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MAGNETISM

Self-Assembly in the Systems of Magnetic Anisotropic Nanoparticles

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Abstract—This paper presents the complex investigation of the system of magnetic anisotropic nanoparticles using computer simulations in a wide range of the system's parameters. The cluster analysis was made, various average characteristics of the formed clusters were calculated and the initial magnetic susceptibility and the radial distribution function were computed. It was shown that via changing the nanoparticles characteristics (their shape and the values of the magnetic moments) it's possible to change macroscopic response of the system, that implements the idea of tuning and design new materials with controllable properties.

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1. INTRODUCTION

In the last few years investigations of systems of magnetic anisotropic nanoparticles have attracted much attention among researchers studying magnetic fluids. These systems containing a new type of particles are of special interest due to their ability to form various liquid-crystalline phases, such as nematic, smectic, etc. [1–4]. These studies are focused on the systems of hard/soft ellipsoids or spherocylinders with point dipole moments located in the center of mass and coaligned to the main axes. Such particles exhibit an interesting feature: their ground state structure changes with shape. The head-to-tail configuration of magnetic moments becomes energetically less favorable than the antiparallel dipole pair arrangement [5]. This structural transition in ground states also leads to changes in the microstructure of anisotropic nanoparticle systems when thermal energy becomes comparable with interparticle interaction energy. The orientation of dipole moment with respect to particle axes also affects the behavior of the particle system as a whole. In this work, we consider ellipsoidal particles whose magnetic moment is directed along the main axis of rotation. For these systems, we performed a detailed analysis of interparticle correlations and macroscopic properties of system in a wide range of parameters with the aim of revealing possible structural transitions and to assess the possibility to manage macroscopic response of the system, which realizes the idea of tuning and design of novel materials with controllable properties.

2. MAGNETIC ELLIPSOIDS

The investigated system consists of magnetic anisotropic nanoparticles that constitute ellipsoids of revolution. The semiaxis ratio is prescribed by parameter $X_0 = b/a$, which shows how the shape of ellipsoidal particle differs from a spherical one. In this work, we considered nanoparticles with values of parameter $X_0 = 1.1, 1.4, 1.7, 2.0, 2.3$. The total interaction potential for these particles consists of two components: steric and magnetic dipole–dipole interactions. To describe magnetic interaction, we used U_d potential:

$$U_d(i,j) = -[3(\mathbf{m}_i, \mathbf{r}_{ij})/r_{ij}^5 - (\mathbf{m}_i, \mathbf{m}_j)/r_{ij}^3], \qquad (1)$$

where $\mathbf{r}_{ij}$ is radius vector of two particles, $\mathbf{m}_{i(j)}$ is magnetic moment of $i(j)$ particle.

To describe steric interaction of anisotropic particles, we used a modified Gay–Berne potential (2) [6, 7], which is widely used to study nonspherical particles. This potential depends on not only the distance between centers of particles, but also their orientation:

$$U_{\mathrm{GB}} = \{4\varepsilon[A^{12} - A^6] + \varepsilon, \quad r_{ij} \le r_c, \quad 0, \quad r_{ij} > r_c, \qquad (2)$$

where

$$A = A(\mathbf{u}_i, \mathbf{u}_j, \mathbf{R}_{ij}) = \sigma_0/[r_{ij} - \sigma(\mathbf{u}_i, \mathbf{u}_j, \mathbf{R}_{ij}) + \sigma_0],$$

$$\sigma(\mathbf{u}_i, \mathbf{u}_j, \mathbf{R}_{ij}) = \sigma_0[1 - \varphi/2(\mathbf{R}_{ij}\mathbf{u}_i + \mathbf{r}_{ij}\mathbf{u}_j)^2/(1 + \varphi\mathbf{u}_i\mathbf{u}_j) + (\mathbf{R}_{ij}\mathbf{u}_i - \mathbf{r}_{ij}\mathbf{u}_j)^2/(1 - \varphi\mathbf{u}_i\mathbf{u}_j)]^{-1/2},$$

$$\varepsilon \equiv \varepsilon(\mathbf{u}_i, \mathbf{u}_j) = \varepsilon_0[1 - \varphi^2(\mathbf{u}_i\mathbf{u}_j)^2]^{-1/2},$$

$$\varphi = [X_0^2 - 1][X_0^2 + 1].$$

In this case, vector $\mathbf{R}_{ij} = \mathbf{r}_{ij}/r_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/r_{ij}$ is taken to be a unit vector collinear to the vector connecting the centers of particles, while $\mathbf{u}_{i(j)}$ is a unit vector directed along the principal axis, and $r_c = (2^{1/6} - 1)\sigma_0 + \sigma(\mathbf{u}_i, \mathbf{u}_j, \mathbf{R}_{ij})$ is a critical radius. Parameter σ_0 is taken to be $\sqrt{2}a$.

Table 1. Average characteristics of clusters at $\rho = 0.08$

Ellipsoid semiaxis ratio X_0	1.1		2.3	
Magnetic moment $\mathbf{m}^2$	1	5	1	5
Average cluster length, L	2.126	3.647	2.02	2.072
Clasterization, P	14.718	71.891	3.441	12.141
Mutual dipole orientation in cluster	60% of head-to-tail configurations	89% of head-to-tail configurations	95% of antiparallel pairs	99% of antiparallel pairs

To perform a detailed study of behavior of a system of magnetic anisotropic particles in a wide range of parameters, we performed molecular dynamic simulations in ESPResSo package [8]. In these simulations we use dimensionless parameters: all values associated with length are normalized to the length of short axis of ellipsoid (it is always equals to 1). Dimensionless temperature $T^* = kT/\varepsilon_0 = 1$, where k_T is thermal energy, and ε_0 is the energetic parameter. Dimensionless magnetic moment m is measured in $1/T^*$ units and disposed in the center of particle. We considered a system composed of 512 particles with periodic boundary conditions, long-range magnetic dipole–dipole interaction was calculated using the P^3M algorithm [8]. To reach equilibrium state, we first performed initial computation with period $10^5\Delta T^*$ and then started investigation of microstructure and macroscopic characteristics of the system. For particles of different shape, we performed studies at the same numerical concentration ρ in a wide range of values. The use of dimensionless parameters provides a possibility to study different nanoparticles showing similar properties. These systems are exemplified by spherical magnetic nanoparticles of magnetite (with saturation magnetization of 480 kA/m) inserted into ellipsoidal nonmagnetic soft nanoparticles. Dimensionless magnetic moment $\mathbf{m}^2 = 5$ for these particles at room temperature corresponds to a particle ~15 nm in diameter, while the moment $\mathbf{m}^2 = 3$ corresponds to a particle 12.5 nm in diameter. One may also consider nickel nanoneedles (saturation magnetization of material is 488 kA/m) coated with nonmagnetic material with a diameter in central cross-section ~50 nm and of different length (for example, equal to 115 nm for $X_0 = 2.3$).

3. SYSTEM MICROSTRUCTURE

A large array of data obtained by computer experiments including information on the particle coordinates and orientation of their dipoles provided a base for cluster analysis, which allows one to determine average characteristics of aggregation in the system. We used graph theory for this purpose: each particle becomes a node of a graph, while bonds between them are prescribed according to the following criterion: the energy of magnetic dipole–dipole interaction (1) should be negative, while interparticle distance should not be longer than a critical value. We calculated average cluster length (the number of particles in it), clusterization (the percentage of particles in clusters), and mutual orientation of magnetic moments.

Table 1 shows the average characteristics of system depending on magnetic moment and shape of nanoparticle. We used concentration $\rho = 0.08$ for this example. However, the same qualitative behavior is observed for systems at all other concentrations; the only difference is quantitative values.

The performed analysis showed that nanoparticles with a shape close to spherical, in contrast to elongated ellipsoidal particles, exhibit a high self-assembly degree; not only the number of clusters in system but also the average number of particles in cluster grows. Increasing the value of the magnetic moment for spherical particles leads to the growth of number of aggregates in the system and to a situation when magnetic moments of particles become practically collinear, which enhances the response of this cluster to external magnetic field. If particles are elongated, the growth of the magnetic moment causes such a mutual dipole orientation that head-to-tail configuration is extremely rare: the number of antiparallel pairs at different concentrations rises from 95% to 99%. Thus, the magnetic moment has less influence on the behavior of system of ellipsoidal particles.

Schematic representation of obtained clusters except single particles is given in Figs. 1a and 1b.

Thus, we can draw a conclusion that particle shape affects the characteristics of clusters resulting from self-assembly.

4. MACROSCOPIC RESPONSE OF SYSTEM

After study of system microstructure, we considered its macroscopic properties. Initial magnetic susceptibility is one of the most important characteristics of magnetic soft materials, because it displays how strong correlations of dipole moments in the system and how the system is sensible to external infinitely small magnetic field.

The dependences of initial magnetic susceptibility on magnetic moment of particle are given in Figs. 2a–2c.

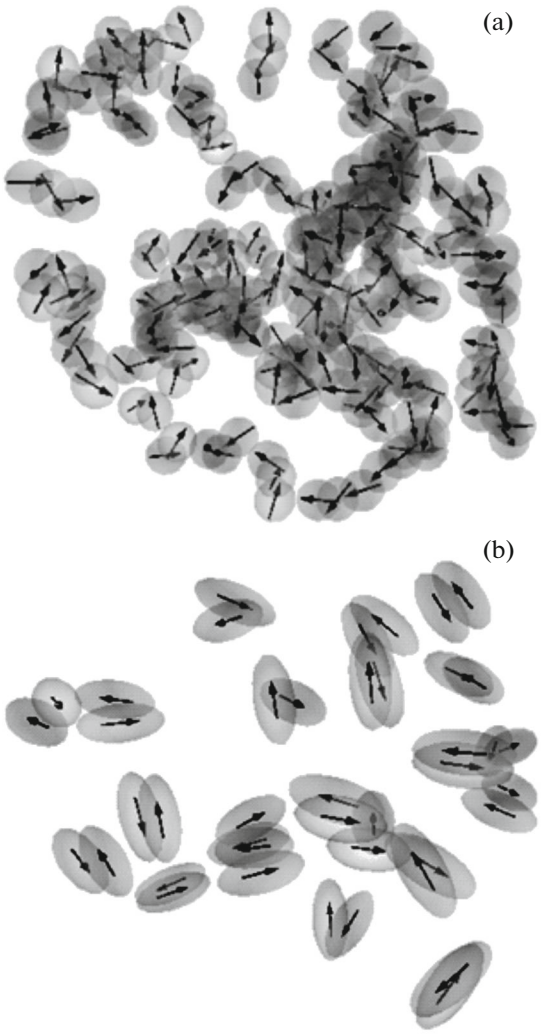

Fig. 1. Snapshots from simulation of clusters in system with concentration ρ = 0.08, parameters $\mathbf{m}^2 = 5$ and $X_0 = 1.1$ (a), 2.3 (b).

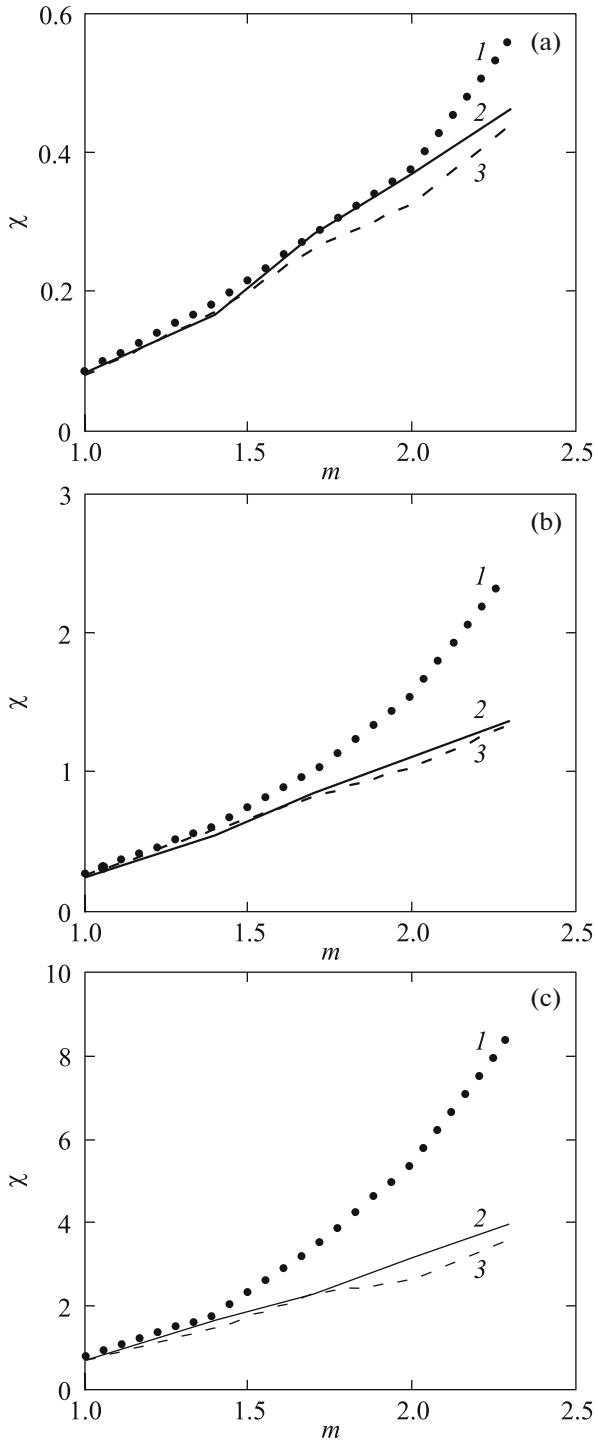

Fig. 2. Dependence of initial magnetic susceptibility on the value of magnetic moment of nanoparticles at concentration ρ = 0.02 (a), 0.06 (b), 0.16 (c); $X_0 = 1.1$ (*1*), 1.7 (*2*), 2.3 (*3*).

On the basis of the presented plots, we can draw a conclusion that the initial susceptibility increases with particle concentration and magnetic moment. The initial susceptibility of spherical particles increases faster and reaches larger values than one for ellipsoidal particles. This is due to the formation of chains in the system, which responds to an external field in a similar way. Increase in particle shape anisotropy leads to decrease of not only absolute value of susceptibility, but also its relative change. The overall decrease of interparticle dipole correlations and observed magnetic response can be explained by the change in the type of particle self-assembly, which is caused by the change of system ground state configuration. Since the entropy of an antiparallel pair is rather small, not many pairs appear, even at large values of magnetic moment. Furthermore, the magnetic moment of this structure equals zero on average; therefore, the susceptibility of such an object is lower than for a doublet with head-to-tail orientation.

Different behavior of nanoparticles of different shape is also observed on the consideration of radial

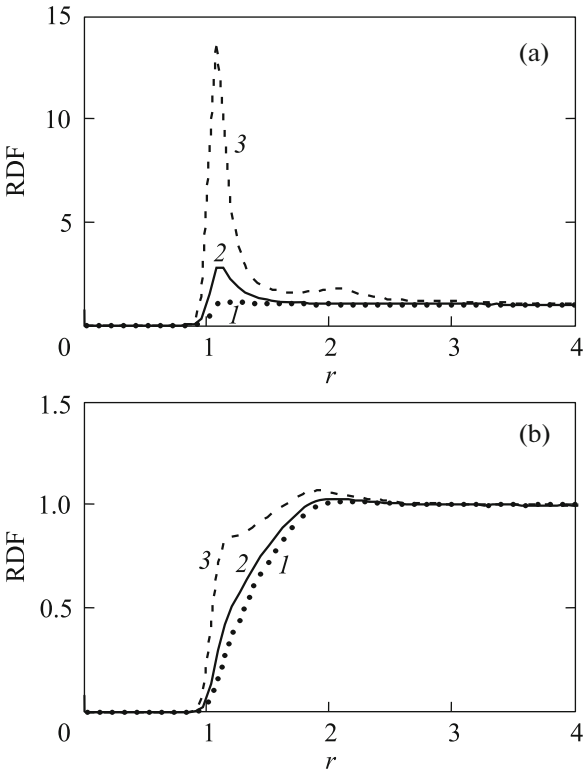

Fig. 3. Radial distribution function as a function of distance between particle centers considered at concentration $\rho = 0.16$, parameter $X_0 = 1.1$ (a), 2.3 (b), $\mathbf{m}^2 = 1$ (*1*), 3 (*2*), 5 (*3*).

distribution function (RDF), the probability density to find particle pair at the prescribed distance (Fig. 3).

One can see that the behavior of radial distribution function for ellipsoidal particles is independent of magnetic moment values. We can say that steric interaction can screen magnetic interaction. In the case of almost spherical particles, the first peak of radial distribution function increases with magnetic moment, which indicates the formation of clusters in the system. Thus, particle shape can rather strongly change the macroscopic response of system.

5. CONCLUSIONS

In this work, we studied self-assembly in the systems of magnetic anisotropic particles and the effect of this process on system behavior at room temperature. For this purpose, we used computer simulations performed by the molecular dynamics method. Cluster formation becomes less pronounced in a wide range of variation in magnetic moment and particle concentration when particle shape anisotropy rises. Antiparallel pairs become energetically more favorable than head-to-tail configuration; consequently, unstable pairs form at room temperature even at large value of dipole moment. Moreover, the total magnetic moment of antiparallel pair is small; therefore, the susceptibility of such an object is considerably lower than that of object with head-to-tail configuration. Therefore the anisotropy has a significant influence on the microstructure of the system of magnetic nanoparticles.

Thus, using particle shape anisotropy as a control parameter allows one to change self-assembly in the system from chains with head-to-tail orientation of magnetic moments (almost spherical particles) to spatially homogeneous system (ellipsoidal particles) without change in the value of saturation magnetization. This feature may be important factor for medical applications when strong magnetic response of nanoparticles should be combined with the absence of considerable particle aggregation. Thus, the shape of nanoparticles can be efficiently used as a control parameter for system microstructure, while the systems themselves will implement the idea of tuning and design new materials with controllable properties.

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