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Abstract. We perform the Brownian-dynamics simulations on dilute suspensions of highly charged colloids with Tokuyama attractive potential. We then show that there exist two kinds of droplet phases in addition to a gas phase, a liquid-droplet phase and a crystal-droplet phase. The detailed structures of those droplets are analyzed by the calculating the radial distribution function.

Recently, we have shown that there exist three phases in dilute highly charged colloidal suspensions, a gas phase, a liquid-droplet phase, and a crystal-droplet phase [1]. In this paper, we discuss the detailed structures of those phases.

We perform the Brownian-dynamics simulations on the charged colloidal suspensions by employing an effective attractive force between colloidal particles proposed by Tokuyama [2]. We consider a 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 $Z \gg q$ and $a \gg a_c$. Here the electrical neutrality is satisfied as $NZ = N_c q$. The volume fraction of the colloidal particles ϕ is given by $\phi = 4\pi a^3 N/3V$, where the total volume of the system is given by V. Then, the particle motion is described by the Langevin-like equation discussed elsewhere [2]

$$\frac{d}{dt}\boldsymbol{r}_i(t) = \frac{D_0}{k_B T}\sum_{j\neq i}^{N}\boldsymbol{F}_T(\boldsymbol{r}_{ij}(t)) + \boldsymbol{\xi}_i(t), \quad (1)$$

where $\boldsymbol{\xi}_i(t)$ is a Gaussian, Markov random velocity with zero mean, and satisfies

$$<\boldsymbol{\xi}_i(t)\boldsymbol{\xi}_j(t')> = 2D_0\delta(t-t')\delta_{i,j}\mathbf{1}. \quad (2)$$

Here D_0 is a diffusion coefficient of a single particle and $\boldsymbol{F}_T(\boldsymbol{r}_{ij})$ is the Tokuyama force between particles i and j and is given by [2]

$$\boldsymbol{F}_T(\boldsymbol{r}_{ij}) = -\nabla U(\boldsymbol{r}_{ij})$$
$$= k_B T(Zql_B)^2\left[z^2 e^{-r_{ij}/\lambda_m} - e^{-r_{ij}/\lambda}\right]\frac{\boldsymbol{r}_{ij}}{r_{ij}^4}, \quad (3)$$

where $U(\boldsymbol{r}_{ij})$ is a potential, $l_B \ (= e^2/\varepsilon k_B T)$ the Bjerrum length, $\boldsymbol{r}_i$ the position vector of particle i, $r_{ij} = |\boldsymbol{r}_{ij}|$,
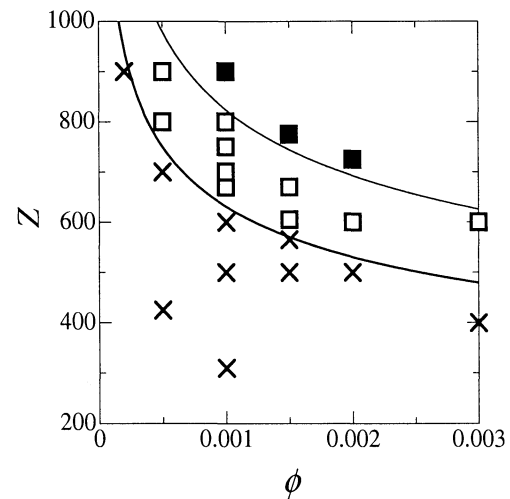

FIGURE 1. Phase diagram in parameter space ϕ and Z at $q = 1$. The symbols indicate each phase; a gas phase ($\times$), a liquid-droplet phase ($\square$), and a crystal-droplet phase ($\blacksquare$). The lower and upper transition lines are drawn at $U_{min}/k_B T \simeq -1.0$ and -3.0, respectively.

$z = Z/q$, and $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$. $\lambda \ (= \sqrt{a/3\phi(r)Zql_B})$ is a Debye screening length, $\lambda_m = z^{1/2}\lambda$, and $\phi(r)$ the local density. In the following, we simply assume that $\phi(r)$ is constant to be ϕ. As one of the parameters, Z, ϕ, and q, increases with the other two parameters being fixed, $\boldsymbol{F}_T$ becomes a more attractive interaction. We are only interested in highly charged dilute suspensions with $\phi \ll 1$. Hence, we can safely neglect the hydrodynamic interactions between the colloidal particles. We simulate Eq. (1) in a cubic simulation cell, where N is chosen to be 3000 here.

In Fig.1, the phase diagram is shown in the parameter space ϕ and Z at $q = 1$. There exist a gas phase, a
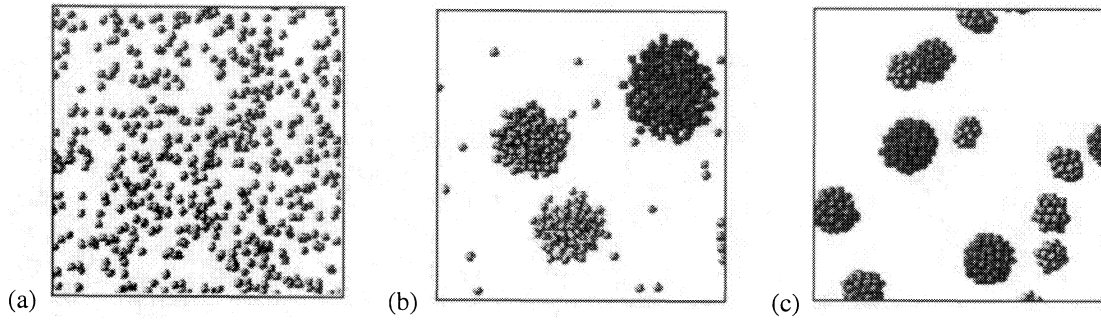
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FIGURE 2. The typical snapshots of particle configurations for different values of Z at $q = 2$ and $\phi = 0.001$; (a) $Z = 400$ on a gas phase, (b) $Z = 500$ on a liquid-droplet phase, and (c) $Z = 700$ on a crystal-droplet phase.
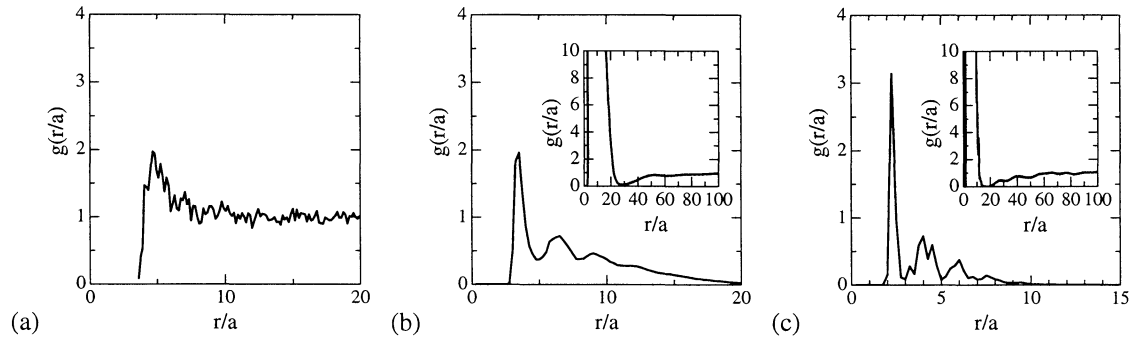

FIGURE 3. The radial distribution functions $g(r)$ versus distance r for different values of Z at $q = 2$ and $\phi = 0.001$; (a) $Z = 400$, (b) $Z = 500$, and (c) $Z = 700$. $g(r)$ in (a) is calculated for the whole system. $g(r)$ in (b) and (c) are calculated for the largest droplet, where those in the insets are calculated for the whole system.

liquid-droplet phase, and a crystal-droplet phase. The simulation results show that each transition line between phases is determined only by the value of the potential minimum U_{min}, which is given by

$$\phi = \left(\frac{-4U_{min}}{3\Gamma^3 k_B T} \right) \frac{\ln z}{z^{-u}(1 - \sqrt{z})^2 + 2f(z)\ln z} \quad (4)$$

with $f(z) = G(u\ln z) - z^3 G(u\sqrt{z}\ln z)$ analytically, where $u = 2/(\sqrt{z} - 1)$ and $G(x) = \int_x^\infty y^{-1} e^{-y} dy$. A gas phase exists for $U_{min}/k_B T > -1.0$, a liquid-droplet phase for $-1.0 \geq U_{min}/k_B T > -3.0$, and a crystal-droplet phase for $-3.0 \geq U_{min}/k_B T$. The phase diagrams are also obtained for values larger than $q = 2$, where the transition lines shift to lower values of Z.

Figure 2 (a), (b), and (c) show typical snapshots on each phase after a long time. The radial distribution functions $g(r)$ of each snapshot on Fig. 2 are also shown in Fig. 3. The configuration of the particles in Fig. 2 (a) is similar to those of the theoretical results in a gas phase, where $g_t(r) = \exp[-U(r)/k_B T]$. In Fig.3 (b), the simulation results does not agree with $g_t(r)$ no longer and shows the liquid-like order in the droplets. On the other hand, the configurations of colloids in droplets in Fig.2 (c) are in local order and the peak positions of $g(r)$

agree with those of face-centered cubic crystal within the fourth nearest peaks. We note that the droplets in both droplet phases are dispersed randomly, because $g(r)$ in the insets of Fig.3 (b) and (c) show disorder-state outside the droplets.

ACKNOWLEDGMENTS

REFERENCES

1. Terada, Y., and Tokuyama, M., *Physica A* (in press).
2. Tokuyama, M., Phys. Rev. E **59**, R2550-R2553 (1999);Phys. Rev. E **58**, R2729-R2732(1998).