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 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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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 [3]. 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 [7].

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 for this effect [12–14].

Furthermore, applying time-dependent external magnetic fields can induce deformations, which makes the materials candidates for the use as soft actuators [5, 14, 15]. 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 [16–18].

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 [19, 20].

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 [22]: 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

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magnetic fields. The following investigations are a first step into this direction.

**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],

\[
E = \frac{\mu_0}{4\pi} \sum_{i,j=1}^{N} \frac{\mathbf{m}_i \cdot \mathbf{m}_j - 3(\mathbf{m}_i \cdot \hat{r}_{ij})(\mathbf{m}_j \cdot \hat{r}_{ij})}{r_{ij}^3} + \frac{k}{2} \sum_{i<j} (\mathbf{r}_{ij} - \mathbf{r}_{ij}^{(0)})^2 + D \sum_{i,j} \left( \mathbf{\hat{m}}_i \cdot \hat{r}_{ij} - \mathbf{\hat{m}}_i^{(0)} \cdot \hat{r}_{ij}^{(0)} \right)^2 \\
+ \tau \sum_{i,j} \left( \mathbf{\hat{m}}_i \times \hat{r}_{ij} \right) \cdot \left[ \mathbf{m}_j \times \mathbf{r}_{ij} \right] - \left[ \mathbf{m}_i^{(0)} \times \hat{r}_{ij}^{(0)} \right] \cdot \left[ \mathbf{m}_j^{(0)} \times \hat{r}_{ij}^{(0)} \right] \right)^2.
\]

(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 \( \hat{x} = \mathbf{x}/x \). All quantities with the superscript \( (0) \) 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 \( \langle \cdot \rangle \).

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 of the polymer matrix. See Ref. [9] for further explanations. In the following we only 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 [23,26] this simplifying picture regularly could capture the experimentally observed effects correctly [27,28]. 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

\[
\frac{\partial \mathbf{y}_i}{\partial t} = -\gamma \cdot \frac{\partial E}{\partial \mathbf{y}_i}, \quad i = 1, ..., N.
\]

(2)

Here, our final simplifying assumption is that the relaxation rate tensor \( \gamma \) 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 \( \gamma = \gamma I \), with \( I \) the unity matrix. In all that follows, we measure time in units of \( \gamma^{-1} \), \( D \) and \( \tau \) in units of \( kl_0^2 \), as well as the magnetic moment \( m \) in units of \( \gamma l_0/\mu_0 \).

We linearize Eqs. (2) with respect to small deviations \( \delta \mathbf{y}_i \) from the energetic ground state. The resulting dynamic equations are rather lengthy and listed in Ref. [29]. We insert an ansatz \( \sim e^{\lambda t} \) and obtain the relaxation rates \( \lambda \) as the eigenvalues of the resulting dynamic system of equations. The eigenvectors characterize the nature of the corresponding relaxatory modes. In our overdamped system, the relaxation rates together with the relaxatory modes characterize the dynamic behavior.

**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 \( \mathbf{\hat{m}}_i^{(0)} \) 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 \( \lambda \mathbf{\hat{m}}_i^{(0)} \cdot \mathbf{r}_{ij}^{(0)} = \pi/4 \), the pairs \( \langle i, j \rangle \) in Eq. (1) denoting nearest neighbors. We consider three different strengths of orientational memory \( (D, \tau) \) that lead to the three different ground states mentioned above, see further Fig. 4.

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. [29] for details. In contrast, for the higher (“quicker”) modes beyond the plateau, spatial relaxation prevails. We find a specific step on the plateau in the antiferromagnetic case. It separates modes dominated by dipolar rotations first around and second towards the chain axis. As Figs. 1 (b) and (c) demonstrate, 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. [29].

**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-
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 since it allows to tune the dynamic properties of the materials in a non-invasive way from outside.

We consider the same set-up 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 characterized in Ref. [30]. It is of cylindrical shape with a diameter of 3 cm. Furthermore, it contains 4.6 wt% of iron particles, the average size of which is around 35 μm. During its synthesis, a strong homogeneous external magnetic field was applied parallel to the cylinder axis. This resulted in the formation of linear chains of magnetic particles spanning the whole sample parallel to the cylinder axis. The chains were resolved by X-ray microtomography. Cross-sectional images in planes perpendicular to the cylinder axis are available and contain information about the chain positions [30].

Each spot in the cross-sectional tomography data identifies magnetic chain particles. We extracted by image analysis the centers of these spots, see Fig. 3(a). Then,
in our model, we place one particle on each center, carrying a magnetic moment \( \mathbf{m} \) oriented perpendicular to the plane. Finally, as shown in Fig. 3 (a), the area between the particles is tessellated by Delaunay triangulation. We insert elastic springs along the edges of the resulting triangles, which sets the pairs described by \( \langle i,j \rangle \) in Eq. (1). 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 [3] [4], 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 perpendicular to the plane. 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. 3 (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. Fig. 3 (c) displays one illustrative but otherwise arbitrarily chosen example of a slow dynamic mode. As is expected, it involves a deformation of the whole irregular lattice structure. Again, an illustration of further modes can be found in Ref. [29].

There are two major differences when compared to the classical phonon modes in crystalline solids [22]. First, our dynamics is overdamped [1]. 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 non-overdamped oscillations [22]. In Eq. (2) this implies a second time derivative on the left, such that \( \omega^2 \sim |\lambda| \).

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 [22] was observed for disordered structures [31]. However, instead of a pure drop of \( g(\omega) \) at higher frequencies, a typical “boson peak” can develop in disordered systems [31], the origin of which is still under debate [22]. In our two-dimensional disordered solid, we obtain a “Debye plateau” of the function \( g(\omega)/\omega \) in Fig. 3 (d) at not too high frequencies. Furthermore, before the curve drops at the end of the plateau, it shows a small hump. It is not possible to decide on the basis of our limited data whether this is the signature of a “boson peak”. On the contrary, what becomes obvious is 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. In combination with the established phononic properties of colloidal systems [33–35], this mechanism could provide a route to tunable sound absorbers.

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 magneto-elastic 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. This represents a first step towards an optimization of the dynamic behavior of magnetic gels. Open problems concern for example more quantitative analyses both on the theoretical and experimental side. We hope that our study can stimulate such further investigations to support the design of these fascinating materials and optimize their tunable dynamic properties.

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