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Coarse-grained molecular dynamics simulation of small ferrogel objects

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ABSTRACT

The microstructure of ferrogels (FG) is investigated with the aid of coarse-grained molecular dynamics. Small FGs samples are considered: about 100 magnetic nanoparticles placed in the nodes of a piece of a quasi-regular polymer mesh. The changes of internal configuration under variations of the intensity of interparticle dipolar interaction, concentration and temperature are monitored. The obtained results evidence that the radial distribution function is a sensitive indicator of self-organization of the magnetic nanoparticles in FGs, thus yielding a robust basis for interpretation of spectroscopic measurements.

1. Introduction

Synthesis, studies and applications of magnetically filled polymers are an intense trend in the smart materials science. Ferrogels (FG) make a special class of this rapidly growing variety. These composites are extremely soft, since the ferro- or ferrimagnetic nanoparticles are embedded in hydrogel matrices with the elastic modulus about units of kPa. FGs display tunable mechanics with respect to shape, density, and stiffness. As highly biocompatible materials, they have wide prospects in medical applications. In particular, FG are used as carriers for targeted drug delivery [1,2] and as quasi-particles for the AC field energy conversion in hyperthermia [2].

To ensure practical implementations, one needs adequate theoretical description of magneto-mechanical behavior of FGs as such and of the samples made thereof. The continuum approaches employed for modeling of functional materials, being quite simple in use, do not provide an insight on interconnections between the overall sample response and the behavior of the material on the mesoscopic scale. Meanwhile, these are indeed the field-induced rearrangements of the filler structures, which fundamentally determine the FG magneto-mechanical response.

Detailed discrete models are able to clarify the behavior of FGs. A powerful method to do so is Molecular Dynamics (MD) simulations [3,4] based on solving the equations of motion of interacting "elementary" particles. The latter, in the classical variants of the method, are atoms and/or small groups of those. This is not appropriate, however, for the systems with multi-scale structure, like FGs, where the reference scale of polymer chains (Angsroms) differs from the magnetic particle dimensions (tens of nanometers) by orders of magnitude.

A convenient solution is offered by the coarse-grained modification of molecular dynamics (CG-MD), where groups of atoms or large molecular fragments (e.g. polymer blobs) are treated as single entities thus making modeling of materials with diverse intrinsic scales computationally affordable. Following this line, a united simulation framework for a FG uses CG description for the polymer subsystem but considers the magnetic particles as they are. Since the FG is studied at finite temperature, one may formally say that this scheme is a "hybrid" of CG-MD (for polymer) and Langevin dynamics (for particles) approaches. Such a combination has already proven itself to be successful for simulating quasi two-dimensional FGs [5].

In this and alike works, two models of intrinsic magnetic behavior of the particles have been employed. One assumes that the magnetic moment rotates freely inside the particle body. In the second case, the moment is "frozen-in" and, thus, rotates only together with the particle. Meanwhile, the nanoparticles of real FGs possess a finite magnetic anisotropy, so that the magnetic moment is subjected to the motions of both types: internal and external. Note that when the magnetic moment responds to an

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applied field, both motions are impeded: the internal one by the magnetic anisotropy, the external one by the presence of polymer mesh.

In this work, we present the results of CG-MD simulations of ferrogel microsamples, where the particles have finite uniaxial magnetic anisotropy. The interest is focused on the structure response of FGs to the external field and temperature. The modeling is performed using ESPResSo (**E**xtensible **S**imulation **P**ackage for **Res**earch on **So**ft matter) package, a powerful and flexible tool of MD developed by an international team [6].

2. Model

In our simulation, we consider FG samples, where the magnetic particles occupy some nodes of a 3D polymer mesh that has a quasi-cubic structure. Each internode chain is built of spherical particles (polymer blobs), which are linked by certain potentials determining the "energy costs" of both stretching and bending of the link. The potential of the i-th monomer is

$$U_i = \sum_{j,\ j\neq i}^{N} V^{\mathrm{LJ}}(r_i, r_j) + \sum_{k,k\neq i}^{n_i} V^{\mathrm{FENE}}(r_i, r_j) + \sum_{l,m,l\neq i,m\neq i}^{n_i} V^{\mathrm{angle}}(r_i, r_l, r_m), \quad (1)$$

where N is the total number of elements (both blobs and magnetic particles) and r_i is the radius-vector of the element. In the second and third terms of Eq. (1), the summation runs only over n_i nearest neighbors of the i-th monomer. The energy terms of U_i are:

1. V^{LJ} is the truncated Lennard-Jones pair potential, i.e., semi-hard sphere repulsion with the cutoff-distance of the order of the particle diameter:

$$V^{\mathrm{LJ}}(r_i, r_j) = \begin{cases} 4\varepsilon\left[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6} + c_{\mathrm{shift}}\right], & 0 < r_{ij} < r_{\mathrm{cutoff}} \\ 0, & r_{ij} \geq r_{\mathrm{cutoff}}; \end{cases} \quad (2)$$

here $r_{ij} = |r_i - r_j|$ and $r_{\mathrm{cutoff}} = 2^{1/6}\sigma$. Parameter ε is the strength of interaction, σ the reference distance, and c_{shift} the shift parameter chosen so that the potential is continuous at the cutoff distance: $V^{\mathrm{LJ}}(r_{\mathrm{cutoff}}) = -\varepsilon + 4\varepsilon c_{\mathrm{shift}} = 0$. For the elements of different types, say α and β, the parameters are defined as $\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_\alpha + \sigma_\beta)$ and $\varepsilon_{\alpha\beta} = \sqrt{\varepsilon_\alpha \cdot \varepsilon_\beta}$.

2. V^{FENE} is the finite extensible non-linear elastic model potential which sets the longitudinal elasticity of the polymer chain:

$$V^{\mathrm{FENE}}(r_i, r_j) = -\frac{1}{2}Kr_{\max}^2 \ln\left[1 - (r_{ij} - r_0)^2/r_{\max}^2\right], \quad (3)$$

where K is the stiffness factor, r_0 and $r_{\max}$ are equilibrium and maximal bond lengths, respectively.

3. V^{angle} is the potential that establishes the bending stiffness of the chain:

$$V^{\mathrm{angle}}(r_i, r_j, r_k) = \kappa\left[1 - \cos\left(\phi_{ijk} - \phi_0\right)\right]; \quad (4)$$

Here κ is the bending stiffness factor, $\phi_{ijk} = \arccos\left[(r_i - r_j)\cdot(r_i - r_k)/r_{ij}r_{ik}\right]$ the angle between vectors connecting the current (central) particle to its two nearest neighbors, and ϕ_0 is the equilibrium value of this angle.

The magnetic particles included in the system are assumed to be spheres, whose diameter d is greater than that of a blob. The energy of such a particle is

$$U_\alpha^{(m)} = -\mu_\alpha \cdot H_0 - E_{\mathrm{A}}\cos^2\theta_\alpha + \sum_{j,\ j\neq\alpha}^{N^{\mathrm{mag}}} V^{\mathrm{D}}\left(r_\alpha, r_j, \mu_\alpha, \mu_j\right) + \sum_{k,\ k\neq i}^{N} V^{\mathrm{LJ}}(r_\alpha, r_k). \quad (5)$$

The first term yields the Zeeman energy of α-th magnetic moment in the external field H_0 and the second term is the energy of uniaxial magnetic anisotropy with θ being the angle between the magnetic moment and the easy axis of the particle. The third term renders the dipolar coupling of the magnetic moments:

$$V^{\mathrm{D}}(r_\alpha, r_\beta, \mu_\alpha, \mu_\beta) = \frac{(\mu_\alpha \cdot \mu_\beta)}{r_{\alpha\beta}^{3}} - \frac{3(\mu_\alpha \cdot r_{\alpha\beta})(\mu_\beta \cdot r_{\alpha\beta})}{r_{\alpha\beta}^{5}}; \quad (6)$$

note that summation of V_D in Eq. (5) runs only over the magnetic particles, their number being N^{mag}. The magnetic grains are linked to the monomers by means of special (lock) particles. These objects are rigidly stuck to their "master" grains but interact with the blobs via potential (Eq. (1)). Due to that, both translational and rotational displacements of the magnetic particles are transferred to the polymer mesh and vice versa.

Calculation implies that the FG sample sits inside a heat bath simulated by a Langevin thermostat [7], so that the equation of motion for a given element has the form:

$$m_i\ddot{r}_i = -\nabla U_i - \eta\dot{r}_i + f_i(t), \quad (7)$$

where t is the system time; m_i mass of the element; η thermal friction coefficient, and $f_i(t)$ random force with the properties of white noise $\left\langle f_i(t)\cdot f_j(t')\right\rangle = 6\eta k_B T\delta_{ij}\delta(t - t')$.

3. Results

We consider a ferrogel microsample as a 3D polymer mesh structure with $5\times5\times5$ nodes. The magnetic particles are distributed over the mesh nodes with a given probability p, each internode chain contains 10 monomers. Fig. 1 presents an example of "dense" sample with $p = 0.9$; the corresponding volume fraction, as defined with respect to the initial volume of the structure, is $\varphi_0 = 0.25\%$. The particles have uniaxial magnetic anisotropy characterized by parameter $\zeta = E_A/k_BT$ being the height of the

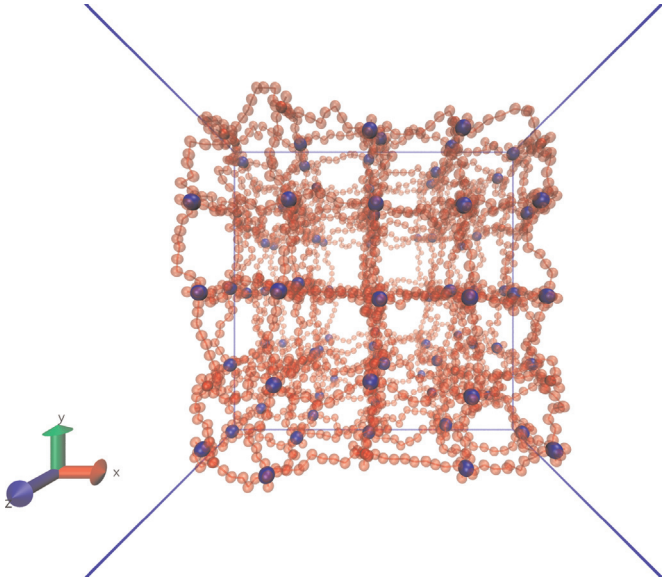

Fig. 1. Initial configuration of a ferrogel sample with $\varphi_0 = 0.25\%$.