Rudolf Weeber*, Patrick Kreissl and Christian Holm

18 Magnetic field controlled behavior of magnetic gels studied using particle-based simulations

Abstract: This contribution provides an overview of the study of soft magnetic materials using particle-based simulation models. We focus in particular on systems where thermal fluctuations are important. As a basis for further discussion, we first describe two-dimensional models which demonstrate two deformation mechanisms of magnetic gels in a homogeneous field. One is based on the change of magnetic interactions between magnetic particles as a response to an external field; the other is the result of magnetically blocked particles acting as cross-linkers. Based on the qualitative behavior directly observable in the two-dimensional models, we extend our description to three-dimensions. We begin with particle-cross-linked gels, as for those, our three-dimensional model also includes explicitly resolved polymer chains. Here, the polymer chains are represented by entropic springs, and the deformation of the gel is the result of the interaction between magnetic particles. We use this model to examine the influence of the magnetic spatial configuration of magnetic particles (uniaxial or isotropic) on the gel's magnetomechanical behavior. A further part of the article will be dedicated to scale-bridging approaches such as systematic coarse-graining and models located at the boundary between particle-based and continuum modeling. We will conclude our article with a discussion of recent results for modeling time-dependent phenomena in magnetic-polymer composites. The discussion will be focused on a simulation model suitable for obtaining AC-susceptibility spectra for dilute ferrofluids including hydrodynamic interactions. This model will be the basis for studying the signature of particle–polymer coupling in magnetic hybrid materials. In the long run, we aim to compare material properties probed locally via the AC-susceptibility spectra to elastic moduli obtained for the system at a global level.

Keywords: AC-susceptibility; computer simulations; gel deformation; magnetic gels; multiscale modeling; simulation models.

18.1 Introduction

In recent years, there has been an increased trend towards miniaturization in diverse fields of application. This includes technical applications, like sensing and actuation

***Corresponding author: Rudolf Weeber**, Institute for Computational Physics, University of Stuttgart, Stuttgart, Germany, E-mail: rudolf.weeber@icp.uni-stuttgart.de

Patrick Kreissl and Christian Holm, Institute for Computational Physics, University of Stuttgart, Stuttgart, Germany

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[1, 2], so-called ‘lab on a chip’ devices, or microrobotics [3, 4] and biomedical treatment. Realizing such systems often relies on the availability of suitable ‘smart materials’, the properties of which can change under external stimuli. Magnetic composite materials are a fascinating example for such smart materials. They typically consist of magnetic nano- or micro-particles which are embedded in a polymer suspension or gel matrix [5–8]. They combine the magnetic properties of a ferrofluid [9, 10] with the elastic and viscoelastic properties of polymers [11]. Application and modification of an external magnetic field allows for the contactless dynamic control of some mechanical properties of the magnetic composites, such as their motion, shape deformation, or (anisotropic) stiffness. These special properties as well as the fact that the human body is transparent to magnetic fields makes magnetic composite materials particularly promising candidates for bio-medical applications [12]. The possible applications range from targeted drug delivery with externally controlled release to magnetic resonance-guided placement and surveillance of artery stents. Moreover, there are cases where treatment is based on the direct injection of magnetic particles or composites into the human body [13] – for example for imaging purposes, dissolving blood clots, or even for cancer treatment via directed chemotherapy [14–16] or externally induced local hyperthermia [17]. All of these applications are affected by or actually rely on the interaction of magnetic particles with their non Newtonian surrounding. Therefore, a deep understanding of the underlying coupling mechanisms is key when it comes to tailoring magnetic particles or composite materials to specific use cases. Examples of typical experimental methods for investigating magnetic composite materials include magnetic particle spectroscopy (MPS) [18], small-angle neutron scattering (SANS) [19–21], small-angle X-ray scattering (SAXS) [22, 23], cryo-transmission electron microscopy (cryo-TEM) [24, 25], and X-ray microtomography [26] which give valuable insight into their structure. Unfortunately however, in many systems, the details of this coupling are not fully known and difficult to determine experimentally.

In such cases, computer simulations can be a valuable tool, as they allow studying well-defined systems, the properties of which can be easily modified. Depending on the length-scales one is interested in, computational modeling requires different levels of detail. On the larger scales – mostly relevant for technical applications – continuum descriptions of magnetic composites [27, 28] can be solved using, e.g., finite element methods (FEM) [29, 30]. On the mesoscale, models include single magnetic particles. A theoretical approach for this scale is density functional theory (DFT) [31]. In this manuscript, we focus on particle-based molecular dynamics approach for simulating the magnetic, deformational and (visco)-elastic response of magnetic gels and magnetic particles in polymer suspensions. We will start with a study of the magnetic field-induced deformation of two-dimensional gel models in Sec. 18.2. The deformation mechanisms in three dimensions will be discussed in Sec. 18.3. Scale-bridging approaches to reduce the computational effort and to transfer knowledge between different levels of descriptions will be given in Sec. 18.4. Finally, in Sec. 18.5 we present

a basic computational strategy for modeling frequency dependent susceptibility measurements on magnetic nanoparticles in polymer solution.

18.2 Direct observation of magnetic-field induced deformation in two-dimensional models

Three distinct mechanisms can lead to the deformation of a magnetic gel in a magnetic field. First, an inhomogeneous magnetic field exerts a force on magnetic moments. This force points along the field gradient. As a consequence, a magnetic gel can be deformed by fixing it at one end and applying a field gradient along the direction in which a deformation is desired [32]. More complex deformations can be achieved, by making the magnetic gel stiffer in certain regions, e.g., through more intense polymerization.

The second and third mechanisms for field-controlled deformation of magnetic gels pertain to homogeneous magnetic fields. This has the advantage of not causing a migration of the gel, even if it is not fixed to a substrate. In a homogeneous field, a deformation can be mediated by the interaction between the magnetic particles. These interactions are, on average, small and isotropic in the field-free case, as the magnetic particles are randomly aligned. In an external field, the magnetic moments in the gel get aligned parallel to the field. This results in an anisotropic interaction between the particles throughout the system. These interactions in turn lead to a repositioning of the magnetic particles and a strain of the surrounding polymer matrix. Macroscopically, this is described by minimizing the sum of two energetic contributions: (I) the energy needed for the elastic deformation and (II) the demagnetization energy [33]. The behavior has also been observed experimentally [34, 35]. This macroscopic description neglects the details of the spatial distribution of the magnetic particles in the system and their local mobility. It has been shown that both factors can influence the deformation [29, 36–38]. A further mechanism for field-induced deformation in homogeneous magnetic fields exists in a special class of magnetic gels. In these gels, magnetically blocked particles act as the cross-linkers of the gel [39–41]. In these so-called particle cross-linked gels, the polymer chains are covalently bound to specific points on the surface of the magnetic particles. Once an external field rotates the magnetic particles, the attached polymer chains have to follow. Their ends wrap around the magnetic particles, effectively shortening the length of the polymers. This leads to shrinkage of the gel.

Although experimental systems are, with very few exceptions [42, 43], three-dimensional, we will begin by introducing two-dimensional simulation models. The deformation mechanisms described above can be observed directly – and visually –, in two-dimensional models. For three-dimensional models, visual inspection is typically no longer useful and the analysis is carried out purely quantitatively. The simulations discussed below have been carried out with the ESPResSo molecular dynamics software [44–46].

18.2.1 Deformation through the change of magnetic interactions

Let us turn to a model demonstrating the deformation of magnetic gels through changing the magnetic interactions between the particles. We call this model I in Ref. [37], where a more technical description can be found. The system has we boundary conditions. The model gel is constructed by placing particles on a regular square lattice. These particles will be the nodes of the network. They are then connected by polymers represented via bead–spring models. Four polymer chains are attached to each node. The network is made magnetic by assigning a randomly aligned magnetic moment to every second particle in the chains. Once the simulation starts, the particles can move freely, but the connections along the chains and at the nodes are maintained. Also the magnetic moments can rotate freely. This combination of a 2D model but 3D rotation is called quasi-two dimensional. The magnetic particles interact via the dipole–dipole interaction. This is suitable for single-domain particles, for magnetizable particles we refer the reader to Ref. [47]. There is no direct coupling between the rotation of the magnetic moments and the polymer chains. We hence describe magnetic particles which are either only loosely connected to the polymer backbone, or which realign their moment internally via the Néel mechanism. Entropy is of importance both, for polymers and for nanometer-size magnetic particles. Therefore, thermal fluctuations are taken into account for both, translation and rotation using the Langevin equation [48]. Due to the fluctuations, for quantitative observations, one has to average over many snapshots. When no external field is applied, the gel keeps a roughly square-like shape originating from its initial construction, see Figure 18.1. When a field is applied, the sample deforms strongly. It elongates parallel to the field direction and shrinks in the perpendicular one. While all chain orientations are equally favorable in the field-free case, this is no longer true in an external magnetic field, where the magnetic moments in the chains are aligned parallel to the field. In all chains aligned roughly parallel to the external field, the magnetic moments are in a head-to-tail configuration which is energetically favorable. In chains oriented perpendicular to the external field, the magnetic moments would be in a parallel side-by-side configuration which is highly unfavorable. Hence, those chains bend towards the field direction. Lastly, the gel is thinner at the ends than in the middle. Macroscopically, this can be related to a lowering of the demagnetization energy which is low for an ellipse aligned parallel to the local magnetization within the gel.

As can be seen in Figure 18.2, the overall area of the gel decreases, when it is exposed to a magnetic field. In this figure, we compare the area of the gel with and without applied fields for different strengths of the dipolar interaction. We use the dipolar interaction parameter

$$\lambda = \frac{\mu_0 m^2}{4\pi\sigma^3} \frac{1}{k_B T}, \quad (18.1)$$

Figure 18.1: Snapshots of gel Model I from Ref. [37] based on polydisperse polymers, i.e., those with randomized chain length. Particles carrying a magnetic moment are highlighted with red color. The model describes a situation in which the interaction between the magnetic particles in the gel is strong compared to the thermal energy. In this case, aligning the dipoles by applying an external magnetic field will result in an interaction between them which is direction dependent throughout the entire system. In combination with the elasticity provided by the network of chains, this results in a deformation of the gel. The field-free case is shown on the left. A field is applied along the x -direction, on the right-hand side. The gel elongates parallel to the external field and shrinks in the perpendicular direction. Chains aligned perpendicular to the field would lead to unfavorable dipolar interactions between the magnetic particles in those chains. Hence, the chains bend towards the field direction. This figure is based on data from Ref. [37].

which compares the interaction energy of two touching magnetic particles of diameter σ and magnetic moment m with the thermal energy $k_B T$. As can be seen the shrinkage of the gel saturates for increasing dipole strengths. This is due to excluded volume and entropic forces limiting a further compression of the gel. Once the nonmagnetic

Figure 18.2: Area of a gel with and without an external magnetic field applied, for different strength of the dipole–dipole interaction λ . It can be seen that for increasing dipole moments, the contraction of the gel saturates quickly, because the internal pressure, caused by entropy and excluded volume, prevents further shrinking. Even without an external magnetic field, the gel area decreases with an increase of λ . Adapted from Ref. [37] with permission from the Royal Society of Chemistry.

particles positioned in between the magnetic ones are pushed aside, a further compression could only be achieved by overcoming the steep excluded volume interactions. This ‘hardening’ of the gel has also been observed in other models [49]. For further details and a more quantitative discussion, we refer to Ref. [37].

18.2.2 Field-controlled deformation of particle cross-linked gels

Let us now turn to gels in which magnetic particles act as cross-linkers. Snapshots of a corresponding model (model II of Ref. [37]) are shown in Figure 18.3. The model is again constructed by initially placing the nodes of the network on a square lattice. Here, however, the nodes are the magnetic nanoparticles. Their magnetic moments are chosen randomly in the model plane, making the model fully two-dimensional. As with the previous model, the nodes are connected by bead–spring polymer chains. The beads, however, have a radius of one-tenth of that of the magnetic particles. This approaches experimentally realistic ratios of the magnetic particle diameter and the polymer persistence length, e.g., 10 versus 1 nm. Furthermore, in the model for particle cross-linked gels, the polymer chains are attached to specific spots on the surface of the magnetic particles. This mimics the covalent bonds which are found in corresponding experimental systems [40, 41]. Numerically, this is realized by a concept called ‘virtual sites’, to which the polymers are connected. These are placed on the surface of the

Figure 18.3: A two-dimensional simulation model of a gel is depicted, in which the magnetically blocked particles (red) act as cross-linkers. The polymer chains are bound to specific spots on the magnetic particle’s surface. The field-free case is shown on the left-hand side. On the right-hand side, an external field is applied. Initially, the model is constructed on a square lattice, but the particles are free to move as the simulation starts. The magnetic moments initially are randomly aligned in the plane. In a homogeneous magnetic field (right-hand side), the gel shrinks isotropically. This is caused by the polymers wrapping around the magnetic particles, effectively shortening the polymer chains. This can be seen especially at the boundary. Reprinted from Ref. [54] with permission from Elsevier.

magnetic particles and rigidly follow their linear and rotational motion. Likewise, forces acting on the virtual sites, e.g., through a stress on the polymer chains, lead to a torque and force on the magnetic particles [45]. As in the previous model, thermal fluctuations are taken into account, and averaging is needed for quantitative observations. Also, as previously, open boundary conditions are applied.

For the field-free case (left image in Figure 18.3), the attachment points of the polymers are roughly oriented along the direction of the polymer chain. As the particles can move and rotate freely in the model plane, some thermal fluctuations compared to the initial, regular construction are observed. When a magnetic field is turned on (right-hand side of Figure 18.3), the gel shrinks. The mechanism is as follows: (I) the magnetic particles coalign to the external field, (II) the attachment points of the polymer chains rigidly follow that rotation, (III) this causes a stress on the polymers. To reduce this stress, the polymer chains wrap around the surface of the magnetic particles. (IV) This wrapping effectively reduces the length of the polymer chains causing the gel's shrinkage. The shrinkage is isotropic in the two-dimensional model, because all magnetic particles rotate around the same rotation axis, namely the one perpendicular to the model plane. In three dimensions this is no longer the case. It is important to note that this deformation mechanism does not depend on the magnetic interactions between the magnetic particles in the system. Rather, it depends on the interaction of the magnetically blocked particles with the external magnetic field, and on a direct coupling between the orientation of the magnetic moments and the polymer chains.

The shrinkage of the gel is limited by two factors, namely the excluded volume forces between the constituents of the system, and the entropic elasticity of the polymers. The latter in particular creates a torque on the magnetic particles which opposes their alignment to the external magnetic field. As a consequence, the magnetization of the gel is hindered. This can be seen from a plot of the magnetization versus the strength of the applied field (Figure 18.4). Here, the field strength is expressed in terms of the dimensionless Langevin parameter

$$\alpha = \frac{\mu_0 m H}{k_B T}, \quad (18.2)$$

which relates the magnetic interaction energy between a particle's dipole moment m and the field H to the thermal energy ($k_B T$). Here, μ_0 is the magnetic constant. We observe a magnetization which lags behind the one predicted by the Langevin law for non-interacting dipoles. This behavior is opposite to what is observed for ferrofluids [50]. Other causes of a hindered magnetization can either be constraints in the rearrangement of magnetic particles in a gel [51], or highly anisotropic magnetic particles [52, 53].

Figure 18.4: Magnetization curve for a gel with 40 and 60 beads per chain, respectively. The magnetization for a single dipole in quasi-2D and 2D are also plotted, for comparison. We observe that the magnetic response of the gel is strongly hindered compared to a single free dipole due to the elasticity of the polymer matrix. When the chains are longer, the gel can be magnetized more easily. At the same time, the amount of shrinkage is lower. It is worth mentioning that the actual error bars for large values of the Langevin parameters α (see Eq. (18.2)) are smaller than those plotted here. Adapted from Ref. [37] with permission from the Royal Society of Chemistry.

18.3 The deformation mechanisms in three dimensions

Now that the basic mechanisms for a ferrogel's deformation in a magnetic field have been illustrated and visualized in two dimensions, let us turn to three-dimensional models, more relevant for experimental systems.

18.3.1 Particle cross-linked gels

A three-dimensional model for particle cross-linked gels has been introduced in Refs. [54, 55]. Like its two-dimensional counterpart it is constructed by initially placing magnetically blocked particles on a regular lattice, then connecting those particles by bead-spring polymer chains. Also, the mechanism by which the polymer chains are bound to specific spots on the surface of the magnetic particles is the same as in the two-dimensional case. Thus, we have the same direct coupling between the magnetic particles rotation and the polymer chains. There are two important differences to the two-dimensional model discussed above. First, instead of open boundary conditions, we apply periodic ones. This is necessary to limit boundary effects which would be more pronounced than in two dimensions for a comparable number of particles in the simulation. Second, two network structures are studied. In the one, based on a

diamond cubic lattice, four chains are connected to each magnetic particle. In the other, based on a simple cubic structure, six chains are connected to a magnetic particle.

Corresponding sketches can be seen in Figure 18.5. The molecular dynamics technique based on the Langevin equation is comparable to the two-dimensional model described in the previous section. However, due to the periodic boundaries, the system

Figure 18.5: Sketch of magnetic nanoparticles in a gel. Upper row (a, b): 2D model, left without an applied external field, right with an applied external field, as marked with the red arrow. One can see four polymer chains rigidly bound to specific spots (light blue, virtual sites) on the surface of a magnetic nanoparticle. When a field is applied and the magnetic particle aligns its dipole to it, the polymer chains wrap around the particle. This exerts a stress on the chain, which leads to a shrinking of the ferrogel (isotropic in 2D). Lower row (c, d) 3D model, left without an external field, right with an external field applied. In sketch c) a 4-fold (diamond) and 6-fold (cubic) crosslinker is shown. In sketch d), an external magnetic field H is applied within the plane, as shown with the red arrow. Notice that only chains within the plane are subjected to the deformation, the polymer chains perpendicular to the plane are not affected. This leads to an anisotropic shrinking of the gel in 3D. Reprinted from Ref. [55], with the permission of AIP Publishing.

cannot deform freely. Instead, averages of the stress tensor were taken and new simulations were done iteratively with an adapted shape of the simulation box. In this way, the equilibrium shape for a given magnetic field was determined. Due to thermal fluctuations and a small system size, the stress tensor fluctuates significantly. Thus, many individual stress calculations are performed at each iteration.

Like in the two-dimensional case, the gel shrinks when it is exposed to an external field. In three dimensions, however, the particles do not all rotate around the same axis. Of the many axes possible, the one parallel to the applied field is special, since a particle's rotation around this axis does not change its interaction energy with the external field. As can be seen in Figure 18.5, this leads to an anisotropic shrinkage of the gel. When comparing the two network structures, we observe significantly different elasticities. This pertains both to the bulk modulus and the Poisson ratio. These differences are not fully understood, since there are counteracting trends at play. On the one hand, adding more polymer chains per magnetic particle enhances the gel's deformation mechanism, which relies on a coupling between the magnetic particles' orientation and the polymer chains. On the other hand, more polymer chains lead to a stiffer material, which counteracts the gel's shrinkage in a magnetic field. For more details, we refer to Ref. [55]. It is worth mentioning that the elasticity of magnetic composites can be strongly nonlinear [56] and frequency-dependent [11, 57]. In addition, some investigations on magnetoactive elastomers show hysteresis effects, suggesting that large rotations of the magnetic particles can lead to detachment of polymer chains from the particle's surface [58]. Both the two-dimensional and the three-dimensional models presented so far could be extended to incorporate this effect, by dynamically removing bonds where a prescribed force limit on the respective bond is exceeded. Using a sufficiently large gel sample in periodic boundary conditions these modeling approaches could be used to study how polymer detachment on a microscopic scale affects the elastomer on a macroscopic scale.

18.3.2 Gels deforming through changing magnetic interactions – role of the magnetic particle configuration

In Figure 18.6, a three-dimensional model gel is depicted which deforms through changes in the interaction between magnetic particles as they align to an external magnetic field (see Figure 18.1 for the two-dimensional model). For this deformation mechanism, the sample shape is of importance, as it affects the demagnetization field [59, 60]. Hence, we cannot use periodic boundary conditions. To limit surface effects, one has to use thousands of magnetic particles in such a model. As a consequence, it is no longer feasible to explicitly model the polymer chains in the bead-spring framework. Instead, the elasticity is provided by connecting the magnetic particles by entropic springs. These can either be viewed as a representation for individual polymers or as a coarse representation of an elastic background, in which the springs describe the ability for

the particles to move locally. The model [38] was developed to study the interplay between the spatial configuration of the magnetic particles in the gel and the structure of the network. To obtain realistic configurations of magnetic particles, we use well-established simulations of ferrofluids similar to those in Refs. [52, 61–63]. Next, the desired sample shape is cut. Here, we will limit the discussion to spherical gels. The model is, however, also suitable to study the interplay between the particle microstructure and the sample shape. To provide the gel's elasticity, all pairs of particles are considered. Whether a polymer is added between the particles is decided based on a distance-dependent criterion. Likewise, the entropic elasticity of the polymer is chosen as a function of its end-to-end distance. Following polymer theory, longer polymers are represented by a weaker elastic spring. A snapshot of a small sample gel is shown in Figure 18.6. The systems used for magnetization and shape measurements are much larger, containing around 10,000 magnetic particles. The main challenge is to calculate the long-ranged dipole-dipole interactions. For the original work, a direct summation over all pairs of particles has been carried out on a graphics processor. By now, an alternative method scaling as $N \log N$ in the number of particles N is available [64]. To further accelerate the simulations, the molecular dynamics technique was supplemented by Monte Carlo moves rotating the entire sample. In particular, rotations around the axis of a magnetic field are likely, thermodynamically, but only happen at very long simulation time scales in a standard molecular dynamics simulation.

Figure 18.6: Model gel in which the polymers connecting the magnetic particles are represented as entropic springs. To visualize the orientations of the magnetic moments, their (magnetically) northern and southern hemispheres are drawn blue and red, respectively. The spatial configuration of the magnetic particles is obtained from a simulation of a standard ferrofluid. This way, correlations between adjacent magnetic particles observed in magnetic fluids are accounted for. A smaller system than that used for production simulations is shown, to improve visibility. Figure adapted from Ref. [38].

Let us turn to the influence of the spatial configuration of the magnetic particles before cross-linking. In experiments, it is possible to cure the gel around a previously prepared ferrofluid. This can be done in the absence of a magnetic field to produce a gel with an isotropic particle configuration or in a field to produce a uniaxial gel [65]. It is worth mentioning that, unless magnetically blocked particles are used and there exists a direct coupling between the particle orientation and the polymers, the gel still has no net magnetization, as long as no external field is applied. In Figure 18.7, we compare the deformation of isotropic and uniaxial gels placed in a magnetic field. As can be seen, in both cases, the gel elongates parallel to the applied field. This is in line with experimental findings obtained for a physical gel [34]. For the perpendicular direction, we see shrinkage for isotropic gels whereas no shrinkage is found for uniaxial gels. A possible explanation would be that in the uniaxial gel, chain-like clusters of magnetic particles are all aligned in a similar direction. Once the field is turned on, the gel rotates to align this direction parallel to the field. In the isotropic case, chain-like clusters are aligned in various directions. Once the field is applied, these chains will all bend towards the field direction. The polymers attached to those clusters will have to follow, which may lead to shrinkage in the direction perpendicular to the field. The rotation of chain-like clusters of magnetic particles into the field direction has also been described in a finite element model [29]. For further details on the model discussed here, we refer to Ref. [38].

Figure 18.7: Relative deformation parallel and perpendicular to an applied field of spherical gel samples with isotropic and uniaxial micro-structures versus the strength of the magnetic field, which is expressed in terms of the Langevin parameter α (Eq. (18.2)). An elongation of the gel is observed parallel to the external field independent of the particle structure. A shrinkage in the perpendicular direction is observed for gels with an isotropic structure, whereas the gels with an uniaxial particle configuration do not deform significantly in the perpendicular direction. Adapted from Ref. [38].

18.4 Scale-bridging approaches

Simulations of magnetic gels tend to be computationally quite demanding. There are two main causes: first, the dipolar interactions are long-ranged. The force and torque on a dipolar particle in the system depends meaningfully on the position and orientation of all other dipole moments in the system. This problem is addressed by a number of specialized algorithms [64, 66–68]. Second, the polymeric nature of the gel results in a rather large number of degrees of freedom. This is the case in particular for bead-spring polymers. Here, each monomer bead results in two or three additional degrees of freedom, depending on the dimensionality. In models such as in Refs. [54, 55], 60 and more beads are used for each of more than a hundred polymer chains. One strategy to reduce the computational effort is to replace the bead-spring chains by entropic springs, modeled via a Gaussian potential. Then, each magnetic particle is connected to its neighbors by a bond with a distance-dependent potential. Harmonic potentials are often used as an approximation [38, 69]. For particle cross-linked gels, this is not sufficient, because the direct coupling between the magnetic particle's orientation and the polymers is not included. To resolve this, a scale-bridging approach was used in Ref. [70]. A pair potential as a function of distance and the angles of the magnetic moments was determined for two magnetically blocked particles connected by a polymer chain grafted to their surface. The polymer was modeled as a bead-spring chain and attached to specific spots on the two particles' surface (see Sec. 18.3.1). The probability to find the particles at a certain distance and at certain relative orientations was then evaluated using a histogram. In total, 10^{11} samples were collected. The resulting pair potential was then obtained numerically by Boltzmann-inversion of the probability distribution. Such techniques are sometimes referred to as 'systematic coarse-graining'. Finally, semiempirical closed-form expressions were fitted to the numeric data. These included the leading correlations. Most importantly, when one of the particles is rotated so that the polymer chain wraps around it, the equilibrium distance between the magnetic particles decreases. This correlation is the signature of the shrinking mechanism found in particle cross-linked gels (see Figure 18.3).

An alternative approach to model the elastic background is to construct a lattice of tracer points. The elasticity is provided by pairwise potentials between neighboring tracers and by potentials placed on the angles between connections ending on a site. This technique is particularly suitable for gels with a low particle concentration, where entropic springs between the particles would not capture the elastic background in sufficient detail. Using such a model, the buckling of a chain of magnetizable particles in a soft quasi two-dimensional gel has been studied [42]. A snapshot can be seen in Figure 18.8. A field is applied perpendicular to the chain of magnetic particles. As a result, the particles get magnetized perpendicular to the chain direction. To avoid the unfavorable dipole-dipole interactions, a free chain

Figure 18.8: Simulation model for a chain of magnetizable particles embedded into a soft polymer gel. The system is quasi two-dimensional. The magnetic moments of the particles in the chain are aligned to an external magnetic field that points to the y -direction. As a consequence, the dipolar interactions between the particles in the chain are unfavorable. To avoid this, the magnetic particles tend to re-arrange. This is limited by the gel's elasticity. The minimization of elastic and magnetic energies makes the chain buckle with a wave-like shape. This behavior can be observed, both, in experiments and in a further theoretical model [42]. Figure adapted from Ref. [42] – published by the Royal Society of Chemistry.

would simply rotate parallel to the field direction. This is not possible due to the surrounding elastic matrix. Consequently, the chain buckles into a wave-like shape to reach a compromise between lowering the dipole–dipole interactions and not expending too much elastic energy. The simulation results are consistent with a second theoretical model and with experimental observations [42]. Modeling the elastic matrix as a network of tracer points or – somewhat related –, using tetrahedral volume elements [56], conceptually lie in between particle-based simulations and the continuum scale as studied using finite element methods [30, 71].

18.5 Obtaining AC-susceptibility spectra in computer simulations

Experimentally, AC-susceptibility measurements are an important tool to assess the properties of magnetic composite materials. The frequency-dependent susceptibility can be obtained by applying an external magnetic field with sinusoidal amplitude modulation to a probe of the material and measuring its magnetization response. The obtained AC-susceptibility spectra give insight into the magnetic properties of the investigated materials. However, using suitable theoretical models these spectra can also be used to assess frequency-dependent mechanical properties such as the local viscosity or mechanical storage and loss moduli [72–75]. Examples for such theories are extended Debye models [75–77], the Gemant–DiMarzio–Bishop model which has been

adapted from dielectric spectroscopy [72, 78, 79], or the theoretical description developed by Raikher et al. [80].

The overall significance of AC-susceptometry for the experimental investigation of magnetic composites makes it an interesting target for studies using computer simulations. The main advantage of simulations is the degree of control that one gets over all aspects of the modeled system. Single aspects of the simulation model such as interaction potentials, length, or stiffness of surrounding polymers etc. can be easily changed, even where it might be quite difficult to do so experimentally. This gives the opportunity to study the signatures that these changes leave in the AC-susceptibility spectra, and to gain further insight into the details of the coupling mechanisms between magnetic particles and the surrounding matrix. For example, the impact of dipolar interactions on the AC-susceptibility has been studied in Ref. [81].

Here, we discuss a simple simulation model suitable for obtaining AC-susceptibility spectra for dilute ferrofluids consisting of magnetic nanoparticles immersed in a polymer suspension. Based on this model, we recently performed a simulation study [82] and compared its results to the experimental system of Ref. [72], a typical example for dilute composite magnetic systems. Such a system includes three main ingredients – the magnetic particles, the polymers, and the solvent. Resolving the system on a coarse-grained molecular dynamics scale, polymers are modeled using as bead–spring chains, where one MD bead corresponds to several monomer units in the experimental system. The beads are connected with harmonic bonds and interact via the purely repulsive Weeks–Chandler–Anderson (WCA) potential [83] to account for excluded volume. In addition, the beads are coupled to a thermalized lattice-Boltzmann (LB) hydrodynamics solver that is used to model the hydrodynamic interactions mediated by the solvent [84, 85]. The magnetic particles are included using the so-called ‘raspberry’ model [86, 87], i.e. the magnetic particles are homogeneously filled with fluid-coupling points that are rigidly fixed with respect to a central MD bead. This bead carries the mass, the moment of inertia tensor, and the magnetic moment of the particle and it is also used to model the monomer–particle interaction. If properly prepared, such raspberry-particles provide not only proper hydrodynamic interactions, but also correct coupling between translational and rotational mobility, which is key when it comes to studying the magnetization response of the system. Since we only consider magnetically blocked particles, the system’s magnetization can solely decay due to Brownian relaxation. Since we consider a dilute ferrofluid, no dipolar interactions are included in the model. Note that this simplification also requires the dipolar interaction parameter λ (see Eq. (18.1)) to be sufficiently small. For the experimental system considered in the next paragraph, both conditions are fulfilled (for more details see Refs. [72, 82]). The MD simulation uses periodic boundary conditions.

Our basic setup is based on the experimental system of Ref. [72]. Therefore, we model spherical magnetic cobalt ferrite particles of radius $R = 7$ nm in polyethylene glycol (PEG) solutions of different concentration. For the solvent, water parameters are used except for the viscosity which we set to $\eta = 0.1 \eta_{\text{water}}$ to speed up the relaxation of

Figure 18.9: Representative snapshot of the simulation model used to reproduce AC-susceptometry. The magnetic particle is modeled as raspberry-particle (green) and surrounded by a polymer solution (yellow: Polymer beads, pink: Bonds). The volume fraction of polymers in this snapshot is $\phi = 0.05$. For clarity, LB fluid is not visualized. The simulation uses periodic boundary conditions.

the system's magnetization. The size of the polymer beads is chosen such that one MD bead corresponds to approximately six ethylene glycol units. A representative snapshot of the model is shown in Figure 18.9.

The straightforward way to measure the susceptibility of such a system using computer simulations would be to add an external magnetic field that interacts with the magnetic moment of the raspberry-particle. Modeling the field amplitude as a sinusoidal function and tracking the instantaneous magnetization response of the system via the vector component of the magnetic moment in field direction, one basically reproduces the experimental setup. While this approach to measuring AC-susceptibility works, there are some drawbacks to this method that render it virtually impracticable. Every simulation is performed at a certain frequency of the external field. Consequently, one obtains only one measurement point for the susceptibility per simulation. Therefore, to resolve an entire spectrum which typically spans several orders of magnitude, a huge amount of such simulations are necessary. Also, in every simulation the magnetization response has to be obtained with sufficient statistics. In order to have a good signal-to-noise ratio it would be advantageous to have a strong field-particle interaction. However, to stay in the linear regime this interaction has to be kept as small as possible, leading to significantly larger simulation times.

We therefore take a different approach to measuring AC-susceptibility. Using linear response theory, we can relate the time autocorrelation function of the magnetic moment of the raspberry particle to the system's susceptibility [88]. As a consequence, we can obtain the whole AC-spectrum from a single steady state simulation (without an external field). While these simulation runs require long sampling times to get sufficient statistics, they still offer a feasible way of measuring AC-susceptibility spectra. Figure 18.10 shows example results for AC-susceptibility spectra obtained in the described

Figure 18.10: AC-susceptibility spectra obtained from simulations using linear response theory. Real parts of the complex susceptibilities (χ') are drawn with solid lines, imaginary parts (χ'') with dashed lines. For these simulations polymers with a length of $N = 25$ monomer beads were used and the polymer concentration varied. With increasing volume fraction ϕ of the polymers in solution, a shift towards lower frequencies occurs in the spectra. For reference, the simple Debye model is also plotted (green curve), corresponding to a purely Newtonian fluid without any polymers. The observed trend is in line with the experimental findings of Ref. [72].

manner, from simulations using polymers of a fixed length and varying the volume fraction of polymers in solution. With increasing polymer volume fraction we observe a shift of the spectra towards lower frequencies, which matches the experimental trends observed in Ref. [72]. Similarly, such shifts towards lower frequencies are experimentally observed with increasing polymer length, for a constant volume fraction [72]. In a recent simulation study [82], we showed that these shifts are qualitatively reproduced as well using the presented modeling approach. In the simulation model, polymers couple to the rotational behavior of the magnetic raspberry particle only hydrodynamically. Increasing the polymer volume fraction and chain length respectively strengthens the coupling within the polymer matrix, increasing the effective viscosity around the raspberry particle, which in turn leads to the frequency shifts in the spectra. This emphasizes the importance of hydrodynamic coupling in dilute composite magnetic systems [82].

The presented model will be the basis for further investigating the impact and importance that specific changes to the magnetic hybrid system have on the measured AC-susceptibility spectra. In the long run, we aim to directly measure elastic moduli for the system on a global level. Note that these measurements are restricted to small deformations when using the linear-response approach. Employing the already mentioned theoretical models will let us obtain the corresponding local observables from the AC-susceptibility – which will provide an opportunity for comparison.

18.6 Summary

In this article we provided an overview of particle-based simulations of magnetic gels and their behavior in an external magnetic field. Particular attention was paid to materials based on magnetic nanoparticles, such that thermal fluctuations are of importance. Two deformation mechanisms for gels in homogeneous magnetic fields were described and underpinned by simulation models. It was also shown that the spatial configuration of magnetic particles can influence the magneto-deformation behavior. Similarly, the structure of the polymer network can influence the material's elastic properties. We discussed scale-bridging techniques which may help to deal with the high computational cost of simulating soft magnetic materials. Here, both, systematic coarse-graining as well as models located somewhere in between particle-based and continuum methods can be of use. We concluded our discussion with an outlook on evaluating the AC-susceptibility spectra in soft magnetic materials. These spectra are experimentally accessible and are useful both for manipulating the systems' properties in a time-dependent fashion, and to probe the local interactions between the magnetic particles and the surrounding polymer. In conclusion, simulations are a valuable tool to study the microscopic mechanisms which are the basis for experimental observations. They may provide guidance for tailoring the materials towards desirable properties.

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