Journal of Magnetism and Magnetic Materials 431 (2017) 192–195

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Structural changes in microferrogels cross-linked by magnetically anisotropic particles

A.V. Ryzhkov[a,b,*], Yu. L. Raikher[b]

[a] Perm National Research Polytechnic University, Perm 614990, Russia
[b] Institute of Continuous Media Mechanics, Russian Academy of Sciences, Ural Branch, Perm 614013, Russia

ARTICLE INFO

Keywords:
Ferrogel
Molecular dynamics
Magnetic nanoparticles
Magnetic anisotropy
Radial distribution function

ABSTRACT

Chaining of magnetic nanoparticles in a microscopic ferrogel (MFG) due to interparticle interaction and external field is analyzed by the coarse-grained molecular dynamics. The embedded nanoparticles, unlike existing conventional models, are assumed to possess uniaxial magnetic anisotropy. By that, the consideration is brought closer to reality. Evolution of particle chains, both in length and straightness, is handled with the aid of "axial" radial distribution function that is sensitive to orientation of the aggregates. The effect of the particle magnetic anisotropy on the structural alterations as well as on volume changes of MFGs is demonstrated.

1. Introduction

The goal of this work is to analyze the structural changes occurring in a ferrogel object in response to an applied magnetic field. We consider a gel sample of microscopic size where the role of cross-linkers is given to properly functionalized magnetic nanoparticles, such entities are known as microferrogels (MFGs) [1,2]. MFGs are considered and tested as remotely controlled containers for drug delivery and release [3–5] and as devices for hypethermia cancer treatment [6,7].

The MFGs have dimensions from hundreds to thousands nanometers and contain several hundreds of magnetic nanoparticles. When an MFG sample is magnetized, its structure changes drastically under the action of interparticle magnetic forces. Cluster and chain formation along with the overall volume changes take place. Evidently, those effects, strongly affecting the magnetomechanics of MFGs, are important to be accounted considering the potential applications.

The absolute majority of theoretical studies of MFGs, when describing the magnetic behavior of nanoparticles, employ the two most simple schemes. The particles are assumed to be either perfectly magnetically soft [8,9] or infinitely magnetically hard [10,11]. The first approximation implies that the magnetic moment is completely free to rotate inside the particle, while the second one treats the magnetic moment as "frozen-in", so that it rotates only together with the particle body. However, to the typical MFG fillers, viz. nanodisperse magnetite [12] and cobalt ferrite [13,14], both assumptions apply quite poorly. In order to overcome this drawback, here we study an MFG filled with the particles which possess uniaxial magnetic anisotropy of finite intensity. This means that the particle magnetic moment is able to turn inside the particle but this rotation is hindered substantially by the presence of the magnetic anisotropy barrier. We show that depending on the parameter of magnetic anisotropy, an MFG might considerably vary its response to the applied field. In what follows we, first, describe in brief the numerical model and the method of structure analysis. The results of simulations obtained in that way and their analysis are presented followed by some conclusions.

2. Model

2.1. Coarse-grained simulation

We use many-particle coarse-grained molecular dynamics (MD) model that imitates a micro-object whose initial structure is that of a simple cubic lattice. A certain fraction of the junctions (nodes) of this lattice are made of magnetic nanoparticles of identical size, the other part of the nodes is nonmagnetic. In the given lattice topology (see Fig. 1A), to each internal magnetic particle six polymer strands are attached. The attachment points are fixed at the particle surface, and due to that the translational and rotational displacements of the particle and the polymer strands affect each other.

All the internode polymer strands of the model MFG comprise equal number of building blocks (blobs) which in the parlance of coarse-grained molecular dynamics are called "monomers". Any monomer (except for those which occupy the lattice nodes) is linked to two of its nearest neighbors by a center-to-center harmonic potential and also is subjected to purely repulsive interaction – Weeks–Chandler–

* Corresponding author at: Institute of Continuous Media Mechanics, Russian Academy of Sciences, Ural Branch, Perm 614013, Russia.
E-mail address: ryzhkov.a@icmm.ru (A.V. Ryzhkov).

http://dx.doi.org/10.1016/j.jmmm.2016.09.056
Received 1 July 2016; Accepted 11 September 2016
Available online 19 September 2016

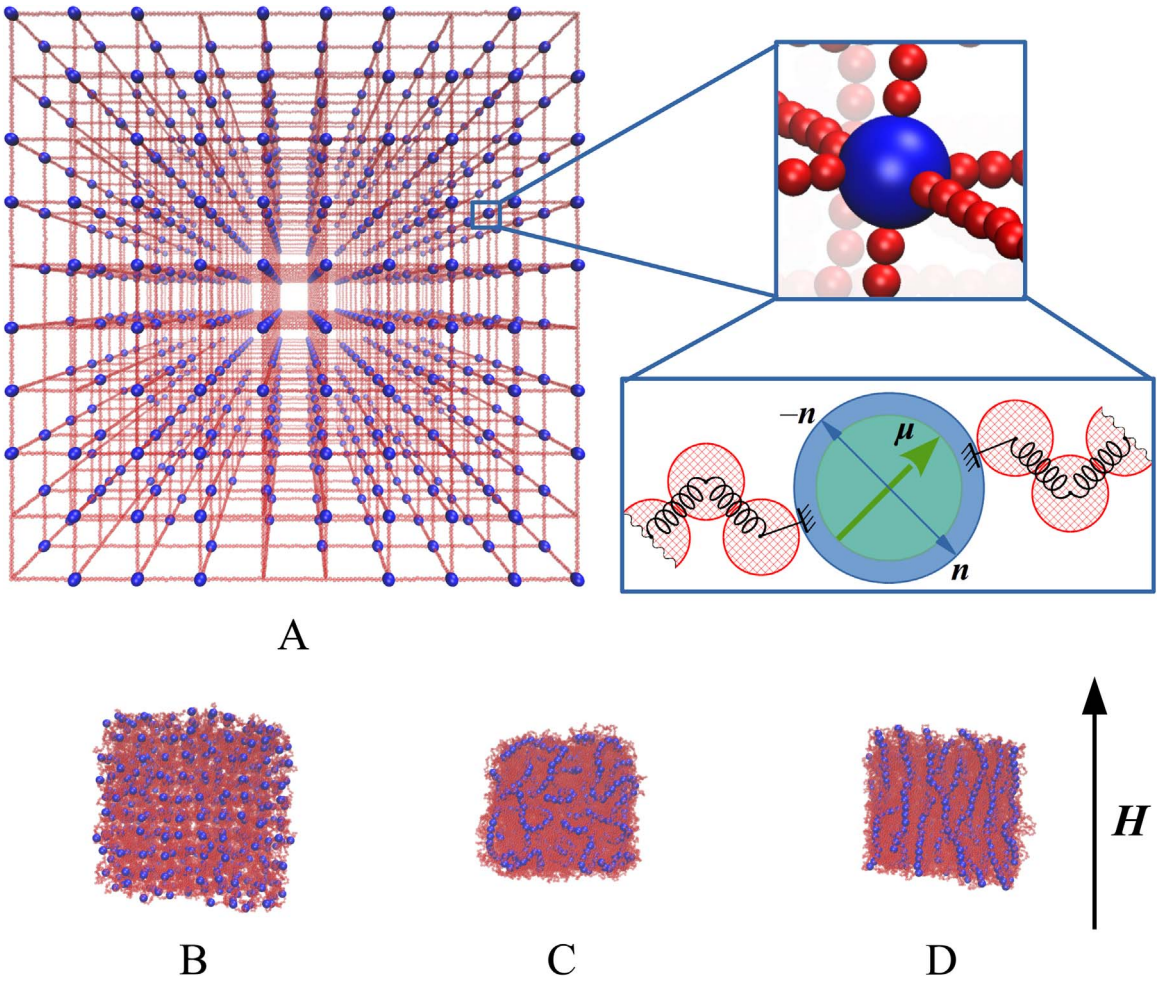

Fig. 1. (A) Pre-initial configuration of a simple cubic lattice network with embedded magnetic particles. The insets show an internal node made of a nanoparticle and the sketch of the internal particle structure, here $\boldsymbol{\mu}$ is the magnetic moment and $\boldsymbol{n}$ is the easy magnetization axis. (B) Thermalized configuration of an MFG put inside Langevin thermostat for the case where the Zeeman and dipole–dipole magnetic interactions are absent. (C) The same but the interparticle magnetic interaction is "switched on". (D) The configuration that evolves from that of (C) under external magnetic field $\boldsymbol{H}$ of the magnitude $|\boldsymbol{H}| = 10k_BT/\mu$.

Andersen (WCA) potential [15] – that prevents their overlapping.

The energy of a magnetic particle that possesses the dipolar magnetic moment $\boldsymbol{\mu}$, along with the Zeeman term and the all-with-all dipole–dipole interaction, includes also the WCA potential. Besides that, vector $\boldsymbol{\mu}$ is coupled inside the particle with the anisotropy (easy magnetization) axis $\boldsymbol{n}$.

All the coarse-grained MD simulations were carried out with the aid of ESPResSo software [16]. First the pre-initial state of fully extended simple cubic lattice is generated. Then the sample is put inside Langevin thermostat for thermalization (Fig. 1B), at the next step the interparticle magnetic interaction is introduced (Fig. 1C), and finally an external uniform magnetic field is applied to the sample (Fig. 1D).

2.2. Structural analysis

As seen from Figs. 1C and D, upon magnetization, in an MFG the particles self-organize into chain-like structures. To monitor the formation of such anisotropic aggregates, we use an angle-resolved radial distribution function (RDF). Unlike the standard definition of RDF [17], this modification renders the distribution of the particles in a narrow cone whose axis points the preferred direction.

The idea of this "axial" radial distribution function (RDFA) is as follows. Two symmetrical spherical sectors with vertex angles 2φ are built (Fig. 2). Their common vertex is positioned on the i-th magnetic particle, while the axes are directed along the anisotropy axis $\boldsymbol{\nu}$. The obtained spherical sectors are divided into thin layers which are perpendicular to the cone axis. Then one defines RDFA as

$$\mathrm{RDFA}^{(\boldsymbol{\nu})}(r) = \frac{1}{N^{\mathrm{magn}}\rho}\sum_{i}^{N^{\mathrm{magn}}}\frac{N_i^{\mathrm{sect}}(r_j,\, r_{j+1},\, \boldsymbol{\nu})}{V^{\mathrm{sect}}(r_j,\, r_{j+1},\, \varphi)} \tag{1}$$

where $N_i^{\mathrm{sect}}(r_j,\, r_{j+1},\, \boldsymbol{\nu})$ renders the number of particles in the portion of spherical sector of the angle 2φ that has inner radius r_j and outer radius r_{j+1}. The sector axis points along $\boldsymbol{\nu}$ and $r = (r_j + r_{j+1})/2$. In Eq. (1) N^{magn} is the total number of magnetic nanoparticles and $\rho = N^{\mathrm{magn}}/V_{\mathrm{box}}$ the net number density of nanoparticles in the simulation box V_{box}.

3. Results

The considered MFG sample (Fig. 1) is an isolated cubic lattice (no periodic boundary conditions are applied) with 1000 nodes about 80% of which are occupied by magnetic nanoparticles of diameter d_{np}. Their magnetic moments have the absolute value μ and randomly distributed directions. Each internode segment of the lattice is a strand of 12 monomers of diameter $d_m = \frac{1}{3}d_{np}$. The parameter defining the strength of dipolar magnetic interaction of the particles in contact is $\lambda = \mu^2/(d_{np}^3 k_B T) = 16$; here k_B is the Boltzmann constant and T the absolute temperature. The effect of magnetic anisotropy is characterized by the ratio of anisotropy energy barrier E_A to thermal energy: $\sigma = E_A/k_B T$.

After step-by-step process of MD calculation (from A to D in Fig. 1),