agreement with the experimental observation of the wrinkles at onset in Fig. 1c and the final oscillatory shape in the inner part of the longer chains in Fig. 2a of the main article.

# 4 Technical description of the coarse-grained molecular dynamics simulations

# 4.1 Magnetic particles

In the molecular dynamics simulations, the centers of the magnetic particles and the nodes of the polymer mesh are treated as point particles in two-dimensional space. The magnetic particles additionally have one rotational degree of freedom, namely around the axis perpendicular to the model plane. As each magnetic particle is superparamagnetic, its magnetic moment is not affected by a rotation of the particle. Rather, the magnetic moment is determined by the magnetic field. Hence, we place the magnetic moment not on the rotating center of the particle, but rather on a separate virtual site which does not rotate. It is placed at the same location as the center of the magnetic particle. Virtual sites are particles, whose position is not determined by integrating an equation of motion, rather their position is calculated from the position and orientation of other particles. In this way, they allow us to introduce rigid extended bodies into a molecular dynamics simulation.<sup>S16</sup> Forces acting on any constituent of such a rigid body are transferred back to its center of mass, and thus included in the equation of motion of the rigid body.

Pairs of magnetic particles interact by the dipole-dipole interaction, Eq. (S6). The dipole moment of the particles is assumed to be determined entirely by the external magnetic field, and its magnitude is deduced from the experimental magnetization curve (Fig. S1b). This assumption is valid as long as the external field is much stronger than the field created by the other magnetic particles. In other cases, a self-consistent approach has to be used to determine the local magnetic fields. In addition to the dipole-dipole interaction, the magnetic particles interact via a truncated and shifted, purely repulsive Lennard-Jones potential mimicking a rigid-sphere interaction. We use the Weeks-Chandler-Andersen potential<sup>S17</sup> in the form

$$V_{WCA}\left(\frac{r}{\sigma}\right) = \begin{cases} 4\varepsilon \left[\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6} + \frac{1}{4}\right] & \text{for } r \le r_c, \\ 0 & \text{otherwise,} \end{cases}$$
(S21)

where *r* is the distance between the particle centers,  $\varepsilon = 1000$  denotes the energy scale of the potential, and  $r_c = 2^{1/6}\sigma$  is the cut-off distance, for which we use the experimental diameter of 1.48  $\mu$ m. The parameter  $\sigma$  denotes the root of the non-shifted potential and is used in the visualizations in Figs. 9 and 10.

# 4.2 Polymer mesh

The polymer matrix is modeled as a bead-spring network based on a hexagonal lattice. We use a lattice constant *a* of one third of the experimentally observed particle diameter, i.e.,  $a \approx 0.49 \ \mu$ m. Along the initial chain direction, we use 601 mesh points, along the perpendicular direction 301. The mesh points on the boundary of the system are fixed, all other mesh points can move in the *x*- and *y*-directions. Adjacent mesh points interact via a non-linear elastic spring based on the FENE-potential.<sup>S18</sup> Here, we use a variant with
different cut-off values for compression and expansion. It is given by

$$V(r) = -\frac{1}{2}K(r_0 - r_{\min})^2 \ln \left[ 1 - \left(\frac{r - r_0}{r_0 - r_{\min}}\right)^2 \right] \quad \text{for } r < r_0,$$

$$V(r) = -\frac{1}{2}K(r_{\max} - r_0)^2 \ln \left[ 1 - \left(\frac{r - r_0}{r_{\max} - r_0}\right)^2 \right] \quad \text{for } r > r_0.$$
(S22)

In these expressions, K = 45 controls the scale of the potential, the equilibrium distance  $r_0 = a$  is equal to the lattice constant, while the minimum and maximum elongations, at which the potential diverges, are  $r_{\min} = 0.1a$  and  $r_{\max} = 3a$ , respectively. The potential, as well as its second derivative, are continuous at the equilibrium extension  $r = r_0$ . In order to prevent any volume element from shrinking to zero, angular potentials are used on all pairs of neighboring springs attached to the same mesh site, encompassing an angle of  $60^{\circ}$  in the unstrained mesh. The potential has the same functional form as the distance-based potential in Eq. (S22), but with the values K = 100,  $r_0 = \pi/3$ ,  $r_{\min} = 0$ , and  $r_{\max} = \pi$ . In the simulations both potentials are tabulated at 100000 equally spaced intervals between the minimum and maximum extensions. Between those points, linear interpolation is used.

# 4.3 Particle-mesh coupling and boundary layer

The mesh spans the entire simulation area, including the area covered by the magnetic particles. In order to couple the polymer mesh to both, the translational and rotational motion of a magnetic particle, the seven mesh sites within the area of each magnetic particle are treated as virtual sites, rigidly following the motion of the magnetic particle. In other words, the mesh sites within the particle and the center of the magnetic particle form a rigid body. This additionally prevents a distortion of the gel matrix in the area occupied by the magnetic particles. Two variants of gel boundary layer around the particles are studied (Fig. 9 in the main article). In the case of a soft boundary layer, the mesh springs emerging from the mesh sites rigidly connected to the particle, are modeled as in Eq. (S22) with the same parameters as for the bulk. In the case of a stiff boundary layer, a potential is used which is stiffer by three orders of magnitude. The following parameters are used in this case: K = 45000,  $r_{min} = -2a$ , and  $r_{max} = 4a$ .

# 4.4 Equation of motion and integration

The simulations are performed in the canonical ensemble at a temperature of 300 K. All particles except for the virtual sites are propagated according to a Langevin equation. For any component in a Cartesian coordinate system, it is given by

$$m_p \dot{v}(t) = -\gamma v(t) + F + F_r, \qquad (S23)$$

where  $m_p$  denotes the mass of the particle, v its velocity, F is the force due to the interaction with other particles,  $F_r$  denotes the random thermal noise, and  $\gamma$  is the friction coefficient. To maintain a temperature T, the thermal noise has to have a mean of zero and a variance of

$$\langle F_r^2 \rangle = 2k_B T \gamma, \tag{S24}$$

where  $k_BT$  denotes the thermal energy. For the rotational degree of freedom of each magnetic particle, the same equation of motion is used, but mass, velocity, and forces are replaced by moment of inertia, angular velocity, and torques, respectively. The friction coefficient, the thermal energy, and the mass of the mesh sites are all chosen to be unity, whereas the mass and rotational inertia of the centers of the magnetic particles are both 100. This slows down the relaxation time of the magnetic particles versus that of the polymer mesh and is helpful in stabilizing the simulation. The Langevin equation is integrated using a Velocity Verlet integrator. For the simulations with a stiff boundary layer, the time step is dt = 0.001, for a soft boundary layer it is dt = 0.0004. The simulations take approximately 100000 time steps to converge.

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# Paper IV. Tailoring superelasticity of soft magnetic materials

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# Statement of contribution

Developing the numerical model and designing the system was a joint effort with AMM, who was my main supervisor for this work. I implemented the computational code, performed the simulations and evaluated the data for the shown results. Writing the manuscript and the supplemental material was done together with HL and AMM. My estimated contribution to the overall work involved in creating this paper is 80%.

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99

# Tailoring superelasticity of soft magnetic materials

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Embedding magnetic colloidal particles in an elastic polymer matrix leads to smart soft materials that can reversibly be addressed from outside by external magnetic fields. We discover a pronounced nonlinear superelastic stress-strain behavior of such materials using numerical simulations. This behavior results from a combination of two stress-induced mechanisms: a detachment mechanism of embedded particle aggregates and a reorientation mechanism of magnetic moments. The superelastic regime can be reversibly tuned or even be switched on and off by external magnetic fields and thus be tailored during operation. Similarities to the superelastic behavior of shape-memory alloys suggest analogous applications, with the additional benefit of reversible switchability and a higher biocompatibility of soft materials. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4934698]

The term "superelasticity" expresses the capability of certain materials to perform huge elastic deformations that are completely reversible.<sup>1,2</sup> Initially, it was introduced in the context of shape-memory alloys.3-5 These metallic materials can perform large recoverable deformations due to stress-induced phase transitions. A transition to a more elongated lattice structure accommodates an externally imposed extension. Typically, this transition shows up as a pronounced "plateau-like" regime on the corresponding stressstrain curve. On this plateau, the samples are heterogeneous with domains of already transitioned material. Then, only relatively small additional stress induces a huge additional deformation. Smart material properties are observed:6-9 upon stress release, shape-memory alloys can reversibly return to their initial state. They self-reliantly adapt their appearance to changed environmental conditions.

In the present letter, we demonstrate that an analogous phenomenological behavior can be realized for a very different class of materials, exploiting different underlying mechanisms. Moreover, we show that during operation the behavior can be reversibly tailored from outside by external magnetic fields. All of these are achieved by employing soft magnetic gels as working materials: colloidal magnetic particles embedded in a possibly swollen elastic polymer matrix.<sup>10</sup> Similar to magnetic fluids,<sup>11–18</sup> magnetic gels allow to reversibly adjust their material properties by external magnetic fields. In this way, switching the elastic properties<sup>19–23</sup> offers a route to construct readily tunable dampers<sup>24</sup> or vibration absorbers,<sup>25</sup> while the possibility to switch the shape<sup>19,26–28</sup> allows application as soft actuators.<sup>29–31</sup>

Here, we show that magnetic gels due to the interplay between magnetic and elastic interactions likewise feature superelastic behavior: it is enabled by a detachment mechanism of embedded magnetic particle aggregates and by a reorientation mechanism of magnetic moments. Both mechanisms are stress-induced and respond to external magnetic fields. also its magnitude and position on the stress-strain curve can be reversibly tailored during operation, as has been realized for some special metallic components.<sup>32,33</sup> The superelastic behavior in our case covers a significantly larger strain regime. Furthermore, soft gel-like materials generally provide a larger deformability and higher degree of biocompatibility<sup>34–38</sup> than metallic alloys. This becomes particularly important for medical applications.<sup>39</sup> There has been a significant effort to transfer the properties of shape-memory alloys to soft materials.<sup>35,37,38,40</sup> Here, we report on reversibly tailoring superelastic properties by external magnetic fields.

Therefore, superelasticity can be switched on and off, and

We concentrate on anisotropic uniaxial magnetic gels.<sup>19,22,41,42</sup> They are manufactured by applying a strong external magnetic field during preparation, which leads to the formation of oriented straight chain-like aggregates of embedded magnetic particles.43-46 After subsequent chemical cross-linking of the embedding polymer network, the position of the particles gets permanently locked.<sup>47</sup> We assume that the magnetic moments carried by the particles are free to reorient. First, for diameters up to 10-15 nm, this applies within the interior of each magnetic particle.48 Second, this is possible when each particle as a whole is free to rotate,<sup>47</sup> e.g., when the polymer is not completely crosslinked in the immediate particle vicinity.49 Another example is yolk-shell particles with a magnetic core that can rotate within the shell.<sup>50,51</sup> If reorientations of the magnetic moments are blocked, only the first of the two mechanisms described below is active.

We identify a superelastic stress-strain behavior of uniaxial magnetic gels by numerically investigating the following model system. Identical spherical colloidal particles, each carrying a permanent magnetic dipole moment, are embedded in a continuous elastic matrix. The elastic deformation energy of the matrix is described by a standard nearly incompressible Neo-Hookean model.<sup>52,53</sup> We tessellate the matrix into sufficiently small tetrahedra by Delaunay triangulation.<sup>54</sup> Each tetrahedron may deform affinely, increasing its elastic energy, from which we extract restoring forces on

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#### 171903-2 Cremer, Löwen, and Menzel

its delimiting nodes. The nodes attached to surfaces of rigid embedded particles transmit forces and torques to these particles. Energy minimization with respect to all nodes and particle positions, as well as all particle and dipole orientations, is performed (see supplementary material for technical details<sup>53</sup>).

Within our model, we study small three-dimensional systems, each containing 96 magnetic particles (Fig. 1(a)). For initialization, we arrange the particles in straight linear chain-like aggregates: each chain is one particle in diameter but several equi-distanced particles in length that are separated by finite gaps filled with elastic material.<sup>22,49,55-57</sup> Initially, the chains are aligned parallel to each other, but otherwise placed in a random non-overlapping way.<sup>53</sup> In the



FIG. 1. (a) A snapshot of an equilibrated system of chain-like aggregates before stretching. The small bar magnets in the embedded particles indicate dipole moments. (b) Uniaxial stress-strain behavior for stretching in chain direction, revealing a pronounced superelastic plateau-like nonlinearity, and adjustability by magnetic fields perpendicular to the chains. (c) Effects of magnetic fields parallel to the chains. As in all subsequent figures, the solid lines represent loading and the dotted lines unloading, highlighting reversibility.

#### Appl. Phys. Lett. 107, 171903 (2015)

presence of the rigid inclusions, the elastic modulus increases<sup>53</sup> by a factor of  $\sim$ 7. Finally, the magnetic moments are switched on, and the system is equilibrated, leading to an initial matrix deformation (Fig. 1(a)).

We quasistatically stretch our systems along the chain direction. To impose a certain extension, the mesh nodes at two opposite system boundaries are displaced into opposite directions in small steps. After equilibration during each step, the forces on the boundary nodes are measured. We check the reversibility of the induced total deformations by repeated loading and unloading cycles. Forces F are measured in units of  $F_0 = ER^2$ , magnetic fields B in units of  $B_0 = \sqrt{\frac{\mu_0}{4\pi}E}$ , and magnetic dipole moments *m* in units of  $m_0 = R^3 \sqrt{\frac{4\pi}{\mu_0}E}$ . Here, E is the elastic modulus of the matrix, R the particle radius, and  $\mu_0$  the vacuum permeability.  $L_0$ denotes the initial total length in stretching direction,  $\Delta L$  is the (absolute) elongation, and  $\Delta L/L_0$  is the elongational strain. We fix the material parameters by setting the Poisson ratio of the matrix to  $\nu = 0.495$  and the magnetic moment to  $m = 10 m_0$ .

Figs. 1(b) and 1(c) illustrate the resulting markedly nonlinear stress-strain behavior. First, the force to achieve a certain elongation steeply increases with the imposed strain. Then, a pronounced superelastic nonlinearity follows. Since our measurements are strain-controlled, and due to the finite size of our systems, we observe a regime of negative slope. A macroscopic sample in this region would become inhomogeneous, leading to a plateau-like superelastic regime<sup>4,6</sup> or likewise show a negative slope under strain control.<sup>58</sup> In this area, a further slight increase in the applied force induces a huge additional deformation. Remarkably, we can reversibly shift the non-linearity to smaller strains by a perpendicular external magnetic field (Fig. 1(b)). High field strengths even switch off the non-linearity. Furthermore, we can alter the shape of the plateau-like regime by a field in stretching direction (Fig. 1(c)). At the end of the plateau, the stressstrain curve crosses over to a relatively constant intermediate slope.

We found that a combination of two effects allows for this adjustable superelastic behavior: a stress-induced detachment mechanism of the individual chain-like aggregates (Fig. 2) plus a reorientation mechanism of the magnetic moments (Figs. 3 and 4). To illustrate the first one, Fig. 2(a) shows the initialized state of an example chain system. Switching on magnetic interactions, the particles attract each other and "pre-compress" the elastic gap material (Fig. 2(b)). Now the particles are located at a small distance from each other, its inverse cube setting the dipolar interaction scale. The initial steep increase in the stress-strain curve (Fig. 2(f)) reflects these strong magnetic interactions. Once the magnetic barrier is overcome, a small further increase in the stretching force is sufficient to detach part of the chain from the remainder (Fig. 2(c)). Such events suddenly elongate the system and lead to spikes in the stress-strain curve (Fig. 2(f)). They repeatedly occur (Fig. 2(d)) until all particles have been detached from each other. In total, a spiky plateau appears (Fig. 2(f)). It smoothens when averaged over different chains (Fig. 1). This is an intra-chain effect. Inter-chain

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171903-3 Cremer, Löwen, and Menzel



FIG. 2. Illustration of the detachment mechanism: (a) A cut through an initialized four-particle single-chain system: the elastic matrix is not yet deformed. (b) Equilibrated state with the pre-compressed gap material. The color maps show the local matrix distortion along the longitudinal stretching direction, here illustrated using the so-called "true strain"  $e_{xx}$ .<sup>59</sup> (c) First and (d) second detachment events of parts of the chain where magnetic energy barriers are overcome by longitudinally applied stretching forces. (e) The equilibrated unloaded state in the presence of a strong perpendicular magnetic field. All magnetic energy barrier. (f) Stress-strain curves for various perpendicular field strengths. Each spike corresponds to a detachment event where a magnetic energy barrier is overcome. An increasing perpendicular magnetic field lowers the detachment threshold, until superelasticity is switched off.

interactions are minor for experimentally reported particle fractions.<sup>22,60</sup> Thus, the finite size of our model systems will not affect the significance of the overall material behavior.

Now, the tunability by a perpendicular magnetic field becomes clear (Figs. 2(e) and 2(f)). Strong perpendicular fields align all dipoles in the perpendicular direction. There is no pre-compression (Fig. 2(e)); hence, no magnetic energy barrier for pulling the particles apart, and thus, no corresponding stress-strain nonlinearity. Smaller magnetic fields do not significantly alter the dipole orientations in the pre-

#### Appl. Phys. Lett. 107, 171903 (2015)

compressed state due to the strong magnetic interactions at short distances. Yet, they affect the threshold for detachment (Fig. 2(f)); the moments can rotate away from the chain axes when the particle separation increases.

The second effect contributing to the superelastic nonlinearity results from the stretching-induced reorientations of the magnetic dipole moments. For illustration, we explain it on a regular cuboid lattice arrangement (Fig. 3). Initially, the edges of the cuboid unit cells are shorter along the stretching direction (Fig. 3(a)). Thus, the dipoles align parallel to it. During elongation (Fig. 3(b)), these distances increase. Simultaneously, due to the overall volume preservation, the system contracts from the sides. This decreases the separation perpendicular to the stretching direction. When the edge lengths of the distorted unit cells become equal in both directions, there is no single favored dipole orientation left (Fig. 3(b)). Further stretching makes the dipoles rotate into the plane perpendicular to elongation (Fig. 3(c)). Thus, during the overall process, the magnetic dipoles reorient ("flip"). This flipping effect is sensitive to the spatial particle arrangement. Yet, it likewise appeared in all of our investigated uniaxial systems. It is obvious from Fig. 3(b) that we can identify the flipping effect by a vanishing orientational order of the magnetic moments (see supplementary material for a quantitative evaluation<sup>53</sup>). A similar orientational analysis for the separation vectors between all nearest-neighbor particles demonstrates that the mechanism is indeed triggered by the changes in the distances mentioned above.<sup>53</sup>

The flipping process is reflected by a steep step in the corresponding stress-strain curve (Fig. 4; see supplementary material for a simplified energetic model, including larger system sizes<sup>53</sup>). Also, this flipping contribution to the superelastic stress-strain behavior can be tuned from outside. Through a perpendicular magnetic field, flipping can be shifted to lower strains or be switched off completely, which largely eliminates the corresponding nonlinearity in the stress-strain curve (Fig. 4(a)). However, also a parallel field has a significant influence: it can postpone flipping to larger deformations and smear out the connected stress-strain nonlinearity (Fig. 4(b)). In Fig. 1(c), it is the dip in the stressstrain curve that is mainly connected to the flipping mechanism and can be switched off by the parallel field. The steep jumps of Fig. 4 appear more rounded in Figs. 1(b) and 1(c) because all stress-strain curves in Fig. 1 were obtained by averaging over twenty characteristic numerical realizations. For larger system sizes, the curves would appear still more rounded.

To amplify the effects and to realize our assumed value of  $m = 10 m_0$ , strong magnetic moments and soft elastic matrices are preferred. A possible route is to use particles made of a material of high remanent magnetization, for example, NdFeB<sup>61</sup> (more than  $2 \times 10^5$  A/m). Soft elastic matrices of  $E \leq 10^3$  Pa can be made of silicone<sup>23,62,63</sup> or polydimethylsiloxane.<sup>64</sup> The problem is qualitatively invariant under rescaling all lengths by a characteristic dimension such as the particle radius *R*. Thus, the particle size is not a critical factor. Our calculations were performed for permanent reorientable magnetic moments. Yet, the reorientation effect could likewise be observed using soft magnetic particles that are magnetized by an external magnetic field. Then, the reorientation

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FIG. 3. An illustration of the reorientation mechanism: snapshots of a stretched regular cuboid-lattice system (here  $m = 8 m_0$ ). (a) Initially, the particles are closest in stretching direction (horizontal), their magnetic moments aligning along this direction. Stretching the system increases the distances along and (due to volume preservation) decreases the distances perpendicular to the stretching direction. (b) When these distances become approximately equal, no particular orientation is preferred. (c) Stretching the system further makes a perpendicular direction the preferred one; the orientations of the magnetic moments "flip."

process must be performed "manually" by switching the external magnetic field direction.

In conclusion, we have identified a superelastic stressstrain behavior of soft uniaxial magnetic gels. These materials consist of chain-like aggregates of magnetic colloidal particles embedded in a soft elastic polymer matrix. Stretching the systems in chain direction reveals a significant nonlinearity in the stress-strain curve. In this regime, the systems can be strongly deformed with hardly any additional load necessary. Two underlying stress-induced mechanisms were identified: a detachment mechanism of the embedded



FIG. 4. Stress-strain curves of the cuboid-lattice system showing a steep drop as reorientation (flipping) occurs. (a) Perpendicular external magnetic fields shift this feature to lower strains, while (b) parallel external magnetic fields smear out the nonlinearity and postpone flipping to higher strains.

chain-like aggregates and a reorientation mechanism of the magnetic moments. Both the processes are reversible upon stress release, in analogy to the superelastic behavior of shape-memory alloys. As an additional benefit, the superelastic properties in the present case can be reversibly switched during operation by an external magnetic field.

These nonlinear stress-strain properties open the pathway to numerous applications. The on-demand tunable deformability could be used for easily applicable packaging or gaskets that become rigid when an external magnetic field is switched off. Under pre-stress, external magnetic fields can trigger significant deformations, qualifying the materials for the use as soft actuators. Combined with an increased biocompatibility, these concepts should be transferable to medical applications such as quick wound dressings, artificial muscles, or tunable implants. Finally, combinations of magnetic gels with other materials can bestow the tunable superelastic properties on the resulting composite.

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# Tailoring superelasticity of soft magnetic materials: Supplemental material

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In the following, we provide additional information concerning three aspects of the main text. First, we list further technical details with regard to our numerical implementation of our model system including some remarks on the increased material stiffness due to rigid inclusions. Second, we illustrate the additional characterization mentioned in the main text concerning the reorientation ("flipping") mechanism in terms of measuring appropriate degrees of orientational order. Third, we provide a simplified description of the flipping process in a regular cuboid-lattice system using energetic arguments and the assumption of globally affine deformations.

# I. TECHNICAL DETAILS CONCERNING THE NUMERICAL IMPLEMENTATION

As mentioned in the main text, we numerically stretch our system along one direction by imposing displacements of two opposite surfaces. Only displacements along the stretching direction and only for the two surfaces facing the stretching direction are prescribed. All other degrees of freedom remain intact. As further mentioned, the displacements are applied in small steps, and after each step the system is equilibrated. Equilibration here means minimization of the total energy of our system under the prescribed uniaxial surface displacements. This total energy consists of elastic and magnetic contributions.

The elastic contributions originate from the deformation of the elastic matrix surrounding the embedded magnetic particles. As described in the main text, we partition the elastic matrix into a set of affinely (uniformly, homogeneously) deformable tetrahedra. The surfaces of the embedded rigid spherical magnetic particles are approximated as sets of planar triangles that form faces of the surrounding matrix tetrahedra. The whole procedure is performed using gmsh<sup>S1</sup>, a mesh generation tool based on Delaunay triangulation. The characteristic length parameter defining the typical lengths of tetrahedra edges is set to 0.35R, where R is the radius of the embedded magnetic particles.

For each tetrahedron, we model the elastic deformation energy  $U_{\rm e}$  using the following nearly-incompressible Neo-Hookean hyperelastic model<sup>S2</sup>:

$$U_{e} = V_{0} \left[ \left( \frac{\mu}{2} \operatorname{Tr} \left\{ \mathbf{F}^{t} \mathbf{F} \right\} - 3 \right) - \mu \left( \det \mathbf{F} - 1 \right) + \frac{\lambda + \mu}{2} \left( \det \mathbf{F} - 1 \right)^{2} \right].$$
(S1)

This is a well-established elasticity model to describe

conventional elastic deformations of polymeric materials. Here  $\mu$  and  $\lambda$  are the Lamé coefficients  $^{\rm S3}$  of the surrounding elastic matrix and are related to the elastic modulus E and the Poisson ratio  $\nu$  given in the main article by  $\mu = \frac{E}{2(1+\nu)}$  and  $\lambda = \frac{E\nu}{(1+\nu)(1-2\nu)}$ .  $V_0$  is the volume of the tetrahedron in the undeformed state, while  ${\bf F}$  is the so-called deformation gradient tensor.  ${\bf F}^t$  denotes its transpose. Since we only allow for affine deformations of each tetrahedron,  $\mathbf{F}$  can easily be expressed in terms of the positions of the four nodes (vertices) of the tetrahedron. For this purpose, we need the positions  $\mathbf{x}_0$ ,  $\mathbf{x}_1$ ,  $\mathbf{x}_2$ ,  $\mathbf{x}_3$  of the nodes in the present deformed configuration, as well as the positions  $\tilde{\mathbf{x}}_0$ ,  $\tilde{\mathbf{x}}_1$ ,  $\tilde{\mathbf{x}}_2$ ,  $\tilde{\mathbf{x}}_3$  in the original undeformed (reference) configuration. We define the matrix  $\mathbf{X} := (\mathbf{x}_1 - \mathbf{x}_0, \mathbf{x}_2 - \mathbf{x}_0, \mathbf{x}_3 - \mathbf{x}_0)$ to describe the deformed state, as well as the matrix  $\mathbf{\tilde{X}} := (\mathbf{\tilde{x}}_1 - \mathbf{\tilde{x}}_0, \mathbf{\tilde{x}}_2 - \mathbf{\tilde{x}}_0, \mathbf{\tilde{x}}_3 - \mathbf{\tilde{x}}_0)$  to describe the undeformed (reference) state of the tetrahedron. In our case of affine deformations, the deformation gradient tensor  ${\bf F}$ is the tensor that connects these two states by  $\mathbf{X} = \mathbf{F}\mathbf{\tilde{X}}$ . Multiplying with  $\tilde{\mathbf{X}}^{-1}$  from the right yields

$$\mathbf{F} = \mathbf{X}\tilde{\mathbf{X}}^{-1}.$$
 (S2)

Thus, we can obtain the deformation gradient tensor  $\mathbf{F}$  of each tetrahedron simply from the knowledge of its node positions in the present deformed ( $\mathbf{X}$ ) and in the original undeformed ( $\tilde{\mathbf{X}}$ ) configuration. Here, the inverse matrix  $\tilde{\mathbf{X}}^{-1}$  has to be calculated only once in the beginning of the whole numerical procedure. A similar strategy to evaluate the deformation gradient tensor was proposed in Ref. S4.

Finally, using Eq. (S2), the force on each node i (i = 0, 1, 2, 3) can be calculated via

$$\mathbf{f}_i = -\nabla_{\mathbf{x}_i} U_e(\mathbf{F}) = -\frac{\partial U_e(\mathbf{F})}{\partial \mathbf{F}} \frac{\partial \mathbf{F}}{\partial \mathbf{x}_i}.$$
 (S3)

If a node is not attached to the surface of an embedded magnetic particle, the force may directly displace the node. Otherwise, the force on that node (particle surface node) is transmitted to the embedded particle. The embedded magnetic particles are treated as rigid objects.

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From the combination of all forces transmitted to an embedded particle via its surface nodes, the net force and torque on the particle are calculated. They lead to rigid translations and rotations of the particle, respectively. In turn, these rigid translations and rotations also determine the repositioning of the particle surface nodes. To accelerate the numerical calculation, the evaluation of the node forces is performed in parallel for different sections of the mesh.

To quantify the magnetic interactions in the system, we assume that all magnetic particles carry a dipolar magnetic moment of equal magnitude. Thus the total magnetic energy for N embedded magnetic particles is given by

$$U_{m} = \frac{\mu_{0}}{4\pi} \sum_{i=1}^{N} \sum_{j=1}^{i-1} \frac{\mathbf{m}_{i} \cdot \mathbf{m}_{j} - 3\left(\mathbf{m}_{i} \cdot \hat{\mathbf{r}}_{ij}\right)\left(\mathbf{m}_{j} \cdot \hat{\mathbf{r}}_{ij}\right)}{r_{ij}^{3}} - \sum_{i=1}^{N} \mathbf{m}_{i} \cdot \mathbf{B},$$
(S4)

where  $\mu_0$  is the vacuum permeability,  $\mathbf{r}_{ij} := \mathbf{r}_i - \mathbf{r}_j$  is the vector pointing from particle j to particle i,  $r_{ij} = |\mathbf{r}_{ij}|$ ,  $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$ ,  $\mathbf{m}_i$  and  $\mathbf{m}_j$  are the respective magnetic moments, and  $\mathbf{B}$  is an externally applied magnetic field. Since we assume that each dipole moment can freely rotate with respect to the frame of its carrying magnetic particle, resulting magnetic torques directly reorient the dipoles. Resulting translational forces are transmitted to the carrying particles.

Finally, a common route to mimic steric interactions between hard colloidal particles is to include the pairwise WCA potential<sup>S5</sup>

$$U_{\rm wca} = \begin{cases} 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} \right], & \text{if } r \le 2^{1/6}\sigma, \\ 0, & \text{if } r > 2^{1/6}\sigma. \end{cases}$$
(S5)

This potential is hard, repulsive, and of finite range. In our case, it accelerates the numerical calculations by its stabilizing effect: it introduces a severe energetic penalty for particles close to touching, allowing for a more efficient equilibration process. The WCA interaction becomes important in the strongly pre-compressed state of the chain-like aggregates, see e.g. Fig. 2b in the main article. We set  $\epsilon = \frac{m^2}{32m_0^2}ER^3$  and  $\sigma = 2R$ . In the situation of Fig. 2b, the attractive magnetic interaction is balanced to 93% by elastic deformation energy and to only 7% by WCA interactions.

Summarizing, the variables describing the state of the system are the positions of the tetrahedral matrix nodes, the particle positions, the particle orientations, and the magnetic dipole orientations. Using these variables, resulting forces and torques can be calculated from Eqs. (S1)–(S5) that drive the system towards the minimum of the total energy. The energy minimization is performed using a nonlinear conjugate gradient algorithm. This algorithm minimizes the energy along a certain direction in parameter space before determining a new direction via the Fletcher-Reeves method, see Ref. S6 for an overview of conjugate gradient methods. The energy optimization along a parameter space direction is performed using Newton-Raphson iteration. The inner product involving the Hessian appearing in this scheme is approximated by finite differences<sup>S7</sup> using the gradient of the energy (forces and torques).

Next, we provide further background information on the initialization of our characteristic numerical systems; see the snapshot in Fig. 1a of the main article for one example realization. In the initially undeformed state before initial equilibration, each system has the shape of a rectangular box of size  $22.5R \times 10.4R \times 10.4R$  (R is again the radius of the embedded magnetic particles). As explained in the main text, we embed initially straight linear chain-like aggregates into these boxes. The chains are aligned parallel to each other and parallel to the long edge of the box, which will become the stretching direction. As further explained in the main text, each chain is only one particle in diameter, but consists of several particles in length. Here, we choose chains of 8 particles in length. Within one chain, neighboring particles are equally distanced from each other by a finite gap, here of thickness R/2. Furthermore, here the systems consist of 12 such parallel chains. Except for being aligned and non-overlapping, the chains are placed at random into the box with a minimum distance of R/4 from the system boundaries. In the resulting configuration, the chains are randomly shifted with respect to each other along their axes by a maximum amount of 2.5R. This is exactly the diameter of a particle plus the thickness of the gap. Consequently, no particular particle-to-gap geometry between two chains is statistically preferred. Finally, the volume containing the elastic matrix is tessellated into a set of affinely deformable tetrahedra as described above. The total number of tetrahedra in the mesh is around 250000. Then, the magnetic moments of the embedded particles are switched on, and the system is equilibrated. Still, the precise values of the above numbers are not important: we confirmed that they do not qualitatively affect our results.

At the end of this procedure, to perform our stressstrain measurements, the outer 10% of the system at both ends pointing towards the stretching direction are clamped. That is, tetrahedral nodes within the clamped regions are not free any more concerning displacements in stretching direction. Instead, their displacements in stretching direction are prescribed from outside. In this way, we impose a strain of defined magnitude (strain control). Forces F on the clamps (identifying the necessary imposed stress) are plotted in our stress-strain curves. They are extracted by calculating the forces exerted on all nodes within the clamped regions.

It is well known that rigid inclusions stiffen the system behavior<sup>S8–S10</sup>. This is illustrated in Fig. S1, where the uniaxial stress-strain behavior for our characteristic system (see Fig 1a of the main article) is compared to

2

3



FIG. S1. Uniaxial stress-strain behavior for the pure elastic matrix without rigid inclusions (pure matrix), for our characteristic system with nonmagnetic rigid particles included (m = 0), and for our magnetized characteristic system under a strong perpendicular magnetic field  $(m = 10 m_0, B_y = 30 B_0)$ . Both systems with rigid inclusions are significantly stiffer than the pure matrix. Since here in the magnetized system  $(m = 10 m_0)$  the detachment and reorientation mechanisms are both deactivated by the strong perpendicular magnetic field  $B_y$ , the stress-strain behavior is similar to the one for nonmagnetic particles (m = 0).

the behavior of the pure matrix material. Through the presence of the rigid inclusions, already with switchedoff magnetization (m = 0) the elastic modulus is increased by a factor of ~ 7. (The elastic modulus is related to the initial slope of the stress-strain curve at small strains  $\Delta L/L_0 \ll 1$ .) If the magnetization is switched on  $(m = 10 m_0)$  and a strong magnetic field  $B_y = 30 B_0$ is applied perpendicular to the stretching direction, the detachment and reorientation mechanisms remain deactivated (see also Figs. 1b,2e,2f,4a of the main article). Then, the stress-strain behavior of the magnetized characteristic system is similar to the one for m = 0, see Fig. S1.

#### II. ORIENTATIONAL DEGREES OF ORDER CHARACTERIZING THE FLIPPING MECHANISM

As became obvious from Fig. 3 in the main article, the reorientation ("flipping") mechanism of the magnetic moments during stretching is associated with an intermediate stage of disorder in the orientations of the magnetic moments (Fig. 3b in the main article). As also mentioned, the intermediate stage of disorder can be used to identify the effect. This is true not only for the regular cuboid-lattice system (Fig. 3 in the main article), but also for our uniaxial system containing the chainlike aggregates (Fig. 1 in the main article). Even more, the measure of orientational order can serve to demonstrate that the flipping mechanism is indeed associated with the distance changes between neighboring magnetic



FIG. S2. Degrees of orientational order  $S_m$  and  $S_r$  for the magnetic moments and for the separation vectors between nearest-neighbor particles, respectively, as a function of imposed strain: (a) for the regular cuboid-lattice system in Fig. 3 of the main article, and (b) for the uniaxial system containing the chain-like aggregates in Fig. 1a of the main article. In both cases,  $S_m$  and  $S_r$  nearly simultaneously go to zero at the point where the reorientation occurs. Solid lines represent loading and dotted lines unloading, respectively.

particles.

To us, the important question is whether the magnetic moments point along the stretching direction or have rotated to a perpendicular orientation. Thus, for each of the magnetic dipole moments  $\mathbf{m}_i$  of the N magnetic particles (i = 1, ..., N), we first measure  $\mathbf{\hat{m}}_i = \mathbf{m}_i / |\mathbf{m}_i|$ ; second, we determine the projections of  $\mathbf{\hat{m}}_i$  onto the stretching direction  $(\mathbf{\hat{m}}_i^{\parallel})$  and into the plane perpendicular to the stretching direction  $(\mathbf{\hat{m}}_i^{\perp})$ ; third, using these projections, we calculate a nematic order parameter tensor<sup>S11</sup>

$$\mathbf{Q}_{m} = \frac{1}{N} \sum_{i=1}^{N} \begin{pmatrix} 2(\hat{m}_{i}^{\parallel})^{2} - 1 & 2\hat{m}_{i}^{\parallel}\hat{m}_{i}^{\perp} \\ 2\hat{m}_{i}^{\parallel}\hat{m}_{i}^{\perp} & 2(\hat{m}_{i}^{\perp})^{2} - 1 \end{pmatrix}.$$
 (S6)

The degree of orientational order  $S_m$  for the magnetic moments follows as the largest eigenvalue of this tensor.  $S_m = 1$ , if all dipoles are simultaneously oriented parallel to the stretching axis or perpendicular to it, while  $S_m = 0$ in the absence of such global ordering.

Fig. S1a quantifies what is qualitatively observed already in Fig. 3 of the main text for the regular cuboidlattice system: at low strains, the dipoles largely align along the stretching direction ( $S_m$  close to 1); at intermediate strains, the dipoles disorder during reorientation (dip in  $S_m$ ); at high strains, the dipoles point into directions perpendicular to the strain axis ( $S_m$  close to 1).

Furthermore, we demonstrate that this reorientation process is correlated with the strain-induced changes in neighboring particle distances. For this purpose, we determine an additional parameter  $S_r$  in the same way as described above for  $S_m$ . Now, however, we use as an input the distance vectors  $\mathbf{r}_{ij}$  separating all pairs of nearest-neighboring particles (i, j), where  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ , instead of the magnetic moments  $\mathbf{m}_i$ . We find (Fig. S2a)  $S_r = 1$  at low strains, i.e. the shortest inter-particle distances are along the stretching direction;  $S_r = 0$  at intermediate strains, where shortest inter-particle distances are equally distributed along and perpendicular to the stretching direction process indicated by the minimum of  $S_m$ ;  $S_r = 1$  at high strains, with the shortest inter-particle distances perpendicular to the stretching direction.

Fig. S2b demonstrates the universality of this concept: also for the uniaxial system containing the chain-like aggregates (Fig. 1 in the main article), we can readily identify the reorientation mechanism via  $S_m$  and  $S_r$ , despite the more irregular particle arrangement. Both  $S_m$  and  $S_r$ become zero at intermediate strains. Also the hysteretic behavior shows up in these quantities.

# III. SIMPLIFIED ENERGETIC DESCRIPTION OF THE FLIPPING MECHANISM

In the following, we present a simplified energetic approach to the flipping mechanism for the cuboid-lattice system illustrated in Figs. 3 and 4 of the main article. The simplified model further supports our underlying picture of this process. As a central approximation, we assume a globally affine deformation of the system. That is, the globally imposed strain is homogeneously mapped to any distance within the system. For a very regular initial cuboid-lattice structure, this represents a plausible approximation, which becomes the better the larger the system size<sup>S12</sup>. As a consequence, the embedded magnetic particles must be considered as point-like inclusions. An immediate benefit of these simplifications is that significantly larger system sizes are addressable: the extensive computational time necessary to allow for inhomogeneous matrix deformations is saved.

We start from a regular cuboid-lattice structure similar to Fig. 3a of the main article, yet now considering up to  $50 \times 50 \times 49$  magnetic point particles. All of their dipole moments are assumed to be initially aligned along the nearest-neighbor axis (horizontally in Fig. 3a). Due to the resulting magnetic interactions, the system tends to initially "pre-compress" along this axis during equilibration. To conserve the volume, this is accompanied by a lateral extension. Already at this stage, we only allow for affine deformations. Elastic interactions again follow from Eq. (S1) and magnetic energies via Eq. (S4).

The effective elastic modulus  $E_{\text{eff}}$  of the composite of rigid particles embedded in an elastic matrix is higher than the elastic modulus E of the embedding matrix itself, see Section I. Our simplified model reduces the stiffening rigid particles to point-like dipoles. Therefore, we must use  $E_{\rm eff} > E$  to represent the overall material response correctly. We find  $E_{\rm eff} \approx 1.6E$  by matching the pre-compression of our simplified model system to that of the actual system in Fig. 3 of the main article. However, forces are still measured in units of  $F_0 = ER^2$  to compare with the simulation where this force scale is used.

Next we impose affine stretching deformations  $\Delta L/L_0$ along the initial nearest-neighbor axis (in analogy to Fig. 3 of the main article). At a certain strain, the distances between initial nearest neighbors and dipoles in perpendicular directions become equal. Thus, the strain creates new pairs of nearest neighbors along perpendicular directions. At still higher strains, these become the only remaining pairs of nearest neighbors (same process as depicted in Fig. 3 of the main article). Therefore, to minimize the magnetic energy, the dipoles flip towards a perpendicular axis (vertical axis in Fig. 3c). We plot the resulting magnetic energies for initial and flipped orientation as a function of strain in Fig. S3a. The flipping strain is given by the intersection point of the two curves. It should be noted that in a laterally symmetric cuboidlattice system there are two equally preferred perpendicular axes. Flipping towards one of them corresponds to spontaneous symmetry breaking. Fig. S3a also compares to the result obtained from the full non-affine numerical calculation in the main article.

It is illustratively clear what happens in the stressstrain curve (Fig. S3b) at the flipping strain. While the dipoles are oriented along the stretching axis, they attract each other along this axis and counteract the strain. This is reflected by a higher mechanical force to keep the system at a certain stretch. After the flip, they are in a repulsive configuration along the stretching axis. This supports the stretch and shows up as a drop in the stressstrain curve at the flipping strain. Thus, directly after the flip, a lower mechanical force is necessary to keep the system in the stretched state. Fig. S3b further compares to the stress-strain curve obtained via the full non-affine numerical simulation (black line in Fig. 4 of the main article). We find good qualitative agreement for the regular cuboid-lattice system.

Finally, Fig. S3c shows the trend for increasing system sizes. For comparison, we have to rescale the measured forces by the number of dipoles in a cross-sectional plane perpendicular to the stretching direction. Then we observe that the magnitude of the jump in the stress-strain curves (Fig. S3c) remains approximately constant. Its occurrence shifts to slightly higher strains, but this shift apparently saturates with increasing system sizes.

In summary, the simplified energetic description provides a reasonable representation of the situation in a regular cuboid-lattice system and can address larger system sizes. It should be kept in mind, however, that macroscopic samples can react in an inhomogeneous way. That is, part of the sample may have "flipped" already, while other parts are still in the state of initial or intermediate orientations. Then the assumption of affinity breaks down. The jumps in the stress-strain curves are replaced

4



FIG. S3. Simplified energetic model for affine elastic deformations of a regular cuboid-lattice system containing point-like magnetic dipoles (same set-up as for the full non-affine calculation presented in Figs. 3 and 4 of the main article; there, however, finite-sized rigid magnetic particles were embedded). (a) Strain-dependent magnetic energies  $U_m^{\parallel}(\Delta L/L_0)$  and  $U_m^{\perp}(\Delta L/L_0)$  for dipole orientations parallel and perpendicular to the stretching axis (horizontal and vertical axes in Fig. 3 of the main article), respectively, measured in units of  $U_0 = F_0 R$ . The flipping strain is identified from the intersection point of the two curves. Results are shown for a system of  $4 \times 4 \times 3$  dipoles for our simplified model and for the simulation in the main article  $[U_m^{sim}(\Delta L/L_0)]$ . (b) Corresponding stress-strain curves. Following the solid lines of magnetic energy in (a), their derivatives are discontinuous at the intersection (flipping) points. In the stress-strain curves, this leads to the characteristic jumps. (The simulation curve corresponds to the black curves in Fig. 4 of the main article.) (c) Stress-strain curves for different system sizes. The cuboid-lattice structures consist of  $N_x \times N_y \times N_z$  dipoles, where x again marks the stretching direction. Our systems shift to higher strains saturates for increasing system size.

by smoothened, flatter, more plateau-like regimes, as partially obtained in Fig. 1b,1c of the main article by averaging over several different realizations of the system.

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5

# Paper V. Superelastic stress-strain behavior in ferrogels with different types of magneto-elastic coupling

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# Statement of contribution

AMM was my main supervisor. Together, we worked out the different magneto-elastic coupling situations discussed in the manuscript. I advanced and adapted the employed numerical code from the previous publication to also address these different types of magneto-elastic couplings. I performed the numerical simulations and evaluated the data for the results shown in the paper. I did most of the writing and created all figures under the guidance of AMM and HL. My estimated contribution to the overall work involved in creating this paper is 90%.

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# 1 Introduction

Ferrogels, <sup>1–3</sup> also known as soft magnetic materials, magnetic gels, magnetic elastomers, or magnetorheological elastomers, are manufactured by embedding colloidal magnetic particles into an elastic matrix that most often consists of a cross-linked polymer. This leads to an interplay between magnetic and elastic interactions, allowing material properties to be reversibly adjusted *via* external magnetic fields.<sup>4–15</sup> Dynamically switching the elastic properties allows applications as tunable dampers<sup>16</sup> or vibration absorbers.<sup>17</sup> Moreover, shape changes<sup>5,18–21</sup> are interesting for the realization of soft actuators.<sup>22–27</sup> Also shape-memory effects have been observed in soft magnetic materials,<sup>28–30</sup> opening the way to even more interesting applications.

Recently we have identified another fascinating feature of soft magnetic materials in a simulation study,<sup>31</sup> namely tunable superelasticity. This term was originally introduced in the context of shape-memory alloys.<sup>32–34</sup> It addresses their special nonlinear stress–strain behavior with a plateau-like regime, where a small additional load leads to a huge additional deformation that is

completely reversible. In shape-memory alloys, the constituents are positioned on regular lattice sites. The observed behavior is enabled by a stress-induced transition of the material to a more elongated lattice structure that can accommodate the deformation. When the load is released, the shape-memory alloy performs the opposite lattice transition, which renders the whole process reversible.

Superelastic stress-strain behavior in ferrogels

Peet Cremer,\* Hartmut Löwen and Andreas M. Menzel\*

with different types of magneto-elastic coupling

Colloidal magnetic particles embedded in an elastic polymer matrix constitute a smart material called a ferrogel. It responds to an applied external magnetic field by changes in elastic properties, which can be exploited for various applications such as dampers, vibration absorbers, or actuators. Under appropriate conditions, the stress–strain behavior of a ferrogel can display a fascinating feature: superelasticity, the capability to reversibly deform by a huge amount while barely altering the applied load. In previous work, using numerical simulations, we investigated this behavior assuming that the magnetic moments carried by the embedded particles can freely reorient to minimize their magnetic interaction energy. Here, we extend the analysis to ferrogels where restoring torques by the surrounding matrix hinder rotations towards a magnetically favored configuration. For example, the particles can be chemically cross-linked into the polymer matrix and the magnetic moments can be fixed to the particle axes. We demonstrate that these systems still feature a superelastic regime. As before, the nonlinear stress–strain behavior can be reversibly tailored during operation by external magnetic fields. Yet, the different coupling of the magnetic moments causes different types of response to external stimuli. For instance, an external magnetic fields.

applied parallel to the stretching axis hardly affects the superelastic regime but stiffens the system beyond it. Other smart materials featuring superelasticity, *e.g.* metallic shape-memory alloys, have already found

widespread applications. Our soft polymer systems offer many additional advantages such as a typically

higher deformability and enhanced biocompatibility combined with high tunability.

In the case of anisotropic soft magnetic gels,5,8,35-39 the superelastic behavior is enabled by stress-induced structural changes. Such samples can be synthesized by applying a strong external magnetic field during the chemical cross-linking process that forms the elastic matrix. Before cross-linking, when the magnetic particles are still mobile, straight chain-like aggregates form along the field direction.<sup>40-43</sup> Cross-linking the polymer locks the particle positions into the elastic matrix even after the external field is switched off. Experimentally, the tunability of the linear elastic modulus of such samples has been investigated by applying external magnetic fields.<sup>5</sup> It turned out that the highest tunability was achieved for deformations and magnetic fields along the axes of the chain-like aggregates. Our previous numerical study of stretching such a magnetic gel along the axis of the chain-like aggregates to the nonlinear regime revealed the following behavior. The strong magnetic attractions within the chains first work against the elongation.

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However, once the magnetic barriers to detach chained particles are overcome, the material strongly extends. A part of the stored stress working against the magnetic interactions is released, leading to an additional strain without hardly any additional stress necessary. This behavior results in a strongly nonlinear, "superelastic" plateau in the stress–strain curve, similar to the phenomenology found for shape-memory alloys. The strain regime that is covered by this plateau, however, is significantly larger. In addition, it is possible to tailor the nonlinear stress– strain behavior during operation by external magnetic fields. Combined with the typically higher degree of biocompatibility of soft polymeric materials,<sup>44–48</sup> medical applications<sup>49–52</sup> might become possible.

In a previous study,<sup>31</sup> we restricted ourselves to the assumption that the magnetic moments of the embedded particles are free to reorient. First, this is possible when each magnetic moment can reorient within the particle interior, which typically can be observed as the so-called Néel mechanism up to particle diameters of 10–15 nm.<sup>53</sup> Second, the type of embedding in the elastic matrix can allow the whole particle to rotate, at least quasi-statically, without deforming the matrix, *e.g.*, when in the vicinity of the particles the cross-linking of the polymer matrix is inhibited.<sup>54</sup> Finally, yolk–shell colloidal particles feature a magnetic core that can rotate relatively to the nonmagnetic shell surrounding it.<sup>55,56</sup>

Herein, we also concentrate on the opposite scenario for spherical, rigid magnetic particles. That is, the magnetic moments are not free to reorient with respect to the embedding matrix. Two ingredients are necessary for this purpose. First, the matrix must be anchored to the particle surfaces. In reality, this can be achieved when chemically the particles themselves act as cross-linkers of the polymer matrix.57-62 Second, the magnetic moments must not rotate relatively to the particle frames. This is the case for magnetically anisotropic monodomain particles that are large enough to block the Néel mechanism. Again we can observe superelastic stress-strain behavior in such systems and again the nonlinearity can be tuned by external magnetic fields. Yet, the response is altered though, due to the different coupling of the magnetic filler particles to the surrounding matrix. An external magnetic field parallel to the chain-like aggregates largely leaves the superelastic behavior intact. In contrast to that, a sufficiently strong perpendicular field rotates the particles out of the initial alignment configuration and gradually removes the nonlinearity from the stress-strain curve. However, due to the covalent coupling to the elastic matrix counteracting particle rotation, the necessary field strengths to deactivate superelasticity are much higher when compared to the case of freely reorientable magnetic moments.

In Section 2 we begin by introducing our numerical model and our simulation technique for the measurement of the stress-strain behavior. Next, in Section 3, we define several ferrogel systems with different coupling properties between the particles and the surrounding elastic matrix. Afterwards, in Section 4, we analyze the resulting stress-strain behavior for these different systems and the various mechanisms and effects leading to the emerging superelastic features. We start with the case of vanishing external magnetic field and then proceed to fields parallel and perpendicular to the chain-like aggregates. Finally, in Section 5, we conclude by reviewing our results and discussing possible experimental realizations as well as prospective applications.

# 2 Numerical model and simulation procedure

The purpose of our simulations is to determine the nonlinear stress–strain behavior of uniaxial ferrogel systems containing chain-like aggregates. To achieve this, we require numerical representations of both the polymer matrix and of the embedded colloidal magnetic particles.

Let us first discuss our representation of the polymer matrix. We assume that all molecular details of the cross-linked polymer can be ignored, so that we can treat the matrix as a continuous and isotropic elastic medium. We tessellate it into a three-dimensional mesh of sufficiently small tetrahedra. Spherical magnetic particles are embedded into this mesh by approximating their surfaces as sets of planar triangles, which become faces of the tetrahedral mesh. This tessellation was enabled by the mesh generation tool gmsh,<sup>63</sup> which is based on Delaunay triangulation.<sup>64</sup> It allows to set a characteristic length scale parameter controlling the typical length of the tetrahedra edges, for which we used 0.35R, where *R* is the radius of the particles.

Each tetrahedron of the mesh may deform affinely, which is associated with an elastic deformation energy  $U_e$  given by the following nearly-incompressible Neo-Hookean hyperelastic model:<sup>65</sup>

$$U_{e} = V_{0} \left[ \left( \frac{\mu}{2} \operatorname{Tr} \{ \mathbf{F}' \cdot \mathbf{F} \} - 3 \right) - \mu (\det \mathbf{F} - 1) + \frac{\lambda + \mu}{2} (\det \mathbf{F} - 1)^{2} \right].$$
(1)

Here the elastic properties of the isotropic matrix enter via the Lamé coefficients  $\mu$  and  $\lambda.^{66}$  They can also be expressed in terms of the elastic modulus E and the Poisson ratio  $\nu$  via  $\mu = \frac{E}{2(1+\nu)}$  and  $\lambda = \frac{E\nu}{(1+\nu)(1-2\nu)}$ .  $V_0$  denotes the volume of the tetrahedron in the undeformed state. **F** is the deformation gradient tensor prescribing the affine transformation that brings the tetrahedron from its undeformed state to the deformed state. The deformed state of the tetrahedron is characterized by the matrix X:=  $(x_1 - x_0, x_2 - x_0, x_3 - x_0)$  that contains the current positions  $x_0,\,x_1,\,x_2,\,x_3$  of the four nodes (vertices), see Fig. 1 for an illustration. Similarly, the matrix  $\tilde{X}{:=}~(\tilde{x}_1~-~\tilde{x}_0,~\tilde{x}_2~-~\tilde{x}_0,~\tilde{x}_3~-~\tilde{x}_0)$  determines the undeformed (reference) state of the tetrahedron with node positions  $\tilde{\mathbf{x}}_0, \tilde{\mathbf{x}}_1$ ,  $\tilde{x}_2,\,\tilde{x}_3.$  Since F is the affine transformation that connects the deformed state to the reference state, we have  $\mathbf{X} = \mathbf{F} \cdot \mathbf{\tilde{X}}$ . Now the deformation gradient tensor F can be obtained<sup>67</sup> by multiplying from the right with  $\tilde{\mathbf{X}}^{-1}$ , yielding

$$\mathbf{F}(\mathbf{X}) = \mathbf{X} \cdot \tilde{\mathbf{X}}^{-1}.$$
 (2)

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Fig. 1 The undeformed state  $\tilde{X}$  of each tetrahedron is determined by the reference node positions  $\tilde{x}_0$ ,  $\tilde{x}_1$ ,  $\tilde{x}_2$ ,  $\tilde{x}_3$  via  $\tilde{X} = (\tilde{x}_1 - \tilde{x}_0, \tilde{x}_2 - \tilde{x}_0, \tilde{x}_3 - \tilde{x}_0)$ , while the deformed state X is characterized by the present node positions  $x_0$ ,  $x_1$ ,  $x_2$ ,  $x_3$  in the form  $X = (x_1 - x_0, x_2 - x_0, x_3 - x_0)$ . Both states are connected via the deformation gradient tensor F.

The undeformed reference state never changes, hence the inverse matrix  $\tilde{\mathbf{X}}^{-1}$  remains constant and has to be calculated only once. This allows to determine the elastic deformation energy  $U_{\rm e}(\mathbf{F}(\mathbf{X}))$  in any deformed configuration from the positions of the tetrahedral nodes.

Calculation of the force  $\mathbf{f}_i$  on each node i (i = 0, 1, 2, 3) is then straightforward,

$$\mathbf{f}_i = -\nabla_{\mathbf{x}_i} U_{\mathbf{e}}(\mathbf{F}) = -\frac{\partial U_{\mathbf{e}}(\mathbf{F})}{\partial \mathbf{F}} \cdot \frac{\partial \mathbf{F}}{\partial \mathbf{x}_i}.$$
 (3)

These forces allow us to determine the displacements of the nodes. The characterization of the elastic matrix is thus completed. In a second step, we turn to the embedded rigid particles. Since they are rigid objects, we have to treat nodes attached to particle surfaces in a special way. The forces on these nodes are transmitted to the corresponding particle, which leads to net forces and torques on the particles. Rotations and translations of the particles due to these forces and torques are calculated. They, in turn, determine the displacements of the surface nodes. We perform a parallel calculation of all node forces in the system by slicing it into different sections that can be handled separately.

Next we discuss our representation of the magnetic interactions. We assume that all N magnetic particles possess permanent dipolar magnetic moments of equal magnitude m. This leads us to a total magnetic interaction energy given by

$$U_m = \frac{\mu_0}{4\pi} \sum_{i=1}^{N} \sum_{j=1}^{i-1} \frac{\mathbf{m}_i \cdot \mathbf{m}_j - 3(\mathbf{m}_i \cdot \hat{\mathbf{r}}_{ij})(\mathbf{m}_j \cdot \hat{\mathbf{r}}_{ij})}{r_{ij}^3} - \sum_{i=1}^{N} \mathbf{m}_i \cdot \mathbf{B}.$$
 (4)

Here  $\mu_0$  is the vacuum permeability,  $\mathbf{m}_i$  and  $\mathbf{m}_j$  are the magnetic moments of particles *i* and *j*, respectively, with  $|\mathbf{m}_i| = |\mathbf{m}_j| = m$ ,  $\mathbf{r}_{ij}$ :=  $\mathbf{r}_i - \mathbf{r}_j$  is the separation vector between both particles,  $r_{ij} = |\mathbf{r}_{ij}|$  is its magnitude,  $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$ , and **B** is an externally applied magnetic field.

The magnetic dipolar interaction can be strongly attractive at short distances, when the magnetic moments of interacting particles are in a head-to-tail configuration. In order to prevent an unphysical interpenetration of the particles due to such an attraction, we additionally introduce a steric repulsion between the particles that counteracts the attraction at short distances. The WCA potential  $^{68}$ 

$$U_{\text{wca}} = \begin{cases} 4\varepsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} \right], & \text{if } r \le 2^{1/6}\sigma, \\ 0, & \text{if } r > 2^{1/6}\sigma, \end{cases}$$
(5)

is hard and finite-ranged and commonly used to represent steric repulsions. Its strong scaling with the particle distance compared to the dipolar interactions ( $r^{-12}$  vs.  $r^{-3}$ ) makes it the dominating contribution for short distances. By setting  $\varepsilon = \frac{\mu_0}{4\pi} \frac{m^2}{32R^3}$  and  $\sigma = 2R$ , the dipolar force between two particles,

 $\varepsilon = \frac{1}{4\pi} \frac{1}{32R^3}$  and  $\sigma = 2R$ , the applier force between two particles, with their magnetic moments aligned in the most attractive head-to-tail configuration, is exactly balanced by the repulsive WCA interaction when they are in contact.

All these ingredients together express the total energy of the system. It is a function of the node positions of the tetrahedral mesh, the particle positions, the particle orientations, and the orientations of the magnetic moments of the particles. We equilibrate our systems by performing an energy minimization with respect to these degrees of freedom. As a numerical scheme, we employ the FIRE algorithm,  $^{69}$  using the forces and torques resulting from eqn (1)-(5) to drive the system towards its energetic minimum. FIRE is a molecular dynamics scheme that introduces artificial velocity modifications to achieve a quick relaxation. In each step of iteration, the equations of motion are integrated using a standard Velocity-Verlet algorithm, causing the system to accelerate towards the direction of steepest descent in energy. The direction is further emphasized by an additional steering contribution that tilts the directions of the velocities and angular velocities more towards the directions of the currently acting forces and torques, respectively. After the system energy has been decreasing for a small number of subsequent iterations, the steering contribution is reduced and the time step is increased, allowing inertia to carry the system further. An eventual increase in system energy is stopped by instantly freezing the system, setting all velocities and angular velocities equal to zero. Subsequently, the system accelerates again with the steering contribution restored to its initial value and reduced time step. The increase and decrease of the time step as well as the steering contribution are controlled using several parameters, for which we use the values suggested in ref. 69. Numerical stability is ensured by an upper bound  $\Delta t_{max}$  for the time step, which may depend on the considered system. We have found  $\Delta t_{\text{max}} = 0.01$  to be sufficient for our systems. From our experience, this rather simple minimization scheme is quite competitive with more sophisticated schemes like nonlinear conjugate gradient<sup>70</sup> that we employed in our earlier work in ref. 31. In extreme situations of deformation, unphysical behavior may result, such as the inversion of individual tetrahedra or their penetration into the spherical particles.

The physical input parameters for our simulations are the elastic modulus *E* and Poisson ratio  $\nu$  of the matrix, the magnitude *m* of the magnetic moments and eventually the external magnetic field **B**. We measure forces *F* in units of  $F_0 = ER^2$ , magnetic

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moments in units of  $m_0 = R^3 \sqrt{\frac{4\pi}{\mu_0}E}$ , and magnetic field strength in units of  $B_0 = \sqrt{\frac{\mu_0}{4\pi}E}$ . Throughout his work, we fix the material parameters by choosing  $\nu = 0.495$  and  $m = 10m_0$ . The Poisson ratio is chosen close to 1/2 to model the typical near-incompressibility of cross-linked polymer matrices while retaining some remnant compressibility required by our numerical simulation method. The choice of *m* sets a sufficiently high ratio between magnetic and elastic interactions to observe pronounced effects and is experimentally realistic as explained later in Section 5.

Besides the material properties, the behavior of a sample depends on its shape<sup>27,71</sup> and on the internal distribution of particles.<sup>72-74</sup> Our characteristic numerical probes are small three-dimensional systems of magnetic particles embedded into an initially rectangular box of an elastic material. The dimensions of the box are  $22.5R \times 10.4R \times 10.4R$ , containing 96 identical spherical particles. These particles are arranged into 12 chain-like aggregates of 8 particles each. All chains are aligned parallel to the long edge of the box (the x-direction). Neighboring particles in the same chain are initially separated by a finite gap of the elastic material of thickness R/2. The positions of the chains are chosen at random, with the constraint that they shall not overlap and have a minimum distance of R/4 to the box boundaries. This results in a configuration of chains shifted with respect to each other along their axes by a maximum amount of 2.5R. Since this maximum shift equals the particle diameter plus the gap thickness, there is no statistical preference of any special particle-gap configuration between two chains. Such an initial arrangement of the chains is supposed to mimic experimental ferrogel systems featuring chain-like aggregates that span the whole sample along one direction.<sup>37,38</sup> They constitute a natural choice for studying tunable deformation effects along the designated direction.5 Our results are based on 20 different systems created in this manner, each with a unique particle configuration. About 250 000 tetrahedra result in each case from the mesh generation.

To measure the uniaxial stress-strain behavior of such a numerical system, we quasi-statically stretch it along the chain direction, using the following protocol. We define two numerical clamps, on the two faces where chains start and end. In our geometry, these faces are normal to the x-direction. All particles on the chain ends are subject to the corresponding numerical clamp. Particles within the clamps may rotate. They may also translate in the y- and z-directions, however, with the constraint that the center-of-mass displacement of all particles in a clamp is zero. This keeps the centers of the clamps fixed in the yz-plane and prevents an overall rotation of the long axis of the system. Finally, we prevent global rotations of the whole system around its long axis at all times. For this purpose, at each timestep, we determine the global rotational modes from which the rotation is eliminated. Overall, this definition of the clamps differs from our approach in ref. 31. There, the clamps consisted of the complete outer 10% of the system at both ends,

that is, besides the particles also all matrix mesh nodes in these volumes were included.

After switching on the magnetic moments, we perform an initial equilibration process. During this period, the clamps are allowed to relatively translate along the x-axis. However, the relative distance between the particles in a clamp is kept constant along the x-direction. Due to this initial equilibration, we can observe an initial matrix deformation and define the resulting state as unstretched. This sets the equilibrium distance  $L_0$  between the clamps as the x-separation between the innermost clamped particles. To apply a uniaxial strain, we increase the distance between both clamps in small steps, displacing all clamped particles uniformly. So we can define the uniaxial strain as  $\varepsilon_{xx} = \Delta L/L_0,$  where  $\Delta L$  is the momentary increase in the distance between both clamps. After each step, we equilibrate the sample again under the constraint of keeping the x-positions of the clamped particles fixed. Subsequently, we can extract the force F that has to be applied to the clamps to maintain the system in the prescribed strained state. We continue the stress-strain measurements up to a maximum strain of  $\Delta L/L_0 = 150\%$ and then gradually unload the system again. To check the reversibility of the deformation, we perform several loading and unloading cycles.

# 3 Definition of the numerical systems

Within our numerical samples defined above, we distinguish between two scenarios of how the magnetic moments are coupled to the surrounding matrix via their carrying particles. Systems showing the first one, which we term free systems, feature magnetic moments that can freely rotate relative to the particle frames and surrounding matrix, see also ref. 31. In this case, a reorientation of a magnetic moment does not directly induce a deformation of the matrix surrounding the carrying particle. Computationally, we treat this system by keeping the orientations of the magnetic moments and the orientations of the carrying particles as separate degrees of freedom. During the initial equilibration, within the particles constituting one chain, the magnetic moments tend to align parallel to the chain axis. The magnetic moments within neighboring chains have the tendency to align in opposite directions to minimize the overall magnetic interaction energy. Fig. 2a illustrates this situation by showing a snapshot of an equilibrated free system before stretching. A cut along the cross-sectional center plane perpendicular to the chain axes in Fig. 2a stresses the different alignment of the magnetic moments in different chains.

In the opposite scenario, we assume that the magnetic moments are fixed to the axes of the carrying particles, while the particles are covalently embedded into the elastic matrix. A torque on a magnetic moment is then equivalent to a torque on the carrying particle, which in turn leads to a deformation of the surrounding matrix. We mark these systems by the term cov and represent them computationally by rigidly coupling the magnetic moment orientations to the particles.

Consequently, the initial orientations of the magnetic moments have a determining influence on the structure of the cov





Fig. 2 Snapshots of characteristic samples containing chain-like aggregates in the equilibrated unstretched state. The two displayed systems are generated from the same initial placement of the rigid embedded particles. Yet, the way of subsequent anchoring of the magnetic moments, here indicated by small bar magnets, is different, leading to the two different equilibrated states. The matrix was tessellated into a mesh of tetrahedra, those faces of which that constitute the overall system boundaries are depicted explicitly. (a) The free system, where the magnetic moments can rotate freely with respect to the carrying particles. This leads to the opposite alignment of the magnetic moments in different chains, as indicated in the top right for the cross-sectional center plane perpendicular to the chain axes. (b) Snapshot for the cov⇒ system, where the magnetic moments are fixed to the particle axes, likewise including a cross-sectional cut. The snapshot for the cov system is by definition again the one shown in (a), because in this system the magnetic moments are fixed to the particle axes only after the initial equilibration in the free system

samples and, thus, on their stress-strain behavior. We distinguish between two sub-scenarios and term the corresponding systems  $cov \rightrightarrows$  and  $cov \backsim$ . In the  $cov \rightrightarrows$  systems, we define all magnetic moments in the sample to initially point in the same direction parallel to the chains. During the initial equilibration, the orientations of the magnetic moments barely change as particle rotations are energetically expensive. The magnetic moments within all chains are still aligned in the same direction, see Fig. 2b for a snapshot. This is different in the

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#### Paper

115

cov  $\leftrightarrows$  systems: here we take the equilibrated state from the free systems, but then fix the magnetic moments to the particle axes before stretching the sample. As a result, the magnetic moments are rigidly anchored to the carrying particles and are arranged into the chains with alternating alignment, see again Fig. 2a for a snapshot. The cov  $\leftrightarrows$  system constitutes a case in-between the free and cov  $\rightrightarrows$  systems. We can, therefore, use it to test separately the effect of the two main modifications from the free to the cov  $\rightrightarrows$  system: anchoring the magnetic moments to the particle frames (free to cov  $\leftrightarrows$ ) and having all magnetic moments point in the same direction (cov  $\leftrightarrows$  to cov  $\rightrightarrows$ ).

If we would apply an external magnetic field before the magnetic moments are anchored, we would destroy the alternating chain morphology that we want to study. Thus, when studying the influence of an external magnetic field on these alternating chain systems, we apply it after the magnetic moments have been anchored. Subsequently, we reequilibrate the systems under these new conditions before performing the stress–strain measurement.

## 4 Results and discussion

In the following, we will present and discuss our results for the three systems free,  $cov \Rightarrow$ , and  $cov \Rightarrow$  as defined above. We begin with vanishing external magnetic field and then proceed to the situation of magnetic fields applied parallel and perpendicular to the stretching direction. For each system and each magnetic field, we show snapshots as well as the uniaxial stress–strain curves and discuss the various mechanisms that lead to our results.

Important insight can be gained by statistically analyzing the orientations of the magnetic moments in the systems. We evaluate them by considering the nematic order parameter  $S_m$ , which is defined as the largest eigenvalue of the nematic order parameter tensor<sup>75</sup>

$$\mathbf{Q}_m = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{3}{2} \hat{\mathbf{m}}_i \otimes \hat{\mathbf{m}}_i - \frac{1}{2} \hat{\mathbf{I}} \right).$$
(6)

Here  $\hat{\mathbf{m}}_i$  are the magnetic moment orientations of the *N* particles in the system,  $\otimes$  marks the dyadic product, and  $\hat{\mathbf{l}}$  is the unity matrix.  $S_m$  measures the degree of alignment of the input orientations without distinguishing between orientation  $\hat{\mathbf{m}}_i$  and its opposing orientation  $-\hat{\mathbf{m}}_i$ . Perfect alignment leads to  $S_m = 1$ , while in the absence of global orientational order  $S_m = 0$ .

In addition to the magnetic order in the systems, also the structural order contains useful information. It can be quantified in a very similar way by defining another nematic order parameter tensor

$$\mathbf{Q}_{r} = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{3}{2} \hat{\mathbf{r}}_{i} \otimes \hat{\mathbf{r}}_{i} - \frac{1}{2} \hat{\mathbf{I}} \right).$$
(7)

In this expression,  $\hat{\mathbf{r}}_i$  is defined as the orientation of the separation vector for each particle *i* to its nearest neighbor.  $S_r$  is the largest eigenvalue of the tensor  $\mathbf{Q}_r$ . We find  $S_r = 1$  when all particles have their nearest neighbor along a common axis.

In the case of linear aggregates, this means that all aggregates are aligned. Such a global structural order is absent for  $S_r = 0$ .

As will be revealed later in more detail, in the free system a "flipping mechanism"<sup>31</sup> plays an important role. "Flips" refer to events during which some magnetic moments suddenly change their direction with respect to the stretching axis from parallel towards perpendicular. They are induced by the stress-induced structural change in the system. To appropriately characterize this flipping mechanism, we define special modified nematic order parameters  $\tilde{S}_m$  and  $\tilde{S}_r$  as described here for  $\tilde{S}_m$ . First, to get rid of the distinction between different perpendicular directions, we determine the projections  $\hat{m}_i^{\parallel}$  of the magnetic moment orientations  $\hat{\mathbf{m}}_i$  onto the stretching axis as well as the projections  $\hat{m}_i^{\perp}$  into the plane perpendicular to the stretching axis. Then we define a two-dimensional nematic order parameter tensor as

$$\tilde{\mathbf{Q}}_{m} = \frac{1}{N} \sum_{i=1}^{N} \begin{pmatrix} 2\left(\hat{m}_{i}^{\parallel}\right)^{2} - 1 & 2\hat{m}_{i}^{\parallel}\hat{m}_{i}^{\perp} \\ 2\hat{m}_{i}^{\parallel}\hat{m}_{i}^{\perp} & 2\left(\hat{m}_{i}^{\perp}\right)^{2} - 1 \end{pmatrix}$$
(8)

and obtain  $\tilde{S}_m$  as the largest eigenvalue of this tensor. Similarly, we can determine the projections  $\hat{r}_i^{\parallel}$  and  $\hat{r}_i^{\perp}$  of the nearest-neighbor separation vectors  $\hat{\mathbf{r}}_i$ , define the tensor

$$\tilde{\mathbf{Q}}_{r} = \frac{1}{N} \sum_{i=1}^{N} \begin{pmatrix} 2\left(\hat{r}_{i}^{\parallel}\right)^{2} - 1 & 2\hat{r}_{i}^{\parallel}\hat{r}_{i}^{\perp} \\ 2\hat{r}_{i}^{\parallel}\hat{r}_{i}^{\perp} & 2\left(\hat{r}_{i}^{\perp}\right)^{2} - 1 \end{pmatrix}, \qquad (9)$$

and identify  $\tilde{S}_r$  as its largest eigenvalue.

#### 4.1 Vanishing external magnetic field (B = 0)

We now start by quasistatically stretching the three systems along the chain axes in the absence of an external magnetic field. The elongation is stepwise increased to a maximum and then, in the inverse way, reduced back to zero. The necessary forces on the clamps are recorded.

Fig. 3 shows the strongly nonlinear stress-strain behaviors resulting for the three systems. In the beginning, all systems show an almost identically steep increase of the stress with the imposed strain. Then, from a strain of about  $\Delta L/L_0 \approx 10\%$  up to  $\Delta L/L_0 \approx 50\%$ , a pronounced superelastic plateau follows. In this regime, a small increase in the applied load leads to a huge deformation that is completely reversible. The shape of the superelastic plateau differs among the systems. In the  $cov \rightrightarrows$  and our strain-controlled measurements we find a regime of negative slope<sup>76</sup> for the free system. Moreover and in contrast to the other systems, we here observe a considerable hysteresis for the free system in the strain interval containing the superelastic plateau. In all cases, subsequent to the plateau, the slope partially recovers, becomes relatively constant, and does not differ much among the different systems. Each stress-strain curve is obtained by averaging the stress-strain curves resulting from 20 different realizations that vary in the initial arrangement of the chain-like aggregates, see Section 2. The standard deviations are indicated by the shaded areas around the curves.



Fig. 5 Unlaxial stress-strain curves for the free, cov $\Xi$ , and cov $\Xi$ , systems, as well as for a corresponding system containing unmagnetized particles (unmag) when stretching along the axes of the chain-like aggregates. The magnetized samples show a superelastic plateau between  $\Delta L/L_0 \approx 10\%$  and  $\Delta L/L_0 \approx 50\%$ . In this regime, they can be deformed by a significant amount by only barely increasing the load. In contrast to that, the curve for the unmagnetized case lacks this appealing feature. The solid lines signify loading and dotted lines unloading processes, as in all subsequent figures. In the free system, our curves show pronounced hysteresis. Each curve results from averaging the curves obtained from 20 different initial particle distributions and the shaded areas illustrate the corresponding standard deviations.

For the free system they are significantly larger than for the other ones.

The main mechanism responsible for the nonlinearities in all systems is a stress-induced detachment mechanism.<sup>31</sup> We briefly illustrate how it can lead to the change from the steep slope at the origin of the stress-strain curve to the subsequent superelastic plateau. Consider again the unstretched states depicted in Fig. 2. In these states, the chains are contracted because of the mutual attraction between the magnetic moments of neighboring particles. Thus, the elastic material in the gaps between neighboring particles on the same chain is pre-compressed and the particles are close to each other. In this situation, the dipolar attraction is strong, since its interaction energy, see eqn (4), scales with the inverse cube of the distance. To stretch the system, work has to be performed against this strong attraction between the particles, which accounts for the steep initial increase in the stress-strain curve. However, when a section of a chain is detached a little from the remainder, the attraction between both parts weakens considerably. Therefore, once overcoming the magnetic barrier, the displaced chain section can be detached from the remainder of the chain. Such a detachment event releases the energy stored in the gap between the detached particles and allows a sudden elongation of the system.

Fig. 4a shows a snapshot of a free sample stretched by 35%, illustrating this process. In the depicted situation, some particles are detached from the chains with increased particle separation, while smaller segments are still intact. Each individual detachment event corresponds to a small localized drop in the stress-strain curve. In a very small and ordered system, this would lead to a spiky appearance of the stress-strain relationship as

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Fig. 4 (a) Snapshot of a free sample stretched by 35%. The freely rotating magnetic moments in this system can minimize their magnetic interaction by aligning along the direction of shortest interparticle distance. When the sample is stretched, perpendicular directions become more and more favored, because the interparticle distance within the chains is increased, while near-incompressibility of the sample forces neighboring chains to approach each other. In the depicted situation, about half of the particles are detached from the chains, their magnetic moments having performed a flip from a direction parallel to the stretching axis towards perpendicular. In the (b)  $cov \Rightarrow$  and (c)  $cov \Rightarrow$  systems, rotations of the magnetic moments necessitate rotations of the carrying particles, causing restoring torques by the surrounding matrix. Still, significant particle rotations can be observed in these samples stretched by 100% with respect to the unstretched states in Fig. 2, caused, however, primarily by inhomogeneous deformations of the surrounding matrix due to the particle embedding. (d) Snapshot of an unmagnetized (unmag) system starting from the same configuration. The bars indicate the initially horizontal particle axes to illustrate the particle rotations. They show a similar pattern as the systems in (b) and (c) although magnetic interactions are absent.

we have demonstrated for a single chain in ref. 31. However, averaging over the many detachment events that occur in a larger, inhomogeneous system with many parallel chains yields a smooth superelastic plateau as in Fig. 3. Upon unloading the system, the individual particles can simply reattach, reform the chains, and restore the energy in their separating gaps, so that the detachment mechanism is reversible.

The second mechanism contributing to the observed superelasticity is the flipping mechanism. It only plays a significant role in the free system. In the unstretched sample, the magnetic moments align along the chain axes in a head-to-tail configuration to minimize their magnetic interaction energy, see Fig. 2. This situation changes when the sample is sufficiently stretched in the direction parallel to the chains. The distances between particles in the same chain eventually increase, see Fig. 4a and ref. 31. Meanwhile, volume preservation in our nearly incompressible systems enforces a contraction in the perpendicular direction, driving different chains closer to each other. Eventually, the interparticle distances in the parallel and perpendicular directions become approximately equal for subsets of particles. For the involved magnetic moments this means a sudden change in their preferred orientation from parallel to the stretching axis towards perpendicular. In the free system, the moments can easily seize this opportunity to minimize their magnetic interaction energy by sudden reorientation. This constitutes a flip event.

Flips are associated with drops in the stress-strain curve for the following reason. As long as the magnetic moments participating in a flip event are still aligned parallel to the stretching axis, their magnetic interaction energy increases with the strain. However, once the flip has occurred and they have aligned towards perpendicular, their magnetic interaction energy decreases with the stretching. Therefore, during a flip event, the slope of the magnetic interaction energy suddenly changes for the participating magnetic moments. Since the stress is the derivative of the energy with respect to the strain, this causes a drop in the stress-strain curve. Or, discussing the situation directly in the force picture: as long as the magnetic moments align along the stretching axis, they counteract the elongation, which requires a higher stretching force; once they flip, they repel each other along the stretching axis, which supports the elongation. In an inhomogeneous sample, flips are local events and can occur over a wide range of global strain magnitudes. As a result, the individual drops are smoothened out in the stress-strain curves resulting from our characteristic systems.

Consider again the snapshot in Fig. 4a. Compared to the particles in the still intact chain parts, the detached particles have a larger interparticle distance along the stretching axis and their magnetic moments indeed prefer an orientation towards perpendicular to this axis. When a detachment event occurs, the corresponding sample section elongates, which can in turn trigger flip events. Conversely, a reorientation of magnetic moments towards the perpendicular direction can induce detachment. So in our characteristic free systems, the detachment and flipping mechanisms are intertwined. Yet, considering suitable

#### Paper

idealized model situations, both mechanisms can be studied in isolation, see ref. 31. The interplay between both mechanisms supports the hysteresis observed in our stress–strain curves for the free system, see Fig. 3. The magnetic attractions pull the particles together along the orientation of the magnetic moments, which in turn self-strengthens the magnetic interaction. In this way, an energetic barrier is created that needs to be overcome every time the magnetic moments are pulled apart and flip, either during initial stretching, or in the flipped state during unloading.

We can further quantify the flipping mechanism by statistically analyzing the orientations of the magnetic moments. Let us evaluate the nematic order parameters  $\tilde{S}_m$  and  $\tilde{S}_r$  defined in eqn (8) and (9) as a function of the imposed strains.  $\tilde{S}_m$  measures the degree of alignment of the magnetic moments and  $\tilde{S}_r$  does the same for the separation vectors between nearest-neighboring particles. The results are plotted in Fig. 5.  $\tilde{S}_m$  and  $\tilde{S}_r$  (as well as  $S_m$  and  $S_r$ ) are themselves per definition obtained from averages, see eqn (6)–(9). We here take the sums in these equations directly over all particles in all 20 different realizations of each system. In this way, the deviations between the different realizations are already contained in these order parameters.

In Fig. 5, for low strains, magnetic moments are aligned parallel to the stretching axis, because this is the direction of smallest interparticle distance. Consequently the system is in a state of high magnetic and structural order, reflected by the high levels of  $\tilde{S}_m$  and  $\tilde{S}_r$ . Upon increasing the strain, the interparticle distances in the stretching direction increase, particles are detached and magnetic moments flip, taking the system into a mixed state.  $\tilde{S}_m$  and  $\tilde{S}_r$  simultaneously decrease and reach a minimum at  $\Delta L/L_0 \approx 35\%$ , where they almost



Fig. 5 Degrees of magnetic order  $\tilde{S}_m$  and structural order  $\tilde{S}$ , for the free system, following the definition in eqn (8) and (9). For vanishing strain, alignment along the initial anisotropy axis is preferred both magnetically and structurally. When the strain is increased, detachment and flip events occur and the system enters a mixed state where the parallel direction becomes less dominant in favor of directions perpendicular to the stretching axis. The minimum is reached at a strain of  $\Delta L/L_0 \approx 35\%$ , corresponding to the situation depicted in Fig. 4a. Subsequently, the degrees of order increase again until all possible detachments and flips have occurred. The hysteretic behavior observed for the stress-strain curves in Fig. 3 shows up as well in the order parameters.

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vanish. This state is depicted in the snapshot in Fig. 4a, where about half of the particles are detached from the chains with their magnetic moments flipped towards a perpendicular direction. From there on, both  $\tilde{S}_m$  and  $\tilde{S}_r$  increase again until finally all particles are detached and all magnetic moments have flipped. The strain regime where the order parameters change significantly coincides with the position of the superelastic plateau in the stress-strain curve in Fig. 3. Finally, at the highest strains, both order parameters again decrease slightly when the lateral contraction of the system squeezes the particles together. This causes them to evade each other when they come too close and makes them shift relatively to each other along the stretching axis, which disturbs the perpendicular alignment. Also for the order parameters, we here observe again the hysteresis discussed already in the context of the stressstrain curves.

Let us now come back to the  $cov \rightrightarrows$  and  $cov \backsim$  systems where the magnetic moments cannot rotate relatively to the particle frames. Then magnetic reorientations cost a significant amount of elastic energy, as this requires a corotation of the elastic matrix directly anchored to the particle surfaces. Fig. 4b and c, show snapshots of the corresponding samples at a strain of 100%. There we can nonetheless observe particle rotations. These particle rotations, however, do not apparently lead to a configuration that minimizes the magnetic interaction energy. In fact, the primary reason for these rotations is not the magnetic interaction between particles, but inhomogeneities in the stiffness across the system. We recall that the particles in our systems are rigid inclusions of finite extension. Consequently, the particles are local sources of increased rigidity within the soft elastic matrix. Already in an unmagnetized system, such rigid inclusions lead to an overall stiffer elastic behavior of the whole system.<sup>77–79</sup> In our case, an increase of a factor of  $\sim$ 7 in the elastic modulus was observed.<sup>31</sup> Placing the particles into the randomly shifted chains when designing our systems adds a certain randomness to the distribution of our localized rigidities. When stretching the systems, the inhomogeneous distribution of rigidity can lead to local shear strains that rotate the embedded rigid particles. Of course, this does not require the particles to be magnetized and occurs in unmagnetized systems (m = 0) as well. In Fig. 4d we show a snapshot of an unmagnetized system stretched by 100% for demonstration. There we indicate the initially horizontal particle axes by bars to visualize the particle rotations. The resulting patterns of particle rotation are qualitatively similar to the ones in the  $cov \rightrightarrows$  and  $cov \leftrightarrows$  systems.

Again we use statistical analysis to further quantify the particle rotations. Due to the different mechanism when compared to the flipping process, we are here only interested in the degree of alignment along the initial anisotropy axis. Therefore, we use the nematic order parameter  $S_m$  defined in eqn (6) for quantification. The results are plotted in Fig. 6a as a function of the imposed strain for the free, cov $\Rightarrow$ , and cov $\Rightarrow$  systems, as well as for the unmagnetized (unmag) case. Let us first consider the unmag system, where the initial horizontal particle axes, see Fig. 4d, are used to calculate  $S_m$ . Up to a strain of  $\Delta L/L_0 \approx 35\%$ ,

#### Phys. Chem. Chem. Phys., 2016, 18, 26670-26690 | 26677



Fig. 6 (a) Nematic order parameter  $S_m$  according to eqn (6) for the magnetic moment orientations of the free, cov rightarrow cov rightarrow systems, as well as for an unmagnetized (unmag) system as a function of the imposed strain  $\Delta L/L_0$ . In the latter three systems, there is a regime of high  $S_m$  at low strains. At a strain of  $\Delta L/L_0 \approx$  35% in the unmag system and  $\Delta L/L_0 \approx$  50% in the cov and cov ⇒ systems, there is a crossover to a regime of declining order, as inhomogeneous stresses begin to rotate the particles. In the free system, again a minimum indicates the occurrence of flip events. The recovery of  $S_m$  beyond the minimum shows that there is one globally preferred perpendicular axis emerging subsequent to flipping. (b) Nematic order parameter  $S_r$  according to egn (7) for the nearest-neighbor separation vectors in the same systems. All curves have a minimum at the point where the preferred directions switch from parallel to the stretching axis towards perpendicular. In the magnetized systems, this minimum is postponed to higher strains. In these systems, the detachment barrier and magnetic interactions along the chains stabilize the chain structure, which is then preserved up to higher strains.

particle rotations barely seem to occur, as  $S_m$  stays close to 1. Then, there is a crossover to a regime of approximately linear decay of  $S_m$ . The particles rotate more and more away from the initial axes of alignment as a consequence of the inhomogeneous stiffness. The behavior in the cov $\rightrightarrows$  and cov $\leftrightarrows$  systems is very similar, the crossover to the regime of declining order merely occurs at a higher strain of  $\Delta L/L_0 \approx 50\%$ , which also roughly marks the end of the superelastic plateau in Fig. 3. In these systems, the dipolar magnetic interactions along the initial, still intact chains counteract particle rotations and stabilize the alignment up to higher strains. When the detachment of the particles from the chains has been completed at the end of the superelastic plateau, this stabilizing magnetic interaction disappears, rendering the particles susceptible to

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#### Paper

119

shear stresses originating from the system inhomogeneity. The curve for the  $\cot \Rightarrow$  system is always below the one for  $\cot \Rightarrow$ , because already the initial unstretched state is less ordered, see again Fig. 2.

The behavior of  $S_m$  for the free system is obviously completely different and should rather be compared with  $\tilde{S}_m$  in Fig. 5.  $S_m$ shows a rapid initial decay up to a minimum and afterwards recovers to reach a relatively low but constant level. This is despite the fact that  $S_m$ , unlike  $\tilde{S}_m$ , distinguishes between different directions perpendicular to the stretching axis. Therefore, beyond the superelastic plateau, one particular axis perpendicular to the stretching axis must emerge along which the magnetic moments preferably align. Such a direction forms as nearby flipped magnetic moments tend to align by magnetic dipolar interaction. In turn, this favors further contraction along such an emerging axis of alignment, providing a self-supporting mechanism. Inherent structural inhomogeneities will affect this mechanism.

The same analysis as for  $S_m$  can be conducted for the nematic order parameter  $S_r$  of the separation vectors between nearest neighbors. It is plotted for all systems in Fig. 6b.  $S_r$  starts at a high value for all systems, because in the unstretched state the nearest neighbor of each particle is always along the chain. The more the sample is stretched, the more the distances along the chains increase, while the distances between separate chains decrease due to volume preservation. Thus, it becomes increasingly likely that the nearest neighbor for a particle is a member of a different chain. In the unmag system, there is no stabilizing attractive interaction keeping the chains together. So the minimum, where nearest-neighbor directions predominantly switch, is reached relatively soon. In the other systems, however, the magnetic attraction makes the chains subject to the detachment mechanism. Segments detach from the chains, while the remainder of the chains remains intact. As a result, partial structural order is preserved up to much higher strains. Again, the strain regime where  $S_r$  changes a lot due to the changes in structural order coincides with the strain interval of the superelastic plateau in the stress-strain curves in Fig. 3.

Finally, we now also understand the different magnitudes of the standard deviations for the displayed averaged stressstrain curves in Fig. 3. Each curve is obtained by averaging of 20 realizations of the particle arrangement. Differences in the initial distribution of the chain-like aggregates lead to differences in the thresholds for flip and detachment events as a major source for the standard deviations. In the unmag system, neither the detachment nor the flipping process is activated, consequently the standard deviation is smallest. Intermediate magnitudes are observed in the cov $\rightrightarrows$  and cov $\leftrightarrows$  systems where the detachment mechanism prevails and flipping is largely inhibited. In contrast to that, the flipping mechanism is activated in the free system and can also trigger detachment events, thus here the largest standard deviations arise.

#### 4.2 External magnetic field along the stretching axis $(B = B_x \hat{x})$

Upon applying an external magnetic field parallel to the chain and stretching axes (the *x*-direction) when recording the stress-strain

26678 | Phys. Chem. Chem. Phys., 2016, 18, 26670-26690

View Article Online



Fig. 7 Results for the free system under the influence of an external magnetic field of varying strength, applied parallel to the stretching axis. (a) Uniaxial stress-strain behavior.† The external field gradually deactivates the flipping mechanism. As a result the superelastic plateau is flattened, the dip at  $\Delta L/L_0 \approx 50\%$  and the hysteresis are removed until the behavior resembles the one for the cov $\Rightarrow$  system in Fig. 3 for vanishing external magnetic field. For better visibility, only the maximum standard deviation on each curve is indicated by a bar where it occurs. (b) Snapshot showing a free system subject to an external field of  $B_x = 1B_0$  at a strain of  $\Delta L/L_0 = 100\%$ . Even in this highly strained state, the magnetic moments assume oblique angles instead of performing full flips towards a perpendicular direction. (c) Degree of magnetic order  $\tilde{S}_m$  and (d) degree of structural positional order  $\tilde{S}$ , as defined by eqn (8) and (9), indicating the deactivation of the flipping mechanism with increasing  $B_x$ . The minimum in  $\tilde{S}_m$  is gradually removed by the parallel external magnetic field. Meanwhile, the minimum in  $\tilde{S}_r$  is shifted slightly.

behavior changes the situation fundamentally in all three systems free,  $cov \rightrightarrows$ , and  $cov \leftrightharpoons$ . In the free system, turning on the field after the initial equilibration quickly causes all magnetic moments to point in the same direction along the field as opposed to the situation in Fig. 2a. There, the magnetic moments carried by particles in different chains can show opposite magnetic alignment. In the free system as well as in the  $cov \Rightarrow$  system, the field also introduces an additional energetic penalty for the rotation of magnetic moments away from the chain axes. The detachment mechanism is not impeded by this, as it relies on the strong magnetic attraction between close neighboring particles within the same chain and the storage of elastic energy within the compressed gap material. The magnetic moments are not rotated away from the alignment along the chain axes during this process. In contrast to that, the flipping mechanism is based on reorientations away from the direction of the applied magnetic field and is, therefore, affected by the aligning magnetic field. In the  $cov \Leftrightarrow$ system featuring anchored magnetic moments of opposite alignment, the external magnetic field has a particularly interesting effect. Roughly half of the magnetic moments are

aligned with the field. The remaining moments are misaligned and the corresponding particles would need to rotate by about 180 degrees to minimize the interaction energy with the external magnetic field.

Fig. 7 revisits our results for the free system for various applied magnetic field strengths. The stress–strain curves in Fig. 7a illustrate the tunability of the material.† Already a small external magnetic field of  $B_x = 1B_0$  removes the dip at  $\Delta L/L_0 \approx 50\%$ , flattens the superelastic plateau, and also reduces the hysteresis considerably. As noted in ref. 31, the dip was mainly generated by flipping of magnetic moments. When a stronger field is applied, the shape of the superelastic plateau becomes almost identical to the one for the cov $\Rightarrow$  system in the case of vanishing external magnetic field, see Fig. 3. The snapshot in Fig. 7b shows a free system for  $B = 1B_0$  at a strain of  $\Delta L/L_0 = 100\%$ . It reveals that the magnetic moments do not perform complete flips anymore and instead show oblique orientation angles.

<sup>&</sup>lt;sup>†</sup> In ref. 31, the magnetic field strengths in the figures containing stress–strain curves were not scaled correctly. Instead of  $10B_0$ ,  $20B_0$ ,  $30B_0$  it should read  $1B_0$ ,  $2B_0$ ,  $3B_0$ , respectively.

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In summary, the flipping transition and the connected bumps in the superelastic plateau together with the hysteresis can be deactivated by the field.

The plot in Fig. 7c of the nematic order parameter  $\tilde{S}_m$ quantifying the magnetic order in the system provides further evidence that the field impedes the flipping mechanism. An external magnetic field of  $B_x = 1B_0$  is sufficiently strong to smoothen the sharp local minimum in  $\tilde{S}_m$  corresponding to the transition from a parallel state towards perpendicular magnetic alignment with respect to the stretching axis. Stronger fields enforce a parallel alignment, remove the local minimum in  $\tilde{S}_m$ and thus deactivate the flipping mechanism. Only the detachment mechanism remains active. Meanwhile, the structural positional order in the sample does not seem to be influenced significantly by the external magnetic field, as the plots of the nematic order parameter  $\tilde{S}_r$  for the separation vectors between nearest neighbors in Fig. 7d suggest. The minimum where the most likely nearest-neighbor direction switches from parallel towards perpendicular is shifted slightly. Beyond the minimum,  $\tilde{S}_r$  decreases with increasing  $B_r$ . This results from an arising competition between two effects. On the one hand, due to overall volume preservation, the particles are driven together along the direction perpendicular to the stretching axis as before. On the other hand, flips are hindered by the external magnetic field, or even suppressed completely. Therefore, the magnetic moments cannot support the perpendicular approach anymore as efficiently, or even counteract it due to the magnetic repulsion when the magnetic moments are forced into the direction of the external magnetic field. This also largely removes the hysteresis from our curves.

Let us discuss the  $cov \rightrightarrows$  system next. The results are summarized in Fig. 8. Fig. 8a shows the corresponding stress-strain behavior. Up to the end of the superelastic plateau, the curves for different external magnetic field strengths hardly differ. This is not surprising, since we have established before that the flipping mechanism plays no role for these systems and that the detachment mechanism is not impeded by an external magnetic field parallel to the chains. However, beyond the plateau, where we have a regime of relatively constant increase of the stress with the imposed strain, we can observe a stiffening of the system when a higher field strength is applied. Only at very high strain, the slopes for all different field strengths become similar again. The explanation for this stiffening influence of the external magnetic field is the suppression of magnetic moment reorientations and, thus, in this  $cov \Rightarrow$  system, of particle rotations. We have seen, however, in Fig. 4b that such particle rotations would arise in the absence of a magnetic field to minimize the elastic energy. Suppressing them increases the necessary mechanical energy input into the system. The snapshot in Fig. 8b shows a sample with an applied field of  $B_r = 10B_0$  at a strain of  $\Delta L/L_0 = 100\%$  for comparison with the analogous situation in Fig. 4b for  $B_x = 0$ .

For a more quantitative analysis of the rotation effects, we evaluate the nematic order parameter  $S_m$  of the orientations of the magnetic moments as a function of the imposed strain, see Fig. 8c. We can distinguish between two major regimes. In the

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first one, the overall strain is still too low to induce significant local shear deformations due to the inhomogeneities, thus, the particles rotate only slightly and  $S_m$  remains at a high and relatively constant level. However, in the second regime, we can observe an approximately linear decay in  $S_m$  as the particles begin to significantly rotate. In the absence of an external magnetic field, the crossover between both regimes occurs at the end of the superelastic plateau. There, the particles are detached from the chains. This reduces the aligning magnetic interactions and the particles become susceptible to rotations due to the elastic inhomogeneities in the system. Interestingly, increasing the strength of the external magnetic field can postpone the crossover far beyond this point by supporting the magnetic moment orientations along the field direction. This stiffens the system in two ways. First, the inhomogeneity shear stresses are prevented from relaxing via the favored channel: the rotation of particles. Second, the magnetic moments in the system keep repelling each other perpendicular to the stretching axis, which occurs against their perpendicular approach. The stronger the external magnetic field strength, the longer the embedded particles can resist a rotation, maintaining the stiffening effect. For all considered magnetic field strengths, the particles eventually begin to rotate, as indicated by the crossover in  $S_m$ . Therefore, the slopes of the stress-strain curves become similar again at the maximum strain.

Finally, we show for completeness in Fig. 8d the nematic order parameter  $S_r$  for the nearest-neighbor separation vectors as a function of the imposed strain. Here, the curves for different magnetic field strengths are largely similar.

Now we come to the  $cov \Leftrightarrow$  system and present the results in Fig. 9. Before the external magnetic field is applied, these systems are in a state like the one depicted in Fig. 2a. Roughly half of the magnetic moments are aligned along to the magnetic field direction, while the other half is oppositely aligned and tends to reorient to minimize the magnetic interaction energy with the external field. This has implications on the stress-strain behavior, as illustrated in Fig. 9a. For small field strengths  $(B_r = 2B_0)$ , the behavior barely changes compared to the case of vanishing external magnetic field. Then for intermediate fields of  $B_x = 4B_0$ , the steep increase at low strains as well as the superelastic plateau become less pronounced. Starting from a field of  $B_x = 6B_0$ , the superelastic features vanish altogether. An explanation is given in the following. As long as the external field strength is low enough  $(B_x = 2B_0)$ , the energy cost of misalignment is not particularly large for the magnetic moments in the metastable configuration antiparallel to the field. However, when increasing the external field, due to imperfections in the initial antiparallel alignment, at some point the magnetic particles can be rotated by a significant amount. Then, the torgues due to the external field get amplified, causing the particles to rotate even further. At this stage, the reorientations of the misaligned moments together with their carrying particles begin to distort the sample substantially. Obviously, for the corresponding chains, the detachment mechanism will seize to function at this point, but also the chains containing aligned magnetic moments in the neighborhood will be disturbed.

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Fig. 8 Same as Fig. 7, but for the cov $\Rightarrow$  system. (a) The stress-strain curves for different external magnetic field strengths are almost identical up to the end of the superelastic plateau. Beyond this point, higher field strengths increase the stiffness until at very high strains the slopes become similar again. (b) Snapshot of a system at a strain of  $\Delta L/L_0 = 100\%$  illustrating that a field of  $B_x = 10B_0$  can effectively prevent the particle rotations favored by local shears due to the elastic inhomogeneities. Here, the internal shear stresses of the system cannot relax via particle rotations and the parallel magnetic moments repel each other in the direction perpendicular to the stretching axis. Both effects stiffen the system against further elongation. (c) Nematic order parameter  $S_m$  for the magnetic moment reorientations only at very high strains. (d) Here, the nematic order parameter  $S_r$  for the nearest-neighbor separation vectors is barely sensitive to a change in the external magnetic field strength.

This chaotic situation is depicted in the snapshot in Fig. 9b for an external magnetic field of  $B_x = 6B_0$  and a strain of 30%. One can still identify the particles that have been aligned along the field direction, but the corresponding chains are distorted. As a result, the detachment mechanism is disabled and the superelastic plateau vanishes.

The plots of the nematic order parameters  $S_m$  and  $S_r$  in Fig. 9c and d support this picture. For small magnetic field strength of  $B_x = 2B_0$ ,  $S_m$  is still very similar to the case of vanishing magnetic field. Further increasing the field strength up to  $B_x = 6B_0$  promotes magnetic disorder in the system, leading to an overall low level of  $S_m$ . From there on, the level of  $S_m$  slightly increases with the magnetic field strength as the orientations of the aligned magnetic moments are stabilized by the field. The structural order measured by  $S_r$  does not change too much as long as  $B_x \leq 4B_0$ . Starting from  $B_x \gtrsim 6B_0$ , however, the misaligned magnetic moments are rotated significantly and distort the system. The increased magnetic order indicated by a higher level of  $S_m$  apparently cannot prevent the structure from becoming more disturbed, so that  $S_r$  is still lowered further.

In conclusion, the effect of an external magnetic field applied parallel to the stretching axis varies substantially among the different systems. In the free system, the main effect is the deactivation of the flipping mechanism, which makes the stressstrain behavior almost identical to the one of the cov $\rightrightarrows$  systems in the absence of an external magnetic field. Within the cov $\rightrightarrows$ system the superelasticity is barely affected. However, the external magnetic field stabilizes the particle orientations at strains beyond the superelastic plateau and thereby stiffens the stress–strain behavior. Finally, in the cov $\leftrightarrows$  system the field promotes a strongly disturbed structure by rotating particles carrying magnetic moments misaligned with the field. As a consequence, the detachment mechanism is disabled and the superelastic plateau vanishes from the stress–strain curves.

# 4.3 External magnetic field perpendicular to the stretching axis $(B = B_y \hat{y})$

An external magnetic field applied perpendicular (here along the *y*-axis) to the stretching axis attempts to rotate the magnetic moments away from their attractive head-to-tail configuration within the chains. This influence is strongest in the free system,



**Fig. 9** Same as Fig. 7 but for the cov = system. (a) Uniaxial stress-strain behavior. Applying an external magnetic field parallel to the stretching axis gradually removes the pronounced nonlinearity. (b) Snapshot of a cov = system under the influence of an external magnetic field of  $B_x = 6B_0$  at a strain of  $\Delta L/L_0 = 30\%$ . The particles carrying the misaligned magnetic moments are strongly rotated towards the external magnetic field and distort their environment in the process, which also affects the chains containing the particles of aligned magnetic moments. As a result, the detachment mechanism is mostly deactivated. (c) Nematic order parameter  $S_m$  for the magnetic moment orientations. Increasing the strength of the external magnetic field first lowers the overall  $S_m$  due to the rotations of particles carrying misaligned magnetic moments and due to the resulting distortions of the rest of the system. At high field strengths,  $S_m$  increases slightly with  $B_{xv}$  as the orientations of the aligned magnetic moments are stabilized. (d) The structural order in the system measured by  $S_r$  is not influenced strongly as long as  $B_x \leq 4B_0$ . Beyond that field strength, however, it significantly decreases because of the induced rotations of the particles carrying misaligned magnets.

where the magnetic moments are free to reorient to minimize their magnetic energy. In the  $cov \Rightarrow$  and  $cov \Rightarrow$  systems, however, rotations of the magnetic moments are counteracted by restoring torques on the embedded particles due to the otherwise induced deformation of the surrounding matrix.

Let us again discuss the free system first. We present the results in the same fashion as before for the parallel field. Fig. 10a shows the resulting stress-strain behavior.† The perpendicular field has two effects. First, it influences the superelasticity, causing the plateau to be confined to a smaller strain interval. Second, it lowers the initial slope of the stress-strain curve. At a high enough magnetic field strength, the superelastic nonlinearities are switched off completely together with the hysteresis, and the stress-strain curve becomes ordinary.

To understand this behavior, it is first noted that the perpendicular magnetic field shifts the flipping mechanism to smaller strains. This is intuitive, as the external magnetic field energetically supports flips to a direction perpendicular to the stretching axis. Analysis of the nematic order parameters  $\tilde{S}_m$  and  $\tilde{S}_r$  in Fig. 10c and d, respectively, confirms this expectation.

The regime of mixed orientations centered around the minimum in  $\tilde{S}_m$  is shifted to lower strains by the field. In this regime, some of the magnetic moments are still aligned along the chains, while others have already flipped. Meanwhile,  $\tilde{S}_r$  is strongly correlated with  $\tilde{S}_m$ . This indicates that the external magnetic field does not only influence the flipping mechanism, but also the detachment mechanism. As noted before, flip events trigger detachment events and *vice versa*. Reoriented magnetic moments do not feel a strong attraction along the stretching axis that could keep the carrying particles attached to the chains. So the threshold strains for both mechanisms are lowered at the same time.

This shift of threshold strains can cause the system to enter a mixed state already without any external strain imposed. The snapshot in Fig. 10b shows a situation of  $B_y = 2B_0$ . Although the system is unstretched in the depicted case, a significant amount of particles has already detached from the chains. Their magnetic moments are aligned along the field direction, perpendicular to the chain axis. So the fraction of particles that can still perform detachment or flip events is lowered.

123

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Fig. 10 Results for the free system under the influence of an external magnetic field of varying strength perpendicular to the stretching axis. (a) The superelastic stress-strain behavior can readily be tuned.† Increasing the field gradually removes the superelasticity and lowers the slope of the initial steep increase. A field of  $B_y = 3B_0$  is already strong enough to remove all superelastic nonlinearities. The maximum standard deviation on each curve is indicated by a bar where it occurs. (b) Snapshot of an unstretched sample with an applied external magnetic field of  $B_y = 2B_0$ . A significant portion of the particles is already detached, their carried magnetic moments already flipped. As a consequence, the detachment and flipping mechanism have less impact on the stress-strain behavior, and superelastic as well as hysteretic features are reduced. (c) Degree of magnetic order  $\tilde{S}_n$  and (d) degree of structural order  $\tilde{S}_r$  using the definitions in eqn (8) and (9). Both order parameters are again strongly correlated. Increasing the magnetic field strength shifts the local minimum marking the regime of mixed orientations to lower strains. That is, the threshold strains for detachment and flip events are lowered, with many events having occurred already in the unstretched state. This limits the amount of events that can still take place when the sample is stretched. At  $B_y = 3B_0$ , the pronounced minima of  $\hat{S}_n$  have vanished as all magnetic moments are already reoriented in the unstretched state. Therefore, there are no remaining flip or detachment events already in the unstretched state and, as a consequence, superelasticity is switched off.

As a result, the features corresponding to both mechanisms are less pronounced in the stress-strain curves. Also the initial slope is lower, because there is less overall magnetic attraction along the stretching direction counteracting the elongation. Consequently, the superelastic plateau spans a smaller strain interval.

We now proceed to the results for the cov $\Rightarrow$  system as shown in Fig. 11. In the case of vanishing external magnetic field, this system features global polar magnetic order in the *x*-direction, see again Fig. 2b. Applying an external magnetic field perpendicular to the stretching axis leads to a new state of rotated global polar magnetic order. Fig. 11b shows a snapshot of an unstretched system subject to a strong external magnetic field of  $B_y = 10B_0$ . The magnetic moments, together with the carrying particles, are rotated towards a configuration of collective polar alignment oblique to the external magnetic field. This occurs against the strong magnetic attractions within each chain and the necessary elastic deformation of the matrix between the particles. The rotations of individual particles are energetically expensive. In fact, the system partially avoids these expensive rotations by allowing chain segments to rotate as a whole towards the field. Undulations and buckling of the chains<sup>80</sup> then lead to a compromise between the minimization of the elastic and magnetic parts of the total energy.

Either way, the magnetic dipolar attraction between neighboring particles along the stretching direction is weakened, which impedes the detachment mechanism. So the influence of the perpendicular external magnetic field on the stress-strain behavior is again a gradual removal of the superelastic plateau, as illustrated in Fig. 11a. A stiffening of the stress-strain behavior beyond the superelastic plateau, as in the case of a parallel external magnetic field, however, cannot be observed. Contrary to the parallel magnetic field, the perpendicular magnetic field breaks the uniaxial symmetry of the system and offers a distinctive direction for the particles to rotate towards. As can be deduced from the nematic order parameter  $S_m$  of the magnetic moments plotted in Fig. 11c, the perpendicular



**Fig. 11** Same as Fig. 10, but for the cov $\Rightarrow$  system. (a) The superelasticity in the stress-strain behavior can again be deactivated by a perpendicular external magnetic field, but only at significantly higher field strengths. (b) Snapshot showing the unstretched state of a system under the influence of a field of  $B_y = 10B_0$ . The system enters a new state of global polar magnetic order, with magnetic moments aligned oblique to the external magnetic field. Energetically expensive rotations of individual particles are avoided, instead whole chain segments rotate as one unit. (c) Plot of the nematic order parameter  $S_m$  for the magnetic moment orientations demonstrating that already a moderate magnetic field strength can maintain a state of global polar magnetic order up to the maximum elongation. (d) Nematic order parameter  $S_r$  for the nearest-neighbor separation vectors. When the external magnetic field is weak,  $S_r$  is high at low strains and then drops to a low and relatively constant level. A strong field removes this large drop so that a relatively constant intermediate level of structural order remains at all strains. This indicates again the tendency of whole chain segments to rotate as one unit, creating a principal axis of structural order oblique to the external magnetic field direction and the initial chain axes.

external field aligns the particles very effectively even up to the highest considered strains. Differences in the rotations of the particles due to elastic inhomogeneities can, thus, be prevented. A field of  $B_y = 2B_0$  is already quite successful in this respect, using stronger fields does not significantly increase the effect much further. The magnetic moments are no longer pointing in the same direction along the stretching axis. Therefore, the mutual repulsion between magnetic moments perpendicular to the stetching axis is reduced and does not counteract an elongation of the system any more. Thus, there is no significant stiffening of the stress–strain behavior when changing the external magnetic field strength.

We also plot the nematic order parameter  $S_r$  of the nearestneighbor separation vectors in Fig. 11d. For  $B_y = 0$ ,  $S_r$  is at a high level for low strains, where it is most likely that the nearest neighbor of a particle is located along the stretching axis within the same chain. Then  $S_r$  quickly drops as the chains are stretched out and subsequently remains at a low level. When a perpendicular magnetic field is applied, such a drop of  $S_r$  never occurs. It remains likely that the nearest neighbor of a particle is within the same chain for the whole considered range of strains. This reflects again the tendency of whole chain segments to rotate as one unit towards the field, staying structurally intact and creating the partial structural order reflected by  $S_{r}$ .

Let us finally discuss the  $cov \Rightarrow$  system under the influence of a perpendicular external magnetic field. Contrary to the case of a parallel external magnetic field, there are no particles that are aligned opposite to the external field. All particles can in principle rotate equally easily into the external magnetic field direction. However, the initial orientation of the magnetic moment of a particle determines the sense of rotation towards the field. Neighboring chains with opposing alignment of the magnetic moments show opposing sense of rotation. As a consequence, in contrast to the  $cov \Rightarrow$  system, the rotations of the complete chain segments towards the magnetic field are largely blocked. Instead, the particles within the chains individually rotate towards the external field, as depicted in the snapshot of an unstretched sample in Fig. 12b. Here, the external magnetic field of  $B_y = 10B_0$  has rotated the particles

#### Paper

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by a significant amount, but the chains are still relatively ordered and aligned along the stretching axis. Depending on their initial alignment, the magnetic moments together with their carrying particles rotate either clockwise or counterclockwise towards the field. In this way, there are two competing magnetic polarities in the system, with roughly the same y-component but oppositely signed x-components. The resulting stress-strain behavior is plotted in Fig. 12a and reveals an influence of the external magnetic field very similar to the cov system. Increasing the magnetic field strength rotates the particles further and weakens their attraction along the stretching axis. This gradually disables the detachment mechanism and, therefore, removes the superelastic plateau from the stressstrain curve. Again, we cannot observe significant stiffening of the system at high strains when increasing the external magnetic field strength, for the same reasons as in the  $cov \rightrightarrows$ system.

The two competing magnetic polarities are reflected by the nematic order parameter  $S_m$  plotted in Fig. 12c. In the unstretched state, when neighboring particles in a chain are close to each other, their magnetic interaction intensifies an alignment of the magnetic moments parallel to the stretching axis. The magnetic field, however, urges the differently orientated magnetic moments and their carrying particles to rotate out of their common initial axis of alignment. More precisely, for magnetic moments of opposite initial orientation, this leads to opposite senses of rotation, which destroys the overall nematic alignment. At low field strengths the particles rotate only slightly in the unstretched state, so that  $S_m$  is initially high. Stronger fields are able to rotate the particles further, see again Fig. 12b, leading to the formation of a lower value of  $S_m$  at zero strain. With increasing strain, the magnetic interactions between neighboring particles in a chain are weakened due to their increased separation. The particles become more susceptible to



**Fig. 12** Same as Fig. 10, but for the cov  $\Leftrightarrow$  system. (a) The stress-strain behavior responds to the external magnetic field in a very similar way as for the cov  $\Leftrightarrow$  system. Increasing the field strength gradually removes the superelastic nonlinearity. (b) Snapshot of an unstretched system with an applied external magnetic field of  $B_y = 10B_0$ . There are two competing polarities for the magnetic moments, sharing a common *y*-component but with opposite *x*-components. (c) Quantification of the magnetic order in the system *via* the nematic order parameter  $S_m$  for the magnetic moment orientations. When the magnetic field strength and the strain are low, the two opposing polarities that are not aligned along a common axis compete, and  $S_m$  is a decreasing function of the strain. The higher the magnetic field strength and the higher the strain, the more the magnetic moments are rotated. Eventually, the magnetic field direction is preferred over the stretching axis by both polarities and  $S_m$  becomes an increasing function of the strain. For  $B_y \gtrsim 8B_0$  this is already the case in the unstretched state, which is consistent with the observation that the corresponding stress-strain curves do not show superelasticity anymore. (d) Nematic order parameter  $S_r$  for the nearest-neighbor separation vectors, quantifying the structural order. The minimum in  $S_r$  shifts to lower strains when increasing the field strength and the overall value beyond the minimum is increased. This is simply a consequence of the particle rotations that lead to less magnetic attraction between particles along the stretching axis and to more attraction along the magnetic field direction.

## PCCP

rotations by the magnetic field. Thus, a decrease in  $S_m$  can be observed.  $S_m$  increases again when the *y*-direction becomes predominant for all magnetic moments so that they again align along a common axis. At even stronger fields of  $B_y = 8B_0$  and  $B_y = 10B_0$ , the *y*-direction is prevalent at all strains, so that  $S_m$  is monotoneously increasing. This is in agreement with the observation, that for these magnetic field strengths superelastic features in the stress-strain curves are absent.

Finally, we show in Fig. 12d the nematic order parameter  $S_r$  for the nearest-neighbor separation vectors. The minimum in each curve indicates the point where it becomes more likely for particles to find their nearest neighbors in a direction perpendicular to the stretching axis than parallel. For low field strengths, this structural bias along the perpendicular axis is not very distinctive. Increasing the field strength, however, shifts the minimum to lower strains and increases the value of  $S_r$  at higher strains. This is intuitive, because for stronger magnetic fields there is simply less attraction within individual chains along the stretching axis between reoriented particles belonging to different chains.

In summary, the main effect of the perpendicular external magnetic field in all systems is the gradual removal of the superelastic plateau from the stress-strain curves. This is mainly caused by the rotation of the magnetic moments in the direction of the magnetic field. When the magnetic attraction disappears between neighboring particles along the stretching axis, the detachment mechanism seizes to function. In the free system, magnetic moment reorientations can be achieved exceptionally easily (see the different scales for  $B_y$  in Fig. 10–12), making this system highly susceptible to the perpendicular external magnetic field. Together with the detachment mechanism, also the flipping mechanism is gradually deactivated. In the cov⇒ system rotations of the magnetic moments are harder to achieve and require significantly stronger magnetic fields. We can observe collective rotations of the particles such that global polar magnetic ordering is preserved with all magnetic moments aligned oblique to the external field. Furthermore, these systems avoid the energetically expensive rotations of individual particles by allowing whole segments of the chains to rotate towards the external magnetic field as one unit. As a result, the chains buckle and undulate as a compromise between minimizing the magnetic and elastic energetic contributions. Finally, the cov system behaves quite similarly concerning the influence of the external field on the stress-strain behavior. However, here the particles do rotate individually towards the field, facilitated by the initially opposite magnetic alignment in different chains. During the rotation process, the opposing magnetic alignments lead to two separate polarization directions of the magnetic moments. Altogether, in both cov systems, particle rotations induced by elastic inhomogeneities of the system are effectively superseded by particle rotations due to the external magnetic field.

# 5 Conclusions

We have numerically investigated the stress-strain behavior of uniaxial ferrogel systems. Our anisotropic numerical systems

26686 | Phys. Chem. Chem. Phys., 2016, 18, 26670-26690

# View Article Online

## Paper

consist of chain-like aggregates of spherical colloidal magnetic particles that are embedded in an elastic matrix of a crosslinked polymer. The particles are rigid and of finite size, while the matrix is treated by continuum elasticity theory. In experimental situations, chain-like aggregates can be generated by applying a strong homogeneous external magnetic field during synthesis. We have considered three different realizations of such uniaxial ferrogel systems. The free system features magnetic moments that can freely reorient with respect to the frames of the carrying particles and the surrounding matrix. In contrast to that, in the cov ⇒ system the magnetic moments are fixed with respect to the axes of the carrying particles. In addition, the particles are covalently embedded into the matrix: particle rotations require corotations of the directly surrounding elastic material, leading to matrix deformations and restoring torques. Initially, all magnetic moments point into the same direction along the chain axes. The third system is the cov 5 system, where the magnetic moments are likewise firmly anchored. However, initially the magnetic moments on different chains can point into opposite directions along the chain axes.

When we stretch these systems along the chain axes, a pronounced nonlinearity in the stress-strain behavior appears. It has the form of a superelastic plateau, along which the samples can be strongly deformed while barely increasing the load. The deformation is reversible and the shape and intensity of the superelastic plateau can be reversibly tailored by external magnetic fields. There are two stretching-induced mechanisms that enable superelasticty. The main mechanism is a detachment mechanism and is active in all systems. It relies on the strong magnetic dipolar attraction between neighboring particles within one chain as long as the magnetic moments align along the chain axis. At certain threshold strains, parts of the chain can detach, leading to a local elongation of the system. This leaves the remainder of the chain intact until the next detachment event is triggered. Besides, a flipping mechanism corresponding to reorientation events of magnetic moments is only active in the free system, where the magnetic moments can easily rotate. A flip event occurs when elongation of the system causes positional rearrangements such that for a subset of magnetic moments a new orientation is suddenly rendered energetically more favorable.

The inhomogeneous distribution of the rigid inclusions in our samples results in regions of elevated stiffness. At high strains, this leads to the formation of local shears that rotate the embedded particles. This is especially apparent in the  $cov \Rightarrow$  and  $cov \Rightarrow$  systems and influences their stress-strain behavior.

Our systems can be reversibly tuned by an external magnetic field as follows. If the field is applied parallel to the chain axes, the detachment mechanism is not affected in the free and  $cov \Rightarrow$  systems, so that the superelastic plateau remains intact. However, in the  $cov \Rightarrow$  system the particles carrying misaligned magnetic moments are forced to rotate. The corresponding chains are strongly distorted, which perturbs the neighboring chains carrying aligned magnetic moments as well. This weakens the required magnetic attractions along the stretching axis that are vital for a pronounced detachment mechanism and

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removes the superelasticity from the stress-strain curve of the cov ⇒ system. Moreover, in the free system the flipping mechanism can be deactivated as well, as the aligning external magnetic field hinders the reorientation of magnetic moments. Consequently, the related features are removed from the stressstrain behavior, leaving only a flat plateau caused by the detachment mechanism. Finally, in the  $cov \Rightarrow$  system, the external field parallel to the chains has another interesting effect. We can observe a stiffening of the system when increasing the field strength at high strains beyond the superelastic plateau. In this situation, all particles have been detached from their chains, leaving them particularly susceptible to rotations due to shears caused by the elastic inhomogeneity of the system. Since the external magnetic field introduces an energetic penalty for particle rotations, the intrinsic inhomogeneitycaused shear stresses cannot relax via particle rotations and the magnetic moments remain parallel to each other. The parallel magnetic moments repel each other in the direction perpendicular to the stretching axis and, thus, work against the volumeconserving stretching deformation. In combination both effects increase the stiffness of the system.

When instead the magnetic field is applied perpendicular to the stretching axis, the detachment mechanism is weakened in all three systems due to an induced rotation of the magnetic moments towards a configuration which is repulsive along the stretching axis. In this way, the superelastic plateau can be gradually removed from the stress-strain curve by increasing the field strength. This works exceptionally well in the free system, where the magnetic moments are not anchored to the particle frames and the flipping mechanism is likewise weakened. In contrast to that, in the  $cov \rightrightarrows$  and  $cov \leftrightarrows$  systems, even a strong external magnetic field cannot rotate the magnetic moments completely. While in the cov system, the magnetic moments feature a global polar magnetic alignment oblique to the external magnetic field, the two opposite initial magnetic alignment directions in the cov system lead to two separate polar alignment directions, each of them oblique to the external magnetic field.

Our effects rely on the sufficiently strong magnetic interactions in our systems when compared to the elastic interactions. To achieve this experimentally, the remnant magnetization of the particle material should be as high as possible. For example, NdFeB can easily exceed  $2 \times 10^5$  A m<sup>-1</sup>.<sup>81</sup> At the same time, the elastic matrix into which the particles are embedded should be soft. Fabrication of matrices with  $E \lesssim 10^3$  Pa is possible using silicone<sup>10,82,83</sup> or polydimethylsiloxane.<sup>80</sup> With these materials, our assumed value of  $m = 10m_0$  can be achieved and is, therefore, experimentally realistic. Also the highest considered magnetic field strength of  $B = 10B_0$  corresponding to 100 mT is readily accessible. We stress that the behavior of our systems does not depend on the length scale of the problem. In an experiment, this freedom can for instance be exploited to adjust the particle size to the effect under investigation. For example, the free system could be realized by relatively small particles where the Néel mechanism<sup>53</sup> is active and the magnetic moments can rotate relatively to the particle frame. Increased particle size would be necessary for the generation of the  $cov \Rightarrow$  and  $cov \Leftrightarrow$  systems.

The free and cov is systems can be generated by applying an external magnetic field during synthesis to form the embedded chains<sup>40-43</sup> from Néel-type particles<sup>53</sup> and from monodomain particles of larger size, respectively, possibly by covalently anchoring appropriately sized particles into the matrix.58-61 For small Néel-type particles, typically of sizes up to 10-15 nm, thermal fluctuations become important. These can suppress the hysteretic behavior as well as the negative slope associated with the dip in our stress-strain curves. Overall, these fluctuations will smoothen the bumps along the plateau, leading to a flatter appearance. Free systems of larger particle size could be realized e.g. using so-called yolk–shell colloidal particles  $^{55,56}$  that consist of a magnetic core rotatable within a shell. To realize the  $\mathsf{cov} \leftrightarrows \mathsf{system}, \ \mathsf{electro-magnetorheological} \ \mathsf{fluids}^{\mathsf{84-86}} \ \mathsf{could} \ \mathsf{be}$ used as a precursor of the anisotropic ferrogel. In such a system, an external electric field can be applied to induce the chain formation of the electrically polarizable magnetic particles, while still allowing for opposite alignments of the magnetic moments in separate chains. Subsequent cross-linking of the surrounding polymer with covalent embedding of the particles should lock the chain structures together with their oppositely directed magnetic alignments into the emerging matrix. The result would be an anisotropic ferrogel with the desired  $cov \Leftrightarrow$  morphology. Possible real example systems that could be analyzed experimentally in view of our effects are discussed in ref. 37, 38, and 80. When measuring the stress-strain behavior, instead of stretching the sample longitudinally, due to the overall volume preservation, it can also be compressed from the sides. This enables the use of experimental compression devices, see e.g. ref. 87-89. Qualitatively the same effects should be induced.

We have assumed permanent magnetic dipoles carried by spherical particles in this work. The particles are arranged in characteristic chain-like structures. Possible quantitative refinements comprise extensions beyond the permanent point-dipole picture<sup>90-92</sup> or to elongated, non-spherical particles.<sup>60,61,93,94</sup> However, the main mechanism leading to superelastic behavior in our systems is the detachment mechanism for which only strong attraction at short distances between the neighboring particles along the stretching axis is necessary. This kind of attraction can likewise be realized for soft magnetic particles magnetized by an external field. The same mechanism could also be realized for nonmagnetic attractive interaction forces. An example is given by electrostatic interactions for particles sufficiently polarizable by an external electric field.<sup>84,85,95</sup> To be able to directly transfer our results to the electrostatic case, these samples need to be sufficient electric isolators. Otherwise electric currents would possibly need to be included into our description. Moreover, also the flipping mechanism could be initiated for soft magnetic particles from outside, when the direction of a magnetizing external field is switched at the corresponding imposed strain.

Particles used in experimental ferrogel systems are often polydisperse and of irregular shape.<sup>37</sup> While variations in the particle size and shape should not principally impede our
129

Paper

### PCCP

mechanisms, strong polydispersity may mask the resulting effects. This occurs if they are too broadly distributed along the stress-strain curve and do not occur within a narrow enough strain interval. Another point is the morphology of the chain-like aggregates. To observe the basic phenomenology, they do not necessarily need to span the whole system. In the most basic opposite situation, embedded pair aggregates would be sufficient.<sup>90</sup> Also the chains do not need to be as perfectly straight as considered here but could for example be slightly wiggled. However, when the wiggling becomes too strong, qualitative variations in the material behavior should arise as discussed in ref. 8. Finally, here we have considered a mesoscopic representative volume element. Macroscopic experimental measurements would include many of these volume elements and average over them. To investigate a system of the same size as in our simulations in an experiment, either large particles can be used as our results are scale invariant, or the stress-strain behavior of a mesoscopic sample volume could be measured using a piezorheometer.<sup>35,42</sup> On the theoretical side, a connection to continuum descriptions on the macroscopic scale shall be established in the future.4,36,96

Exploitation of the described reversibly tunable nonlinear stress-strain behavior of our systems should enable a manifold of applications. When a pre-stress is applied to the material, such that it is pre-strained to the superelastic regime, it becomes extremely deformable.97 This is an interesting property for easily applicable gaskets, packagings, or valves.<sup>2</sup> Moreover, in such a state, the ferrogel can be operated as a soft actuator,<sup>22,23,25-27</sup> as external magnetic fields can trigger significant deformations. Passive dampers based on superelastic shape-memory alloys are already established<sup>98,99</sup> and utilize hysteretic losses under recoverable cyclic loading to dissipate energy. Our results for the free system might stimulate the construction of analogous soft passive dampers with the additional benefit of being reversibly tunable from outside. Finally, the typically increased biocompatibility of polymeric materials allows for medical applications exploiting the above features, e.g., in the form of quickly fittable wound dressings, artificial muscles, 100,101 or tunable implants. 50,51

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Phys. Chem. Chem. Phys., 2016, 18, 26670-26690 | 26689

130

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### Paper VI. A density functional approach to ferrogels

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### Statement of contribution

I implemented the numerical codes for the density functional theory and Monte-Carlo simulations, and produced all results related to these methods. HL provided guidance concerning density functional theory. I wrote the more technical and result-centered parts of the paper under the supervision of HL and AMM, who themselves concentrated on the introduction and the conclusions. We developed the models and ideas that enable statistical mechanical methods for our systems in a joint effort. MH performed the Zerah-Hansen liquid-integral calculations and wrote significant parts of the supplementary material. My estimated contribution to the overall work involved in creating this paper is 80%.

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## A density functional approach to ferrogels

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### Abstract

Ferrogels consist of magnetic colloidal particles embedded in an elastic polymer matrix. As a consequence, their structural and rheological properties are governed by a competition between magnetic particle-particle interactions and mechanical matrix elasticity. Typically, the particles are permanently fixed within the matrix, which makes them distinguishable by their positions. Over time, particle neighbors do not change due to the fixation by the matrix. Here we present a classical density functional approach for such ferrogels. We map the elastic matrix-induced interactions between neighboring colloidal particles distinguishable by their positions onto effective pairwise interactions between indistinguishable particles similar to a 'pairwise pseudopotential'. Using Monte-Carlo computer simulations, we demonstrate for one-dimensional dipole-spring models of ferrogels that this mapping is justified. We then use the pseudopotential as an input into classical density functional theory of inhomogeneous fluids and predict the bulk elastic modulus of the ferrogel under various conditions. In addition, we propose the use of an 'external pseudopotential' when one switches from the viewpoint of a one-dimensional dipole-spring object to a one-dimensional chain embedded in an infinitely extended bulk matrix. Our mapping approach paves the way to describe various inhomogeneous situations of ferrogels using classical density functional concepts of inhomogeneous fluids.

Keywords: density functional theory, colloids, ferrogel, magnetorheological elastomer, classical Monte Carlo simulation, soft condensed matter

S Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

### 1. Introduction

Classical density functional theory for inhomogeneous fluids is nowadays used for many-body systems governed by a pair potential (such as hard or soft spheres) and has found widespread applications for phase separation, freezing and interfacial phenomena, for reviews see [1–4]. In a corresponding one-component system, though classical, the particles are indistinguishable in principle according to standard statistical mechanics [5], which implies that the interaction between two particles is the same for any pair of particles provided they are at the same separation. This standard assumption breaks down for particles embedded in an elastic polymeric gel, if the particles are anchored to the surrounding gel matrix and/or cannot diffuse or propagate through it. In this case, the particles can be labeled according to their position in the matrix with their interaction energy persistently depending on the labeling. Thus, they are distinguishable. As a basic example, this situation is encountered for a simple bead-spring model, where the springs represent the elasticity and connectivity provided by the matrix and the beads represent the particles.

Particle distinguishability leads to a different combinatorial prefactor in the classical partition function and therefore affects the entropy [6]. However, at high density, a fluid of indistinguishable particles typically undergoes a freezing transition into a crystal. At low temperature, this crystal can be modeled by a harmonic solid [7–9], where the neighboring particles are connected by springs. In fact, this effective model

### J. Phys.: Condens. Matter 29 (2017) 275102

of distinguishable particles provides a good approximation as the free energy of the system is dominated by the particle interactions that overwhelm the combinatorial contribution.

In the present paper, we exploit this idea to introduce a density functional approach for ferrogels and related systems. Such ferrogels consist of magnetic colloidal particles that are embedded in a polymeric gel matrix [10-14]. Examples of similar materials are given by magnetic elastomers, magnetorheological elastomers, or magnetosensitive elastomers, where often these terms are used interchangeably. Remarkably, the structural properties and rheological behavior of these materials are governed by a competition between the magnetic particle-particle interactions and the mechanical elasticity of the embedding polymeric gel matrix. As a consequence, it is possible to tune their properties during application by modifying the magnetic interactions via external magnetic fields. Therefore, these magnetorheological systems have many prospective and promising applications, such as tunable dampers [15] or vibration absorbers [16].

The theoretical description of these materials is challenging. While the specific properties arise on the mesoscopic colloidal particle scale, for practical applications one is interested in the overall macroscopic response. To connect these scales in simulations, large numbers of individual particles need to be covered. For this purpose, recent work has focused on simplified minimal models. Starting on the microscale, at most a few individual polymer chains are resolved by coarsegrained bead-spring models [17-19]. In still more reduced mesoscopic dipole-spring models, the elasticity of the matrix is directly represented by effective spring-like interactions between the particles, combined with long-ranged magnetic dipolar interactions between them [20-24]. More explicit approaches treat the matrix directly by continuum elasticity theory, yet at the price of reduced accessible overall particle numbers [25-28]. A kind of compromise between the two concepts can be found in [29] and [30]. Previous analytical approaches to link the different scales often relied on substantially simplifying idealizations concerning the positional particle configurations [31-33]. Therefore, it is desirable to develop statistical means that allow for a more profound connection between the different scales in the future. As a step in this direction, we now suggest to employ the framework of classical density functional theory for a characterization of these complex materials.

Here we mainly follow the dipole-spring concept of distinguishable particles often used for the description of ferrogels. In order to keep the models simple, we study effective onedimensional set-ups. Such a situation is realized, for instance, for elongated magnetic particle chains embedded into an elastic matrix [34], but also for magnetic filaments [35] made, e.g. of magnetic colloidal particles connected by DNA polymer strands [36]. We map this system with its particle-distinguishing connectivity onto another one with an effective connectivity and indistinguishable particles [37]. Based on the considerations above, one expects a good agreement between real and effective connectivity at least for strong particle–particle interactions. We use Monte-Carlo computer simulations of both situations and P Cremer et al

confirm that the results agree at high packing fractions and/or strong particle interactions. This opens the way to employ statistical-mechanical theories like classical density functional theory to also describe systems of particles that are, in principle, distinguishable. For the one-dimensional model, we use the exact Percus free-energy functional for hard rods [38] combined with a mean-field theory for the elastic and dipolar interactions and minimize the resulting grand canonical free energy functional with respect to the equilibrium one-body density field.

We study two different models. In the first one, the elastic matrix is represented by harmonic springs between nearestneighboring particles. Including thermal fluctuations, such a simple one-dimensional bead-spring model cannot show a phase transition [39, 40]. Thermal fluctuations have a strong impact in one spatial dimension and fuel the Landau–Peierls instability [7, 41, 42], which impedes periodic ordering. This fact is captured by our Monte-Carlo simulations, which take all contributions by thermal fluctuations into account exactly. Our mean-field density functional theory, however, introduces an artificial crystallization at low temperatures. Still, at higher temperatures we can obtain qualitative agreement between density functional theory and Monte-Carlo simulations for the pressure and compressibility of the system. These provide key material properties for the practical use of ferrogels.

Later in this paper, we turn to an extended model, including an additional external elastic pinning potential for the colloidal magnetic particles. Such pinning potentials arise when the particles are embedded in a three-dimensional elastic bulk matrix [34]. Similarly, the displacement of one embedded particle results in a matrix-mediated force on all other particles, so that we have additional long-ranged elastic particle-particle interactions. In combination with the pinning potential, this suppresses the Landau-Peierls instability even though our model is effectively one-dimensional. Consequently, our density functional theory immediately shows much better agreement with Monte-Carlo simulations for both, the model with real connectivity and the version mapped towards indistinguishable particles. During the synthesis of ferrogels such permanent straight one-dimensional magnetic particle chains embedded within three-dimensional ferrogel blocks are readily generated by applying external magnetic fields during the manufacturing process [34, 43–48].

We remark at this stage that the problem of mapping from distinguishable to indistinguishable particles also occurs in density functional descriptions of polymeric bead models [49, 50]. Typically, in tangential bead models for hard spheres [51, 52], one neglects the linking constraints of the chain and maps the excess free energy of the system onto an unconstrained hard-sphere fluid.

Our analysis paves the way to a future application of density functional theory of freezing also to two- and threedimensional ferrogel models. There, we anticipate thermal fluctuation effects to be of less influence, leading to a better agreement with simulations. It will further be useful to characterize other particulate systems embedded in a permanent elastic matrix such as electrorheological elastomers [53, 54] or possibly even drug carriers and compartments within biological tissue [55].





**Figure 1.** Sketch of our one-dimensional dipole-spring model for a ferrogel. Two outer particles (blue) form the system boundary and are at a fixed distance *L*. Additionally, there are *N* mobile particles (dark gray) in between. Each particle carries a magnetic dipole moment of magnitude *m*, all of which point into the same direction along the system axis. Finally, harmonic springs of spring constant *k* and equilibrium length  $\ell$  connect each particle to its nearest neighbors.

This paper is organized as follows. In section 2, we describe our first one-dimensional dipole-spring model and offer a method to map the real connectivity to an effective one. Next, we describe the various methods used to study our systems in section 3. These methods are mainly mean-field density functional theory and canonical Monte-Carlo simulations. The supplemental material<sup>3</sup> contains an additional treatment using the Zerah-Hansen liquid-integral equation. Then we complete the discussion of the first dipole-spring model in section 4, where we present results from our density functional theory and compare them to Monte-Carlo simulations. Subsequently, we proceed to our extended model in section 5. Following a motivation of this extended model, we again compare results from density functional theory and Monte-Carlo simulations, showing their improved agreement. Finally, in section 6, we revisit our overall approach and discuss prospective uses and extensions beyond the one-dimensional models discussed here.

### 2. Dipole-spring model

We consider the following one-dimensional dipole-spring model, which is sketched in figure 1. There are two outer particles at a fixed distance L, forming the system boundary, and N mobile particles in between. All particles have a hard core of diameter d, which limits the closest approach of two particle centers to this distance. Additionally, all particles carry magnetic dipole moments of magnitude m that all point in the same direction aligned with the system axis. Finally, each particle is connected to its nearest neighbors by a harmonic spring of spring constant k and equilibrium length  $\ell$ .

As we will discuss below, the connectivity introduced by the harmonic springs renders the particles distinguishable. We label the particles with indices i = 0, ..., N + 1 according to their position  $x_i$  in ascending order. The indices i = 0 and i = N + 1 are used for the left and right boundary particles, respectively. The total potential energy of the system consists of three contributions

$$U = U_{\rm h} + U_{\rm m} + U_{\rm e},\tag{1}$$

<sup>3</sup> See supplemental material at (stacks.iop.org/JPhysCM/29/275102/mmedia) for a treatment of our dipole-spring model (mapped to indistinguishable particles) using the Zerah-Hansen liquid-integral equation in comparison to Monte-Carlo simulations. Furthermore, an overview of typical computation times for our various numerical methods is provided. Finally, for the density functional theory, a discussion of system size effects is included. P Cremer et al

i.e. the hard core repulsion  $U_{\rm h}$ , the magnetic dipolar interaction  $U_{\rm m}$ , and the elastic interaction  $U_{\rm e}$ . We can write the former two as sums over the interactions between all particle pairs *i*, *i* with i > i

$$U_{\rm h} = \sum_{i=0}^{N+1} \sum_{j>i} u_{\rm h}(x_{ij}); \quad u_{\rm h}(x) = \begin{cases} \infty & \text{for } x < d, \\ 0 & \text{for } x \ge d, \end{cases}$$
(2)

$$U_{\rm m} = \sum_{i=0}^{N+1} \sum_{j>i} u_{\rm m}(x_{ij}); \quad u_{\rm m}(x) = -2\frac{\mu_0}{4\pi} \frac{m^2}{x^3}, \qquad (3)$$

where  $\mu_0$  is the vacuum permeability and  $x_{ij} := |x_j - x_i|$  is the distance between a pair of particles. Since the pair interactions  $u_h(x)$  and  $u_m(x)$  do not depend on any particular labeling of the particles, the total interactions  $U_h$  and  $U_m$  are invariant under a relabeling of all particles. In contrast to that, the elastic interactions between nearest neighbors

$$U_{\rm e} = \frac{k}{2} \sum_{i=0}^{N} (x_{i,i+1} - \ell)^2 \tag{4}$$

persistently depend on the labeling and therefore render the particles distinguishable.

We note that one spatial dimension generally constitutes a special case for hard-core particles because there is no dynamical pathway for them to switch places. Thus, from a dynamical viewpoint they are distinguishable even in the absence of a spring-like interaction  $U_e$  as they can be persistently labeled according to their position [38, 56]. However, we remark that it is likewise possible to state the partition function for these systems in terms of indistinguishable particles, as long as their labeling does not affect the total interaction energy U. The partition function counts the number of possibilities to distribute N particles anywhere in the system, where each configuration is weighted with  $\exp(-U/k_{\rm B}T)$ , and a prefactor 1/N! corrects for the interchangeability. From there, the partition function corresponding to the viewpoint of distinguishable particles can be recovered by introducing an ordering among the particles, for which there are N! possibilities. Consequently, these one-dimensional systems can be treated in both ways, as ensembles of distinguishable or indistinguishable particles. However, in our model systems the elastic interaction  $U_e$  renders the particles strictly distinguishable.

To facilitate a description of our model system with the tools of statistical mechanics, we map it onto a system of indistinguishable particles. This can be achieved by replacing the elastic interaction (4) with an approximative potential  $\tilde{U}_e$  that can be decomposed into pairwise interactions  $\tilde{u}_e(x)$ . Ideally, such an approximative potential should still affect only nearest neighbors and provide the same result as equation (4) under realistic circumstances. We make the choice

$$\tilde{U}_{e} = \sum_{i=0}^{N+1} \sum_{j>i} \tilde{u}_{e}(x_{ij});$$

$$\tilde{u}_{e}(x) = \begin{cases} \frac{k}{2} \left[ (x-\ell)^{2} - (2d-\ell)^{2} \right] & \text{for } x < 2d, \\ 0 & \text{for } x \ge 2d. \end{cases}$$
(5)



**Figure 2.** Illustration of how the pseudo-spring pair potential  $\tilde{u}_{c}(x)$  combined with the hard-core repulsion  $u_{h}(x)$  serves to approximate the effect of harmonic springs between nearest neighbors. A harmonic well of spring constant k (here  $k = 40k_{B}T/d^{2}$ ) is centered around a distance  $\ell = 1.5d$ . It is cut at a distance x = 2d and shifted to zero in order to confine the interaction to nearest neighbors only. The sketch on the left depicts a situation where a particle (blue) interacts with its nearest neighbor (red), as both particles are at a distance x < 2d. In the sketch on the right no interaction takes place since the distance is  $x \ge 2d$ . In any case, only nearest neighbors can ever interact as we always have  $x \ge 2d$  for all other pairs of particles.

The 'pseudo-spring' pair potential  $\tilde{u}_e(x)$  is illustrated in figure 2 and consists of a harmonic well of spring constant k centered around a distance  $\ell < 2d$ . The harmonic well is cut and shifted to zero potential strength at a distance  $x \ge 2d$ . For two particles at a distance x < 2d, this potential acts as a common harmonic spring. Beyond this distance, the spring 'breaks' leading to zero interaction. The combination with the hard-core repulsion  $u_h(x)$  in equation (2) limits the possible harmonic interaction to pairs of nearest-neighbors. Only nearest neighbors can be at a distance x < 2d. Next-nearest neighbors are always at a greater distance and, thus, excluded from the interaction.

In the following, we refer to this potential as 'pseudospring' interaction as opposed to the 'real-spring' permanent connectivity between nearest neighbors. Good agreement between the real-spring system and its mapped version using pseudo-springs can be expected in situations where the pseudo-springs do not break. First, this is the case at high packing fraction, when the confinement enforces small distances between nearest neighbors. The packing fraction in our finite system is defined as

$$\phi = \frac{Nd}{L-d},\tag{6}$$

because L - d is the system length enclosed between the two hard boundary particles. At  $\phi > (L - 2d)/(L - d)$ , the distance between nearest neighbors is smaller than 2*d* everywhere, such that breaking of pseudo-springs becomes impossible. Another limit is reached at high potential strength (large value of *k*) and moderate packing fraction of  $\phi \gtrsim d/\ell$ . Under these conditions, the harmonic well, as illustrated in figure 2, is deep compared to the thermal energy  $k_{\rm B}T$  and the system is sufficiently filled such that all particles are effectively trapped in the harmonic wells created by their nearest neighbors.

For fixed values of *L*, *N*, and *d*, the physical input parameters determining all interactions are the magnetic moment *m*, the spring constant *k*, and the spring equilibrium length  $\ell$ . From now on, we measure all energies in units of  $k_{\rm B}T$  and

P Cremer et al

all lengths in units of the particle diameter *d*. This implies to measure the spring constant in units of  $k_0 = k_{\rm B}T/d^2$  and the magnetic moment in units of  $m_0 = \sqrt{\frac{4\pi}{\mu_0}}k_{\rm B}Td^3$ , while the pressure and the compression modulus are given in units of  $p_0 = K_0 = k_{\rm B}T/d$ .

### 3. Methods

We use three different methods to study our dipole-spring model. The first and most notable one is our density functional theory (DFT) description, for which we use the pseudo-spring approximation to make particles indistinguishable. Second, we perform canonical Monte-Carlo (MC) simulations for real springs as well as for pseudo-springs as a benchmark to test our DFT results. Finally, we have also solved the Zerah-Hansen liquid-integral equation to show that our pseudo-spring approximation is meaningful beyond the scope of DFT, see the supplemental material<sup>4</sup> for results and a description of the method.

### 3.1. Density functional theory

The central statement of classical DFT is that for a fixed temperature *T* and interparticle pair potential u(x), the Helmholtz free energy  $\mathcal{F}[\rho]$  is a unique functional of the one-body density distribution  $\rho(x)$ . Likewise, there is a unique grand canonical free energy functional  $\Omega[\rho]$  describing the system when it is exposed to an external potential  $U_{\text{ext}}(x)$  and a particle reservoir at chemical potential  $\mu$ . This grand canonical free energy functional has the form [3]

$$\Omega[\rho] = \mathcal{F}[\rho] + \int_0^L \rho(x) (U_{\text{ext}}(x) - \mu) \,\mathrm{d}x \tag{7}$$

and is minimized by the equilibrium one-body density profile  $\rho_{eq}(x)$ . The minimum  $\Omega[\rho_{eq}]$  corresponds to the thermodynamic grand canonical free energy in equilibrium.

Unfortunately, the exact free energy functional  $\mathcal{F}[\rho]$  is usually unknown, so that one has to resort to approximations. These approximations usually start by splitting the free energy functional  $\mathcal{F}[\rho] = \mathcal{F}_{id}[\rho] + \mathcal{F}_{ex}[\rho]$  into the exact free energy for the ideal gas

$$\mathcal{F}_{\rm id}[\rho] = k_{\rm B}T \int_0^L \rho(x) (\ln(\Lambda \rho(x)) - 1) \,\mathrm{d}x \tag{8}$$

with  $\Lambda$  the thermal de Broglie wavelength, plus an excess contribution  $\mathcal{F}_{ex}[\rho]$ . For some special problems in one spatial dimension, the exact excess contribution can be derived [57]. One such example is the Percus excess functional [38] for the one-dimensional hard-rod fluid,

$$\mathcal{F}_{ex}^{P}[\rho] = -k_{B}T \int_{0}^{L} \frac{\rho(x+d/2) + \rho(x-d/2)}{2} \\ \times \ln(1-\eta(x)) \, dx, \\ \text{with } \eta(x) = \int_{x-d/2}^{x+d/2} \rho(x') \, dx'.$$
(9)

<sup>4</sup> See footnote 3.

4

### J. Phys.: Condens. Matter 29 (2017) 275102

It takes one-dimensional hard repulsions exactly into account and, thus, provides a good starting point for the construction of a functional describing our dipole-spring model. Here, we combine it with an approximate mean-field excess functional accounting for the soft pair interactions consisting of our pseudo-spring pair potential  $\tilde{u}_e(x)$  and the magnetic dipolar pair interaction  $u_m(x)$ ,

$$\mathcal{F}_{\text{ex}}^{\text{MF}}[\rho] = \int_{0}^{L} \int_{0}^{L} \left( \tilde{u}_{\text{e}}(|x - x'|) + u_{\text{m}}(|x - x'|) \right) \\ \times g(|x - x'|)\rho(x)\rho(x')\,\mathrm{d}x'\,\mathrm{d}x, \tag{10}$$

where the distribution function g(x) satisfies the no-overlap condition g(x) = 0 for x < d. The mean-field approximation assumes that the pair potentials are soft enough to regard the particle positions as basically uncorrelated [3]. Here we make the simplifying assumption that g(x) = 1 for all distances x > d. In total, our free energy functional is given by

$$\mathcal{F}[\rho] = \mathcal{F}_{id}[\rho] + \mathcal{F}_{ex}^{P}[\rho] + \mathcal{F}_{ex}^{MF}[\rho]. \tag{11}$$

The boundary of our finite systems consists of the leftmost and rightmost particles, which are fixed but otherwise identical to the enclosed particles, see figure 1. Their influence on the enclosed density profile enters via an external potential

$$U_{\text{ext}}(x) = u(L - x) + u(x),$$
 (12)

where  $u(x) = u_h(x) + u_m(x) + \tilde{u}_e(x)$ . This completes our grand canonical free energy functional  $\Omega[\rho]$ .

Functional derivation of equation (7) leads to the Euler-Lagrange equation

$$\frac{\delta\Omega\left[\rho\right]}{\delta\rho(x)} = \frac{\delta\mathcal{F}[\rho]}{\delta\rho(x)} + U_{\text{ext}}(x) - \mu = 0, \qquad (13)$$

which can be used to determine the equilibrium density profile minimizing  $\Omega[\rho]$ . In practice, however, we numerically calculate our equilibrium density profile  $\rho(x)$  by performing a dynamical relaxation of  $\Omega[\rho]$  [58]. This scheme fixes the average particle number  $\langle N \rangle$  instead of the chemical potential  $\mu$  and is described in detail in the appendix.

After the relaxation, we have access to the grand canonical free energy  $\Omega$ . This enables us to calculate a pressure  $p = -\frac{\partial \Omega}{\partial L}\Big|_{\langle N \rangle, T}$  and a compression modulus  $K = -L\frac{\partial p}{\partial L}\Big|_{\langle N \rangle, T}$ by varying the system length *L* at fixed average particle number  $\langle N \rangle$  and probing the corresponding change in  $\Omega$ .

In addition to that, we have also tested other forms of the distribution function g(x) [59, 60] as an input into the mean-field functional in equation (10). In particular, we tried in our DFT calculations the g(x) extracted from corresponding bulk Monte-Carlo simulations (see section 3.2). However, such a g(x) is characterized by peaks at typical distances corresponding to the minimum of the interaction pair potential u(x), with which it is multiplied in the mean-field functional. This overestimates the tendency to form patterned structures, leading to larger deviations from the simulations. The simple form of g(x) used here seems to partially mitigate the incomplete representation of thermal fluctuations in our one-dimensional mean-field approach, see below.

#### 3.2. Monte-Carlo simulation

We perform canonical Monte-Carlo (MC) simulations at fixed particle number N, system length L, and temperature T [61]. After equilibrating the systems, we sample the pressure p, the compression modulus K, and the equilibrium density profile  $\rho(x)$ . To sample the pressure, we affinely deform the system by a factor  $(L + \Delta L)/L$  and probe the corresponding change in Helmholtz free energy F(N,L,T).  $\Delta L$  is a small change in system length. It can be shown that the pressure is related to the acceptance ratio of such volume moves by [62]

$$p = -\frac{\partial F(N, L, T)}{\partial L} \approx -\frac{F(N, L + \Delta L, T) - F(N, L, T)}{\Delta L}$$
$$= \frac{k_{\rm B}T}{\Delta L} \ln \left\langle \left(\frac{L + \Delta L}{L}\right)^N \exp(-\Delta U/k_{\rm B}T) \right\rangle.$$
(14)

 $\Delta U$  is the change in system energy associated with the volume move and  $\langle \cdot \rangle$  denotes the ensemble average. In order to capture the pressure contributions of the hard repulsions in our systems, the volume moves must be compressive ( $\Delta L < 0$ ). Given the pressure, the compression modulus can be calculated using  $K = -L \frac{\partial p}{\partial L}$ 

tted using 
$$K = -L \frac{\partial p}{\partial L}\Big|_{N,T}$$
.

### 4. Results

In the following, we present results for our one-dimensional dipole-spring model. First we concentrate on a non-magnetic system to test the feasibility of the mapping onto indistinguishable particles. Then we add the magnetic interaction and discuss how this affects the density profile and the pressure in our systems. Finally, we turn to the thermodynamic compression modulus, which is a key quantity to characterize ferrogel systems as it can be controlled by changing the magnetic properties.

#### 4.1. Non-magnetic system

First of all, we confirm within our MC-simulations that the pseudo-spring pair potential is an appropriate replacement for real springs between nearest neighbors. Figure 3 compares the equations of state  $p(\phi)$  for both situations in a system of length L = 51d. The spring parameters  $k = 40k_0$  and  $\ell = 1.5d$  are the same as in figure 2. Using these parameters, we can confirm that at packing fractions  $\phi \gtrsim d/\ell = \frac{2}{3}$  the mapping to indistinguishable particles using pseudo-springs works well.

Let us now compare MC and DFT results using the same parameters. Figure 4 shows three density profiles  $\rho(x)$  at a packing fraction  $\phi = \frac{2}{3}$ , one from the real-spring MC, one from the pseudo-spring MC, and one from DFT. While the two MC density profiles expectedly agree with each other and display a liquid-like behavior near rigid boundaries, the DFT density profile is qualitatively different and resembles a crystal.

This crystalline appearance displayed by the DFT is unphysical. Our system is one-dimensional, all particle

P Cremer et al



**Figure 3.** Comparison of the equations of state from MCsimulations of the real-spring system with the mapped version using pseudo-springs instead. In both systems we have L = 51d,  $k = 40k_0$  and  $\ell = 1.5d$ . At a packing fraction  $\phi \gtrsim d/\ell = \frac{2}{3}$ , the pseudo-spring system is filled with particles trapped in the harmonic wells of their nearest neighbors and, thus, behaves essentially identical to the system featuring real springs. For lower packing fractions in the real-spring system, the springs between nearest neighbors are stretched on average, so that the system would contract if the boundaries were not fixed. Thus, the pressure is negative for these packing fractions.



**Figure 4.** Density profiles  $\rho(x)$  obtained from real-spring and pseudo-spring MC as well as from DFT calculations at a packing fraction  $\phi = \frac{2}{3}$  and otherwise with the same parameters as in figure 3. For this packing fraction, the two MC-simulations are in good agreement and show a liquid-like behavior as expected in one spatial dimension. However, the density profile obtained from DFT is qualitatively different and displays an artificial crystalline behavior.

interactions are short-ranged and there are no external fields. For such systems, the existence of a phase transition can be ruled out [39, 40, 63, 64]. This fact is accurately captured by our MC-simulations that display a liquid phase even for this high value of  $k = 40k_0$ , as they explicitly include all effects of thermal fluctuations. In one spatial dimension, thermal fluctuations have a particularly strong effect. They can escalate into long-ranged fluctuations scaling in amplitude with the system size, capable of destroying periodic ordering. This is the well-known Landau–Peierls instability [7, 41, 42]. Within the DFT, some thermal fluctuations are introduced by the ideal gas term (see equation (8)), which pushes the system towards disorder. However, the mean-field term (see equation (10)) excludes other contributions by fluctuations. We conclude that this term is responsible for the unphysical crystallization. Our



**Figure 5.** When setting k = 0 and m = 0, we recover the hard-rod fluid and observe perfect agreement between MC and DFT. In this case, both density profiles  $\rho(x)$  show liquid-like behavior and the

equations of state (inset) match the exact result  $p(\phi) = \frac{\phi}{1-\phi}p_0$ [38]. This demonstrates that the mean-field term in equation (10) is responsible for the disagreement between DFT and MC, as it disregards some of the contributions by thermal fluctuations.



**Figure 6.** Density profiles as in figure 4 but using a ten times lower spring constant  $k = 4k_0$ . Now the depth of the harmonic well of the pseudo-spring pair potential is of the order of  $k_BT$  such that pseudo-springs frequently break. As a result, DFT and pseudo-spring MC both show liquid-like behavior and are in much better agreement. However, this comes at the price of worse agreement between the pseudo-spring MC and the real-spring MC. The inset shows equations of state  $p(\phi)$  for these three systems which confirm these observations. There is agreement between DFT and the pseudo-spring MC at least in the range around  $\phi \approx \frac{2}{3}$  but the pseudo-spring and real-spring MC only agree at very high packing fractions.

conjecture is supported by setting k = 0 and m = 0, i.e. setting the mean-field term to zero. Then, we recover the hardrod fluid also for the DFT and find perfect agreement with MC-simulations, see figure 5.

The Landau–Peierls instability is well-known to be most prominent in one spatial dimension. In future studies in two and three dimensions, we therefore expect a significantly weaker effect of the thermal fluctuations, which should lead to a better agreement between simulations and mean-field DFT. For now, we achieve qualitative agreement between DFT and MC by raising the temperature (which means decreasing k) until the DFT system enters the liquid state.



**Figure 7.** Density profile  $\rho(x)$  as well as equation of state  $p(\phi)$  obtained from DFT and pseudo-spring MC upon activating the magnetic moments. In the DFT, all density peaks increase in amplitude (right insets), while in the MC only the first peak is affected. This is probably again due to the underestimation of thermal fluctuations in our mean-field DFT. The more patterned structure puts less emphasis on configurations where two particles are close and magnetic attractions are strong. Thus, the DFT predicts a much smaller downward shift for the pressure *p* when increasing the magnetic moments than the MC (left insets).

7

Figure 6 shows a comparison between density profiles as well as equations of state for the same systems as in figure 4, but with a ten times lower spring constant  $k = 4k_0$ . The depth of the harmonic well in the pseudo-spring potential is now of the order of  $k_BT$  so that breaking of pseudo-springs is a common event. This renders the density profile in DFT more liquid-like, which improves the agreement with the pseudo-spring mapping becomes a bad approximation for the real connectivity. Only at high packing fractions, where the confinement prevents pseudo-spring breaking, we can reach agreement between the pseudo-spring mC again.

### 4.2. Influence of magnetic interactions

We now activate the magnetic dipolar interactions and discuss the resulting changes for our systems. Figure 7 demonstrates that increasing m increases the amplitudes of all peaks in the DFT, whereas in the pseudo-spring MC only the first peak is affected.

Again, our mean-field DFT seems to overestimate the tendency to form a patterned structure because of its incomplete representation of thermal fluctuations. The reason is that, effectively, the particles do not fluctuate as much around their average positions and do not come as close to each other, where the pseudo-spring interaction and the dipolar interaction increase (the latter with inverse cubic distance). As a consequence, the DFT underestimates the averaged strength of the pair interactions in the system. This becomes apparent in the equation of state, where the MC predicts a much stronger downwards shift when increasing the magnetic moments (see the insets of figure 7).

As a liquid-state approach alternative to DFT, we have also solved the Zerah-Hansen liquid-integral equation. Corresponding results in comparison to MC-simulations can be found in the supplemental material<sup>5</sup>.

<sup>5</sup> See footnote 3.

#### 4.3. Thermodynamic compression moduli

Finally, we evaluate the elastic moduli of the DFT and pseudospring MC systems for various magnitudes *m* of the magnetic moment. We present them as a function of packing fraction  $\phi$  in figure 8. The DFT predicts only a very slight downward shift of the compression modulus when increasing the magnetic moment. In contrast to that, the shift is significantly more pronounced in the pseudo-spring MC. Additionally, the overall value of the compression modulus at high packing fractions is lower in the DFT.

These observations are in line with our earlier results. The mean-field DFT overestimates the tendency to form patterned structures. It therefore underestimates both, contributions by magnetic and elastic pair potentials. If the fluctuations of the particle positions were more pronounced, there would be more emphasis on configurations with strong elastic and magnetic interactions and their influence on the compression modulus would be stronger.

### 5. Embedding into the elastic matrix

So far, we have considered a simple one-dimensional dipolespring model. There, the elastic matrix is solely represented by springs between nearest-neighbor magnetic particles. Now we turn to an extended model, explicitly describing a single linear chain of magnetic particles that is embedded in a threedimensional elastic matrix.

### 5.1. Dipole-spring model for a linear embedded chain

We begin by constructing an effective pinning potential  $U_{\rm mp}$  for the embedded particles within the three-dimensional matrix as well as an effective pair interaction  $u_{\rm pp}$  between two embedded particles *mediated* by the matrix. Subsequently, we translate these potentials into a network of springs describing the overall elastic interactions.



**Figure 8.** Compression modulus *K* as a function of packing fraction  $\phi$  for various magnetic moments. In the DFT calculations the curves are only very slightly shifted downwards when increasing the magnetic moment, a trend that we have already seen in the pressure in figure 7. Furthermore, compared to the pseudo-spring MC-simulation, the compression modulus is overall lower, especially at high packing fractions. Again, this is due to the mean-field nature of our DFT, which underestimates the contributions of the magnetic and elastic pair interactions by not taking thermal fluctuations fully into account. In the MC-simulations, the particles fluctuate more in their positions, increasing the influence of these pair interactions on the compression modulus. Thus, increasing the magnetic moment has a greater effect.

If a single spherical particle of diameter *d* embedded in an infinitely extended homogeneous elastic matrix is displaced by a vector  $\Delta \mathbf{R}$ , it distorts the elastic environment. Then the restoring force  $\mathbf{F}_{mp}$  that the matrix exerts onto the particle is given by [65–68]

$$\mathbf{F}_{\rm mp}(\Delta \mathbf{R}) = -\frac{12\pi(1-\nu)Gd}{5-6\nu}\Delta \mathbf{R},\tag{15}$$

where  $\nu$  is the Poisson ratio that equals  $\nu = 1/2$  for incompressible matrices and *G* is the shear modulus. The force can be connected via  $\mathbf{F}_{mp} = -\nabla U_{mp}$  to a harmonic potential

$$U_{\rm mp}(\Delta \mathbf{R}) = \frac{1}{2} k_{\rm mp}(\Delta \mathbf{R})^2 \tag{16}$$

with the spring constant  $k_{\rm mp} := (12\pi(1-\nu)Gd)/(5-6\nu)$ .

Now we consider two embedded particles, labeled as '1' and '2', respectively. Upon displacing these particles by vectors  $\Delta \mathbf{R}_1$  and  $\Delta \mathbf{R}_2$ , they experience the forces  $\mathbf{F}_1$  and  $\mathbf{F}_2$ . In our one-dimensional set-up, we only consider forces and displacements along the particle center-to-center vector  $\mathbf{r}$ . To first order in the particle distance, i.e. to order 1/r with  $r = |\mathbf{r}|$  we then obtain [65–68]:

$$\begin{pmatrix} \mathbf{F}_{1} \\ \mathbf{F}_{2} \end{pmatrix} = \begin{pmatrix} -k_{\mathrm{mp}} & \frac{k_{\mathrm{mp}}^{2}}{4\pi G r} \\ \frac{k_{\mathrm{mp}}^{2}}{4\pi G r} & -k_{\mathrm{mp}} \end{pmatrix} \cdot \begin{pmatrix} \Delta \mathbf{R}_{1} \\ \Delta \mathbf{R}_{2} \end{pmatrix}.$$
 (17)

Here, entries on the diagonal represent the restoring pinning forces (15). The off-diagonal contributions result from the matrix distortions that are caused by the displacement of one particle but affect the other embedded particle. To construct an effective pair potential, we here only consider symmetric situations where  $\Delta \mathbf{R}_1 = -\Delta \mathbf{R}_2$ . Then, the change in distance between the two particles is  $\Delta \mathbf{r} = \Delta \mathbf{R}_1 - \Delta \mathbf{R}_2 = 2\Delta \mathbf{R}_1$ . Per particle, we can thus rewrite the effective matrix-mediated inter-particle interaction as a function of  $\Delta \mathbf{r}$  in the form of an effective potential



**Figure 9.** Sketch of our extended dipole-spring model for a onedimensional chain of magnetic particles of diameter *d* embedded into a three-dimensional elastic matrix. The elastic embedding is represented by a harmonic potential with spring constant  $k_{mp}$ , pinning each particle *i* (labeled from left to right) to its initial position  $x_i^0 := i\ell$ . The elastic particle–particle interaction *mediated* by the matrix is represented by the springs connecting the particles. Between nearest neighbors, there are springs of spring constant  $k_{pp}$ and equilibrium length  $\ell$ . Next-nearest neighbors are connected by springs of spring constant  $k_{pp}/2$  and equilibrium length  $2\ell$ , thereafter the parameters are  $k_{pp}/3$  and  $3\ell$ , and so forth. Finally, all particles carry a fixed magnetic dipolar moment of magnitude *m* aligned with the system axis.

$$u_{\rm pp}(\pm\Delta\mathbf{r}) = \frac{1}{2}k_{\rm pp}(r)(\Delta\mathbf{r})^2,$$
(18)

with a distance-dependent spring coefficient

$$k_{\rm pp}(r) := \frac{k_{\rm mp}^2}{8\pi G} \frac{1}{r} = \frac{3}{2} \frac{1-\nu}{5-6\nu} k_{\rm mp} \frac{d}{r}.$$
 (19)

Using the two potentials  $U_{\rm mp}$  and  $u_{\rm pp}$  as an input, we now motivate an extended dipole-spring model for a linear, initially homogeneous chain of *N* particles embedded into an elastic matrix, see figure 9. We label the particles from left to right by i = 1, ..., N, according to their equilibrium positions  $x_i^0 := i\ell$  within the chain. The total pinning potential based on equation (16) then becomes





**Figure 10.** Illustration of the pseudo-spring external potential in equation (22) representing the pinning effect of the embedding elastic matrix in our DFT. There are *N* harmonic wells at a spacing  $\ell$  with spring constant  $k_{\rm mp} = \frac{8\ell}{3d}k_{\rm pp}$  (here  $\ell = 2d$ ,  $\nu = 1/2$ , and  $k_{\rm pp} = 4k_0$ , which translates to  $G = \frac{8\ell}{9\pi d^2}k_{\rm pp} = \frac{64}{9\pi}\frac{k_0}{d}$ ). The corresponding harmonic potentials of the individual wells are cut where they overlap with the potential of another well. This leaves the leftmost and rightmost wells unbounded to the sides and, therefore, the whole particle chain remains confined.

$$U_{\rm mp} = \sum_{i=1}^{N} \frac{1}{2} k_{\rm mp} (x_i - i\ell)^2.$$
 (20)

To approximate the matrix-mediated particle–particle interactions between two particles i, j we replace the 1/r dependence of the spring constant (19) by  $1/|j - i|\ell$ . Thus, we have for the total interaction between all pairs of particles

$$U_{\rm pp} = \sum_{i=1}^{N} \sum_{j>i} \frac{1}{2} \frac{k_{\rm pp}}{|j-i|} (x_{ij} - |j-i|\ell)^2, \qquad (21)$$

where  $k_{pp} := \frac{3}{25-6\nu} \frac{1-\nu}{\ell} k_{mp}$ . Essentially, this means that each particle *i* is connected to all other particles *j* with harmonic springs of spring constant  $k_{pp}/|j-i|$  and spring equilibrium length  $|j-i|\ell$ , see figure 9. From now on, we assume incompressibility of the elastic matrix and set  $\nu = 1/2$ .

Of course, in this extended dipole-spring model the particles are again distinguishable by their positions. As before, it needs to be mapped to the use in our DFT. For this purpose, we replace the harmonic springs in the model by 'pseudosprings', following the ideas outlined in section 2. To include the pinning potential  $U_{mp}$ , we use an external potential consisting of a series of *N* harmonic wells

$$U_{\text{ext}}(x) = \min_{i=1,...,N} \left\{ \frac{1}{2} k_{\text{mp}}(x - i\ell)^2 \right\}$$
(22)

as depicted in figure 10. To represent the network of springs in equation (21) between one particle and all other particles by 'pseudo-spring' interactions, we use

$$\begin{split} \tilde{u}_{e}(x) &= \frac{k_{pp}}{2} \left[ (x-\ell)^{2} - \frac{\ell^{2}}{4} \right] \mathbb{1}_{[0,\frac{3}{2}\ell]}(x) \\ &+ \sum_{i=2}^{\infty} - \frac{k_{pp}}{2i} \left[ (x-i\ell)^{2} - \frac{\ell^{2}}{4} \right] \mathbb{1}_{[(i-\frac{1}{2})\ell,(i+\frac{1}{2})\ell]}(x), \quad (23) \\ &\text{ with } \mathbb{1}_{[a,b]}(x) = \begin{cases} 1 & \text{for } x \in [a,b], \\ 0 & \text{else.} \end{cases} \end{split}$$

This pair potential is illustrated in figure 11 and consists of a series of harmonic wells. The spring constants of the wells



**Figure 11.** Effective elastic pair potential in equation (23) to represent the network of springs in equation (21) in our DFT calculations. The harmonic wells with width  $\ell = 2d$  have a spring constant  $k_{pp}/i$ , where *i* is the index of the well and  $k_{pp} = 4k_0$ .

decay with the neighbor number *i* from the origin just like the individual springs connecting a particle to all other particles in the dipole-spring model, see figure 9. Furthermore, the boundaries of the wells are shifted to zero so that we have a vanishing pair potential at infinite distance. Since the depth of the wells roughly decays as 1/x, the interaction is long-ranged.

The width of the wells in both, the external and the pair potential, is given by  $\ell$ . This width should be larger than dand here we choose  $\ell = 2d$ . Thus, both potentials in principle allow more than one particles to occupy a single well. However, the external potential pinning the particles to their equilibrium positions in the matrix is relatively strong. The particles should, therefore, remain centered in their respective wells on average.

### 5.2. Results

9

We now discuss our results for our extended dipole-spring model for a magnetic particle chain embedded in a threedimensional elastic matrix. To this end, we consider a chain of N = 40 particles, with an equilibrium interparticle distance

 $\ell = 2d$  and spring constants  $k_{pp} = 4k_0$ ,  $k_{mp} = \frac{8\ell}{3d}k_{pp} = \frac{16}{3}k_{pp}$ . To evaluate the contribution of the magnetic chain to the pressure and compression modulus as well as to evaluate the DFT numerically, we address one part of the elastic matrix of length L = 100d that contains the magnetic chain. This choice of *L* is arbitrary, the only requirement for *L* is to be larger than the total equilibrium length  $N\ell = 80d$  of the chain by a reasonable amount.

Figure 12 shows density profiles obtained from DFT, pseudo-spring MC, and real-spring MC when setting the magnetic moment to m = 0. In contrast to our former dipole-spring model, periodic structures appear here in the density profiles resulting from all three methods, even though this model is still effectively one-dimensional. The reason is, first, that the elastic particle–particle interaction decays only slowly with the distance and is effectively long-ranged. This applies to both, the real-spring and the pseudo-spring version. Second, we have a pinning potential suppressing large amplitude fluctuations of the particles around their pinning positions. Together, both contributions counteract the Landau–Peierls instability and can facilitate periodic structures also in one spatial dimension [39, 40, 63, 64, 69]. In this way, the role of thermal fluctuations is substantially reduced, and our



**Figure 12.** Density profiles for a non-magnetic chain of N = 40 particles at an equilibrium interparticle distance  $\ell = 2d$  embedded in an elastic matrix ( $k_{pp} = 4k_0, k_{mp} = \frac{16}{3}k_{pp}, m = 0$ ). The density profiles are sharply peaked around the equilibrium positions of the particles. There is good agreement between DFT, pseudo-spring MC and real-spring MC.



**Figure 13.** Pressure contribution  $\Delta p$  and contribution  $\Delta K$  to the compression modulus as a function of the squared magnetic dipole moment  $m^2$ . Both quantities show a linear monotonous decrease with  $m^2$ . The DFT shows a small offset in  $\Delta p$  of the order of  $0.01p_0$  compared to the MC, but the slopes are almost identical. For the compression modulus, the deviations are of the order of  $0.001K_0$ .

mean-field DFT performs much better when compared to the MC-simulations.

Let us now address the pressure and compression modulus. As before, they can be determined by probing the energetic change of the system upon deformation. However, we keep in mind that we have one system (the chain of particles) embedded into another system (the surrounding matrix, where here we present our results for one part of length L of this infinitely extended matrix). When we perform a small affine deformation  $\Delta L$  of the part of the matrix containing the chain, we alter the properties of the embedded system. In particular, the equilibrium distance  $\ell$  between the embedded particles changes by a factor  $(L + \Delta L)/L$ . In our approach, this affects the pinning positions  $x_i^0 = i\ell$  of the particles as well as the spring constant  $k_{\rm pp} = \frac{3d}{8\ell} k_{\rm mp}$ , which is accounted for in the energetic change upon deformation. Furthermore, what we can calculate from this energetic change are only the contributions  $\Delta p$  and  $\Delta K$  of the embedded chain to the overall pressure and compression modulus of the composite. To obtain the overall pressure or compression modulus of the whole composite, the energetic change associated with the macroscopic deformation of the three-dimensional matrix would need to be included as well, which is beyond our particle-based approach.

Figure 13 shows the contribution  $\Delta p$  to the pressure as well as the contribution  $\Delta K$  to the compression modulus as a function of the magnetic dipole moment. We can observe a linear decrease with  $m^2$  in both quantities with good agreement between the DFT and MC calculations. The linear behavior is expected, because the magnetic interaction energy scales with  $m^2$  and the particle chain remains relatively homogeneous while increasing the magnetic moment.

As a final result, we present the contribution of the embedded chain to the stress-strain behavior of the composite material. For this purpose, we compress the surrounding matrix by  $\Delta L$ and measure the pressure contribution of the embedded chain as a function of this compression. The results are shown in figure 14 for values of the squared magnetic moment in the range  $m^2 = 0.0 m_0^2 - 1.0 m_0^2$ . At vanishing magnetic moment, the pressure contribution slightly increases when compressing the system. This is probably due to entropic effects that favor an elongated chain and, thus, work against a compression combined with a slight increase in the spring constant  $k_{\rm pp}$  in our description. Increasing  $m^2$ , however, leads to a stronger magnetic attraction between the particles. This renders an overall compression more favorable. Since decreasing the particle distance also enhances the magnetic attraction, we have a negative pressure contribution that increases in magnitude when compressing the system further.

Again, we can observe good agreement between DFT and MC. The best agreement is observed at small compressions and low magnetic moments. Remarkably, the pseudo-spring and the real-spring MC agree exceptionally well at all considered values of  $\Delta L$  and  $m^2$ . This demonstrates, that our approach to map the spring network to effective interactions between indistinguishable particles is promising also beyond the scope of our mean-field DFT. Moreover, in the supplemental material<sup>6</sup>, we also show how the overall number of particles on the chain

<sup>&</sup>lt;sup>6</sup> See footnote 3.



J. Phys.: Condens. Matter 29 (2017) 275102

**Figure 14.** Pressure contribution  $\Delta p$  as a function of an overall matrix compression  $\Delta L$  for squared magnetic moments in the range of  $m^2 = 0.0 m_0^2 - 1.0 m_0^2$  in steps of  $0.1 m_0^2$ . These results constitute the contribution of the embedded chain to the overall stress-strain behavior in one part of the composite material. At vanishing magnetic moment, the pressure increases with the compression. Increasing the magnetic moment, however, leads to stronger magnetic attractions so that the pressure contribution decreases when the surrounding matrix is compressed. We find good agreement between DFT and MC results, especially for low compressions and magnetic moments. The deviations for high compressions already described in figure 7. Agreement between the pseudo-spring and real-spring MC is excellent under all conditions.

influences its contribution to the stress-strain behavior and we present corresponding DFT results in analogy to figure 14.

### 6. Conclusions

In summary, we have proposed a density functional theory to address ferrogel model systems, here evaluated in one spatial dimension. These systems are in principle non-liquid, because the particles are arrested by the elastic matrix surrounding them. To enable the investigation with statistical-mechanical theories, we map the elastic interactions onto effective pairwise interactions and, thus, make the particles indistinguishable.

The one-dimensional nature of the ferrogel model systems investigated here poses a challenge, because thermal fluctuations have a special impact in one dimension. Fluctuations can become long-ranged and destroy periodic structural order. These fluctuations, driving the Landau–Peierls instability, are not resolved within our mean-field density functional theory. Therefore, within our first dipole-spring model we observe deviations from Monte-Carlo simulations where these fluctuations are included.

In a second, more advanced approach, we explicitly model a linear particle chain embedded into a three-dimensional matrix. Within this model, the Landau–Peierls instability is counteracted by a stronger long-ranged coupling between the particles and a pinning potential that localizes the particles within the elastic matrix. Since the role of the fluctuations is therefore reduced, our density functional theory now provides results that are in good agreement with Monte-Carlo simulations. Numerous experimental realizations of such systems exist [34, 43–48], see particularly the set-up in [34].

### P Cremer et al

145

For the future, it would be promising to extend the concept proposed here to higher spatial dimensions, that is to two-dimensional sheets of ferrogels or full three-dimensional samples. In those dimensions, the Landau-Peierls instability will be less relevant. We expect that especially for regular crystal-like particle arrangements, where the one-body density is regularly peaked, density functional theory is reliable and provides a useful framework to study the properties of these promising materials. It will be interesting to extend the present analysis to include the dynamics of the colloidal particles by using the concept of dynamical density functional theory [70-73]. For this purpose, one should smoothen our non-differentiable external potentials because the dynamic theory entails their spatial derivatives. Our likewise non-differentiable pairwise interactions are already smoothened by the convolution in the mean-field functional. The dynamics should be reasonably tractable by using schemes similar to those in [74] or a pseudospectral approach such as the one detailed in [75]. For particles of different sizes, or different dipole moments, the same ideas can be used to map the system onto binary and multicomponent systems. Moreover, orientational degrees of freedom, such as rotating dipole moments or anisotropic particle shapes, can be tackled by density functional theory as well, both in statics [76, 77] and dynamics [78, 79], and can therefore be treated within the same framework as proposed here.

Our results show that density functional theory can be used to describe non-liquid systems like ferrogels, still leading to reasonable results. More generally, we have established that mapping bead-spring models to effective potentials is a feasible approach to make them accessible to statistical-mechanical theories.

These theories often make use of correlation functions as an input [80], which here are related to the particle distribution in the ferrogel. Experimental extraction of the particle distribution and the corresponding correlation functions is still challenging [48]. However, this route could be explored in the future once the available experimental techniques for particle detection in ferrogel materials are more advanced and particularly can address larger system sizes. These correlation functions could then help to construct effective pair potentials representing the real connectivity in the gel [81], providing a formal route for the mapping onto systems of indistinguishable particles.

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### Appendix. Numerical relaxation scheme to obtain the equilibrium density profile from our DFT

Here, we describe in detail our numerical relaxation scheme to obtain the equilibrium density profile  $\rho(x)$  minimizing  $\Omega[\rho]$  within our DFT. Instead of directly solving equation (13), we perform a dynamical relaxation of the Lagrange functional

J. Phys.: Condens. Matter 29 (2017) 275102

$$\mathcal{L}[\alpha] = \int_0^L \frac{1}{2} \dot{\alpha}(x)^2 \, \mathrm{d}x - \Omega[\alpha] - \lambda \left( \int_0^L \exp(\alpha(x)) \, \mathrm{d}x - \langle N \rangle \right)$$
(A.1)

with respect to the logarithmic density profile  $\alpha(x) = \ln(\rho(x))$ [82]. Minimizing with respect to the logarithmic density profile ensures that  $\rho(x) = \exp(\alpha(x))$  remains positive during the relaxation. The artificial kinetic term  $\int_0^L \frac{1}{2}\dot{\alpha}(x)^2 dx$  drives  $\alpha(x)$ and thus  $\rho(x)$  towards the minimum in the grand canonical free energy  $\Omega[\rho]$ . The Lagrange multiplier  $\lambda$  with the corresponding constraint  $\langle N \rangle = \int_0^L \exp(\alpha(x)) dx = \int_0^L \rho(x) dx$ allows us to set the average particle number  $\langle N \rangle$  instead of the chemical potential  $\mu$ . This is more convenient for evaluating the pressure and the compression modulus defined as

$$p = -\frac{\partial \Omega}{\partial L}\Big|_{\langle N \rangle, T}$$
 and  $K = -L\frac{\partial p}{\partial L}\Big|_{\langle N \rangle, T}$ , respectively.

Solving the Euler–Lagrange equation

$$\frac{\mathrm{d}}{\mathrm{d}t} \frac{\delta \mathcal{L}[\alpha]}{\delta \dot{\alpha}(x)} - \frac{\delta \mathcal{L}[\alpha]}{\delta \alpha(x)} = 0 \tag{A.2}$$

then leads to the equation of motion for  $\alpha(x)$ 

$$\ddot{\alpha}(x) = -\rho(x) \left( \frac{\delta \Omega[\rho]}{\delta \rho(x)} + \lambda \right).$$
(A.3)

The Lagrange multiplier  $\lambda$  is determined by

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2} \int_0^L \exp(\alpha(x)) \,\mathrm{d}x = 0 \quad \Leftrightarrow \\ \int_0^L \rho(x) (\dot{\alpha}(x)^2 + \ddot{\alpha}(x)) \,\mathrm{d}x = 0 \quad \Leftrightarrow \\ \lambda = \int_0^L \rho(x) \bigg( \dot{\alpha}(x)^2 - \rho(x) \frac{\delta \Omega\left[\rho\right]}{\delta \rho(x)} \bigg) \mathrm{d}x \, \bigg/ \int_0^L \rho(x)^2 \,\mathrm{d}x.$$
(A.4)

In order to perform the numerical relaxation, we discretize the system into *n* equally spaced sampling points such that one particle diameter *d* is represented by 100 points. The density profile, the potentials, and the radial distribution function are all defined on this numerical grid. All integrals appearing in the calculation of the 'acceleration'  $\ddot{\alpha}(x)$  can then be solved numerically, making use of fast-Fourier-transforms in the case of convolution integrals.

We iterate the equation of motion for  $\alpha(x)$  forward in time using the standard Velocity-Verlet scheme, obtaining the 'velocity'  $\dot{\alpha}(x)$  and an update for the density profile  $\rho(x)$  in each time step  $\Delta t$ . To ensure that the constraint  $\langle N \rangle = \int_0^L \rho(x) dx$ remains fulfilled, we renormalize  $\rho(x)$  after each time step. The time step is variable and increases by a factor 1.1 up to a maximum  $\Delta t_{max} = 0.01$  when the grand canonical energy has decreased for 5 consecutive time steps. The decrease in energy is monitored by the 'power'  $P = \int_0^L \dot{\alpha}(x)\ddot{\alpha}(x) dx$ , which is supposed to be positive. If  $P \leq 0$  occurs, we set  $\dot{\alpha}(x) = 0$ and halve the time step. We consider the density profile  $\rho(x)$  P Cremer et al

sufficiently close to equilibrium when our measure for the error  $\varepsilon := \sqrt{\int_0^L \ddot{\alpha}(x)^2 dx}$  becomes smaller than  $10^{-6}$ . At that stage, the left hand side of equation (A.3) as well as  $\lambda$  are close to zero, so that we have  $\frac{\delta \Omega[\rho]}{\delta \rho}(x) \approx 0$  as required by equation (13). A brief discussion of typical computation times is given in the supplemental material<sup>7</sup>.

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J. Phys.: Condens. Matter 29 (2017) 275102

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P Cremer et al

### Supplemental material to: A density functional approach to ferrogels

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In the main article, we have mapped our one-dimensional dipole-spring model containing magnetic particles that are distinguishable by their positions onto a description using pairwise interactions in terms of effective "pseudo-springs", such that the particles can be treated as indistinguishable. Using this mapping, we have then compared results from density functional theory to those of Monte-Carlo simulations. Here, in a similar fashion, we compare results obtained from solving the Zerah-Hansen liquid-integral equation in comparison to those of Monte-Carlo simulations for various magnitudes of the magnetic moments of the particles. These results demonstrate that other liquid-state theories using our pseudo-spring approximation lead to reasonable predictions as well. Additionally, we provide typical computation times for our various numerical methods. Finally, we discuss finite-size effects on our density-functional-theory results in the framework of our advanced dipole-spring model for a linear embedded chain of magnetic particles in an infinitely extended elastic matrix.

### I. ZERAH-HANSEN LIQUID INTEGRAL EQUATION

Let us first describe the method of using the Zerah-Hansen (ZH) liquid-integral equation to obtain the equation of state, before we proceed to the comparison with Monte-Carlo (MC) simulations. We use a numerical spectral method [S1–S3] to solve the Ornstein-Zernike equation [S4]

$$\gamma(x) = \bar{\rho} \int_{-\infty}^{\infty} dx' \big(\gamma(x') + c(x')\big) c(x - x') \qquad (S1)$$

for a bulk liquid of mean density  $\bar{\rho}$ . The functions  $\gamma(x) = g(x) - 1 - c(x)$  and c(x) are the indirect and direct correlation functions, respectively. The latter is approximated here by the thermodynamically partially self-consistent Zerah-Hansen (ZH) closure [S5]

$$c(x) = \frac{e^{-\beta u_{\rm r}(x)} \left[ f(x) - 1 + e^{f(x)(\gamma(x) - \beta u_{\rm a}(x))} \right]}{f(x)} - \gamma(x) - 1,$$
(S2)

where  $\beta = 1/k_BT$  and the interaction potential  $u(x) = u_{\rm h}(x) + u_{\rm m}(x) + \tilde{u}_{\rm e}(x)$  between indistinguishable particles is split into the sum  $u(x) = u_{\rm r}(x) + u_{\rm a}(x)$  of a repulsive part

$$u_r(x) = \begin{cases} 0 & \text{for } x > x_{\min} ,\\ u(x) - u_{\min} & \text{otherwise,} \end{cases}$$
(S3)

and an attractive part

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$$u_{\rm a}(x) = \begin{cases} u(x) & \text{for } x > x_{\rm min} ,\\ u_{\rm min} & \text{otherwise.} \end{cases}$$
(S4)

Here,  $u_{\min} = u(x_{\min})$  denotes the minimum of u(x). The mixing function  $f(x) = 1 - e^{-\alpha x}$  depends on the nonnegative mixing parameter  $\alpha$  which is adjusted to achieve thermodynamic consistency with respect to the compression modulus: At the numerically determined value of  $\alpha$ , the fluctuation-route expression [S4, S6]

$$K = \bar{\rho}k_B T \left( 1 - 2 \ \bar{\rho} \int_0^\infty c(x) \ dx \right)$$
(S5)

gives the same result as the virial-route expression [S4, S6]

$$K = \bar{\rho} \left. \frac{\partial p_{\rm v}}{\partial \bar{\rho}} \right|_T,\tag{S6}$$

in which  $p_{\rm v}$  is the virial pressure. The derivative in Eq. (S6) is numerically approximated by a finite difference and the virial pressure is calculated by numerical integration and solution of

$$\frac{p_{\rm v}}{\bar{k}_B T} = 1 + \bar{\rho} dg(d^+) - \bar{\rho}\beta \int_d^\infty x \, \frac{du(x)}{dx} \, g(x) \, dx. \quad (S7)$$

Here,  $g(d^+) = \lim_{x \to d} g(x > d)$  is the contact value of the radial distribution function.

We compare the equations of state obtained from this method with MC-simulations of a bulk pseudo-spring system. For the latter we use a periodic box of width L = 500d and otherwise proceed as for our finite systems in the main article. Figure S1 shows the equations

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FIG. S1: Equations of state obtained from bulk MCsimulation and ZH liquid-integral theory for various magnitudes of the magnetic moment and a spring constant of  $k = 4 k_0$ . Thermodynamic consistency cannot be found for many parameter combinations, explaining the lack of ZH data points. Where it can be found, however, there is good agreement with the MC, especially at high packing fractions. Also the magnitude of the downward shift when increasing the magnetic moment seems to be accurately captured.

of state obtained from both methods, ZH and MC, for various values of the magnetic moment.

Unfortunately, there are many parameter combinations for which the numerical ZH equation solver does not converge, because thermodynamic consistency with respect to the compression modulus is not found for any value of the mixing parameter  $\alpha$ . Nevertheless, for those parameters at which ZH solutions are available they agree remarkably well with the MC results. Especially at high packing fractions, the equation of state is accurately predicted by the ZH equation. Furthermore, the ZH solution captures correctly the decrease in pressure when the magnetic moment is increased. In contrast to density functional theory (DFT), the employed ZH equation is a theory for homogeneous, isotropic bulk liquids that is not expected to overestimate the tendency of the system to form regular structures and, in fact, does not even include the possibility of symmetry-breaking phase transitions. This might explain why the agreement between MC and ZH in Fig. S1 is better than between MC and DFT in Fig. 7 of the main article. However, the missing feature of reproducing localized density peaks at pre-set equilibrium positions, as required for the extended model in the main article, is an obvious drawback when compared to the DFT approach.

We have also solved the hypernetted chain (HNC) integral equation [S7] and the Percus-Yevick (PY) integral equation [S8] (results not shown). Both the HNC and the PY equations can be readily solved numerically in the complete parameter range of Fig. S1. However, the (virial and fluctuation-route) equations of state predicted by the HNC and PY equation solution exhibit distinctive disagreement with our MC-simulation results. We conclude that thermodynamic consistency with respect to the compression modulus — which is satisfied in the ZH equation solution, and which is lacking in both the HNC and the PY equations — is a crucial feature. In order to overcome the problem of missing solutions of the ZH equation in extended physical parameter ranges, it might be worthwhile to test alternative thermodynamically partially self-consistent closures of the Ornstein-Zernike equation in future work.

### II. COMPUTATION TIMES FOR OUR VARIOUS NUMERICAL METHODS

We indicate typical computation times for the three numerical methods we have used. In the MC-simulations, the pressure is sampled by a virtual-volume-move method and therefore subject to statistical fluctuations. To obtain an accurate value for the compression modulus, the derivative of the pressure, a relatively large amount of statistics has to be gathered. Typical simulations, thus, take around 30–50 hours.

The calculation times for the DFT can strongly vary. For our first dipole-spring model defined in Sec. II of the main article, a calculation finishes in only two minutes. However, when the density becomes strongly peaked as in our advanced model for an embedded chain of particles (Sec. V), small variations in the density lead to huge energetic changes in the Percus functional [see Eq. (9) in the main article]. Then, the time step in our numerical relaxation scheme (see the Appendix) has to adapt itself to a small value, which increases the computation time to 2–8 hours. Still, the DFT calculations are significantly faster than the corresponding MC-simulations.

Finally, the runtime for solutions of the ZH liquid integral equation amounts to 5–10 minutes.

### III. EFFECT OF SYSTEM SIZE FOR THE LINEAR EMBEDDED CHAIN

In Fig. 14 of the main article, we have shown the pressure contribution  $\Delta p$  of the chain of particles for various matrix compressions  $\Delta L/L$  and magnitudes of the squared magnetic moments. Here, we are interested in how this stress-strain behavior changes when we increase the number of particles in the chain from N = 40 to N = 80 and further to N = 160 while accordingly scaling the considered part of the elastic matrix from L = 100dto L = 200d to L = 400d, respectively. We perform the calculations using only DFT and present the results in Fig. S2 in a way analogous to Fig. 14 of the main article. The effect of increasing the system size seems to be fairly weak. For small compressions, there is a slight shift of all curves to higher  $\Delta p$ . For larger compressions and stronger magnetic interactions, a slight shift to lower  $\Delta p$ occurs. These shifts seem to be more pronounced when doubling the system size from N = 40 to N = 80 than

 $\mathbf{2}$ 



FIG. S2: Contribution of the chain of embedded particles to the overall stress-strain behavior in a part of length L of the composite material as in Fig. 14 of the main article. Here, however, DFT results for three different systems of N = 40, N = 80, and N = 160 particles are compared. We consider parts of the (in principle infinitely extended) embedding elastic matrix of length L = 100d, L = 200d, and L = 400d, respectively. Increasing the system size accordingly has only a small effect, shifting the curves slightly upwards at small compressions  $\Delta L/L$  and slightly downwards for larger compressions and stronger magnetic interactions.

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for doubling it again from N = 80 to N = 160. In total, we do not expect the shifts to become significant when going to even larger system sizes.

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### Paper VII. Statistical analysis of magnetically soft particles in magnetorheological elastomers

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### Statement of contribution

TG performed the experimental parts and wrote the corresponding sections of the paper. I did the statistical analysis of the data involving the distribution functions and wrote the corresponding sections and the supplemental material. AMM, HL, and SO acted as supervisors and guided the writing of the paper and offered corrections. I estimate my overall contribution to this work to be around 40%.

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# Statistical analysis of magnetically soft particles in magnetorheological elastomers

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### Abstract

The physical properties of magnetorheological elastomers (MRE) are a complex issue and can be influenced and controlled in many ways, e.g. by applying a magnetic field, by external mechanical stimuli, or by an electric potential. In general, the response of MRE materials to these stimuli is crucially dependent on the distribution of the magnetic particles inside the elastomer. Specific knowledge of the interactions between particles or particle clusters is of high relevance for understanding the macroscopic rheological properties and provides an important input for theoretical calculations. In order to gain a better insight into the correlation between the macroscopic effects and microstructure and to generate a database for theoretical analysis, x-ray micro-computed tomography (X- $\mu$ CT) investigations as a base for a statistical analysis of the particle configurations were carried out. Different MREs with quantities of 2–15 wt% (0.27–2.3 vol%) of iron powder and different allocations of the particles inside the matrix were prepared. The X- $\mu$ CT results were edited by an image processing software regarding the geometrical properties of the particles with and without the influence of an external magnetic field. Pair correlation functions for the positions of the particles inside the elastomer were calculated to statistically characterize the distributions of the particles in the samples.

Supplementary material for this article is available online

Keywords: magnetism, rheology, magnetorheological elastomers, pair correlation, computertomography, digital image processing, statistical analysis

(Some figures may appear in colour only in the online journal)

### 1. Introduction

Magnetorheological elastomers (MRE) are an interesting class of actively controllable smart materials. They consist of magnetic particles embedded into an elastic polymer matrix [1–4]. This combination of materials allows to dynamically influence many material properties simply by applying an external magnetic field, opening the way for a wide range of applications in technology [5–15]. The magnetic particles are usually made of a ferromagnetic material, e.g., carbonyl-iron powder [10–15] or neodymium-iron-boron [16] in a size range of a few nanometers up to several micrometers. To generate the polymeric matrices, polydimethylsiloxane (PDMS) or poly(N-isopropylacrylamide) is frequently used.

Applying a magnetic field to such a kind of MRE, internal magnetodipolar forces can cause changes in static and dynamic properties [17–24]. Structurally, during synthesis, these forces can lead to a rearrangement of the particles towards chain-like aggregates oriented parallel to the direction of the applied magnetic field [25–28]. Inducing these forces in the final product, counteracting elastic restoring forces by the surrounding matrix oppose to the reorganization. The magnitudes of the magnetodipolar forces are largely dependent on the distribution of the particles inside the matrix, particularly on the distance between neighboring particles.

During the last years, a noninvasive method for the threedimensional investigation of the morphology of materials

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T Gundermann et al

using x-ray micro-computed tomography (X- $\mu$ CT) was developed [29–31]. This measuring technique enables a quantitative analysis of the geometrical properties of single particles in MRE materials. It is possible to perform X- $\mu$ CT investigations under the influence of an external magnetic field by implementing a magnetic field setup into the CT-system [31, 32].

The main interest of the current study is to observe and analyze the particle distribution within different samples. We have investigated isotropic samples with and without exposure to an external magnetic field during measurement. Samples with an already imprinted chain structure (anisotropic samples) due to initial polymerization under the influence of an external magnetic field are addressed as well. The initially isotropic samples show a formation of small chainlike aggregates when applying an external magnetic field. Consequently, there is a structural difference between the cases with and without an external magnetic field switched on [32]. For both cases, pair correlation functions (PCF) are calculated and compared to the situation in the anisotropic samples, where chain-like aggregates are always present. These PCF are of interest as an input for statistical theories, see also their previous use in the characterization of dipolar liquids [33-40].

The experimental samples were based on magnetically soft iron particles with a mean diameter of about 45  $\mu$ m and a particle content of 2, 5, 10, and 15 wt% which corresponds to 0.27, 0.70, 1.47, and 2.32 vol%, respectively. These particles were embedded into a PDMS matrix supplied by Wacker Chemie AG (Germany). Applying the external magnetic field was achieved by two permanent magnets in the X- $\mu$ CT system that create an external homogeneous magnetic flux density of approximately B = 270 mT [31].

### 2. Experimental

### 2.1. Setup

To carry out the investigations we used an X- $\mu$ CT system based on a nano-focus tube with a maximum acceleration voltage of 160 kV, a movable sample holder with two cylindrical permanent magnets to adjust the magnetic field, and a detector with a photodiode array of 2000 × 2048 (vertical × horizontal) pixels [29–31]. The permanent magnets were mounted in a displaceable fashion and could generate a homogeneous magnetic field parallel to the direction of gravity in the range of B = 0-270 mT. This enables investigations of cylindrical regions of 4 mm both in height and in diameter, within a magnetic field with a degree of homogeneity of 97% in radial and 94% in axial direction [31]. More details on the measuring setup can be found in [31, 32].

During the CT investigations, the temperature was kept constant at 20 °C. The projection images in the experiments were generated by rotating the sample with  $0.25^{\circ}$  angular increment for a tube current of  $170 \,\mu\text{A}$  and an acceleration voltage of 90 kV. The exposure time was varied between 2

and 6.5 s to achieve a suitable image quality. The magnification was 15, which resulted in a resolution of 1 pixel =  $3.2 \,\mu$ m. CT-reconstruction was carried out using a home-made software.

#### 2.2. Samples

Our samples were of cylindrical shape of diameter d = 3.5 mm and height h = 3.5 mm. The polymer host matrix was prepared from the elastomer kit Elastosil® RT 745 A/B, provided by Wacker Chemie AG Germany. Elastosil is a two-component silicon with a curing agent in one of the two components. The components were mixed in a mass ratio of 1:1. After mixing the components, a highly viscous silicon oil of viscosity  $\eta = 100$  Pas (at 23 °C), produced by Wacker Chemie AG (Germany), was added as a softener in a content ratio of 60 wt% related to the two silicon components. This softener leads to an adjustment of the elastic moduli of the polymer matrix and to a reduction of the sedimentation rate due to gravitation. After mixing the components and the softener, magnetically soft iron powder ASC200, supplied by Höganäs AB (Sweden), was added. The average particle size was approximately 45  $\mu$ m. Further details about the particle size distribution can be found in [29].

To investigate the statistical particle distribution in MREs, different samples with particle contents of 2, 5, 10, and 15 wt% (0.27, 0.70, 1.47, 2.32 vol%, respectively) were produced. Samples with isotropic particle distributions were synthesized by pouring the final mixture (with particles added) into a mold that was then placed into a 95 °C water bath for 2 h to guarantee the polymerization of the samples. Samples with anisotropic particle distributions were produced by exposing the final mixture to a homogeneous magnetic field of B = 270 mT generated by a laboratory electronic magnet from the company Bruker Corp. (Germany) during polymerization amounted to 2 h at a temperature of 95 °C.

After preparation of the samples, CT-scans were performed. We anticipated a particle rearrangement upon application of an external magnetic field [32]. Therefore, each sample was investigated in the absence and the presence of an external magnetic field. In this process, it was found that the particles within the anisotropic samples already featuring chain-like aggregates do not show significant rearrangement when the magnetic field is applied parallel to the chain structures. Thus, the cases we discuss in the following are isotropic samples at B = 0, isotropic samples at B = 270 mT, and anisotropic samples at B = 0. Example tomograms of the samples with different particle distributions are shown in figures 1(a) and (b).

### 3. Evaluation

A quantitative analysis identifying single particles inside the elastomeric matrices becomes possible by evaluating the reconstructed tomographic scans with an image processing



**Figure 1.** Tomograms of cylindrical MRE samples of 5 wt% particle content with (a) isotropic structure in the absence of an external magnetic field. The anisotropic sample (b) was generated by applying an external magnetic field in axial direction during the polymerization process. The host matrix is shown in dark red (dark gray) and the particles in yellow (light gray).

software. For the quantitative analysis, the software MATLAB 7.10.0 with the image toolbox DIPimage was used. Due to a lower absorption coefficient of the elastomer relatively to the particles, the matrix in figure 1 (in dark red/ dark gray) can be distinguished from the particles (in yellow/ light gray). A threshold criterion based on the gray value in the tomographic data was used to separate the particles from the matrix. After separation of the components, individual particles in clusters were identified (segmented) using a watershed algorithm [41]. To avoid an incorrect separation of the particles, it was important to adjust the parameters of the watershed algorithm. To guarantee an accurate particle segmentation, the threshold criterion and the watershed algorithm were calibrated to the size distribution of the magnetic particles obtained by a laser diffraction method. Figure 2 illustrates a segmented cluster of particles within an anisotropic sample for a particle content of 5 wt%.

After segmentation of the clustered particles, the particles were labeled and their size and center coordinates were determined and organized into a database. The particle distribution was determined from this database. In a homogeneous sample, a useful approach to statistically characterize the distribution of particles is to consider the PCF [42, 43]

$$g(\mathbf{r}) = \frac{V}{N^2} \left\langle \sum_{i} \sum_{j \neq i} \delta(\mathbf{r} - (\mathbf{r}_j - \mathbf{r}_i)) \right\rangle, \tag{1}$$

where *N* is the number of particles, *V* is the sample volume,  $\mathbf{r}_i = (x_i, y_i, z_i)$  and  $\mathbf{r}_j = (x_j, y_j, z_j)$  denote the positions of particles *i* and *j*, respectively,  $\delta$  is the Dirac delta function,



Figure 2. Segmented individual particles in one chain of an anisotropic MRE sample with a particle content of 5 wt% as opposed to the still non-segmented particles in the other chain structures.

and  $\langle \cdot \rangle$  denotes an ensemble average. The PCF is proportional to the probability density for finding a pair of particles in the sample at a separation as given by the vector **r**. In an ideal gas

155

of particle density N/V, where the ensemble-averaged distribution of particles is uniform, this probability density is given by  $(N/V)^2$ . So  $g(\mathbf{r})$  relates the actual nonuniform distribution to the uniform ideal-gas distribution. For very short distances smaller than the finite particle size,  $g(\mathbf{r}) = 0$ because the rigid particles cannot interpenetrate. At very long distances, there is no correlation between two particles anymore so that the probability density to find a particle at a separation  $\mathbf{r}$  from another particle becomes uniform as for the ideal gas and  $g(\mathbf{r}) = 1$ .

Our anisotropic samples were produced in an external magnetic field parallel to the cylinder axis ( $\hat{z}$ -direction). Moreover, our isotropic samples were probed under the influence of an equally oriented magnetic field. These samples possess a cylindrical symmetry and, therefore, the probability density to find a particle pair at a certain separation only depends on the particle distances  $r_{||}$  in the axial direction and  $r_{\perp}$  perpendicular to it. That means a PCF of only two variables given by

$$g(r_{\parallel}, r_{\perp}) = \frac{V}{4\pi r_{\perp} N^2} \left\langle \sum_{i} \sum_{j \neq i} \delta(r_{\parallel} - |z_j - z_i|) \times \delta(r_{\perp} - \sqrt{(x_j - x_i)^2 + (y_j - y_i)^2}) \right\rangle$$
(2)

contains the same information as  $g(\mathbf{r})$  and can be termed cylindrical distribution function. For the analysis of the isotropic samples in the absence of an external field we can proceed one step further and consider the radial distribution function

$$g(r) = \frac{V}{4\pi r^2 N^2} \left\langle \sum_{i} \sum_{j \neq i} \delta(r - |\mathbf{r}_j - \mathbf{r}_i|) \right\rangle$$
(3)

with  $r := |\mathbf{r}|$ . See the supplemental material available online at stacks.iop.org/SMS/26/045012/mmedia for a detailed discussion on why equations (2) and (3) are equivalent to equation (1) when the particle distribution features cylindrical symmetry or is isotropic, respectively.

In practice, the computation of g(r) was performed in the following way. The possible values for the distance r are sorted into *n* discrete bins of thickness  $\Delta r$  with possible distance values  $r_k = (k + 1/2)\Delta r$ , where  $k \in \{0, ..., n - 1\}$ . A histogram of the occurrences of particle distance is computed. The occupation number of the kth bin is incremented whenever  $|\mathbf{r}_{i} - \mathbf{r}_{i}| \in [k\Delta r, (k + 1)\Delta r]$ . This procedure reflects the sum of  $\delta$ -distributions in equation (3). Since each bin represents a spherical shell of finite thickness  $\Delta r$ , the normalization by  $4\pi r^2$ is replaced with the normalization by  $\frac{4}{3}\pi((k+1)^3 - k^3)(\Delta r)^3$ . However, our samples are finite, so there is one complication here. Let  $b_i$  be the distance of particle *i* to the sample boundary. If the interparticle distance  $|\mathbf{r}_j - \mathbf{r}_j|$  would fall into a bin, but  $b_i < |\mathbf{r}_i - \mathbf{r}|$ , the normalization becomes complicated because the spherical shell corresponding to the bin centered around  $\mathbf{r}_i$ intersects with the boundary. We have circumvented this problem by only taking those pairs of particles into account for which  $b_i \ge |\mathbf{r}_i - \mathbf{r}_i|$ . But then a bin only gets the chance to

#### T Gundermann et al

grow if  $b_i \ge (k + 1)\Delta r$ , the outer radius of the spherical shell. Therefore, one division by *N* in equation (3) has to be replaced with a division by the number of particles *i* for which  $b_i \ge (k + 1)\Delta r$ . To summarize, we have used the following formula for the calculation of the radial distribution function

$$g(r_k) \approx \frac{V}{N} \\ \times \left\langle \frac{\sum_i \sum_{j \neq i} \mathbf{1}_{[k\Delta r, (k+1)\Delta r} \left[ (|\mathbf{r}_j - \mathbf{r}_i|) \mathbf{1}_{[0,b_i]} (|\mathbf{r}_j - \mathbf{r}_i|) \right]}{\frac{4}{3} \pi ((k+1)^3 - k^3) (\Delta r)^3 \sum_i \mathbf{1}_{[(k+1)\Delta r, \infty[} (b_i)} \right\rangle, \\ \mathbf{1}_{[a,b]}(x) = \begin{cases} 1 & \text{for} \quad x \in [a, b[, 0] \\ 0 & \text{else.} \end{cases}$$
(4)

The calculation of the cylindrical distribution function  $g(r_{\parallel}, r_{\perp})$  was performed in an analogous fashion. Here, both distances  $r_{\parallel}, r_{\perp}$  have to be discretized. Bins represent cylindrical shells with discretized radii and heights and again count the number of times a separation  $|\mathbf{r}_{j} - \mathbf{r}_{j}|$  falls within their shell. Also the same considerations for the sample boundary apply.

In evaluating the statistics for our experimental systems, the averages were performed for each individual sample separately. For this purpose, sufficiently homogeneous regions were identified as described in the following.

### 4. Results

### 4.1. Statistical analysis of MREs with isotropic particle distribution

First, we had to make sure that the requirement of the homogeneity of the sample is sufficiently met. The criterion was based on the homogeneity of the particle number density within the sample. Imagine around the geometrical center of our cylindrical sample a smaller cylinder of height H and radius R. If the particle number density  $\rho(H, R)$  within the enclosed volume is a sufficiently constant function of H and R, then the sample can be regarded as homogeneous. As an example, we plot in figure 3 for an isotropic sample with a particle content of 15 wt% the particle density  $\rho(H, R = 1.5 \text{ mm})$  within a cylinder of variable height and fixed radius as well as  $\rho(H = 3.0 \text{ mm}, R)$  within a cylinder of fixed height and variable radius. While the former shows stronger fluctuations, especially for large H before the full sample height is reached, the latter remains relatively constant up to the full radius of the sample. The spikes at very low radii and heights are due to the poor statistics when only a few particles fit into the cylinder. The significant decrease at high values of H and R is to some extent due to slight deviations of the sample from a perfect cylindrical shape, which is also visible in figure 1. When the test cylinders that are fitted into the sample for our evaluation reach the overall extent of the sample, these shape irregularities become important. If voids are included in the probe volume, the density drops. We therefore chose a maximum height  $H_m = 3.0$  mm and radius



**Figure 3.** Particle number density  $\rho(H, R)$  within a cylinder of height *H* and radius *R* centered around the geometrical center of an isotropic sample with a particle content of 15 wt%. (a) When the cylinder radius is kept fixed at R = 1.5 mm and its height is varied, the particle density  $\rho(H, R = 1.5 \text{ mm})$  shows some fluctuations, indicating that the sample is not perfectly homogeneous in the axial direction, especially when going beyond H = 3.0 mm. (b) When the height is kept fixed and the radius is varied, the particle number density  $\rho(H = 3.0 \text{ mm}, R)$  shows less fluctuations, up to at least R = 1.5 mm. Since the sample shape slightly deviates from that of a perfect cylinder, here is a significant decrease for both  $\rho(H > 3.2 \text{ mm}, R)$  and  $\rho(H, R > 1.6 \text{ mm})$  when the test cylinder reaches the overall extent of the sample and voids are included in the evaluation.

 $R_m = 1.5$  mm and only used the enclosed sample volume in our calculations.

After determining a sample region that is approximately homogeneous, we calculated the radial distribution function. The results are shown in figure 4. For small interparticle distances we have g(r) = 0, because even the smallest particles in the sample show a finite separation distance between their centers. Starting with  $r \approx 20 \ \mu m$ , g(r) rapidly increases as more and more configurations become possible where also particles of larger size do not overlap. Saturation is already reached at  $r \approx 70 \ \mu m$ . This represents a reasonable value, considering the mean particle diameter of approximately 45  $\mu$ m. From there on g(r) remains at a constant level of 1. Our results suggest that mainly approximate repulsive hardsphere-like interactions between the particles determine the particle arrangement in the sample. If this is the case, almost the same radial distribution function should be recovered when the same particles are redistributed in a random and non-intersecting way. We performed this test by generating artificial statistical ensembles of hard spheres within the same overall volume and with the same distribution of volumes of the individual particles as extracted from the real sample. The protocol is the following. For each particle in the real sample, we generate a spherical particle of identical volume. Then we insert this particle into the available sample volume, one at a time. During each event of insertion, the corresponding particle is placed at a random position, avoiding overlap with previously placed spheres. If there is any overlap with any previously inserted particle, a new random position is generated, otherwise we proceed to the next particle, and so on. When all particles are inserted, the result is an isotropic distribution of hard spheres that have the same volume



**Figure 4.** Radial distribution function for the isotropic sample with a particle content of 15 wt% and vanishing magnetic field. The data are in agreement with the results from a polydisperse hard-sphere model where all particles are transformed into spheres, keeping their volumes as determined experimentally and then randomly distributing them. This suggests that repulsive hard-core-like interactions dominate the particle arrangement during the preparation process of the sample.

distribution as the particles in the real experimental sample. 100 of these artificial distributions were created and the resulting radial distribution functions were averaged. The distribution function obtained from this polydisperse hardsphere model is plotted in figure 4 and shows reasonable qualitative agreement with the real sample. Isotropic samples 158





**Figure 5.** (a) Cylindrical distribution function  $g(r_{\parallel}, r_{\perp})$  for the isotropic sample with a particle content of 15 wt% under the influence of an external magnetic field of B = 270 mT. There is a pronounced peak in the direction parallel to the external field, indicating that the particles prefer to have their neighbors in a direction along the external field. Since this peak is absent in the absence of an external magnetic field, it indicates internal rearrangement upon field application. The radial direction  $g(r_{\parallel} = 0, r_{\perp})$  is mostly featureless. (b) Tomographic scan to visualize the chain formation when an external magnetic field is applied to the initially isotropic sample. These data were obtained in the same way as described in [32].

with a lower particle content lead to very similar results, albeit with worse statistics due the lower total number of particles.

The situation changed when an external magnetic field of B = 270 mT was applied to the sample in axial direction when measuring the particle distribution. In figure 5(a) we illustrate the cylindrical distribution function  $g(r_{\parallel}, r_{\perp})$ . While no significant structure of  $g(r_{\parallel}, r_{\perp})$  is observed in the direction perpendicular to the field, there is a strongly increased probability for each particle to find another one in close vicinity in the parallel direction. In particular, there is a peak at  $r_{\perp} \approx 0$  and  $r_{\parallel} \approx 45 \ \mu m$ . The latter distance corresponds to the mean particle diameter within our samples. Beyond this peak, however, the correlation rapidly decays and there are no striking features anymore. These observations are in agreement with the picture of magnetic particles attracting each other along the external field direction. The attraction seems to be strong enough to put the particles close to contact in spite of the counteracting forces generated by a deformed matrix environment, see figure 5(b). This is in agreement with the picture of chains of magnetic particles forming in the sample under the influence of the external magnetic field [21]. However, higher-order correlation peaks are not clearly identified, possibly due to the relatively low particle content, due to the elastic interactions preventing particles from moving too far, and due to the polydispersity of the particles.

Since the PCF does not contain any direct statement on the number of particles in a chain, a database searching algorithm was developed to determine this number. For this purpose, a cylinder with  $R = 25 \ \mu m$  and  $H = 400 \ \mu m$  was defined around each particle. Each particle that was found inside this cylinder with a center-to-center distance from the initial particle smaller than the sum of the two particle diameters is defined to belong to the same chain. After the assignment, the number of particles organized in chains of a



**Figure 6.** Numbers of particles organized in chains of given size for different particle contents. The chains formed in the isotropic samples when a magnetic field of B = 270 mT was applied. Their average size increases with increasing particle content.

given size were determined and are plotted in figure 6 for the different particle quantities. We observed that the lengths of the chains increase with increasing particle content.

### 4.2. Statistical analysis of MREs with anisotropic particle distribution

As already shown in figure 1, the anisotropic samples created by applying an external magnetic field during the polymerization process feature chain-like aggregates in the direction of the originally applied field. These chains span the entire sample from bottom to top. It has previously been observed that the structure of chains in anisotropic MREs

159



Figure 7. Tomographic results for the horizontal cross-sections through the center of the anisotropic samples with particle contents of (a) 2 wt%, (b) 5 wt%, (c) 10 wt%, and (d) 15 wt%.



**Figure 8.** Two different illustrations of the cylindrical distribution function  $g(r_{\parallel}, r_{\perp})$  for an anisotropic sample with a particle content of 2 wt%. The left plot illustrates the behavior for smaller separation distances. There is a pronounced peak at low  $r_{\perp}$ , which reflects the preferred nearest-neighbor positioning along the axial direction. The correlations in this direction are overall very high and decay slowly. Contrary to that, in the perpendicular direction there are no striking features and the correlation is lost very quickly. The right plot aims to demonstrate the correlations between separate chains. For long distances  $r_{\perp}$ , there is first a depleted region corresponding to the voids between separate chains. After that, however, there is a series of peaks reflecting the positioning of neighboring chains.

typically depends on the particle content [29]. This is also the case for our anisotropic samples. We illustrate horizontal cross-sections through our samples with different particle content in figure 7, where the structural changes with increasing particle content are evident. At low particle content of 2 wt%, the chains are thin and orientated in the direction along the magnetic field initially applied during polymerization. With increasing particle content, the structures begin to thicken and to expand in the direction perpendicular to the magnetic field (figure 7(d)). Obviously, in the directions perpendicular to the anisotropy axis, the particles are not distributed uniformly. Instead, they rather appear to be clustered at certain mutual distances. Such inhomogeneous distributions are known to be able to significantly affect the mechanical response [44].

Again we determined the cylindrical distribution functions. Results for particle contents of 2 and 15 wt% are plotted in figures 8 and 9, respectively. There are obviously huge differences between the directions parallel and perpendicular to the anisotropy axis. Along the direction of the chains the correlation is much stronger and long-ranged, especially for the samples with low particle content. In both samples, there is again a peak at  $r_{\parallel} \approx 45 \ \mu \text{m}$ ,  $r_{\perp} \approx 0$  identifying nearestneighboring particles in the axial direction. In the direction perpendicular to the chains, the correlations are lost much more quickly, especially for the 2 wt% sample. In contrast to that, the sample with 15 wt% particle content features chains of larger thickness in the perpendicular directions, so that the correlations in these directions decay much more slowly. At long distances in the perpendicular direction, we can first observe a depleted region where the probability to find other particles becomes very low and  $g(r_{\parallel}, r_{\perp})$  almost vanishes. Beyond this depleted region, the values increase again and indicate the presence of other chains. This manifests itself as a series of discrete peaks at  $r_{\perp} \ge 500 \,\mu\text{m}$  in the sample with low particle content and as one smeared-out peak in the sample with high particle content. In figure 10 this is illustrated more clearly and also for the other particle contents. There we plot the cylindrical distribution function  $g(r_{\parallel} = 0, r_{\perp})$  only as a function of the perpendicular distance, setting the distance in the axial direction to zero.

T Gundermann et al



Figure 9. Same as figure 8 but for a particle content of 15 wt%. The chains in these systems are typically much thicker and less ordered. Thus, compared to the particle content of 2 wt% there is less correlation between particles along the chains but more in the directions perpendicular to the chain axes. For long distances in the perpendicular directions there is again a depleted area where  $g(r_{\parallel}, r_{\perp})$  drops close to zero. Beyond this depletion zone one smeared-out peak reflects the positioning of neighboring chains.



**Figure 10.** Cylindrical distribution functions  $g(r_{\parallel} = 0, r_{\perp})$  of anisotropic samples for different particle contents, where only  $r_{\perp}$  is varied and  $r_{\parallel}$  is set to zero. This plot illustrates more clearly the correlations between separate chains and the depleted region due to the voids between the chains where it is very unlikely to encounter another particle.

To further quantify the correlations between the particle chains, we also performed an analysis using a Delaunay triangulation method [29, 45]. First, for different cross-sectional planes, see figure 7, the centers of the chains were detected. Using Delaunay triangulation, each plane was tessellated into triangles with their vertices located in the chain centers. The distances between the chains were then determined as the lengths of the edges of these triangles.

An example for the resulting distributions is shown in figure 11(a) for a particle content of 15 wt%. Approximately, the distances between the particle chains follow a Gaussian distribution. Extracting the average chain separation distance, we found for our samples that the chain distances first decrease from the 2 wt% to the 5 wt% case, see figure 11(b). content. For the particle content of 5 wt%, the chains still remain thin and aligned, as already shown in figure 7. When the particle content is further increased, the chains start to expand in the direction perpendicular to the magnetic field. This leads to a decreasing number of chains and, therefore, to an increase in chain distance. 5. Summary

For the higher particle contents of 10 and 15 wt%, we then

observed both the chain separation distances and the chain

thicknesses to increase. This behavior is connected to the

dependence of the total number of chains on the particle

This work demonstrates the possibility to extract and quantify particle distributions within MRE via X-µCT tomographic measurements. A statistical analysis of these distributions leads to insights into the particle interactions within such materials. X-µCT provides a method to detect individual particles inside these systems and to track their rearrangement when an external stimulus is applied. In a measured tomogram, particles are still clustered and not individually visible. By using methods of digital image evaluation, clustered particles can be distinguished. This provides the possibility to analyze their geometrical properties and to generate a database for statistical processing. From the database, PCF characterizing the particle arrangements were calculated. Several different experimental samples were produced in this work, all of them consisting of particles of carbonyl-iron powder embedded into a polymeric matrix made of PDMS. Isotropic and anisotropic samples were synthesized with particle contents of 2, 5, 10, and 15 wt%. The anisotropic samples were created by applying a magnetic field during the polymerization process, which led to the formation of chains along the field direction. For the isotropic samples, tomographic studies with and without an external magnetic field of B = 270 mTapplied during data collection have been carried out. The 0.2 0.4 0.6 0.8 1.0 1.2

chain separation distance [mm]

0.0

(a)



Figure 11. (a) Histogram of the distances between particle chains obtained from the Delaunay triangulation for a particle content of 15 wt%. The chain distances obviously follow a Gaussian distribution, from which an average chain distance can be extracted. (b) Plots of the average chain distances and the number of chains for all considered particle contents.

1.4

analysis of the PCF for these isotropic samples indicated the absence of structures in the absence of external magnetic fields. When an external magnetic field is applied, the nearest particle neighbors are most likely found along the magnetic field direction as the particles attract each other along this direction. Apparently, smaller chain-like structures are formed under the influence of the external field in the isotropic samples. However, larger anisotropic structures seem to rarely emerge. The tomographic measurements on the anisotropic samples were carried out without an external magnetic field applied during data acquisition, because the field did not significantly alter the structures. We characterized the morphology of the chain-like aggregates in these anisotropic samples by determining corresponding PCF. The chain morphology strongly depends on the particle content of the samples. An increasing particle content leads to increased chain thicknesses perpendicular to the magnetic field. Furthermore, we were able to address correlations in the positioning of separate chains.

In summary, a tool was described to characterize the distribution of particles in particle-matrix systems. In the future, measurements on samples with higher particle contents should be performed. Also the statistics for the calculation of the PCF can be improved by combining the tomographic results of more samples. The obtained correlation functions can then be used as an input for statistical theories. Moreover, measurements on samples with still higher particle contents and, additionally, measurements on anisotropic samples exposed to an external magnetic field perpendicular to the chain axes should be performed.

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(b)

0 2 4 6

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particle content [wt.%]

10 12 14 16

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### Supplemental material to: Statistical analysis of magnetically soft particles in magnetorheological elastomers

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**Abstract.** In the main article, we have introduced a cylindrical distribution function to characterize particle distributions with an overall cylindrical symmetry. We have used this function to analyze our anisotropic cylindrical samples that were produced or probed under the influence of a magnetic field in axial direction. Here, we show that this approach in the case of cylindrical symmetry contains the same information as the full pair correlation function. In the case of an overall isotropic distribution, also the radial distribution function contains an equal amount of information.

The pair correlation function is a standard approach to characterize statistical particle distributions in fluids [1, 2, 3]. It is defined in the main article for overall spatially homogeneous distributions as

$$g(\mathbf{r}) = \frac{V}{N^2} \left\langle \sum_{i} \sum_{j \neq i} \delta \left( \mathbf{r} - (\mathbf{r}_j - \mathbf{r}_i) \right) \right\rangle \,. \tag{1}$$

Here N corresponds to the number of particles, V to the sample volume,  $\mathbf{r}_i = (x_i, y_i, z_i)$ and  $\mathbf{r}_j = (x_j, y_j, z_j)$  are the positions of particles i, j, respectively, i, j = 1, 2, ..., N, and  $\langle \cdot \rangle$  denotes the ensemble average. Let  $\rho^{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N)$  be the probability density of finding the N particles in the sample at positions  $\mathbf{r}_1, \ldots, \mathbf{r}_N$ . In a sufficiently large statistical ensemble,  $\rho^{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N)$  does not depend on the ordering of its arguments. Then the probability density  $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$  to find any two particles at positions  $\mathbf{r}_1, \mathbf{r}_2$ , irrespective of the positions of the other particles, is given by

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int \rho^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) \, d\mathbf{r}_3 \dots d\mathbf{r}_N \,. \tag{S1}$$

With this we can show the following relation between  $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$  and the pair correlation function  $g(\mathbf{r})$ 

$$g(\mathbf{r}) = \frac{V}{N^2} \int \rho^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) \sum_i \sum_{j \neq i} \delta\left(\mathbf{r} - (\mathbf{r}_j - \mathbf{r}_i)\right) d\mathbf{r}_1 \dots d\mathbf{r}_N$$

2

Supplemental Material

$$= \frac{V}{N^2} \sum_{i} \sum_{j \neq i} \int \rho^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) \,\delta\left(\mathbf{r} - (\mathbf{r}_j - \mathbf{r}_i)\right) d\mathbf{r}_1 \dots d\mathbf{r}_N$$

$$= \frac{V}{N^2} N(N-1) \int \rho^{(N)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \,\delta\left(\mathbf{r} - (\mathbf{r}_2 - \mathbf{r}_1)\right) d\mathbf{r}_1 \dots d\mathbf{r}_N$$

$$= \frac{V}{N^2} \int \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \,\delta\left(\mathbf{r} - (\mathbf{r}_2 - \mathbf{r}_1)\right) d\mathbf{r}_1 \,d\mathbf{r}_2$$

$$= \frac{V}{N^2} \int \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_1 + \mathbf{r}) \,d\mathbf{r}_1$$

$$= \frac{V^2}{N^2} \rho^{(2)}(\mathbf{r}), \qquad (S2)$$

where  $\rho^{(2)}(\mathbf{r}) := \frac{1}{V} \int \rho^{(2)}(\mathbf{r}', \mathbf{r}' + \mathbf{r}) d\mathbf{r}'$  gives the probability density to find two particles at a separation  $\mathbf{r}$  in a homogeneous sample. This shows what has already been mentioned in the main article: that the pair correlation function  $g(\mathbf{r})$  relates the actual nonuniform distribution  $\rho^{(2)}(\mathbf{r})$  for the separations  $\mathbf{r}$  of particle pairs to the uniform distribution  $(N/V)^2$  in the ideal gas.

In the case of a particle distribution that is not only homogeneous but also isotropic,  $\rho^{(2)}(\mathbf{r}) = \rho^{(2)}(r)$  holds, and we define  $\rho^{i(2)}(r) := 4\pi r^2 \rho^{(2)}(r)$ .  $\rho^{i(2)}(r)$  gives the probability density of finding a pair of particles at a distance  $r := |\mathbf{r}|$ . Then there is no loss of information in considering the radial distribution function  $g^i(r)$ , defined in the main article as

$$g^{i}(r) = \frac{V}{4\pi r^{2} N^{2}} \left\langle \sum_{i} \sum_{j \neq i} \delta\left(r - |\mathbf{r}_{j} - \mathbf{r}_{i}|\right) \right\rangle \,. \tag{3}$$

We briefly show that this definition is analogous to Eq. (S2) in the isotropic case, in the sense that it relates the probability density  $\rho^{i(2)}(r)$  of finding a pair of particles at a certain distance to the distribution of particle distances in the ideal gas:

$$g^{i}(r) = \frac{V}{4\pi r^{2} N^{2}} \int \rho^{(N)}(\mathbf{r}_{1}, \dots, \mathbf{r}_{N}) \sum_{i} \sum_{j \neq i} \delta\left(r - |\mathbf{r}_{j} - \mathbf{r}_{i}|\right) d\mathbf{r}_{1} \dots d\mathbf{r}_{N}$$

$$= \frac{V}{4\pi r^{2} N^{2}} \int \rho^{(2)}(\mathbf{r}_{1}, \mathbf{r}_{2}) \delta\left(r - |\mathbf{r}_{2} - \mathbf{r}_{1}|\right) d\mathbf{r}_{1} d\mathbf{r}_{2}$$

$$= \frac{V}{4\pi r^{2} N^{2}} \int \delta\left(\mathbf{r}' - (\mathbf{r}_{2} - \mathbf{r}_{1})\right) \rho^{(2)}(\mathbf{r}_{1}, \mathbf{r}_{2}) \delta\left(r - |\mathbf{r}_{2} - \mathbf{r}_{1}|\right) d\mathbf{r}_{1} d\mathbf{r}_{2} d\mathbf{r}'$$

$$= \frac{V}{4\pi r^{2} N^{2}} \int \rho^{(2)}(\mathbf{r}_{1}, \mathbf{r}_{1} + \mathbf{r}') \delta\left(r - r'\right) d\mathbf{r}_{1} d\mathbf{r}'$$

$$= \frac{V^{2}}{4\pi r^{2} N^{2}} \int \underbrace{\rho^{(2)}(\mathbf{r}')}_{=\rho^{i(2)}(r')/4\pi r'^{2}} \delta\left(r - r'\right) d\mathbf{r}'$$

$$= \frac{V^{2}}{4\pi r^{2} N^{2}} \rho^{i(2)}(r) . \tag{S3}$$

Together with Eq. (S2), we have  $g^i(r) = g(\mathbf{r})$ , and we may therefore drop the superscript <sup>*i*</sup>. For isotropic distributions, g(r) and  $g(\mathbf{r})$  as introduced in the main article therefore contain the same amount of information.

Finally, for the analysis of our anisotropic distributions with cylindrical symmetry, we made use of the cylindrical distribution function  $g^c(r_{\parallel}, r_{\perp})$  defined in the main article

164
Supplemental Material

as

$$g^{c}(r_{\parallel}, r_{\perp}) = \frac{V}{4\pi r_{\perp} N^{2}} \left\langle \sum_{i} \sum_{j \neq i} \delta\left(r_{\parallel} - |z_{j} - z_{i}|\right) \delta\left(r_{\perp} - \sqrt{(x_{j} - x_{i})^{2} + (y_{j} - y_{i})^{2}}\right) \right\rangle.$$
(2)

In this situation, due to the cylindrical symmetry,  $\rho^{(2)}(\mathbf{r}) = \rho^{(2)}(r_{\parallel}, r_{\perp})$  holds, and we define  $\rho^{c(2)}(r_{\parallel}, r_{\perp}) := 4\pi r_{\perp} \rho^{(2)}(r_{\parallel}, r_{\perp})$ .  $\rho^{c(2)}(r_{\parallel}, r_{\perp})$  is the probability density of finding a pair of particles with a distance of  $r_{\parallel}$  in axial direction and a distance  $r_{\perp}$  in the transversal direction. Therefore, the cylindrical distribution function  $g^{c}(r_{\parallel}, r_{\perp})$  likewise depends only on these two distances. Again, we briefly verify that Eq. (2) gives a result in analogy to Eq. (S2) in the case of a particle distribution of cylindrical symmetry:

$$g^{c}(r_{\parallel}, r_{\perp}) = \frac{V}{4\pi r_{\perp} N^{2}} \int \rho^{(N)}(\mathbf{r}_{1}, \dots, \mathbf{r}_{N}) \sum_{i} \sum_{j \neq i} \delta\left(r_{\parallel} - |z_{j} - z_{i}|\right) \\ \times \delta\left(r_{\perp} - \sqrt{(x_{j} - x_{i})^{2} + (y_{j} - y_{i})^{2}}\right) d\mathbf{r}_{1} \dots d\mathbf{r}_{N} \\ = \frac{V}{4\pi r_{\perp} N^{2}} \int \rho^{(2)}(\mathbf{r}_{1}, \mathbf{r}_{2}) \delta\left(r_{\parallel} - |z_{2} - z_{1}|\right) \\ \times \delta\left(r_{\perp} - \sqrt{(x_{2} - x_{1})^{2} + (y_{2} - y_{1})^{2}}\right) d\mathbf{r}_{1} d\mathbf{r}_{2} \\ = \frac{V}{4\pi r_{\perp} N^{2}} \int \delta\left(\mathbf{r}' - (\mathbf{r}_{2} - \mathbf{r}_{1})\right) \rho^{(2)}(\mathbf{r}_{1}, \mathbf{r}_{2}) \delta\left(r_{\parallel} - |z_{2} - z_{1}|\right) \\ \times \delta\left(r_{\perp} - \sqrt{(x_{2} - x_{1})^{2} + (y_{2} - y_{1})^{2}}\right) d\mathbf{r}_{1} d\mathbf{r}_{2} d\mathbf{r}' \\ = \frac{V}{4\pi r_{\perp} N^{2}} \int \rho^{(2)}(\mathbf{r}_{1}, \mathbf{r}_{1} + \mathbf{r}') \delta\left(r_{\parallel} - r'_{\parallel}\right) \delta\left(r_{\perp} - r'_{\perp}\right) d\mathbf{r}_{1} d\mathbf{r}' \\ = \frac{V^{2}}{4\pi r_{\perp} N^{2}} \int \underbrace{\rho^{(2)}(\mathbf{r}')}_{=\rho^{c(2)}(r'_{\parallel}, r'_{\perp})/4\pi r'_{\perp}} \delta\left(r_{\parallel} - r'_{\parallel}\right) \delta\left(r_{\perp} - r'_{\perp}\right) d\mathbf{r}'$$
(S4)

Thus, for cylindrically symmetric distributions,  $g(r_{\parallel}, r_{\perp})$  and  $g(\mathbf{r})$  as introduced in the main article contain the same amount of information. Together with Eq. (S2), we have  $g^{c}(r_{\parallel}, r_{\perp}) = g(\mathbf{r})$ , and we may therefore drop the superscript <sup>c</sup>.

In summary, the pair correlation function in Eq. (1) gives the most general and applicable form for homogeneous particle distributions. For particle distributions featuring cylindrical symmetry, the cylindrical distribution function in Eq. (2) contains the same amount of information. In the case of an isotropic particle distribution, the radial distribution function in Eq. (3) may be used and it is then equivalent in information to both, Eqs. (1) and (2).

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## Chapter 3. Concluding remarks

Magnetic elastomers and gels are fascinating smart composites of colloidal magnetic particles embedded into a cross-linked polymer matrix. Their physical properties can be reversibly tuned on demand by external magnetic fields. Many studies on magnetic elastomers have demonstrated that the mesoscopic processes have a strong influence on the properties that can be observed on the macroscale. It is, therefore, important to understand the mesoscale behavior also when moving over to a macroscopic description. Contributing by the present thesis to this effort, we have investigated how the mesoscopic structure influences the magneto-responsive properties, we have uncovered a new fascinating superelastic stress-strain behavior, and we have devised a framework to apply density functional theory to magnetic elastomers.

Important structural aspects are, for example, the particle distribution as well as the type of magneto-elastic coupling between the magnetic filler particles and the polymer matrix. To investigate their influence, we have begun by considering minimal models. In **Paper I**, using a simple dipole-spring representation for the composite, we have analyzed how the distribution of magnetic particles controls the tunability of the elastic modulus by external magnetic fields. In this context, we have also demonstrated that coarse-grained models for the material, that are restricted to affine deformations, are prone to mispredict the behavior if the particle configuration is not regular enough, such as is often the case in typical experimental samples. This work could provide future modeling approaches with a guideline to when the approximation of affine deformations is justified.

Understanding how the structure determines the dynamic relaxation behavior of the materials is important for applications like tunable dampers or vibration absorbers, as well as to predict the response times of actuators. In **Paper II**, we have extended our dipole-spring model to also include a rotational magneto-elastic coupling between particles. We have then characterized the appearance of the dominant relaxation modes as well as their corresponding relaxation rates in dependence of the magneto-elastic coupling, the distribution of the particles, and the strength of an applied magnetic field. We have found that all three can have a significant influence on the relaxation behavior.

Also the buckling behavior of paramagnetic chains embedded in a soft gel, that was

observed experimentally in **Paper III**, depends on the structure of the chains and the surrounding matrix. There we have seen that chains of different length display a different number of half-wave oscillations. The buckling amplitude can be controlled by the strength of the applied magnetic field as well as the softness of the matrix. Furthermore, our experimental observations and theoretical models suggest that a certain bending rigidity of the chains is necessary to explain the observed buckling behavior. This might be a hint that such a bending rigidity is an important structural property also in other experimental systems containing chain-like aggregates.

Of course, the importance of the mesoscopic structure does not only pose challenges, but also offers opportunities to engineer the material on this level. So far, during synthesis, the structural arrangement of the particles within the composite is mostly controlled by applying an external magnetic field, e.g., to create anisotropic samples with a certain chain morphology. Perhaps, a finer control over the particle distribution could be achieved by additionally using electric fields together with magnetic particles that are also electrically polarizable [274–276].

As the main topic of this thesis, we have revealed by numerical simulations in **Paper IV** that the non-linear stress-strain behavior of anisotropic magnetic elastomers can contain a fascinating feature called superelasticity under uniaxial elongation. The superelastic behavior appears as a plateau-like regime in the stress-strain curve, where the sample becomes susceptible to large-scale deformations while the applied load is barely increased. We have identified two deformation-induced restructuring processes within the material that generate the superelasticity. The most important one is a detachment mechanism of embedded chain-like particle aggregates gradually breaking up into smaller segments. Additionally there is a flipping mechanism of magnetic moments. Both mechanisms respond to applied external magnetic fields allowing to tune, tailor, and switch off the superelastic behavior on demand. This on-demand response could be interesting for for applications like actuators, passive dampers, or easily applicable gaskets or wound dressings.

Again, the behavior can be influenced via the mesoscopic structure. In **Paper V**, we have investigated how different types of rotational magneto-elastic coupling affect the appearance of the superelastic plateau. In the case of magnetic moments that can freely reorient with respect to the carrying particles, the flipping mechanism is active and the superelastic plateau is characterized by a pronounced hysteresis. Furthermore, because of the easy reorientation of the magnetic moments, the material is particularly tunable by magnetic fields. An applied magnetic field parallel to the axes of the chain-like aggregates and the imposed strain switches the flipping mechanism off. This removes the hysteresis, and alters the shape of the superelastic plateau. When a field is applied perpendicular to the axes of the chains instead, the detachment mechanism can be deactivated, which completely switches off the superelasticity. Due to the easy reorientation of magnetic moments, these changes can be induced with relatively low external field strengths. In contrast, when the magnetic moments are fixed to the particle axes and, thus, rotationally coupled to the surrounding polymer matrix, it

becomes harder to reorient them. Then the flipping mechanism is basically inactive and there is no pronounced hysteresis from the start. Additionally, significantly stronger perpendicular magnetic fields are required to switch off the superelastic behavior.

Probably, the structure of the anisotropic numerical samples can be further optimized towards even stronger superelasticity effects. For the particle distribution in the anisotropic elastomer, we have so far assumed straight chain-like aggregates that percolate the sample, with finite gaps of elastic material separating neighboring particles in a chain. The gaps strongly support the detachment mechanism because they provide a medium to store elastic pre-stresses within the chains. These pre-stresses can then be released when the sample is elongated. For a given magnetization of the particles, there should be an optimum gap thickness that maximizes the pre-stresses. As a next step, also samples with smaller staggered chain-like aggregates of varying length should be investigated. Exploring a certain waviness of the chains should not affect detachment mechanism too much. However, strong deviations from straight aggregates should lead to a qualitatively different behavior [149]. Finally, in many experiments the particles are of irregular shapes and sizes, so it should be tested if this affects the behavior [70, 71, 277].

As an approximation, in our numerical representation of the anisotropic magnetic elastomer, we have assumed dipolar magnetic interactions between the particles, although their mutual distance in our numerical samples can be quite small. Nevertheless, the crucial prerequisite for superelasticity is that there is a strong attraction at short distances between neighboring particles in the chains, such that there is a high magnetic energy barrier for their detachment. This is, of course, still fulfilled when the magnetization of the particles is resolved in more detail [169, 173]. Another approximation we have made concerns the representation of the elastic matrix as a mesh of affinely deformable tetrahedra. In our case of a nearly-incompressible elastomer, each tetrahedron is associated with a corresponding constraint of quasiincompressibility. However, the number of tetrahedral nodes in the complete mesh, and therewith the number of deformational degrees of freedom, is significantly lower than the number of constraints. Such tetrahedral meshes are known to overestimate the stiffness of the material for this reason. By using more sophisticated tetrahedral volume elements, the number of constraints can be adjusted to the number of degrees of freedom [278–280]. Implementing these schemes into our numerical approach would allow for a better quantitative agreement with experiments and detailed continuum mechanical calculations [149, 155–159].

Since we have identified the mesoscopic processes that lead to superelastic stressstrain behavior in anisotropic magnetic elastomers, it should be possible to introduce them also into a coarse-grained macroscopic description. For this purpose, the ongoing restructuring due to detachment and flip events could be expressed by corresponding macroscopic variables. Detachment could be expressed by relative strains between parts of the chains and the surrounding matrix, which take stress storage and release within the chain-like aggregates into account. Reorientation of magnetic moments could be expressed by relative rotations between the chain axes and the macroscopic, possibly staggered, magnetization [177].

The phenomenology of superelasticity that we have observed in magnetic elastomers shows some analogies to the superelastic behavior in shape-memory alloys. In the latter, the superelastic behavior is fueled by stress-induced phase transitions. This raises the question whether the flipping and detachment restructuring mechanisms that enable the superelasticity in magnetic elastomers show the characteristics of a phase transition as well. In our approach, we have only considered small system sizes and neglected thermal fluctuations so that it is not possible to draw a definite conclusion on the basis of existing results. Using minimalistic mesoscopic models that can access much larger system sizes and include thermal fluctuations could shed some light on this question.

As the final topic of this thesis, we have pursued a statistical description of magnetic elastomers. Most importantly in **Paper VI**, we have devised a framework to apply density functional theory to magnetic elastomers. Such statistical approaches offer the possibility to calculate macroscopically relevant material parameters while taking the mesoscopic particle correlations as well as the particle–particle interactions into account. Normally, such a description is restricted to ensembles of indistinguishable particles. This poses a challenge, because in magnetic elastomers the particles can be distinguished by the positions inside the elastic matrix at which they are permanently embedded. Here we have successfully mapped the distinguishable particles within a one-dimensional dipole-spring model to an ensemble of indistinguishable particles governed by effective pair interactions. In this way, we have opened up density functional theory as a new method for describing these materials. Moreover, other statistical mechanical tools that rely on indistinguishable particles, such as liquid integral theory, become applicable as well.

Future extensions of this work could include more degrees of freedom, such as rotations of magnetic moments, or different shapes and sizes of the particles [281–284]. Transferring our static approach to dynamical density functional theory [285–290] should be straightforward as well and open up the description of dynamical relaxation processes or the behavior under cyclic deformation. Our ideas and concepts might also act as a guideline to transfer statistical mechanical descriptions like density functional theory to higher spatial dimensions.

Experimentally realistic particle distributions could be a valuable input for these theories, as they encode the mesoscopic structural informations. In **Paper VII**, we have statistically analyzed the particle distributions in experimental samples for which the structural data had been provided by X-ray tomography. In particular, we have determined how the particle correlation functions change when homogeneous magnetic fields are applied to the samples. When the field is applied to an already cured isotropic sample, small chain-like clusters oriented in the direction of the field temporarily form. This is reflected by the pair correlation functions in the form of

an increased statistical probability that two particles are close to each other in this direction. In contrast, when the field is applied before and during the synthesis, longer chain-like aggregates form that remain permanently imprinted in the sample. For such samples, we have analyzed what kind of chain morphology arises when the filler content of magnetic colloidal particles in the samples is varied. At the current stage, the particle detection within experimental samples is still challenging. Hence, the available statistical data for the calculation of pair correlation functions are limited. However, once these methods become more advanced, a statistical characterization of experimental samples might serve as an input to statistical theories.

In conclusion, magnetic elastomers and gels will remain an exciting topic for future research. In the last years, there has been much progress on enhancing the magnetoelastic effects that are relevant for applications. A better theoretical understanding and the discovery of new fascinating effects will open up the pathway to the development of new and the optimization of existing applications.

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