Novel Phase States in Highly Charged Colloidal Suspensions

Y. Terada [1], K. Muramoto [2], M. Tokuyama [1]
1. Institute of Fluid Science, Tohoku University, Sendai 980-8577, Japan
2. Department of Machine Intelligence and Systems Engineering, Tohoku University, Sendai 980-8577, Japan

Corresponding author ***Y. Terada*** *(terada@ifs.tohoku.ac.jp)*

Abstract

Brownian-dynamics simulation on highly charged colloidal suspensions is performed by employing Tokuyama effective force recently proposed. The radial distribution function suggests that there exist three novel phases, a gas phase, a liquid droplet phase, and a face-centered cubic (FCC) crystal droplet phase, depending on the minimum values of that potential. The dynamics of droplet growth is also investigated both in liquid droplet phase and in crystal droplet phase. Thus, different types of characteristic growth stages are found.

Keyword: Charged Colloidal Suspension, Droplet Growth, Novel Phase State

1. Introduction

Charged colloidal suspensions have been extensively studied on experimental and theoretical research over the past 50 years. This is mainly because of various industrial applications of those systems for biological technologies, food technologies, and etc. Recently Tokuyama proposed the effective attractive force between the highly charged colloidal particles [1]. In this paper, we perform a Brownian-dynamics simulation on the dilute highly charged colloidal suspensions by employing that force. We consider the simple model system, which consists of N highly charged colloidal particles with bare charge Ze and radius a and N_c counter ions with charge $-qe$ and radius a_c in an equilibrium solvent with a dielectric constant ε and temperature T, where the total volume of the system is given by V and $Z >> q$ and $a >> a_c$. Here the electrical neutrality is satisfied as $NZ = N_c\, q$. The volume fraction of the colloidal particles ϕ is given by $\phi = 4\pi a^3 N/3V$. Since $\phi << 1$, the hydrodynamic interactions between colloidal particles are safely neglected. The Tokuyama force $\boldsymbol{F}(\boldsymbol{r}_{ij})$ between particles i and j is given by [1]

$$\boldsymbol{F}(\boldsymbol{r}_{ij}) = -\nabla_{\boldsymbol{r}} U(\boldsymbol{r}_{ij}) = k_B T \Gamma^2 a^2 \left[\left(\frac{Z}{q} \right)^2 \exp\left(-r_{ij}/\lambda_m\right) - \exp\left(-r_{ij}/\lambda\right) \right] \frac{\boldsymbol{r}_{ij}}{r_{ij}^4}, \quad (1)$$

where $U(\boldsymbol{r}_{ij})$ is a potential, $\Gamma (= Zql_B/a)$ a dimensionless parameter, $l_B (= e^2/\varepsilon k_B T)$ the Bjerrum length, $\boldsymbol{r}_i$ the position vector of particle i, $r_{ij} = |\boldsymbol{r}_{ij}|$, and $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$. Here $\lambda\,(= a/(3\phi\Gamma)^{1/2})$ is a Debye screening length and $\lambda_m = (q/Z)^{1/2}\,\lambda$. The particle motion is then described by the Langevin-like equation discussed elsewhere [1]

$$\frac{d}{dt}\boldsymbol{r}_i(t) = \frac{D_0}{k_B T} \sum_{j(\neq i)}^{N} \boldsymbol{F}(\boldsymbol{r}_{ij}) + \boldsymbol{R}_i(t), \qquad \langle \mathbf{R}_i(t)\mathbf{R}_j(t') \rangle = 2D_0\delta(t-t')\delta_{ij}\mathbf{1}, \quad (2)$$

where $\boldsymbol{R}_i(t)$ is a Gaussian, Markov random force and D_0 a diffusion coefficient of a single particle. We simulate Eq. (2) in the cubic simulation cell, where N=3000 here.

2. Results and Discussion

In Fig. 1 the typical snapshots of spatial configuration of particles and the radial distribution functions $g(r)$ are shown. There exist three novel phases. The first is a gas phase shown in Figs. 1(a) and (b), where the particles disperse at random in the solvent. The second is a liquid droplet phase shown in Figs. 1(c) and (d), where the particles behave like a liquid inside the droplets. The last is a crystal droplet phase shown in Figs. 1(e) and (f), where the particles form a FCC structure inside the

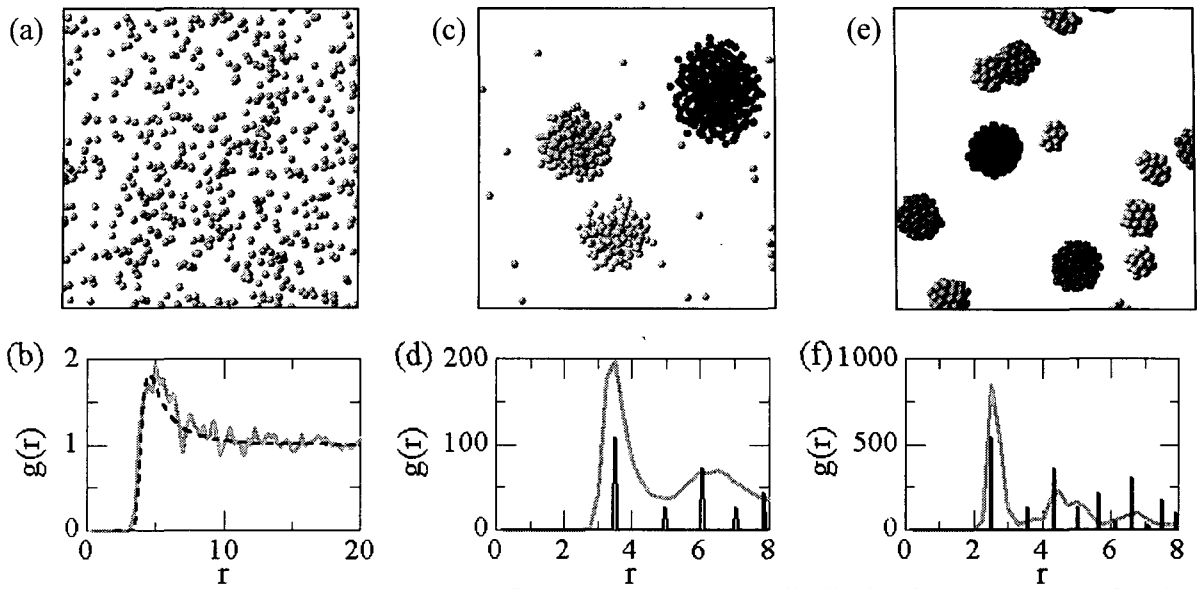

Fig.1 The typical snapshots of particle configurations and the radial distribution functions $g(r)$ as a function of the distance r for different values of Z at q=2 and ϕ=0.001; (a) and (b) for Z=400, (c) and (d) for Z=500, and (e) and (f) for Z=700. The light grey particles indicate the isolated particles and the dark grey particles indicate the biggest droplets. The dashed line denotes the theoretical radial distribution function in a gas phase and the solid black line the theoretical one for a FCC crystal.

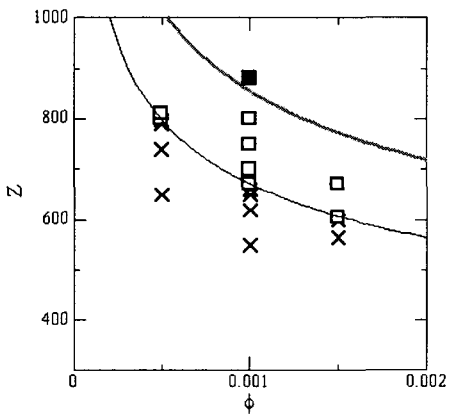

Fig.3 Phase diagram in parameter space ϕ and Z. Crosses indicate a gas phase, open squares a liquid droplet phase, and filled squares a crystal droplet phase. The lower and upper transition lines stands for U_{min}= - 1.3 and - 3.5, respectively.

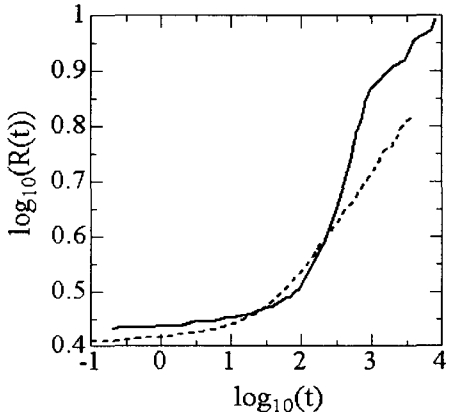

Fig.4 A log-log plot of the average droplet radius $R(t)$ versus time t. The solid line stands for a liquid droplet phase and the dashed line for a solid droplet phase.

droplets. In Fig. 3 the phase diagram in parameter space ϕ and Z are also shown at q=1. The simulation results show that the transition lines are determined only by the potential minimum U_{min} and obey the theoretical line given by $\log Z = 2.05(-U_{min})^{1/20} - 0.25\log\phi$. The average radius of the droplets $R(t)$ is also calculated in liquid droplet phase and in crystal droplet phase (see Fig.4). It seems that depending on time scales after the nucleation, the droplets are described by different growth processes. This situation is similar to that seen in phase separation. The details will be discussed in the meeting.

This work was partially supported by Grants-in-aid for Science Research with No. 14540348 from Ministry of Education, Culture, Sports, Science and Technology of Japan. The calculations were performed using the ORIGIN 2000 in the Institute of Fluid Science, Tohoku University.

References

[1] Tokuyama M., "Effective forces between macroions in highly charged colloidal suspensions", *Phys. Rev. E* Vol. 59, (1999), pp. R2550-R2553.