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MOLECULAR DYNAMICS SIMULATIONS OF AUXETIC FERROGEL

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Abstract. A ferrogel model based on a polymer network with single-domain magnetic particles is constructed. The non-magnetic matrix is represented by a two-dimensional bead-spring model where beads interacting via Lennard-Jones potential are connected by harmonic springs. It is assumed that in each polymer chain of beads some bonds include magnetic grains. In the considered model, a conformation of polymer chains is analyzed in terms of bead positions and magnetic grains are introduced into the model via magnetic torque acting on the bond connecting neighboring beads. The magnetic torque is absent if the external magnetic field is set to zero. We examine the case when the polymer matrix under consideration exhibits unusual auxetic behavior, i.e., it expands under a stretching force applied to the ends of the chain. The analysis of the ferrogel model presented in this paper is a result of molecular simulations in which the motion of grain magnetization is described by the Landau-Lifshits-Gilbert equation.

1. INTRODUCTION

The search for new functional materials leads to new ideas which appear in material science and in theoretical physics. An example is offered by the class of materials with negative Poisson's ratio [1]. Such materials [2,3], known also as auxetics [3] or dilational materials [4], exhibit mechanical properties which are counter-intuitive - they become thicker when stretched and thinner when compressed. In this paper we restrict our attention to a special class of auxetics whose mechanical properties are similar to those discussed recently in Ref. [5]. A good representative of this class are liquid crystalline polymers. Other studies of auxetics at the molecular levels may be found in [3,5-27].

The model of ferrogel used in the present paper has auxetic properties and it describes a non-magnetic polymer matrix into which single-domain magnetic particles have been incorporated. Such a system can exhibit large changes of shape when the external magnetic field is applied. It can model ferrofluids or ferrogels which usually consist of magnetic grains, with typical dimensions of about 10 nm, dispersed in a non-magnetic liquid or gel carrier, see e.g. Refs. [28,29].

The recent methods of precipitation of magnetic particles directly into polymer matrix open new technological possibilities for the ferrofluid with nanoparticles. In particular, liquid crystal elastomers in which magnetic nanoparticles are encapsulated are more and more extensively investigated, see

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e.g., [30,31]. Recently, some suggestions on auxetic properties of the ferrogels has been made by Gouskos and Typek [32].

2. MODEL PRESENTATION

To mimic the general physical properties of a ferrofluid in a computationally cheap manner, it is convenient to choose a two-dimensional model. Apart from a qualitative description of three-dimensional systems, such a model can be used to model the properties of very thin films. Below we discuss a simplified two-dimensional bead-spring model where a conformation of polymer chains is described by bead positions and magnetic grains are represented by magnetic torques acting on the bonds connecting neighboring beads. The model network consists of N beads at position $\vec{r}_i(t)$ (i = 1, . . . ,N) with three kinds of interactions:

– all beads interact through the Lennard-Jones potential

$$U^{LJ}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \qquad (1)$$

where r_{ij} is the distance between bead i and j, ε determines the well depth of the interaction energy, and σ scales the range of the interaction (in the following, we use reduced units, where ε=σ=k_B =M = 1),

– in addition, the nearest-neighboring beads are connected by harmonic springs,

– the magnetic torque acting on the beads i and j is produced by the uniaxial anisotropy of the magnetic particle (Fig. 1) located in the bond (i,j).

A fragment of two polymer chains with the bonds including magnetic grains has been shown in the schematic picture in Fig. 1. The magnetic anisotropy energy of a uniaxial magnetic particle is given (see, e.g., Refs. [28,33]) by the formula:

$$U_M = K_a V \sin^2\theta, \qquad (2)$$

where K_a is the anisotropy constant, θ is the angle between the particle magnetization and the easy axis of the particle, and V is the particle volume. We introduce the anisotropy field H_{Ka} defined as

$$H_{K_a} = \frac{2K_a}{\mu_0 m}, \qquad (3)$$

where

$$m = |\vec{M}| = M_s V \qquad (4)$$

and M_s is the saturation magnetization.

One can define the effective magnetic field $\vec{H}^{eff}$ acting on the grain magnetization $\vec{M}$:

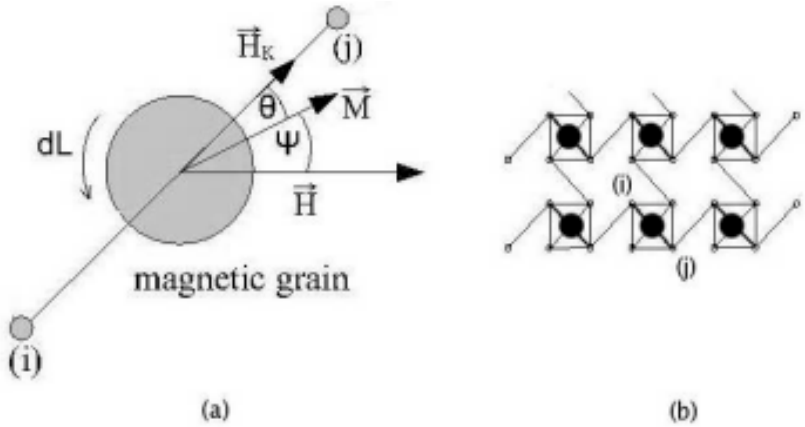

Fig. 1. Schematic draft of the magnetic grain located between beads i and j (part (a) of the figure) and the fragment of two polymer chains of beads with magnetic grains included (part (b) of the figure). The filled disks in the figure represent magnetic grains and are only graphical symbols. The bonds in the chains of beads represent harmonic bond interaction. The uniaxial anisotropy of the single-domain magnetic grain introduces a magnetic torque acting on the bond which plays the role of the magnetic easy axis. The angles θ and ψ are the angles between the easy axis and magnetization and the magnetization and the magnetic field H, respectively. All beads interact via the Lennard-Jones potential.

$$\vec{H}^{eff} = \vec{H} + \frac{H_k}{m}(\vec{M}\cdot\vec{n})\vec{n}, \quad (5)$$

where $-\vec{n}$ is a unit vector along the easy axis and $\vec{M} = m\vec{s}$ with $\vec{s}\cdot\vec{s} = 1$. In this work we consider the simplest case without the dipole-dipole magnetic interaction between the magnetic grains.

In the discussed model, the presence of the magnetic anisotropy of the bond (*i*,*j*) caused by the magnetic grain located between the beads *i* and *j* introduces an additional force applied directly to the bead *i* and *j*, as in Fig. 1. The force results from the magnetic torque acting on the magnetic grain in the non-zero magnetic field $\vec{H}$. The larger the magnitude of the angle $\theta + \psi$, the larger the magnetic torque. We have calculated the strength of the magnetic force acting on the beads *i* and *j* using the geometry of a rotating disk, representing magnetic grain with the radius $R = r_{ij}/2$, and we have considered the bond (*i*,*j*) to be the magnetic anisotropy axis. Then, the infinitesimal rotation of the whole disk along its center by the distance *dL* of the arc length *L* of the disk perimeter defines the tangential force at *i* and *j* with the strength

$$|\vec{F}^M| = \left|-\frac{dU_M}{dL}\right| = \left|-\frac{\partial U_M}{\partial\theta}\frac{d\theta}{dL}\right| =$$
$$\left|-\frac{\partial U_M}{\partial\theta}\frac{1}{R}\right| = \frac{2}{r_{ij}}|mH_{K_a}\sin(2\theta)|, \quad (6)$$

where U_M is the magnetic anisotropy energy defined in Eq. (2). If the strength of the harmonic bond interaction is large then the bond (*i*,*j*) behaves as a rigid body and the result of the force $\vec{F}^M$ acting on the particles *i* and *j* is the rotation of the bond about its center. We could notice that $\vec{F}^M$ is inversely proportional to the distance r_{ij}.

The dynamics of our bead-spring model is described by the Landau-Lifshitz equation [34,35] for magnetization $\vec{M}_{ij}$ of magnetic grain in the bond (*i*,*j*) and by Newton equations for beads at position $\vec{r}_i$ as follows:

$$\frac{d\vec{M}_{ij}}{dt} = \gamma_0\vec{M}_{ij}\times\vec{H}_{ij}^{eff} - \alpha\frac{\gamma_0}{M_s}\vec{M}_{ij}\times(\vec{M}_{ij}\times\vec{H}_{ij}^{eff}), \quad (7)$$

$$m_i\frac{\partial^2\vec{r}_i}{\partial t^2} = \vec{F}_i^{LJ} + K\sum_j(\vec{r}_j - \vec{r}_i) + \vec{F}_i^M + \vec{F}_{ext}, \quad (8)$$

where γ_0 is the gyromagnetic ratio and α is the damping constant, F_i^{LJ} is the net Lennard-Jones force acting on bead at $\vec{r}_i$, *K* scales the harmonic interaction, $\vec{F}_{ext}$ is the external force which is applied to the first and last bead in each polymer chain (otherwise it is equal 0), and $\vec{F}_i^M$ is the magnetic force defined in Eq.(6) acting on the bead *i* in the bond (*i*,*j*) if it contains magnetic grain:

$$\vec{F}_i^M = |\vec{F}_i^M|\left(\cos(\theta_{ij}+\psi_{ij}), \sin(\theta_{ij}+\psi_{ij})\right) \quad (9)$$

and

$$\vec{F}_i^M = -\vec{F}_j^M \quad (10)$$

for the bond (*i*,*j*). We have set the external magnetic field of the form $H = (H_x,0,0)$ and the value of the harmonic strength *K* for bonds including magnetic grain is chosen by an order of magnitude larger than for the remaining bonds.

3. THE SIMULATION METHOD

The simulations were performed by the molecular dynamics method. As the presence of magnetic degrees of freedom introduces a strongly nonlinear behavior of the whole system, which might cause serious numerical difficulties during the calculation of the approximate trajectory of the particles, we combined two different numerical methods, a new, non-finite difference method of the formal polynomials described in Refs. [36,37] and the commonly used finite-difference velocity – Verlet method. The first method was applied to the magnetization of the magnetic grains, $\vec{m}$ (where the components read as $m_x(t) = ms_x(t)$, $m_y(t) = ms_y(t)$, $m_z(t) = ms_z(t)$) whereas the latter was applied to the non-magnetic degrees of freedom.

At each time step, $t = nh$ (n = 0, 1, 2, ...), we calculated the approximate magnetization of the magnetic grains described by the Landau-Lifshitz equations Eq. (7), using the method described in [36,37]. The obtained numerical values contribute to the magnetic force $\vec{F}^M$ in the set of Eqs. (8) which are solved using the velocity-Verlet algorithm. For magnetization we chose the approximating polynomials to be of the second degree in the formal parameter λ which is always set equal to one $\lambda = 1$ in the numerical part of the algorithm [36] and [37].

In the numerical calculations we assumed that the numerical errors introduced by the calculation of the magnetization should be smaller than 10^{-6} per time step *h*. When the value of *h* was too large to keep this accuracy, we changed its value to a smaller one, *h*/10, as many times as it was necessary. This value of *h* was then used in the Verlet algorithm. The starting value of *h* in this self-adapting procedure, was always the value 0.001.

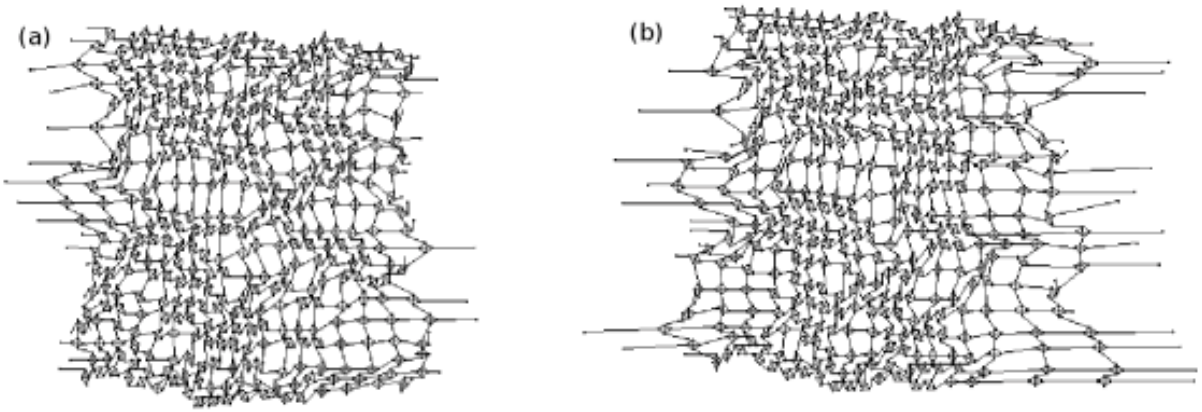

Fig. 2. Snapshots of the configuration of the polymer network under the action of the periodic force, long time after the force started acting on the system. The lines represent harmonic bonds. The panel (a) is the case of zero force half-period and (b) maximum force half-period. The width of the sample expands when it is stretched. The external magnetic field is applied in *x*-direction.

We introduced an additional condition for the numerical calculation of the next time step for the particle *i*. Namely, if the angle between the bonds, (*i*, *i*+1) and (*i* + 1, *i* + 2) or (*i*, *i* + 1) and (*i* - 1, *i*), exceeded the value $|\Delta\psi| = \pi$ then we set the velocity of the particle *i* to 0. Thus, if initially the angle between two bonds is convex than it cannot become concave later on. This correction ensured that the shape of the zig-zag structure of the polymer chains was locally conserved during the computer simulation.

4. RESULTS

The model of ferrogel introduced in the present paper has magnetic properties which are typical of ferrofluids and it also shows mechanical properties of auxetic materials.

We assumed that dipolar interactions between magnetic grains are negligible and they do not contribute to the effective magnetic field H^{eff} in Eq.(5). Thus we have a paramagnetic model in which the total magnetization (the sum of all grain magnetizations) is non-zero only if the external magnetic field is switched on. In the case of strong uniaxial anisotropy of magnetic grains both the anisotropy easy axes and grain magnetization tend to be aligned in the same direction as the external magnetic field. Consequently, we could expect large changes of shape of the non-magnetic matrix in our model after the external magnetic field is applied because the easy axes of magnetic grains are directed always along the bonds of the polymer chains. The processes of magnetization of the whole system and polymer deformation compete. We chose a simplified case in which the magnetic field direction is the *x*-direction. Then, it is clear that if the initial configuration of the polymer matrix is the same as in two polymer chains presented in the right hand side of Fig. 1 the width of the polymer matrix should expand after the magnetic field is applied because the polymer bonds which contain magnetic grains will try to follow the direction of the magnetic field. Notice that the polymer matrix is constructed in such a way that its width will expand if an external stretching force is applied to the ends of the polymer chains in Fig. 1. In our computer experiment the constant external force was applied to the first and the last bead in each polymer chain of beads in the considered polymer matrix and the force was alternately held fixed and then released to zero with period τ. During the simulation run both the longitudinal and lateral dimension of the polymer network were measured as well as its magnetization. In Fig. 2, we present a typical snapshots of the polymer configuration a long time after the external force was switched alternately on and off for a period of time. The expansion of the width of the polymer matrix with the length increase is easily seen. The external field introduces an additional trend to keep the easy axes of the magnetic grains in its direction. The strength of the effect can be observed in Fig. 3 where the time

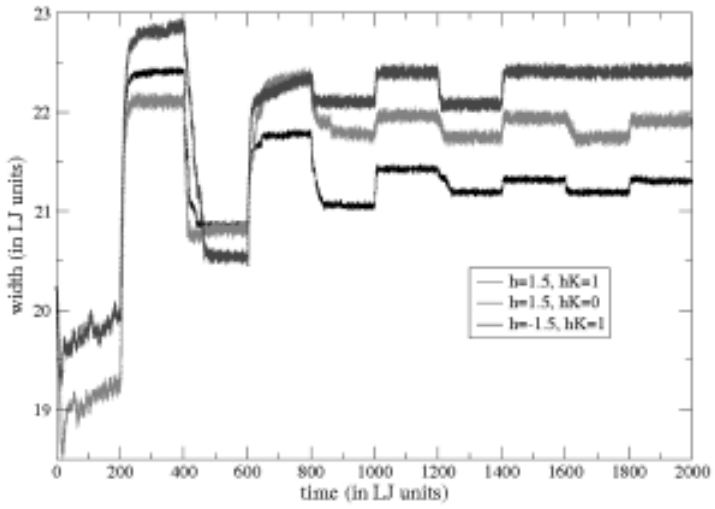

Fig. 3. Time dependence of the width of the polymer network in the case of the external force switched alternately on and off with period τ = 200 in the Lennard-Jones (LJ) time units. In the figure, the time intervals [200, 400], [600, 800], [1000, 1200] relate to the case of the non-zero external force. The three examples are shown for the reduced magnetic field H/K_BT = 1.5, 1.5,-1.5 and the reduced anisotropy field H_k/K_BT = 1.0, 0, 1.0, respectively.

dependence of the sample width is presented for different values of anisotropy field and external magnetic field.

The auxetic-like behavior of the discussed ferrogel model is evident from Fig. 4 (see also Fig. 3) where the time dependence of the length and width of the polymer network (has been) is presented for some time interval in the case of the external force switched alternately on and off. We can observe that the sample expands both in longitudinal and transverse direction when the longitudinal stress is applied. Thus, one can explicitly

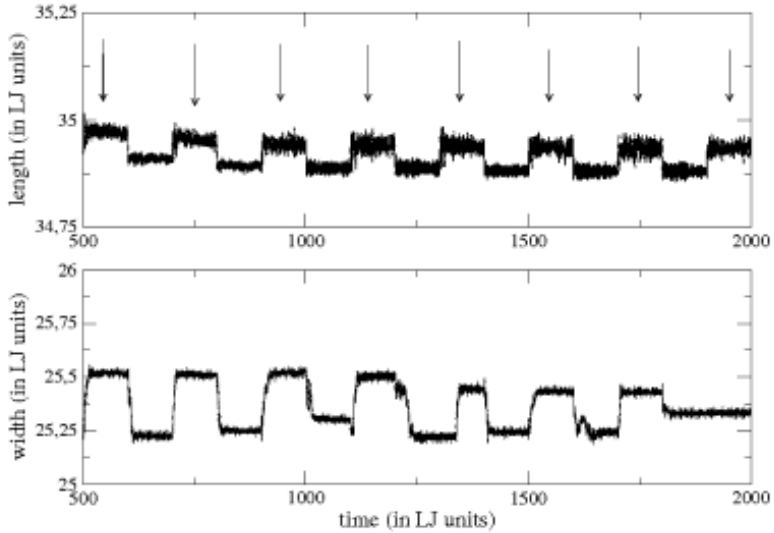

Fig. 4. The evidence for negative Poisson coefficient in the polymer network model - the length and width of the polymer network increase and decrease together according with the external force alternately switched on and switched off. The initial time range has been skipped where the whole system starts from the initial configuration of beads as in Fig. 1. The Lennard-Jones system units have been used. The arrows show time intervals when the external force was applied. The sample in the example is consisting of 20×20 magnetic grains and 20×40 beads.

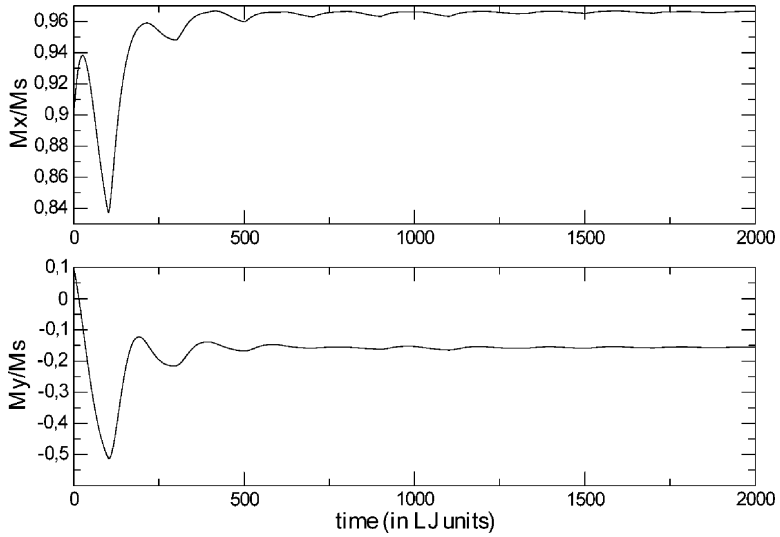

Fig. 5. Time dependence of the normalized magnetization with the external force switched alternately on and off as in Fig. 4. The initial values s_{0x} =0.9, s_{0y} = 0.1, s_{0z} = 0.

observe the negative Poisson's ratio. The corresponding behavior of the total magnetization (per magnetic grain), represented by $s_x(t)$ and $s_y(t)$, is shown in Fig. 5. It could be observed that although the external stretching force is alternately switched on and off the total magnetization saturates after some time. With an abrupt appearance or disappearance of longitudinal stress in the polymer matrix the polymer conformation and consequently also the direction of the anisotropy axes of the magnetic grains are locally disturbed by the propagating mechanical stress.

5. CONCLUSIONS

In this paper we show a "marriage" of magnetic materials with auxetic behavior. Our model shows that it may be possible to produce magnetic "anti-rubbers", corresponding to the existing elastic magnetic materials like magnetic rubbers. It is also possible to investigate magnetic elastomers or liquid crystals with the auxetic properties.

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