Two-Dimensional Monte Carlo Simulations of a Polydisperse Colloidal Dispersion Composed of Ferromagnetic Particles

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1. Introduction

A Ferrofluid is classed as a functional fluid because it exhibits attractive functional properties in an applied magnetic field. Under the influence of a strong external magnetic field, the ferromagnetic particles in the ferrofluid tend to aggregate to form thick chain-like clusters. These clusters give rise to a large resistance in a flow field. Therefore, several fluid engineering applications using this phenomenon are under development: for example, mechanical dampers and actuators, so that the aggregate structures for various conditions have to be clarified in order to develop new functional fluids which can apply to wide fields of science and technology.

A microscopic simulation approach such as the Monte Carlo method is a powerful technique used to clarify the particle aggregation phenomena. Hence, several molecular simulations using this method have already been conducted on ferromagnetic colloidal dispersions. However, these previous investigations have generally tended to use an idealized dispersion comprising of identical spherical particles with the same diameter.

On the other hand, investigations on polydispersity of the aggregate structures are indispensable for clarifying aggregate structures and magnetic properties of a real ferrofluid. There are a number of studies on polydisperse ferromagnetic particle system (A.O. Ivanov and S.S. Kantorovich, 2003; P. Bhatt et. al., 1998; T. Kristof, and I. Szalai, 2003; T. Kruse et. al., 2003; Z. Wang and C. Holm, 2003). However, these studies have mainly investigated the system for relatively weak magnetic interaction between particles. That is, they have studied the short chain-like clusters in detail. This is because a particle rarely moves away from a cluster due to the large energy barrier when the particle-particle interactions are very strong for the ferromagnetic particle system. Thus, the conventional Monte Calro method based on a Metropolis method can not reproduce aggregate structures of thick chainlike clusters.

If the particle-particle interaction increases, a number of complicated microstructures are expected to be detected. In this study, we introduced a cluster-moving MC method (Satoh, 1992), which is suitable for reproducing physically reasonable aggregate structures for strong particle-particle interactions. This method has a much higher rate of convergence in achieving an equilibrium state because the clusters formed during the simulations can move as composite single particles.

The objective of the present study is to clarify the aggregate structures of polydispersed ferromagnetic colloidal dispersion by the cluster-moving MC method. Influences of both particle-particle and particle-field interactions on the internal structures of the aggregate structures are analyzed in terms of a pair correlation function and a radial distribution function. In addition, the cluster size distribution and angular distribution function have been

investigated.

2. Polydisperse System of Ferromagnetic Colloidal Particles

In this study we consider a two-dimensional system comprising of N spherical particles with a distribution of particle diameters, d, and a magnetic dipole at their center. We also take into consideration the fact that the particles are coated with a steric layer of thickness δ. In the present study, we assume that the system possess a normal particle-size distribution with an average particle diameter d_0 and a standard deviation $\sigma = 0.35$.

If the magnetic moment of particle i and the uniform magnetic field strength are denoted by $\mathbf{m}_i$ ($m_i = |\mathbf{m}_i|$) and $\mathbf{H}$ ($H = |\mathbf{H}|$), respectively, the energy of interactions between particle i and the magnetic field, $u_i^{(H)}$, the energy of magnetic dipole-dipole interaction, $u_{ij}^{(m)}$, and the interaction energy due to the overlapping of the steric layers, $u_{ij}^{(v)}$, are expressed as follows:

$$u_i^{(H)} = -kT\xi_i \mathbf{n}_i \cdot \mathbf{H} / H \,, \tag{1}$$

$$u_{ij}^{(m)} = kT\lambda_{ij} \frac{d_0^3}{r_{ji}^3} \left\{ \mathbf{n}_i \cdot \mathbf{n}_j - 3\left(\mathbf{n}_i \cdot \mathbf{t}_{ji}\right)\left(\mathbf{n}_j \cdot \mathbf{t}_{ji}\right) \right\}, \tag{2}$$

$$\begin{aligned} u_{ij}^{(v)} = {} & \frac{\lambda_{vi} kT}{2} \left\{ 2 - \frac{2C_i}{t_{\delta i}} \ln\left(\frac{t_{\delta i} + 1}{C_i} \right) - 2\frac{C_i - 1}{t_{\delta i}} \right\} \\ & + \frac{\lambda_{vj} kT}{2} \left\{ 2 - \frac{2C_j}{t_{\delta i}} \ln\left(\frac{t_{\delta i} + d_j / d_i}{C_j} \right) - 2\frac{C_j - d_j / d_i}{t_{\delta i}} \right\}, \end{aligned} \tag{3}$$

in which

$$\begin{aligned} C_i &= \frac{(1 + t_{\delta i})^2 - (d_j / d_i + t_{\delta i})^2 + 4r_{ji}^2 / d_i^2}{4r_{ji} / d_i}, \\ C_j &= \frac{(d_j / d_i + t_{\delta i})^2 - (1 + t_{\delta i})^2 + 4r_{ji}^2 / d_i^2}{4r_{ji} / d_i}, \end{aligned} \tag{4}$$

where k is Boltzmann's constant, T is the absolute temperature of the fluid, r_{ji} is the magnitude of the vector $\mathbf{r}_{ji}$ drawn from particles i to j, $\mathbf{n}_i$ and $\mathbf{t}_{ji}$ denote the unit vectors given by $\mathbf{n}_i = \mathbf{m}_i / m_i$ ($m_i = |\mathbf{m}_i|$) and $\mathbf{t}_{ji} = \mathbf{r}_{ji} / r_{ji}$. The parameter $t_{\delta i}$ in Eqs. (3) and (4) is the ratio of the thickness of the steric layer δ to the radius of the solid portions of particle i, and is expressed as $2\delta / d_i$. The dimensionless parameters λ_{vi} and λ_{vj} in Eq. (3) are written as

$$\lambda_{vi} = \left(\frac{d_i}{d_0} \right)^2 \lambda_v \,, \quad \lambda_{vj} = \left(\frac{d_j}{d_0} \right)^2 \lambda_v \,, \quad \lambda_v = \frac{\pi d_0^2 n_s}{2} \,, \tag{5}$$

in which λ_v is a dimensionless parameter representing the strength of steric interactions between two particles with the same average ensemble diameter d_0, and n_s is the number of surfactant molecules per unit area on the particle surface.

If we assume that the magnitude of the magnetic moment of particles, m (= $|\mathbf{m}|$), is in proportion to its particle volume $\pi d^3/6$, then the dimensionless parameters ξ_i and λ_{ij} in the Eqs. 1 and 2 can be written as

$$\xi_i = \left(\frac{d_i}{d_0}\right)^3 \xi_0 , \quad \lambda_{ij} = \left(\frac{d_i d_j}{d_0^2}\right)^3 \lambda_0 , \tag{6}$$

in which ξ_0 and λ_0 are the dimensionless parameters for the particles with the mean diameter d_0, representing the strength of particle-field and particle-particle interactions, relative to the thermal energy. These parameters are written as

$$\xi_0 = \mu_0 m_0 H / kT , \quad \lambda_0 = \mu_0 m_0^2 / 4\pi d_0^3 kT . \tag{7}$$

3. The Simulation Parameters

Two-dimensional MC simulations have been conducted under the following conditions. The simulation region used here is a square unit cell with side length L, and the periodic boundary condition is adapted. The number of particles N and the area fraction of particles ϕ_a are taken as N = 900 and ϕ_a = 0.1, respectively. The particle-size distribution is assumed to be Gaussian, and we have considered the standard deviation σ = 0.35, with the average diameter d_0 = 1.0. The smooth Gaussian distribution curve is discretized into increments such as Δd = 0.035d_0 for specifying the diameter of each particle, as shown in Figure. 1. According to the discretized Gaussian distribution, the number of particles with a specific diameter can be determined.

The side length of the square simulation box, L, is taken as L = 89.12d_0 for the polydisperse systems of σ = 0.35, and L = 84.07d_0 for a monodisperse system, respectively. The initial configuration of particles and the initial directions of the magnetic moments are taken randomly. The thickness of the steric layer is taken as δ = 0.15d_0, and the dimensionless parameter, λ_v, representing the strength of the steric interactions between the two particles, as λ_v = 150. If the distance between the surfaces of the steric layer of the two particles is smaller than 0.2d_0, then these particles are assumed to form a cluster. The cutoff radius for the particle-particle interactions, r_{coff}, is 10d_0.

Under these parametric conditions, we performed the MC simulations for various cases of the dimensionless parameters λ_0 and ξ_0 such as λ_0 = 4, 6, 8 and ξ_0 = 0, 1, 2, 4, 30. Each simulation was executed up to approximately 450,000 MC steps, in which the cluster-moving algorithm was employed after every 80 MC steps up to the first 270,000 MC steps, and it was ensured that the system attains equilibrium. In the subsequent 180,000 MC steps, the conventional Metropolis algorithm was conducted instead of the cluster-moving procedure until the end of each run. The mean values were evaluated using the data of the last 180,000 MC steps.

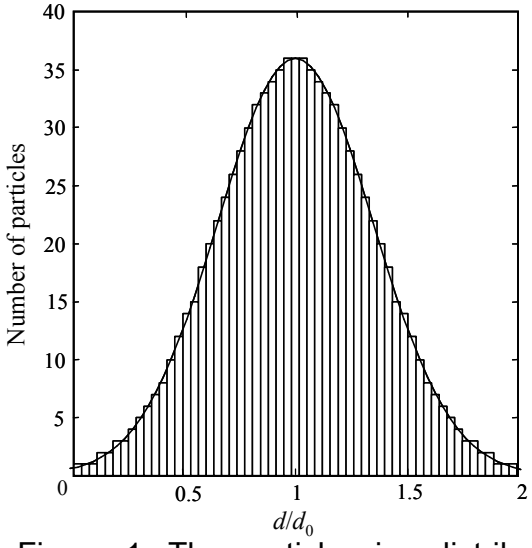
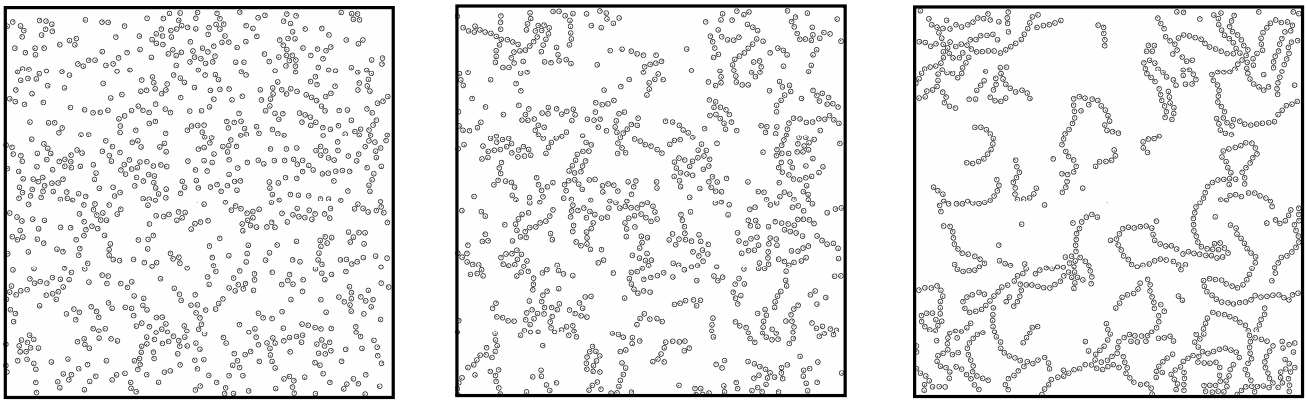
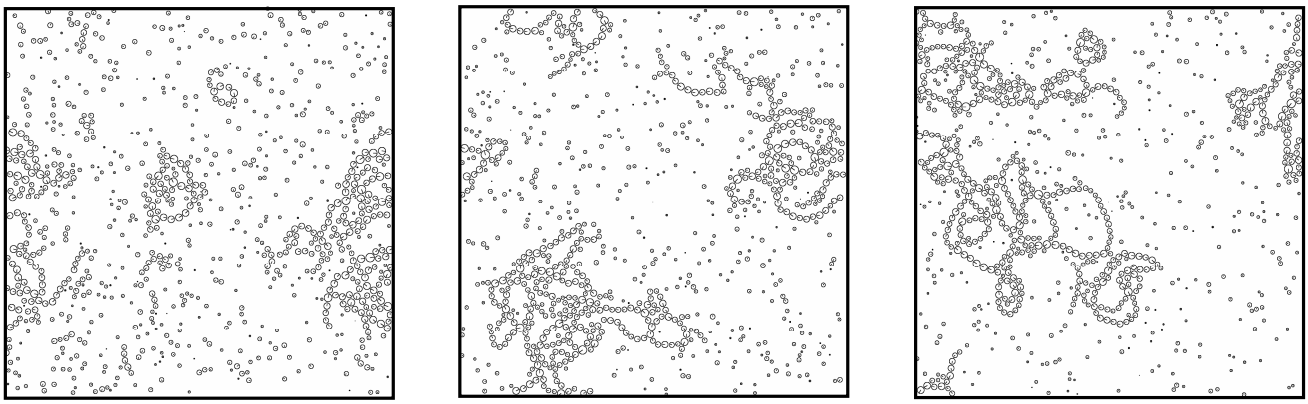


Figure 1. The particle size distribution for σ = 0.35



(a) (b) (c)

Figure 2: The influence of the interactions between particles on the aggregate structures for the monodisperse system: (a) $\lambda_0 = 4$; (b) $\lambda_0 = 6$; (c) $\lambda_0 = 8$.



(a) (b) (c)

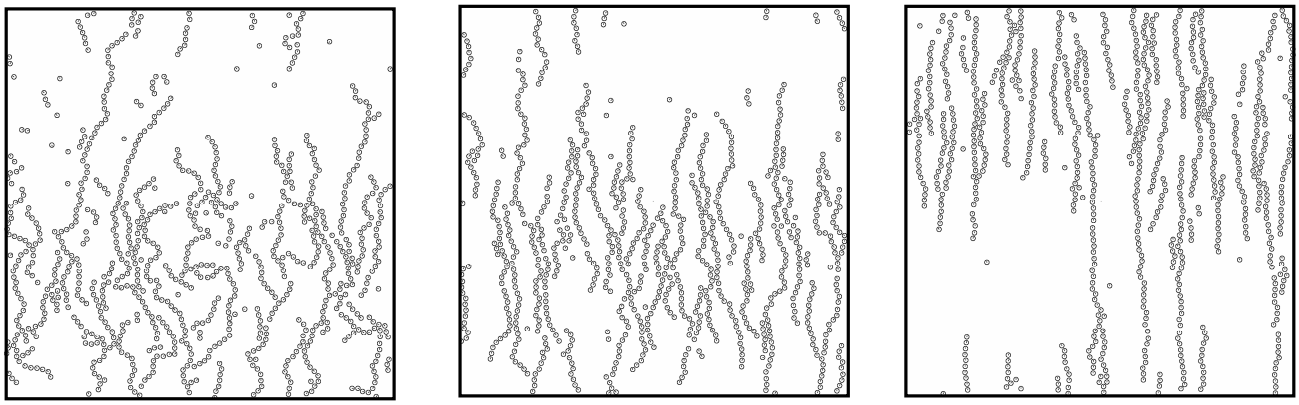
Figure 3: The influence of the interactions between particles on the aggregate structures for the polydisperse system: (a) $\lambda_0 = 4$; (b) $\lambda_0 = 6$; (c) $\lambda_0 = 8$.

4. Results and Discussion

First we obtained aggregate structures in an absence of external magnetic field and we compared it for a polydisperse system with that for a monodisperse system. In the monodisperse system as shown in Figure 2, open necklace-like clusters are formed and they extend with increasing strength of the magnetic particle-particle interaction: however, there are few clusters which are larger than those composed of about thirty particles. The reason for this characteristic may be interpreted as follows. Single-moving particles have to be combined with short chainlike clusters in order for these clusters to grow to form long open necklace-like clusters. However, after open necklace-like clusters have grown to a certain degree, the number of single-moving particles significantly decreases, so that the cluster size distribution attains equilibrium and does not change.

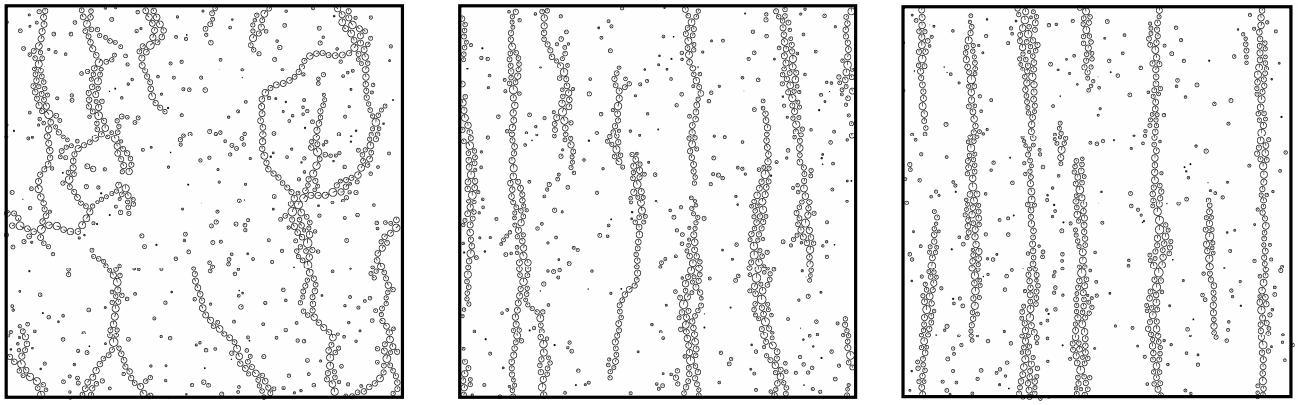
In a polydisperse system with a larger standard deviation, $\sigma = 0.35$, clump-like clusters are formed for a weak magnetic particle-particle interaction (Figure 3). For a stronger magnetic interaction, larger size clusters that exhibit a complicated network structure are formed.

Then we consider the aggregate structures for the strong magnetic interactions between particles. The influence of the magnetic field on the aggregate structures for a monodisperse system and polydisperse system are compared.



(a) (b) (c)

Figure 4: The influence of magnetic field on the aggregate structures for the monodisperse system: (a) ξ_0 = 1; (b) ξ_0 = 4; (c) ξ_0 = 10.



(a) (b) (c)

Figure 5: The influence of the interactions between particles on the aggregate structures for the polydisperse system: (a) ξ_0 = 1; (b) ξ_0 = 4; (c) ξ_0 = 10.

In the case of the monodisperse system, thin, bent chain-like clusters become straight with an increase in the strength of the magnetic field (Figure 4). In the case of a large standard deviation of σ = 0.35, large clump-like clusters are formed in the initial stages of the chain-like cluster formation during the simulation (Figure 5). This is because there are several large particles that possess a particle-particle interaction strong enough to form the clump-like clusters. However, as the influence of the magnetic field dominates, the particles align along the magnetic field direction to form the straight chain-like clusters. This leads to the formation of the rather thick straight chain-like clusters, whereas the number of branch-like and bent structures found in the chain-like clusters decrease.

One of the characteristics of the particle aggregation in the polydisperse system is the appearance of various interesting structures, such as the clump-like and the branch-like structures, due to the strong interaction of the larger particles. In order to investigate the formation of these structures, we consider a case in which the three particles are in contact with each other (Figure 6). We assume that two particles *j* have the same fixed diameters d_j and the other has the variable diameter d_i. We then propose two representative configurations of these three particles: linear and triangular, and we investigate the influence of the diameter d_i of the particle *i* on potential energies of the two typical configurations.

The obtained potential energy curves implies that the triangular configuration is more

stable than the linear configuration when the ratio of particle diameter d_i/d_j is larger than 2.1. This is because the influence of the attractive interaction between particles *i* and *j* dominates over the influence of the repulsive interaction between the two particles *j* with an increase in the particle diameter. The formation of the triangular configuration for the polydisperse system enhances the formation of the branch-like or the clump-like structures.

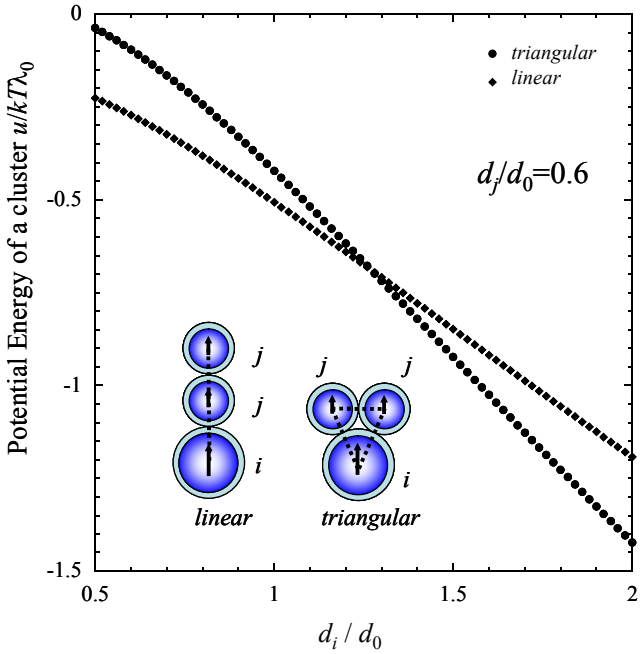


Figure 6: Influence of particle-size on the interaction energy between three particles in a cluster.

5. Summary

We have investigated the aggregation phenomena occurring in a polydisperse colloidal dispersion composed of ferromagnetic particles, simulated by means of the cluster-moving Monte Carlo method.

In a monodisperse system, open necklace-like clusters are formed and they extend with increasing strength of the magnetic particle-particle interaction. In a polydisperse system with a larger standard deviation, σ = 0.35, clump-like clusters are formed for a weak magnetic particle-particle interaction. For a stronger magnetic interaction, larger size clusters that exhibit a complicated network structure are formed. These complicated cluster formations found in a polydisperse system are mainly due to the effect of the presence of larger particles. With an increase in the external magnetic field, these structures reorganize to form the straight chain-like clusters.

The formation of the triangular configuration for the polydisperse system enhances the formation of the branch-like or the clump-like structures.

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