Molecular dynamics of magnetic particulate dispersions

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A computational investigation using the method of molecular dynamics was undertaken to characterize the state of magnetic particle dispersions. The simulations revealed that the microstructure of spherical particulate dispersions consists of chainlike clusters resulting from magnetic dipole alignment. Acicular particles formed clusters such as dimers, chains, and rings. The effect of fluid viscosity on the dispersion quality and the response of the magnetic dispersions to an external DC magnetic field are also reported.

I. INTRODUCTION

The dispersion quality and stability of magnetic particle dispersions (magnetic inks) is controlled by the balance between attractive and repulsive forces between particles in a dispersion medium of a specific chemistry. The attractive forces arise from van der Waals and magnetic interactions whilst the electrostatic and steric interactions give rise to repulsive forces between particles. Calculations have shown that van der Waals and electrostatic contributions to the total energy of interaction between particles are much smaller than the other two forces.[1,2]

The classical energy of interaction–distance plots found in colloid chemical literature are useful in predicting whether a dispersion is stable or not but do not yield information on the dispersion quality (i.e., presence of magnetic agglomerates), especially as a function of time. One computational method which can yield information on the dispersion quality of a magnetic particulate dispersion is molecular dynamics (MD). In this method, the state of a system of interacting particles is simulated by solving the classical equations governing the motion of each individual particle.

II. METHOD AND MODEL

The total energy for a system containing N interacting magnetic particles is the sum of a kinetic energy and a potential contribution. The kinetic energy consists of two parts: translational and rotational. In our model, the potential energy includes only magnetic attractive and steric repulsive energies.

The magnetic interaction energy for spherical particles is based on the magnetic dipole–dipole interaction and is given by

$$U_{\text{mag}}=\sum_{j>i}^{N}\sum_{i=1}^{N-1}\frac{\mu_0}{4\pi}\frac{1}{|r_{ij}|}\left(\mathbf{m}_i\cdot\mathbf{m}_j-\frac{3}{r_{ij}^2}(\mathbf{m}_i\cdot\mathbf{r}_{ij})(\mathbf{m}_j\cdot\mathbf{r}_{ij})\right), \tag{1}$$

where $\mathbf{m}$ is the magnetic moment, μ_0 is the permeability, and $\mathbf{r}_{ij}$ is the separation vector between spherical particles. For the calculation of the magnetic interaction energy between cylindrical particles, a pole–pole interaction approach is used and the resulting expression is as follows:

$$U_{\text{mag}}=\sum_{k=1}^{2}\sum_{l=1}^{2}\sum_{j>i}^{N}\sum_{i=1}^{N-1}\frac{\mu_0}{4\pi}\frac{P_i(k)P_j(l)}{r_{ij}(k,l)}, \tag{2}$$

where $r_{ij}(k,l)$ is the separation distance between poles of two different particles i and j, and P is the pole strength. Signs of the magnetic energy for cylindrical particles is determined by the signs of the interacting poles.

Available expressions for the calculation of steric repulsion energy between dispersant coated spherical particles are rather complex and require quantities that are not easily measured. Hence, a simple form of steric repulsion energy is employed in this simulation and is given by a truncated parabola:

$$U_{\text{st}}=\sum_{j>i}^{N}\sum_{i>1}^{N-1}\Phi_{ij}^{s}=\sum_{j>i}^{N}\sum_{i>1}^{N-1}A(r_1-r_{ij})^2,\quad \text{if}\quad r_{ij}\leqslant r_1. \tag{3}$$

The parameters A and r_1 are chosen such that the equilibrium center-to-center distance between two particles is no less than $2.3a$, where a is the radius of a particle.

The steric interaction energy between two cylindrical particles, i and j, is also represented by a truncated parabola

$$\Phi_{ij}^{s}=A\cdot(r_1-r_s)^2,\quad \text{if}\quad r_s\leqslant r_1, \tag{4}$$

where r_s is the minimum distance of separation between the longitudinal axis of the particles. The parameters A and r_1 are also chosen to simulate a steric layer of thickness $0.15a$.

The equations of motion of each particle have two forms: (1) translational ($Md^2\mathbf{r}_i/dt^2=\mathbf{F}_i$) and (2) rotational ($Id\boldsymbol{\omega}_i/dt=\mathbf{T}_i$), where $\mathbf{F}_i$ is the force on particle i, I is the moment of inertia, $\boldsymbol{\omega}_i$ is the angular velocity, and $\mathbf{T}_i$ is the torque. In the case of spherical particles, the torque arises from the magnetic interactions, whereas for cylindrical particles, both magnetic and steric contributions to the torque have to be taken into account. For spherical particles a drag term can be included in the translational equation of motion by adding to the force a term in the form $-6\pi a\eta\mathbf{V}_i$, where η is the viscosity of the fluid and $\mathbf{V}_i$ is the translational velocity of particle i. At this stage, rotational motion in a viscous fluid is not accounted for.

To study the dynamical and structural response of the magnetic dispersions containing spherical particles to an external dc field, we include the contribution of an external torque, $\mathbf{T}_{\text{ext}}$ ($=\mathbf{m}_i\times\mathbf{B}$, where $\mathbf{B}$ is the applied dc field), to the rotational equation of motion.

For both spherical and cylindrical geometries, the dipole moment is assumed to be attached physically to the particle. In the latter case the moment is parallel to the long axis of the cylindrical particle. In stead of Euler angles, the orientation of the particles is described by a set of four parameters

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FIG. 1. Relaxing configuration of a suspension of spherical particles after 4000 integration time steps in absence of fluid viscosity and external field. (a) and (b) mark two ends of chains linked through periodic boundary conditions.

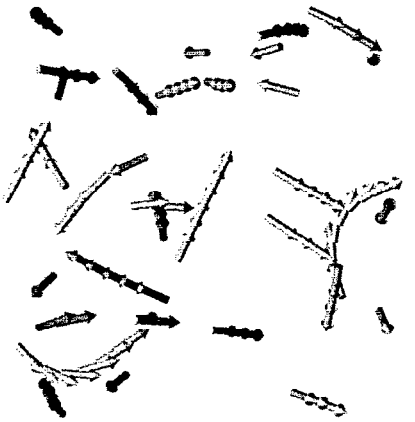

FIG. 2. Suspension of spherical particles at step 6000 in a fluid with a viscosity of 0.001 P.

(quaternions) developed by Evans *et al.*[3] Contrary to Euler angles, these parameters lead to equations of motion without singularity.[4]

Our simulation system is a three dimensional box with an edge length of $50a$ containing 100 particles ($N=100$). A periodic boundary condition is used. The physical and magnetic properties of magnetic particles are $M=3\times10^{-18}$ kg, $a=500$ Å, $m=380$ emu/cm^3 ($=4.75\times10^{-16}$ A m^2), and adsorbed polymer layer thickness=75 Å. In the case of cylindrical particles, the radii of the hemispheric tip and of the cylindrical body are assumed to be 500 Å with an aspect ratio of 2:1. The equations of motion are solved numerically using a finite difference approximation for the time derivatives. The time integration step in these simulations is 6.76×10^{-9} s. All simulations were carried out under the constraint of a constant kinetic energy of 1.66×10^{-22} J/particle.

III. RESULTS AND DISCUSSION

In all the simulations reported in this article, the same initial set of positions and magnetic moment orientations were used. The orientations were generated at random according to a normal distribution. Random numbers were also used for the positions of each particle. However, random positions leading to overlapping pairs of particles were excluded.

A. Spherical particles

Three simulations were conducted under the following conditions: (A) time=4000 integration steps, no fluid viscosity, and no external magnetic field; (B) time=6000 integration steps, viscosity=0.001 P, and no external field; and (C) time=4000 integration steps, zero fluid viscosity, an external magnetic field of 300 Oe applied after 2000 time steps.

Figure 1 shows the structure of the magnetic dispersion at the final stage in simulation A. In the case of spherical particles, minimization of energy takes place by alignment of magnetic moments. Here the particles form chains with nearly aligned dipole moments. Obviously, the lowest energy state corresponds to a single infinite chain. In our simulation such a state can be approached at large time steps. It may be noted that the periodic boundary condition imposed on the simulation cell permits a chain from exiting the cell from one side and reentering it on the other side. This feature is clearly seen in Fig. 1.

Simulation B was run to test the effect of fluid viscosity on the state of the dispersion. An increase in viscosity of the dispersion medium augments the time for relaxation. Minimization of energy is achieved by the formation of chains of particles in the initial stage of the calculation. However, since the motion of chains is more sluggish than that of single particles, further energy minimization by attachment of pieces of chains is strongly impeded by the fluid viscosity. The resulting suspension is therefore only composed of short pieces of chains as shown in Fig. 2, this despite the longer simulation time.

In Fig. 3 we illustrate the final structure of a suspension subjected to an external magnetic field (simulation C). The stimulation of the suspension with a magnetic field results in a strong structural anisotropy. Here, upon application of the field after 2000 time steps, those long chains of spherical particles which were perpendicular to the field break off into pieces which subsequently align with the field. All other

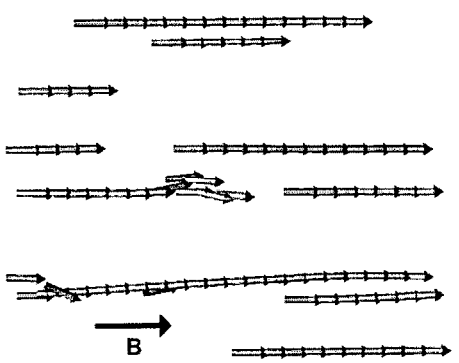

FIG. 3. Orientation of chains of spherical particles in an external magnetic field, B, of 300 Oe.

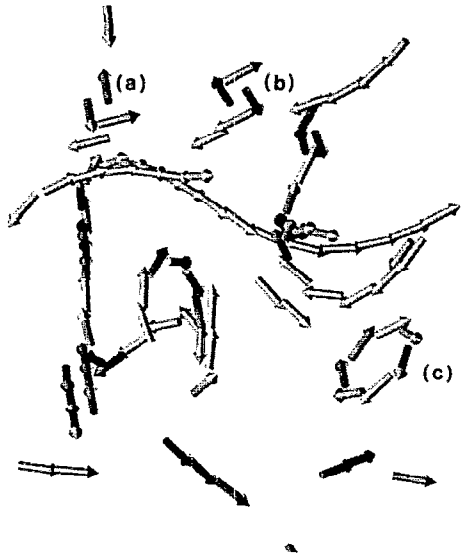

FIG. 4. Suspension of acicular particles after 4000 integration time steps (see text for details).

chains respond to the stimulus by directly aligning in the direction of the external field. Attachment of chains to form longer chains is also observed.

B. Acicular particles

The lowest energy state formed by two acicular particles interacting through pole–pole interactions can be shown to be a dimer with magnetic moments in opposite directions. A configuration composed of aligned particles constitutes only a metastable state. Moreover, rings of three, four,..., particles with opposite poles in contact are more stable than linear chain configurations. A simulation of 100 acicular particles with an aspect ratio of 2:1 was run for a period of 4000 integration steps. The final configuration of the suspension of acicular particles is shown in Fig. 4. As expected, stable dimers and rings are observed. For instance, a dimer, a four-particle ring, and a seven-particle ring are labeled on the figure as (a), (b), and (c), respectively. Similar ring configurations have already been observed in Monte Carlo calculations of dispersion of acicular magnetic particles with an aspect ratio of 10:1.[5] In addition to the observation of stable ring configurations, metastable pieces of chains are also seen. The structure of the suspension of acicular particles also shows aggregated configurations involving dimers, rings, and pieces of chains.

IV. CONCLUSION

We have developed a computational tool to understand at the microscopic level the dynamical behavior of dispersions of magnetic particles. The preliminary results reported in this article show the potential of the MD method to simulate the structure and behavior of dispersions of magnetic particles. Of particular interest are the relationships between particle geometry, steric repulsion, and the stability of the suspension. Further refinement of the model such as the inclusion of the translational and rotational motion of acicular particles in a viscous medium will lead to future progress in the understanding of the complex rheology of magnetic suspensions.

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