Microstructures in Strongly Interacting Dipolar Fluids *

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The formation of ring- and chain-like microstructures in ferrofluids consisting of interacting magnetic particles coated by a surfactant layer is studied by Monte Carlo simulations. For thin coating layers, it is found that ring- and chain-like structures coexist. The ring-like structures are suppressed by thicker coating layers. These observations are in agreement with recent experiments. Also, the ring-like structures are formed by dynamical aggregation of particles, instead of bending of linear chains. The latter process is forbidden by a substantial energy barrier. More generally, it is found that the ring structures exist when the parameter $\alpha = \mu^2/[k_B T(d+2\delta)^3]$ *is higher than a critical value* α_c*, where* μ *is the magnitude of magnetic moment,* d *is the diameter, and* δ *is the coating thickness of a particle. We find that when* $\alpha < \alpha_c$*, the ring structures cannot be formed spontaneously, while the chain-like structures still exist. Furthermore, the critical value* α_c *is almost independent of magnetic particle volume density in the low density range.*

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Ferrofluids provide both challenging fundamental physics problems and opportunities for important potential applications.[1,2] Ferrofluids have exhibited strong anisotropic properties, such as magneto-optic effect and viscosity, after applying a magnetic field. These effects should stem from the change of the inner structures of ferrofluids. Therefore, one of the key issues relates to the aggregation of magnetic particles and the corresponding changes in microstructures. Typically, magnetic fluids are stable colloidal dispersions of single domain magnetizable particles of about 10 nm in diameter. The particles, usually made of magnetite, carry weak magnetic moments, and a thin layer of surfactant (about 2 nm in thickness) is sufficient to prevent the particles from sedimentation at room temperature.[2] For particles of strong magnetic materials (such as Co and Fe), aggregation of the particles, however, occurs even in the presence of a thin surfactant layer due to the strong dipolar interactions between the particles. Aggregations in strongly interacting dipolar fluids result in intricate microstructures. As the properties of ferrofluids depend critically on the microstructures in the fluid, it is important to study the possible structures and the changes between structures in ferrofluids. It has theoretically and computationally been described[3−7] that strongly interacting dipolar particles may show chain- and ring-like structures at low particle densities. Wen *et al.*[8,9] studied the microstructures formed by microspheres by using of experimental and computer simulation methods. Their experiment showed that the microspheres prefer to forming ring-like structures in low concentrations. Also, their computer simulation results based on the magnetic dipolar interaction and neglected the thermal effect were in good agreement with their experiment. When the size of magnetic particles decreases to nanometres, can the chain- or ring-like structures still be formed? Tavares *et al.*[5] showed that the chains and rings coexist in their simulation of quasi-two-dimensional dipolar fluid at low densities. Attempts on observing these structures experimentally have not been successful[10,11] until recently.[12,13] Puntes *et al.*[12] observed that large Co particles with a 2-nm-thick surfactant coating could assemble into rings. Butter *et al.*[13] however only observed chain-like aggregations of large Fe particles with thick (about 6 nm) surfactant coating. Many works have been focused on the existence of liquid-vapor phase transition[14] and a few works studied the microstructure transition behaviour of chain-ring aggregations without applied magnetic field.[4,9] Undoubtedly, many rich phenomena in the formation of microstructures in ferrofluids are expected to be explored.[14]

Motivated by the experimental observations, we study how the microstructures in ferrofluids with interacting magnetic particles may change when the coating thickness is varied. The spontaneous formation of microstructures is a dynamical process in which the size of these structures changes when particles aggregate. Such processes are most conveniently studied by using Monte Carlo (MC) simulations in consideration of the thermal effect. The magnetic dipole–dipole interaction energy between two particles is given by

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$$E_{ij} = \frac{\mu^2}{r_{ij}^3}[-3(\boldsymbol{\mu}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{\mu}_j \cdot \boldsymbol{r}_{ij}) + \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j], \quad (1)$$

where r_{ij} is the distance between the centres of particle i and j, $\boldsymbol{r}_{ij} \equiv (\boldsymbol{r}_i - \boldsymbol{r}_j)/r_{ij}$ is an unit vector pointing from particle i to j, μ is the magnitude of magnetic moment of the particles, and $\boldsymbol{\mu}_i(\boldsymbol{\mu}_j)$ is a unit vector giving the direction of the dipole moment of particles $i(j)$. For simplicity, we consider our model ferrofluid to be a thin film approximately as thick as the particle size. Particle aggregation can, therefore, be regarded to take place in a two-dimensional plane. Note that the magnetic moment of each particle may orientate to any direction in a three-dimensional space. Such quasi-two-dimensional system is widely used to study the ferrofluids.[15,16] The particles are assumed to be spherical with a coating surfactant shell, as shown in Fig. 1.

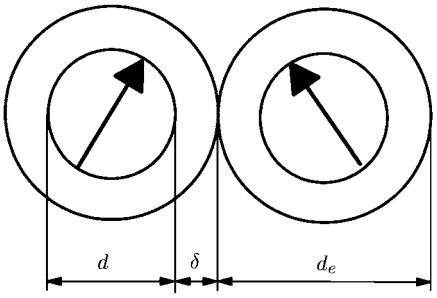

Fig. 1. Schematic sketch of magnetic particles coated with surfactant. The smallest separation between two particles is $(d + 2\delta)$, which is also the effective diameter d_e of a coated particle.

Here d is the diameter of magnetic particle, and δ is the thickness of the coating surfactant layer. Thus the particle has an *effective* diameter of $d_e = d+2\delta$. In order to study the effect caused mainly by dipolar interaction to the dynamic formation of micro-structures and the Van der Waals (VDW) force between the magnetic particles is very weak because of the coating surfactant, we neglect the VDW force and treat the repulsive force between the nearest-neighbouring particles as infinite when the surfactant layers overlap, i.e. the smallest separation between two particles is $(d + 2\delta)$. For numerical calculations, it is convenient to measure lengths in units of d. Thus, we define a reduced coating thickness $\delta^* = \delta/d$ and a reduced separation between two particles $r_{ij}^* = r_{ij}/d$. Taking the ratio of the interacting energy and the thermal energy k_BT, Eq. (1) can be rewritten in reduced quantities as

$$E_{ij}^* = \frac{(\mu^*)^2}{(r^*)_{ij}^3}[-3(\boldsymbol{\mu}_i \cdot \boldsymbol{r}_{ij})(\mu_j \cdot \boldsymbol{r}_{ij}) + (\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j)], \quad (2)$$

where E_{ij}^* is the reduced interaction energy and $(\mu^*)^2 = \mu^2/d^3k_BT$ is the ratio of the dipolar interaction energy for two non-coated touching particles to the thermal energy. Extensive numerical simulations are carried out in a two-dimensional system of reduced size of $L^* = L/d = 100$ consisting of $n = 381$ particles, under periodic boundary conditions. We have taken $(\mu^*)^2 = 12.0$. Values of the size of strong magnetic particles (such as Fe, Co, Ni) are approximately 10 nm at room temperature. To treat the long-range dipolar interactions, one approach is to use the Ewald summation method,[15] and another is by means of the truncation approximation.[17] Here the long-range character of the interaction is taken into consideration by summing over nearest-neighbouring particles within three times the average separation between particles in a random dispersion of particles in systems of the same size. It has been shown that such treatment gives sufficient accuracy for calculations of most physical quantities.[18,19] In each MC step, a randomly selected magnetic particle is allowed to move a maximum displacement (equal to $0.2d$) in a randomly chosen direction and the magnetic moment of the particle is also allowed to change its direction randomly according to the Metropolis algorithm.[20] Namely, when a particle is assumed to have a displacement and a change of its moment orientation, the system energy will be changed due to the dipolar interaction between particles. The acceptance of such movement is determined by the Metropolis algorithm. No particle overlap is allowed. For an n-particle system, equilibrium is achieved typically after $n \times 10^6$ steps.

Figure 2 shows the microstructures in a ferrofluid for different thicknesses of the surfactant coating layer. For thin coating layer [$\delta^* = 0.1$ in Fig. 2(a)], the ring and chain structures co-exist. As the surfactant coating thickness increases [$\delta^* = 0.25$ in Fig. 2(b)], the ring-structures disappear while chains, curves, and branched structures still exist. For thick coating layer [$\delta^* = 0.5$ in Fig. 2(c)], the microstructures become of stable ferrofluids without aggregation due to thermal effects. The coating thickness, which affects the strength of the dipolar interaction through the smallest allowed separation, is thus crucial in the formation of ring-like microstructures. For the cases of thin coating layers, we observed that the ring-structures are formed by the dynamic aggregation of particles, i.e. a few particles first form an arch and then more particles join in and close the arch into a ring. This process is possible for thin coating layers because the magnetic dipolar interaction between particles that temporarily form a chain or a curved chain (an arch) is sufficiently strong to hold the particles in place long enough against thermal fluctuations so that other particles can join the arch and close the structure. As the coating becomes thicker and hence the magnetic interaction becomes weaker, it becomes increasingly difficult that a close structure can be formed.

As the dipolar interacting energy tends to align the moments of nearest-neighbouring particles "nose to tail", one might have thought that a ringed structure could be formed by the bending of a chain of fixed length. Such a process, however, is *not* observed in the simulations.

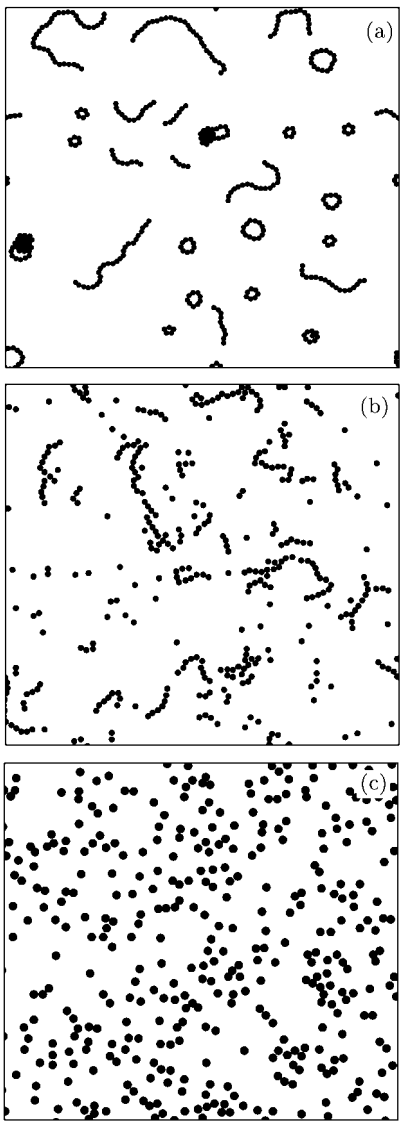

Fig. 2. Snapshots of magnetic particles in a ferrofluid with different coating thicknesses for (a) $\delta^* = 0.1$, (b) $\delta^* = 0.25$, and (c) $\delta^* = 0.5$.

To understand the absence of such process, it is instructive to study the energetics of chain and ring structures of a fixed number of particles. It turns out that for a finite chain consisting of n dipoles, the energy of a closed ring is lower (hence more stable) than that of a straight chain[4,8] for $n > 3$. Consider magnetic particles of diameter d and $\mu^2/d^3 k_B T = 12.0$. As before, we take the chains with fixed particles for $n = 3$, 4, and 6 and calculate the energy change when a chain is gradually curved into a ring based on Eq. (1). The energy of a curve $E_r(\Omega)$ characterized by an angle Ω ($0 < \Omega < 2\pi$) subtended by the two ends of the curve at the centre of curvature is found to depend on Ω non-monotonically (see Fig. 3). The magnetic moments are assumed to point tangentially to the radius of curvature so as to make use of the dipolar interaction to lower the energy. The results show that there is an energy barrier between a linear chain ($\Omega = 0$) and a closed ring ($\Omega = 2\pi$), where we have denoted the energy at $\Omega = 0$ by E_c with $E_c < 0$. The energy barriers $\Delta E_{c\to r}/k_B T$ for transforming from a chain-structure to a ring-structure (solid line) and $\Delta E_{r\to c}/k_B T$ from ring to chain (dotted line) are shown in the insert of Fig. 3 as a function of n. This energy barrier makes it hard to bend a chain into a ring, unless the chain is sufficiently long. However, when the chain is quite long, it will form labyrinthine structures but not simple bending structures or large rings [see Fig. 2(a)]. The existence of labyrinthine structures makes it difficult for the long chain to curve into a large ring.

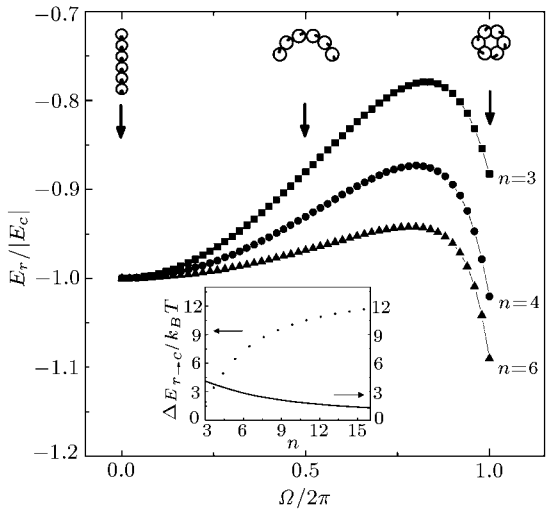

Fig. 3. The ratio of the energy of a curved chain subtending an angle Ω to the energy of a linear chain, $E_r/|E_c|$, as a function of the angle $\Omega/2\pi$. Results for a system with $n = 3$ (squares), $n = 4$ (circles), and $n = 6$ (triangles) particles are shown. Schematic sketches of the structure with 6 particles are also shown for $\Omega/2\pi = 0$, 0.5, and 1.0. The inset gives the energy barriers for transforming from a linear chain-structure to a ring-structure and vice versa, as a function of the particle number.

The simulation results (Fig. 2) are of relevance to recent experimental observations of ring and chain structures in ferrofluids[12,13] in which the ring structures only appears for sufficiently thin coating layer [see Fig. 2(a)], i.e. for sufficiently strong dipolar interaction between the particles. For fixed values of magnetic moment and particle diameter at a given temperature, there exists a critical coating thickness above which the ring structures disappear in the ferrofluids spontaneously. We have performed a series of simulations and found that it is indeed the case. Inspecting Eq. (2) more closely reveals that, for fixed

magnetic particle volume density, the important parameter is the combination $\alpha \equiv \mu^2/(k_BT(d+2\delta)^3) = (\mu^*)^2/(1+2\delta^*)^3$. The parameter reflects the comparison between the interaction energy for coated particles in contact and the thermal energy.[13,21] We have carried out detailed simulations as those discussed in Fig. 2 to determine the critical coating thickness for a given magnitude of dipole moments. The results show that for $\alpha > \alpha_c \approx 3.6$, the ring and chain structures coexist in the dilute volume density studied here, while for $\alpha < \alpha_c$, the particles still aggregate but only chain structures exist. The microstructure transition versus the dipolar interaction strength is shown in Fig. 4. The upper region separated by the line represents the coexistence of the ring- and chain-like structures, while the lower region denotes the chain-like structures only. The calculated critical value α_c seems to be almost independent of the volume density in the studying range of our simulations (from 0.03 to 0.08). Note that the increase of the coating thickness also causes the increase of the effective density of magnetic particles at the same time. It is the case that high density can make the particles have less "free" space to move, this limits the particles to grow into ring structures but forms net-like structures.[8] In our case, however, the condition of formation of ring structures are related to the dipolar interaction strength and thermal perturbation, the particle volume density has little effect on the ring-like structure formation.

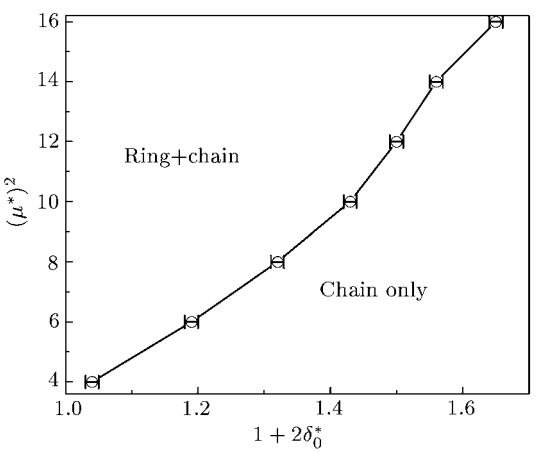

Fig. 4. The microstructure transition of ring- and chain-like aggregations at different dipolar interaction strengths under fixed temperature. The symbols represent the simulation results, the line guided to the eyes separates the region into two parts. The one (upper region) denotes coexistence of the ring- and chain-like structures, the other (lower region) denotes the chain-like aggregation only.

In summary, we studied the formation of ring-like and chain-like structures in ferrofluids consisting of interacting magnetic particles using Monte Carlo simulations. Snapshots of the aggregation process revealed that rings are not formed by bending of chains, but instead by a dynamical aggregation process of particles. Though the model used here was quite simple, the numerical results showed that a thin layer of surfactant coating favors the formation of ring structures; while a thick coating layer suppresses ring-structure formation. The results are in agreement with recent experimental observations.[12,13] More generally, it is found that ring structures exist when the parameter $\mu^2(k_BT(d+2\delta)^3)$ is higher than a critical value. Thus, formation of ring structures can also be controlled by tuning the magnitude of the magnetic moment (e.g., using different magnetic particles) or the temperature.

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