

## Phase Transition of Colloidal Particles with Electric Dipole Moment

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### Abstract

We investigate an effect of electrical dipole moment on the crystallization of charged colloidal systems by simulation. The particles' dynamics obey Langevin equation and the interaction potential is screened Coulomb potential. Consequently, the crystallization point is raised by the moment effect. That is, it becomes difficult to crystallize when the dipole moment is larger. This phenomenon is observed in both cases that crystallize into bcc and into fcc crystal. In polarized colloidal systems, the directions of the moments arrange to lower the energy of the systems when the system is crystallized.

KEYWORDS: charged colloid, moment, crystallize, repulsive, Poisson-Boltzmann, DLVO, simulation

### 1. Introduction

A charged colloidal system is one of notable systems in the view of crystal growth research, because it crystallizes by repulsive interaction of each particle. This is a good experimental example of the Alder's Phase transition.<sup>1-3)</sup> Crystallization of colloidal systems is investigated enthusiastically in recent years,<sup>4)</sup> and new curious phenomena which show phase separation into crystal and fluid phase after crystallization were discovered.<sup>5,6)</sup> These new phenomena cannot be explained by the classical Derjaguin-Landau-Verwey-Overbeek (DLVO) model<sup>7,8)</sup> and become controversial issues.

Within the limit of two-body repulsive interaction, many interesting phenomena occur when the particles have inner structures. We consider crystallization of colloidal particles having the electric dipole moment. In the DLVO model, particles are treated on the assumption that particles have spherically symmetric interaction potential, but the real particle surface is rough and the surface charge distribution is not uniform.<sup>9)</sup> It was reported that this non-uniform distribution changes the interaction potential between the charged sphere and a charged wall depending on the direction of the particle's charge distribution.<sup>10)</sup> An effect of non-uniformity of surface charge will also appear on the crystallization of charged colloids, and this effect is clearer if we can produce artificially the dipole electric particles. However there is neither experimental report nor theoretical report of this effect. So we investigate an effect of the moment on crystallization of charged colloids, and show

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that the parameters determining crystallization points are not only the total charge of particle but the electric moment.

We use the simulation method for investigation of phase transition. For simplicity, we treat this non-uniform distribution of surface charge as the dipole moment. We describe our simulation model in §2 and simulation condition in §3. The main result is that the effect of the moment raises of the crystallization point and it is described in §4.

## 2. Model

Ideal colloidal systems are constructed by dispersed particles, and water as a surrounding medium. The diameter of particles is a few hundred nanometer. In charged colloidal systems, the particles have large charge on their surface, and the water contains many micro ions that arise from surfaces of particles and added salt. We adopt the DLVO model basically among many models for colloid,<sup>7,8)</sup> and reform it for taking account of the moment of colloidal particles. This is because this model is the most classical one and easy to apply to computer simulation.

The original DLVO free energy is

$$F = \frac{1}{2} \sum_{l=1}^N \sum_{m \neq l}^N \frac{Z^2 e^2 \exp(2\kappa a) \exp(-\kappa r_{lm})}{4\pi\epsilon(1 + \kappa a)^2 r_{lm}}, \quad (1)$$

$$\kappa^2 = \sum_i z_i^2 e^2 \tilde{n}_i / (\epsilon k_B T). \quad (2)$$

Here,  $Ze$  is the charge of one macro-ion,  $a$  is a radius of a macro-ion,  $1/\kappa$  is the Debye's screening length,  $\epsilon$  is the dielectric constant of water,  $k_B$  is the Boltzmann constant,  $T$  is temperature and  $r_{lm}$  is a distance between particle  $l$  and particle  $m$ . The summation of eq. (2) is all kinds of counter ions, which charge is  $z_i e$  and typical density is  $\tilde{n}_i$ . We choose  $\tilde{n}_i$  as average density,  $\kappa^2 = e^2(2C_s + n_p|Z|)/(\epsilon k_B T)$ , where  $C_s$  is a number density of added salt,  $n_p$  is a number density of macro-ions.

DLVO model is one of the linearized Poisson-Boltzmann models. The charge of a macro-ion is regarded as an effective point charge in the center of particle sphere. This is a good approximation when a radius of a particle is smaller than the Debye's length. The magnitude of effective charge is determined to reproduce the electric field by the surface charge.

We represent the bias of surface charge distribution as the moment in the center of sphere. Modified DLVO free energy is

$$\begin{aligned} F &= \frac{c_0}{2} \sum_l \sum_{m \neq l} (Z + \mathbf{p}_l \cdot \nabla)(Z - \mathbf{p}_m \cdot \nabla) \frac{\exp(-\kappa r_{lm})}{r_{lm}} \\ &= \frac{c_0}{2} \sum_l \sum_{m \neq l} \left[ Z^2 + Z(\mathbf{p}_m - \mathbf{p}_l) \cdot \mathbf{r}_{lm} \frac{1 + \kappa r_{lm}}{r_{lm}^2} - (\mathbf{p}_l \cdot \mathbf{r}_{lm})(\mathbf{p}_m \cdot \mathbf{r}_{lm}) \frac{3 + 3\kappa r_{lm} + \kappa^2 r_{lm}^2}{r_{lm}^4} \right] \end{aligned} \quad (3)$$

$$c_0 = \frac{e^2 \exp(2\kappa a)}{4\pi\epsilon(1 + \kappa a)^2} + (\mathbf{p}_l \cdot \mathbf{p}_m) \frac{1 + \kappa r_{lm}}{r_{lm}^2} \left] \frac{\exp(-\kappa r_{lm})}{r_{lm}} \right. \quad (4)$$

Here,  $\mathbf{p}_l e$  is electrical moment of  $l$ -th macro-ion and  $\mathbf{r}_{lm} = \mathbf{r}_l - \mathbf{r}_m$ .

The Brownian dynamics of a particle is expressed in the Langevin equation. An equation of motion of center-of-mass of  $l$ -th particle is

$$m \frac{d^2 \mathbf{r}_l(t)}{dt^2} = \mathbf{f}_l(t) - \zeta \frac{d\mathbf{r}_l(t)}{dt} + \mathbf{g}_l(t), \quad (5)$$

where  $m$  is a mass,  $\mathbf{r}_l(t)$  is position of a particle,  $\mathbf{f}_l(t)$  is interaction potential force,  $\zeta = 6\pi\mu a$  is a coefficient of friction for particle of radius  $a$  in water.  $\mathbf{g}_l(t)$  is random force satisfying the conditions:

$$\langle g_{li}(t) \rangle = 0 \quad , \quad \langle g_{li}(t) g_{lj}(t') \rangle = 2\zeta k_B T \delta_{i,j} \delta(t - t'). \quad (6)$$

The equation of rotational motion is written as

$$I \frac{d\boldsymbol{\Omega}_l}{dt} = \mathbf{p}_l e \times \mathbf{E}_l - \zeta_\Omega \boldsymbol{\Omega}_l, \quad (7)$$

where  $I = 2ma^2/5$  is rotational inertia,  $\boldsymbol{\Omega}_l$  is rotational moment,  $\mathbf{E}_l$  is electric field at the point of particle,  $\zeta_\Omega = 8\pi\mu a^3$  is a coefficient of friction. Here, we neglect the rotational random force.

We discretize eq. (5) using Euler's method. In colloidal systems, the inertia term can be neglected, and turns to

$$\mathbf{r}_l(t + \Delta t) = \mathbf{r}_l(t) + \frac{1}{\zeta} \Delta t \mathbf{f}_l(t) + \Delta \mathbf{G}_l(t) \quad (8)$$

$$\Delta \mathbf{G}_l(t) = \int_t^{t+\Delta t} dt' \frac{\mathbf{g}_l(t')}{\zeta} \quad (9)$$

Distribution function of random noise  $\Delta \mathbf{G}_l(t)$  is Gaussian distribution, that satisfies

$$\langle \Delta G_{li}(t) \rangle = 0 \quad , \quad \langle \Delta G_{li}(t) \Delta G_{lj}(t') \rangle = 2D \Delta t \delta_{i,j} \delta_{t,t'}. \quad (10)$$

### 3. Simulation

To investigate the moment effect on crystallization points, we prepare some systems that have various number densities. The number density  $n_p$  is controlled by changing volume of systems, and the number of particles  $N$  is constant. The boundaries are periodic for each direction, and the interaction is limited by a finite cut-off length. This cut-off length is 1/3 of the box size of the  $y$ -direction and it is in the range of a few times of the Debye's screen length.

Figure 1 shows an initial arrangement of particles. The initial condition is coexistence of random phase and ordered phase to prepare seeds of fluid and crystal phases, because it takes

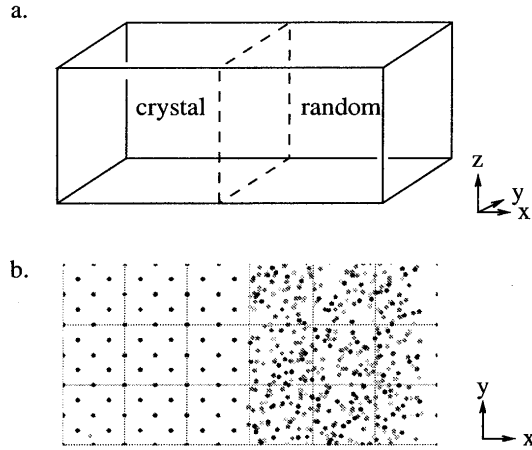


Fig. 1. Initial arrangement of colloidal particles. A rectangular of a. is a simulation container, b. is seen from z-direction.

much time to nucleate a stable phase from a metastable phase. We prepare two crystal phases. One is bcc and another is fcc.

Fixed physical parameters for simulations are shown in table I. We determine them referring to the experiments by Yoshida et.al.<sup>5)</sup> In their experiments, the crystal states are hcp structure. Simulation variables and investigation ranges are shown in table II. The system size  $N$  is limited by computer power. The range of a ratio of the electrical dipole moment to a total charge of a particle  $pe/|Z|e$  is chosen within repulsive interactions. A contact attraction appears at the moment value of  $pe/|Z|e > a$ , but our algorithm is not adaptable to the contact of particles, so the simulation sometimes ends unsuccessfully in the region of  $pe/|Z|e > 0.05[\mu\text{m}]$  and high density.

Table I. fixed parameter

Particle charge	$Ze$	$-500e$
Diameter	$2a$	$0.1[\mu\text{m}]$
Temperature	$T$	$25.00[^\circ\text{C}]$
Belumn length	$\lambda_B = e^2/(\varepsilon k_B T)$	$8.967 \times 10^{-3}[\mu\text{m}]$
Viscosity of water	$\mu$	$0.89 \times 10^{-3}[\text{Pa s}]$
Density of micro-ion from add salt	$Cs$	$2.408 \times 10^3[\mu\text{m}^{-3}]$
Resistance of motion	$\zeta_v/k_B T$	$2.241 \times 10^{-3}[\mu\text{m}^{-2}\text{s}^4]$
Resistance of rotation	$\zeta_\Omega/k_B T$	$9.040 \times 10^{-4}[\text{s}^4]$

Table II. parameter for each systems

System		BL864	BL500	FL512
Initial condition		bcc-random	bcc-random	fcc-random
Number of particles	$N$	864	500	512
Electrical dipole moment	$pe/ Z e[\mu\text{m}]$	0.00 – 0.06	0.00 – 0.06	0.00 – 0.06
Density of particles	$n_p[\mu\text{m}^{-3}]$	6.36 – 8.81	6.96 – 9.26	6.75 – 8.93
Debye's screening length	$1/\kappa[\mu\text{m}]$	0.141 – 0.128	0.138 – 0.126	0.139 – 0.127
Coefficient of potential	$Z^2c_0[\mu\text{m}]$	198 – 202	198 – 202	198 – 202
Time division	$\Delta t[\text{s}]$	$5 \times 10^{-5}$	$5 \times 10^{-5}$	$5 \times 10^{-5}$

## 4. Result

### 4.1 Time evolution of melting and crystallization

Figure 2 shows time evolutions of melting and crystallization. In the case of Figs. 2-a. and 2-b., the systems are transform into liquid state, and it crystallizes in the case of Figs. 2-c. and 2-d. In the system of repulsive particles, the crystallization occurs when the number density of particles is high.

### 4.2 The moment effect on the crystallization point

The relaxization state from the initial conditions of bcc-fluid coexistent state is shown in Fig. 3. For each point, we prepare 10 initial conditions which are made by different initial random seeds. Over the number density of these plots, bcc crystal is more stable than fluid, and in the area of lower number density, fluid is more stable than bcc crystal. These results show that the crystallization point is raised by the moment effect. The moment effect on the crystallization of charged colloids is to prevent the crystallization.

Figure 4 is the distributions of the moment direction of some samples with different parameter after relaxation. The patterns of fig. 4-a.,b.,c. are not so different from initial random distribution. Ordering is clearly seen in fig. 4-d. where the colloidal system with large moment crystallizes. These 8 directions correspond to the directions of nearest neighbor particles of bcc crystal.

Figure 5 shows that the system energy decreases with increasing the moment. Solid and dashed lines show the energy of the system in a crystal phase and a disordered phase, respectively. The energy  $U$  is the summation of potential energy of each particles.

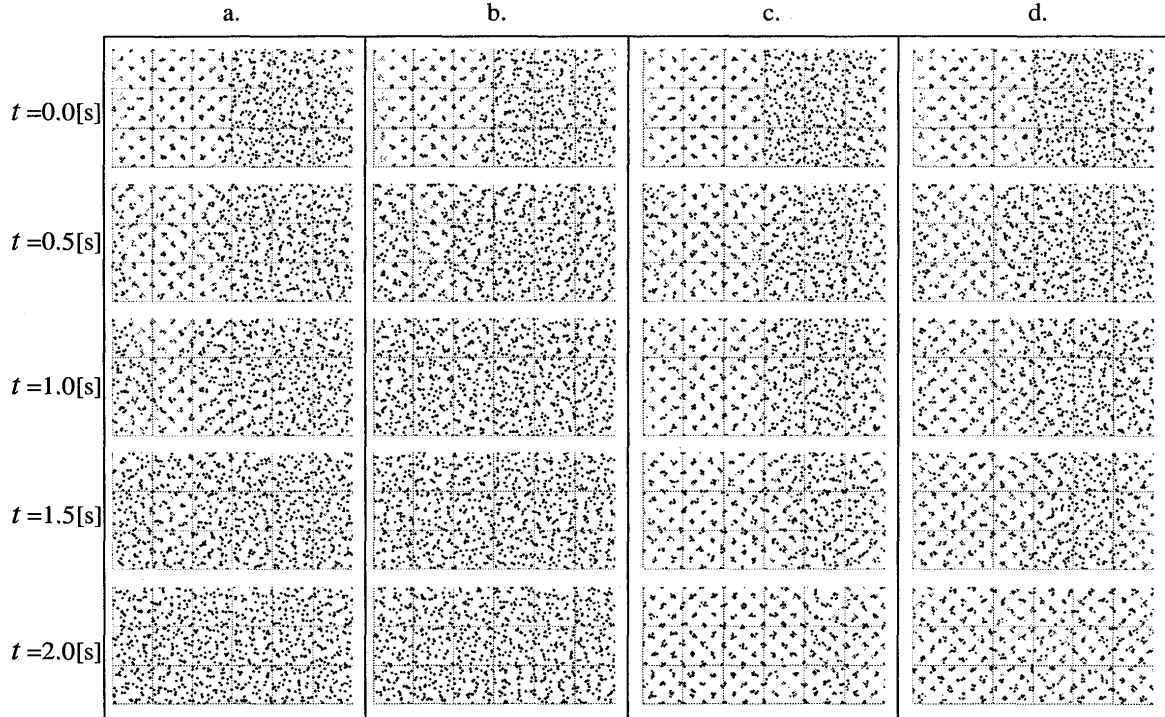


Fig. 2. Time evolution of melting and crystallization. Systems are BL864. a.  $n_p = 7.45[\mu\text{m}^{-3}]$ ,  $p/|Z| = 0.01[\mu\text{m}]$ , b.  $n_p = 7.45[\mu\text{m}^{-3}]$ ,  $p/|Z| = 0.05[\mu\text{m}]$ , c.  $n_p = 8.81[\mu\text{m}^{-3}]$ ,  $p/|Z| = 0.01[\mu\text{m}]$ , d.  $n_p = 8.81[\mu\text{m}^{-3}]$ ,  $p/|Z| = 0.05[\mu\text{m}]$ .

### 4.3 FCC-liquid phase transition

For comparison, we make a plot of the relaxation state from the initial conditions of fcc-fluid coexistence states (Fig. 6). This is made using same method with Fig. 3. The rising of crystallization point is seen in this system. Figure 7 is an energy plot. The line types are common with Fig. 5. Energy falling is also seen in the fcc-fluid system.

Comparing Fig. 3 and Fig. 6, the crystallization point of fcc is higher than bcc. In this system, bcc state is more stable than fcc in the area between these crystallization lines.

## 5. Conclusion

The effect of electrical moment is the rising of the crystallization point. The ordering of the moments lowers the total energy, and prevents crystallization of a system. If we can produce artificially the moment colloid, the crystallization point is different from the uniform-surface-charge colloidal system.

Comparing phase diagrams of the bcc-liquid transition (Fig. 3) and the fcc-liquid transition (Fig. 6), the bcc crystallization point is smaller than that of the fcc system with the same moment. This is interpreted as that the bcc crystal is more stable than the fcc one near the crystallization point.

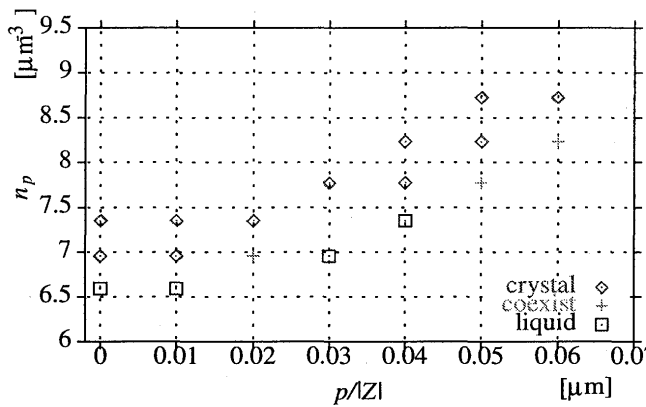


Fig. 3. Relaxation state from the initial conditions of bcc and liquid coexistence. The system is BL500, and the result is average of 10 time runs.

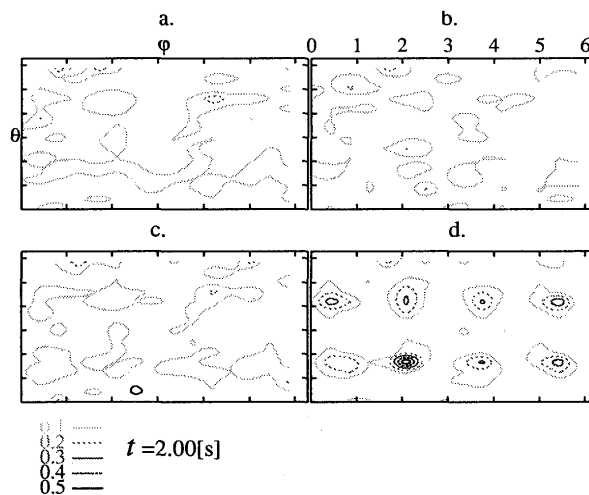


Fig. 4. The distribution of the moment direction. These systems are BL800. a. liquid state,  $p/|Z| = 0.01[\mu\text{m}]$ ,  $n_p = 7.45[\mu\text{m}^{-3}]$ , b. liquid state,  $p/|Z| = 0.05[\mu\text{m}]$ ,  $n_p = 7.45[\mu\text{m}^{-3}]$ , c. crystal state,  $p/|Z| = 0.01[\mu\text{m}]$ ,  $n_p = 8.81[\mu\text{m}^{-3}]$ , d. crystal state,  $p/|Z| = 0.05[\mu\text{m}]$ ,  $n_p = 8.81[\mu\text{m}^{-3}]$ .

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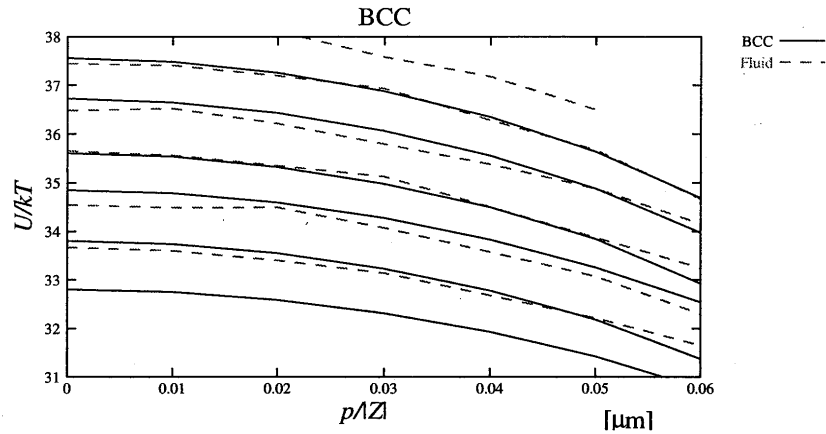


Fig. 5. The energy of bcc and fluid systems at  $t = 1.00[s]$ . The solid lines connect between crystal states points and dashed lines connect liquid states.

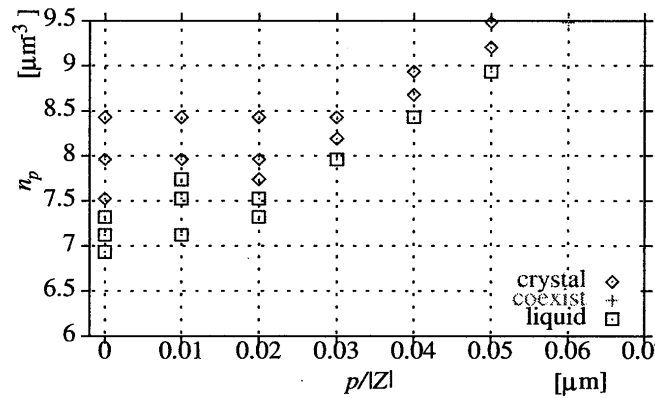


Fig. 6. Relaxation state from the initial conditions of fcc and liquid coexistence. The systems are FL512, and the result is average of 10 time runs.

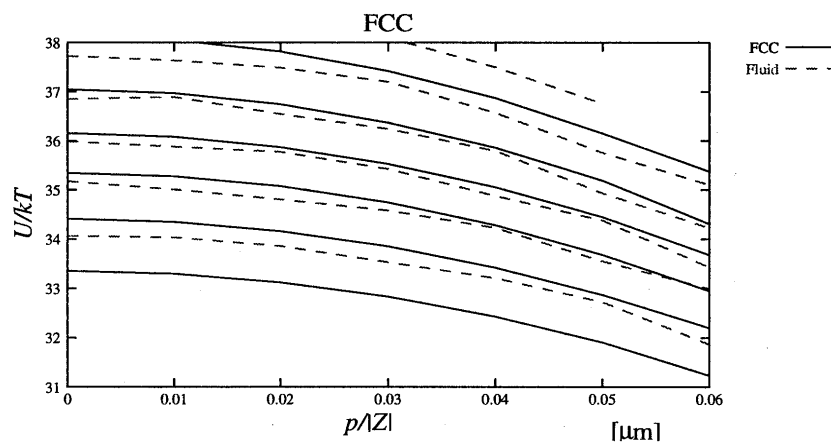


Fig. 7. The energy of bcc and fluid systems at  $t = 1.00[s]$ . The solid lines connect between crystal states points and dashed lines connect liquid states.



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