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Magnetic gels as smart materials

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Abstract

Magnetic gels show a promising possibility for medical applications and micro robots such as controlled drug delivery and release or actuation [1]. Because of their ability to control their shape and size by applying external magnetic fields, artificial muscles can be made of magnetic gels [2]. Due to the tolerance of biological matter to magnetic fields they can be used in medicine as well. If one applies an external magnetic field gradient, the gel will follow this inhomogeneous field. Thus drugs which are embedded in the magnetic gel can be carried to the affected body part. The shrinkage as well as shaking the gel in an alternating field can be used to release the drug [3]. If the field is alternating fast enough internal heating of the gel is possible. In cancer therapy this internal heating can be used to destroy cancer cells without affecting the whole body.

To give an insight to these gels, magnetic particles and their interactions are provided. Magnetic gels are characterized to clarify their different architectures and the connected properties. Besides that, there are also some simulation models presented.

1 Magnetic Particles

Magnetic gels are hybrid materials consisting of a polymer matrix with embedded magnetic particles. Latter can be made of different materials and can differ in size, depending on the field of application the gel is used. Possible materials are e.g. metals, such as Fe, Co or Ni, iron oxides or metal ferrites [1]. In ferromagnetic particles so called magnetic domains usually occur. If magnetic nanoparticles are used in these gels, it is possible that there is only one domain due to their size. The size at which several magnetic domains appear are very different and depending on the material.

We will now have a look at these particles and their interactions in more detail for a better understanding of how magnetic gels behave. The different interactions can be split into interparticle and field interactions and relaxation processes.

1.1 Particle-field interaction

Particle-field interaction play an important role for understanding the properties of magnetic gels. Because of their size it has been proven suitable to approximate the magnetic moment of the particle as a point dipole in their center to receive a valid description of the magnetic gel's microstructure. This interaction is given by the Zeeman energy

$$U_{df} = -\mu_0 \langle \vec{m}, \vec{H} \rangle = -\mu_0 m H \cos(\theta) \quad (1)$$

where μ_0 is the vacuum permittivity, \vec{m} is the magnetic moment with the magnitude m , \vec{H} denotes the external magnetic field and θ indicates the angle between the magnetic moment of the particle and the external field. If no external field is applied, they are arranged randomly. This is why the total magnetization of the system is zero. By applying an external field the magnetic moments co-align in the direction of the field to minimize energy, which is why the whole system has a non-zero magnetization. This response behavior is called superparamagnetic. Thermal motion counteracts this alignment. The Maxwell-Boltzmann distribution

$$f(E) = A \exp\left(\frac{-E}{k_B T}\right) = A \exp\left(\frac{\mu_0 m H \cos(\theta)}{k_B T}\right) \quad (2)$$

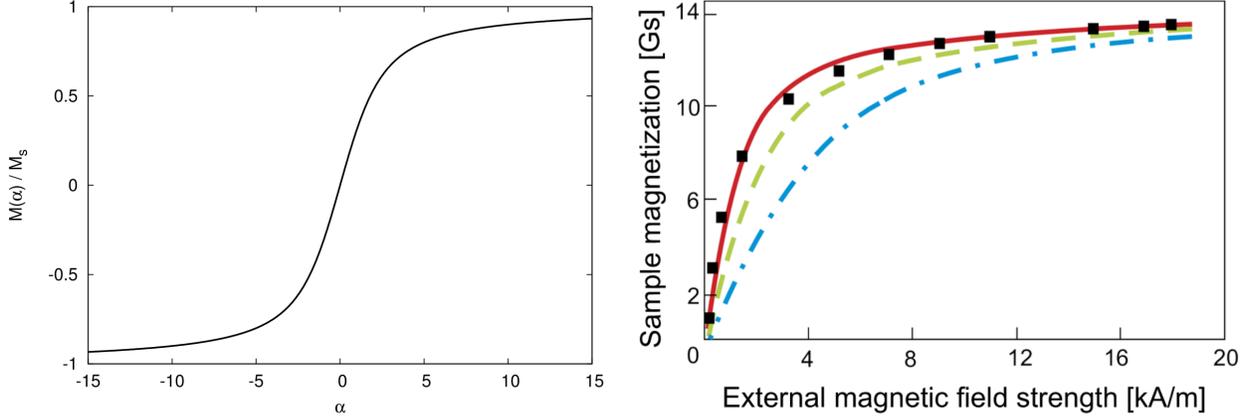
where A is a normalization constant and $k_B T$ is the thermal energy, describes the probability that in thermal equilibrium between field direction and a magnetic dipole an angle θ occurs. Regarding all dipoles the sum of the resolved components of the magnetic moments normalized by the number of all dipoles leads to the average magnetic moment in field direction. Multiplying with the number of dipoles per volume gives the total magnetization of the system. For neglected particle-particle interactions the magnetization is

$$M(\alpha) = M_s L(\alpha) \quad \text{with} \quad M_s = \frac{1}{V} \sum_i m_i \quad (3)$$

in which M_s is the saturation magnetization and V denotes the volume. The Langevin function is given by $L(\alpha) = \coth(\alpha) - 1/\alpha$ and is diagrammed in figure 1a. Here, α is the dimensionless Langevin parameter

$$\alpha = \frac{\mu_0 m H}{k_B T} \quad (4)$$

which compares the thermal energy to the minimum Zeeman energy per particle.



(a) Langevin magnetization curve neglecting particle-particle interactions [1].

(b) Magnetization curve in a ferrofluid considering particle-particle interactions. Modified from [4].

Figure 1: For non-interacting magnetic particles the Langevin magnetization curve is plotted in figure (a), which is dependent of the Langevin parameter i.e. of the external field. Considering interactions between dipoles like in (b) the curve changes especially for intermediate field strengths but for nearly all superparamagnetic systems the general profile is similar. Here the blue dash-dotted line refers to the Langevin function, the green dashed line shows a modified mean-field model and the red line illustrates the flexible chain model. The black dots are data points of a ferrofluid with big magnetic particles, i.e. $\lambda = 4.4$.

1.2 Relaxation processes

When an external magnetic field is applied there are in principal two ways for the magnetic moment to align parallel to it. This alignment is called relaxation process and is divided into Néel and Brownian relaxation. These two processes lead to different behavior especially in connection to a polymer which will be seen later on.

Néel relaxation

The magnetic dipole reorients itself inside the particle to the external field. This happens against an energy barrier [5]. This mechanism is much more sensitive to the particle diameter than the Brownian relaxation because the Néel relaxation time

$$\tau_N = \tau_0 \exp\left(\frac{KV}{k_B T}\right) \quad (5)$$

increases exponential with the volume V . K is the anisotropy constant, its product with the volume is the height of the energy barrier and τ_0 is a material-specific length of time [6].

Brownian relaxation

Another possible mechanism to adjust to an external field is the rotation of the whole particle. The Brownian relaxation time is given by

$$\tau_B = \frac{3V_{\text{hyd}}}{k_B T} \eta = \frac{\pi \sigma_{\text{hyd}}^3}{2k_B T} \eta. \quad (6)$$

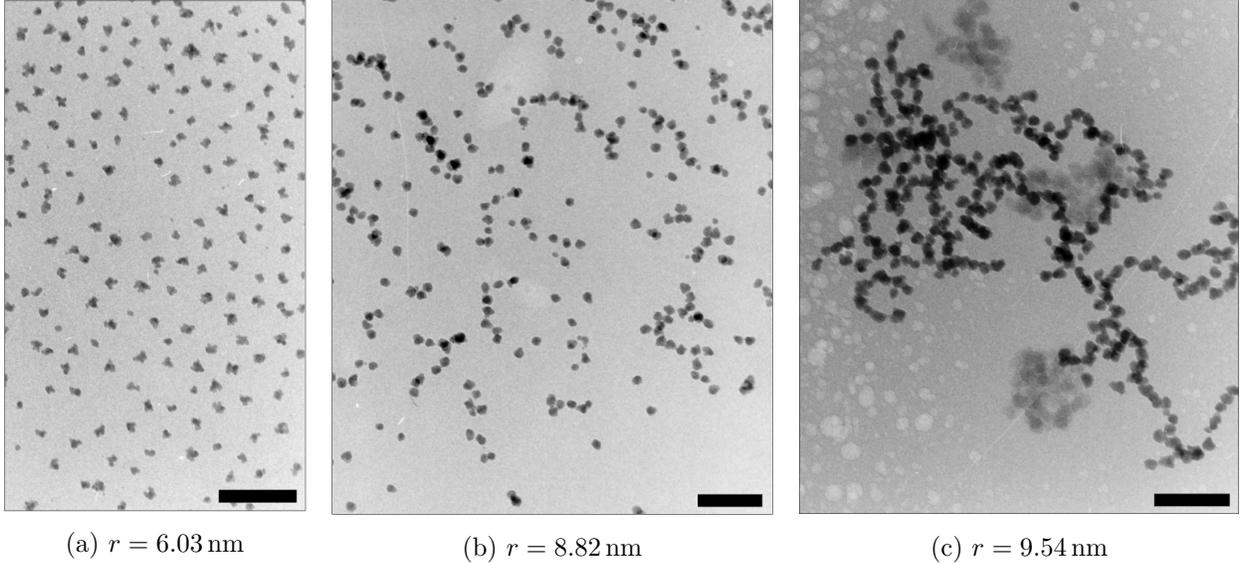


Figure 2: Cryo-TEM images for different particle size of iron dispersions. For small particle radii thermal motion is dominant and only single particles are observable. For increasing particle size chains are built because of the dipole-dipole interaction between the magnetic particles [8].

The dynamic viscosity of the suspension, e.g. the magnetic gel, is denoted by η and the hydrodynamic particle volume hence the diameter is described by V_{hyd} and σ_{hyd} [7].

Which mechanism dominates is depending on the relaxation time. The one with the shorter relaxation time is the dominant process in the system. For this reason Brownian relaxation is regnant for large particles and dominant Néel relaxation occurs mainly in single domain nanoparticles. In real systems both mechanisms appear but for convenience often just the dominant one is considered in calculations or simulations.

1.3 Dipole-dipole interaction

Besides particle-field interaction, particle-particle interaction also plays an important role for understanding the properties of magnetic gels. For two interacting particles the interaction term is given by

$$U_{\text{dd}} = -\frac{\mu_0}{4\pi} \left[3 \frac{\langle \vec{m}_i, \vec{r}_{ij} \rangle \langle \vec{m}_j, \vec{r}_{ij} \rangle}{r_{ij}^5} - \frac{\langle \vec{m}_i, \vec{m}_j \rangle}{r_{ij}^3} \right] \quad (7)$$

with the particles' magnetic moment $\vec{m}_{i,j}$ and their distance \vec{r}_{ij} . The preferred configuration, corresponding to the global minimum of equation (7), is the so called 'head-to-tail' configuration where both dipoles are co-aligned. The global maximum refers to the 'head-to-head' configuration. Like the Langevin parameter α (eq. (4)) the dipolar interaction parameter λ is used to determine the strength of this dipolar interaction. It connects thermal energy with the minimum energy per particle of two touching particles [1] and is given by

$$\lambda = \frac{\mu_0 m^2}{4\pi \sigma^3 k_B T} . \quad (8)$$

Here the diameter of the magnetic particles is denoted by σ , m stands for their magnitude of the magnetic moment and $k_B T$ is the thermal energy. In magnetic nanoparticles with only one domain λ can reach a value within the range of below one and eight. In figure 2 one can see cyro transmission electron microscopy (TEM) images for different particle sizes. If the particles are too small, when their magnitude of the magnetic moment ($m \propto \sigma^3$) is too small to overcome the thermal energy, no chains will be built (fig. 2a). With rising particle size the particles start building chains which however can easily be broken in consequence of thermal motion [8]. That is why there are still many single particles (fig. 2b). For large particles long chains are observable because they are big enough to conquer the thermal energy (fig. 2c).

Particle-particle interactions influence the particle-field interaction and thus the magnetization curve. The first order mean field approach includes the dipole-dipole-interaction of the surrounding particles and is given by

$$M_1(\alpha) = M_s L(\alpha + cL(\alpha)) \quad (9)$$

with a dimension and density dependent constant c . Considering this interaction usually yields to an increasing magnetization, mainly for intermediate external fields (see fig. 1b). This is based on the field created by the surrounding magnetic particles [9, 10]. Because it is only a first order approach and thus not accurate enough to describe the difficult interaction, better theoretical models are needed. In figure 1b the Langevin function is compared to a modified mean-field model as well as a flexible chain model (FCM). This FCM fits best to the data points of a ferrofluid with big magnetic particles. Further information on this model is given in [11].

1.4 Simulation

To simulate systems including magnetic particles such as magnetic gels, one needs to model them and calculate their interactions.

Dipolar hard and soft sphere model

In this model two interactions are considered. The dipole-dipole interaction, where the dipole of a particle is approximated as a point dipole in the center of a particle modeled via a vector, and the excluded volume interaction which ensures that particles do not overlap. Latter can be described as soft or hard sphere in which hard spheres are commonly used in theoretical research as well as Monte Carlo simulations for simplicity. Soft spheres on the other hand take the coating layers of the magnetic particles into account and are used in molecular dynamics (MD) simulations. The Weeks-Chandler-Anderson potential

$$U(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + \frac{1}{4} & , r < 2^{\frac{1}{6}}\sigma \\ 0 & , \text{otherwise} \end{cases} \quad (10)$$

is an example for a soft sphere potential. Here ε denotes an energy scale and r represents the distance. It is a purely repulsive and shifted Lennard-Jones potential with a cut-off radius which is quite simple. To model the surface coating more complicated potentials than equation (10) are required.

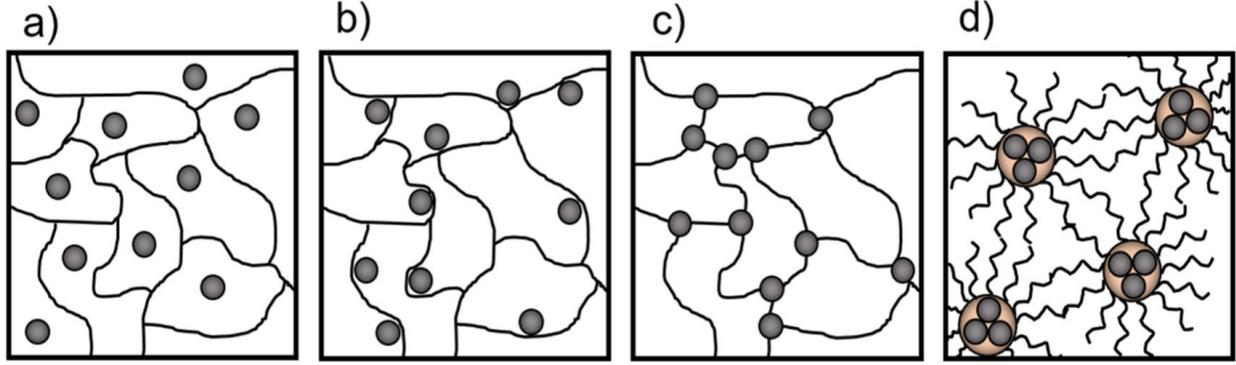


Figure 3: Each picture shows a schematic drawing of a magnetic gel in which the magnetic particles (gray dots) and the polymer (gray lines) are connected in different ways. The polymer can be chemically cross-linked with entrapped particles (a) or with physical interactions between particles and polymer (b). The magnetic particles can also act as cross-linkers (c) or build bridged micelles (d) [1].

P³M

An easy way to simulate many particles and their interactions would be direct summation over all particles. However this is really time consuming due to a slow convergence and a scaling of $\mathcal{O}(N^2)$ where N is the number of particles [12]. A better solution is to use P³M which scales with $\mathcal{O}(N \log(N))$. First of all, the short ranged interactions are computed in real space. To get the long ranged interactions, the particles are mapped from the continuum onto a mesh. Via a fast Fourier transform the potential as well as the electric field are obtained. The last step is to map back to the continuous system [13]. Additionally the mapping onto a mesh allows to consider periodicity without further effort. Yet to cover open boundaries other methods have to be used.

2 Magnetic gels

2.1 Different magnetic gels

Hybrid materials such as magnetic gels can be divided into two classes [14]. One differentiates between:

- **Class I**

Particles and polymer are not connected or only weakly bonded and have small interactions e.g. van der Waals forces, weak electrostatic bonding or hydrogen bonding. An example is shown in figure 3 where magnetic particles are entrapped in a chemical cross-linked polymer without a bond between particles and polymer (a) or with weak physical interactions between them (b).

- **Class II**

Particles and polymer are strongly physical or chemical coupled e.g. through covalent, strong coordinative or strong hydrogen bonds or strong electrostatic interactions. Figure 3 illustrates a class II magnetic gel in which the polymer is cross-linked via magnetic particles (c).

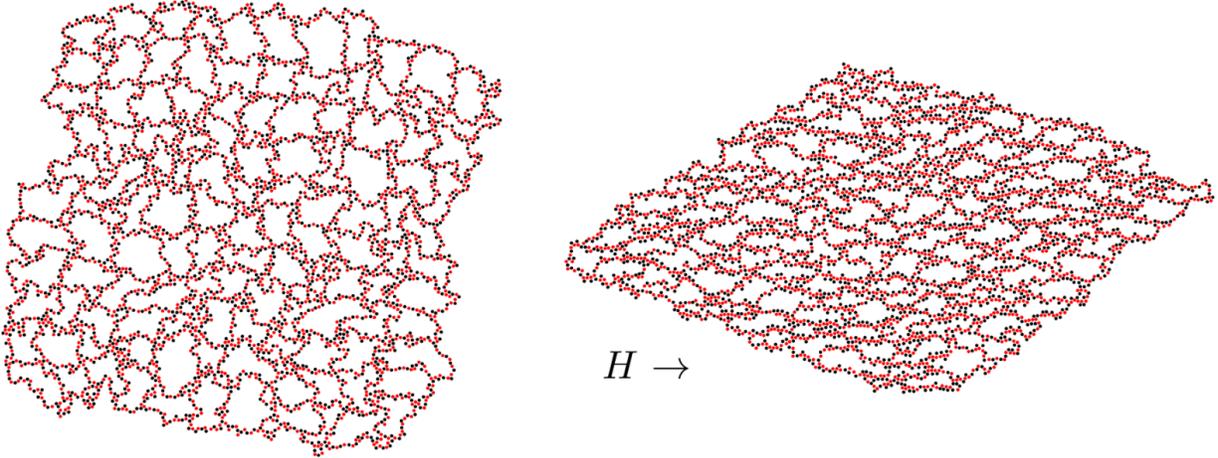


Figure 4: A magnetic gel modeled as bead-spring chains in which the polymer bonds are polydisperse. The black dots represent beads with an assigned dipole moment. When applying an external magnetic field (right) the gel extends parallel to it and contracts perpendicular [15].

The properties of a magnetic gel strongly depend on how it is set up especially when applying an external magnetic field. Every kind of gel has its strengths and weaknesses so it really depends on the research question or the intended purpose.

When magnetic particles have no or only weak interactions with the polymer matrix, the particles are very flexible and thus particle loss, which could be toxic and also decreases magnetic properties of the gel, is possible. Due to the high flexibility, particle-particle interactions are more frequent and the response to an external magnetic field is enhanced as well. Thus e.g. internal magnetic heating is possible.

However in particle cross-linked networks particle loss is inhibited due to a strong coupling between particles and polymer which in addition leads to an improved mechanical stability. Because of the coupling, detailed information primarily for the particle-polymer interaction can be obtained by studying the characteristics of the magnetic particles.

To analyze these different magnetic gels simulations play an important role which will be covered in the next section.

2.2 Simulation methods

Simulations are used to get a deeper insight into e.g. magnetic response behavior of different magnetic gels. Therefore different methods such as continuum model, entropic springs and bead spring chains are used.

Continuum model

There are different possibilities to simulate magnetic gels. In a continuum model the polymer is an elastic continuum which allows to explicitly define their elastic properties. It is used for simulations of big systems but due to this continuum modeling details in the architecture of the polymer can not be considered.

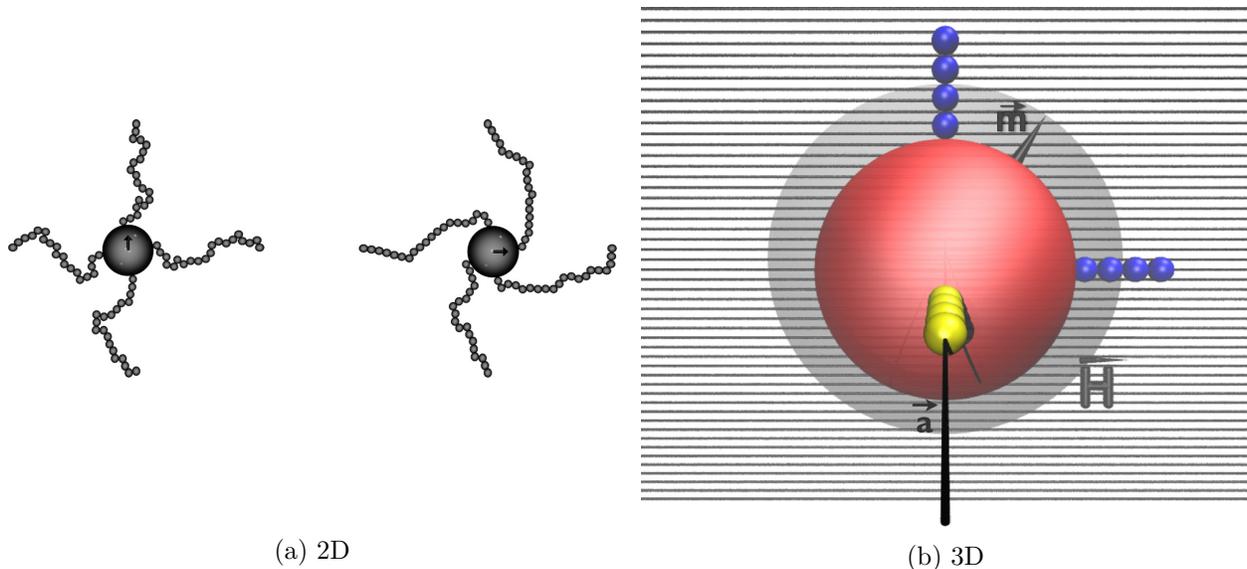


Figure 5: Magnetic particles are sketched as cross-linker in 2D (a) as well as 3D (b). When the magnetic particle align to an external field the polymer chains wrap around them which leads to a contraction of the gel. This shrinkage is isotropic in 2D but not in 3D [16].

Entropic springs

Another strong method is to treat the polymer as entropic springs in which the magnetic particles are explicitly modeled. These springs, modeled via a potential, connect the particles which is why one can easily modify the connections and thus analyze different polymer structures and their details [15]. Another advantage is that still huge systems to the extent of 10 000 magnetic particles can be simulated for which reason one can compare different particle arrangements as well as different sample sizes. Because of this computational efficiency longer time scales can be estimated as well. To simulate such a system one first takes a magnetic particle distribution e.g. from a ferrofluid simulation. Afterwards one has to declare the shape of the gel. To get magnetic particles as cross-linkers a probability function is used to add entropic springs between some of them. The length of these springs can vary which influences their stiffness. Depending on the probability function as well as the particle distribution different gels and their properties can be investigated.

Bead-spring chains

If one is interested in the different couplings and interactions of polymer and magnetic particles bead-spring chains are the best choice. The computational cost is much higher but it can be used as basis for larger systems. The deformation of a two dimensional (2D) magnetic gel in an external field can be seen in figure 4. It is constructed by bead-spring chains in which some beads refer to a magnetic particle due to an assigned dipole moment [16, 17]. Polymer chains are not directly coupled to the orientation of the magnetic moments and thus represent van der Waals and other weak interactions or Néel relaxation. As shown the gel extends parallel to an external magnetic field and contracts orthographic.

In figure 5 two models of directly coupled polymers to the dipole moments' orientation are sketched.

Here, the magnetic moment of the particle aligns to an external field via Brownian relaxation. In a 2D system the reorientation of the magnetic moment yields to a shrinkage of the whole gel due to the wrapping of polymer chains around magnetic particles (fig. 5a) [16, 17]. This contraction is isotropic because of a single rotation axis orthographic to the 2D plane. Extending this model to three dimensions (3D) leads to one significant difference [16, 18]. Due to several rotation axes the shrinkage is non-isotropic (fig. 5b). Polymer chains parallel to the magnetic field are most affected whereas chains parallel to the rotation axis, which is perpendicular to the plane of magnetic moment and field, are not influenced. This is why the gel contracts more parallel to the field than orthographic to it.

3 Conclusion

Magnetic gels show potential for many different applications especially in medicine. Their behavior mainly depends on magnetic properties such as dipole-dipole interactions between magnetic particles and particle-field interactions. The interactions of the system are characterized by the two dimensionless parameters α (eq.(4)) and λ (eq. (8)).

The polymer architecture as well as their coupling with magnetic particles play an important role. One differs between weak interactions between particles and polymer and strong coupling e.g. magnetic particles as cross-linkers. Due to these different interactions and types of gels, shrinkage, elongation and other behavior are observable.

To simulate magnetic gels different methods can be used. Entropic spring models allow to model large systems on long time scales. But to get more information about the coupling and interactions of polymer and particles, bead-spring chains are favorably.

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