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Monte Carlo simulations on phase change in aggregate structures of ferromagnetic spherocylinder particles

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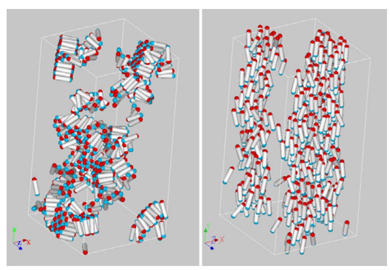
HIGHLIGHTS

- Raft-like clusters are preferred in no applied magnetic field.
- Raft-like clusters disappear within a small field change.
- Long and thick chain-like clusters are formed in a certain situation.
- Longer magnetic particles yield raft-like clusters more significantly.
- Typical aggregate phases are raft-like, thick chain-like and no clusters.

GRAPHICAL ABSTRACT



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ABSTRACT

A suspension of ferromagnetic rod-like particles can be expected to exhibit strong magneto-rheological characteristics, which is a significantly important factor for application of magnetic particle suspensions to mechanical dampers and actuators. Hence, in the present study, we address a suspension composed of ferromagnetic rod-like particles in thermodynamic equilibrium. We here investigate the dependence of the phase change in aggregate structures on the various factors such as magnetic field strength, magnetic particle–particle interaction strength and volumetric fraction of magnetic particles. Monte Carlo simulations have been carried out to obtain results of snapshots, radial distribution function and order parameter of the system. In a weak applied magnetic field, the magnetic rod-like particles tend to aggregate to form raft-like clusters if the magnetic particle–particle interaction is much larger than thermal energy. If the magnetic field is increased, these raft-like clusters drastically dissociate into single-moving particles, that is, the phase change in aggregate structures arises. Moreover, the phase change in the aggregate structures is induced by the magnetic particle–particle interaction strength, from no cluster formation to long and thick chain-like clusters, in a strong applied magnetic field circumstance. As the length of the magnetic rod-like particles is increased, the orientational configuration comes to have a more significant effect on the cluster formation.

1. Introduction

Magnetic particle suspensions exhibit the effect of resistance in a flow field in a certain situation of both an applied magnetic field and a flow field. This is called the magneto-rheological effect and a fluid exhibiting this effect is called a magneto-rheological fluid [1]. A ferrofluid is a representative magneto-rheological fluid, and this functional fluid is a colloidal suspension that is composed of spherical magnetic particles with approximately 10 nano-size in a base liquid [2]. The main target of magneto-rheological fluids for application is mechanical dampers and actuators in the fluid engineering field [1,2]. In general, magnetic spherical particles are used for synthesizing magneto-rheological fluids. However, if magnetic rod-like particles are used instead of the more common spherical

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particles, they exhibit a more significant resistance to a flow field, leading to a larger magneto-rheological effect [3–10]. Recently, there may be another hopeful application to use magnetic particles in the different fields. For instance, there is a magnetically targeted drug delivery in the bioengineering field [11–13], and a recovering technology for specific substances such as hazardous heavy metal molecules (environmental waste and pollutants) or valuable noble metal molecules from water (sea, lake, etc.) in the environmental resources engineering field [14–16].

On the other hand, hematite particles are magnetized in a direction normal to the particle axis direction, and exhibit much weaker magnetization than magnetite [17–19]. This feature regarding magnetization gives rise to exhibiting quite different characteristics. For instance, suspensions composed of spindle-like hematite particles have been found to exhibit negative viscosity in a certain situation of an applied magnetic field. This negative viscosity has been predicted by the theory based on the orientational distribution function and verified by an experimental study using a cone-plate-type rheometer that can function in the situation of an external magnetic field [20–22]. However, it is noted that the viscosity component due to the magnetic properties of particles becomes negative, but the net viscosity of the fluid remains positive. Currently, development of new magneto-rheological fluids has been challenged and several researchers have succeeded in obtaining new hematite particles with a variety of shapes such as rod-like, oblate spheroidal and cubic-like [23,24].

Although hematite particle suspensions are quite attractive to be investigated, we here address a usual magnetic suspension composed of ferromagnetic rod-like particles. This is partially because they are usually magnetized in the particle axis direction, and exhibit significant orientational feature of a single-peak-type orientational distribution under the circumstance of an applied magnetic field and a flow field, leading to a large magneto-rheological effect [25–31]. The biomedical and environmental resources engineering fields require more sophisticated functional properties for the application of magnetic particles and composites [32–34]. In the fluid engineering field, researchers have been applying synthesis technology to generate magnetic particles with particular magnetization characteristics by modifying the particle shape and size [35–38]. The magneto-rheological effect has a strong relationship with aggregate structures of magnetic particles that are dependent on a variety of factors such as magnetic particle–particle and particle-field interaction strengths. In a suspension composed of magnetic spherical particles, several typical phases of aggregates structures have been found to arise, dependent on values of the above-mentioned factors.

In the present study, therefore, we address a ferromagnetic rod-like particle suspension in order to investigate the phase change in aggregate structures of the particles in the situation of an external magnetic field. Characteristics of the phase change are investigated by Monte Carlo (MC) simulations for thermodynamic equilibrium. We attempt to clarify the dependence of the phase change in aggregate structures on the field strength, the magnetic particle–particle interaction strength, the volumetric fraction, etc.

2. Simulation method

2.1. Particle model

As shown in Fig. 1, a ferromagnetic rod-like particle is idealized as a spherocylinder with a point dipole moment $\boldsymbol{m}$ at the particle center in the particle axis direction. The length of the cylindrical part is l_0, the diameter of hemispherical part is d, and the total length of the spherocylinder is l (=l_0+d). The particle is assumed to be covered by a uniform steric layer with thickness δ. In MC simu-

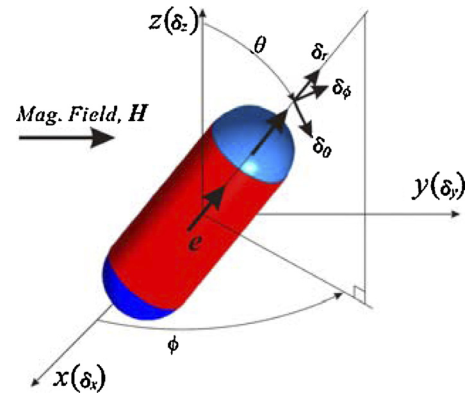

Fig. 1. Magnetic rod-like particles in a simple shear flow under the circumstance of an applied magnetic field in the y-direction.

lations, a suspension composed of these magnetic spherocylinder particles is assumed to be in a uniform external magnetic field $\boldsymbol{H}$ =$H\boldsymbol{h}=(0, H, 0)$, where $\boldsymbol{h}$ (=$\boldsymbol{H}/|H|$) is the unit vector denoting the field direction. The situation of an arbitrary spherocylinder particle i is described by the position vector $\boldsymbol{r}_i$ and the orientational unit vector $\boldsymbol{e}_i$, denoting the particle direction.

Employing subscript i for an arbitrary spherocylinder particle i, the interaction energy of particle i with the magnetic field, $u_i^{(H)}$, and the interaction energy between particles i and j, $u_{ij}^{(m)}$, are expressed, respectively, as [39]

$$u_i^{(H)} = -kT\xi e_i \cdot \mathbf{h} \tag{1}$$

$$u_{ij}^{m} = kT\lambda \frac{d^3}{r_{ij}^3} \left\{ e_i \cdot e_j - 3(e_i \cdot t_{ij})(e_j \cdot t_{ij}) \right\} \tag{2}$$

in which $\boldsymbol{r}_{ij}=\boldsymbol{r}_i-\boldsymbol{r}_j$, $r_{ij}=|\boldsymbol{r}_{ij}|$, $\boldsymbol{t}_{ij}=\boldsymbol{r}_{ij}/r_{ij}$, k is Boltzmann's constant, and T is the temperature. Also, ξ and λ are the non-dimensional parameters representing the strengths of magnetic particle-field and particle–particle interactions, respectively. These expressions are expressed as

$$\xi = \mu_0 mH/kT, \lambda = \mu_0 m^2/4\pi\ d^3 kT \tag{3}$$

in which μ_0 is the permeability of free space and $m=|\boldsymbol{m}|$.

If the steric layers of the two particles overlap, a repulsive interaction arises between the two particles. However, it is difficult to express this interaction energy as a mathematical expression for the two spherocylinder particles, so that we here apply the fully established expression for the two spherical particles to the present spherocylinder particle system. To do so, the spherocylinder is modeled as a linear sphere-connected particle coated with a steric layer with thickness δ [39]. In this sphere-connected particle model, the repulsive force due to the overlap of the two spherocylinders can be evaluated by summing the energy between constituent spheres belonging to the two different spherocylinder particles. The repulsive interaction energy due to the overlap of the steric layers of the two spherical particles, $u_{ij}^{(V)}$, is written as [2]

$$u_{ij}^{(V)} = kT\lambda_V \left(2 - \frac{2r_{ij}/d}{t_\delta}\ln\left(\frac{d+2\delta}{r_{ij}}\right) - 2\frac{r_{ij}/d-1}{t_\delta}\right) \tag{4}$$

in which t_δ is the ratio of the thickness of the steric layer to the particle radius, i.e. $t_\delta=2\delta/d$. The non-dimensional parameter λ_V represents the strength of the interaction due to the overlap of steric layers, expressed as

$$\lambda_V = \quad n_s d^2/2 \tag{5}$$

in which n_s is the number of surfactant molecules per unit area on the surface of the spherical particles.