Simulating formation of voids in charged colloids by Brownian dynamics

K. G. Wang
Department of Applied Physics, Beijing Institute of Technology, Beijing 100081, China
and Tohwa Institute for Science, Tohwa University, Fukuoka 815-8510, Japan
(Received 7 July 2000)

Using Brownian dynamics simulations and Sogami's effective pair potential with a long-range attractive term for the colloidal particles, we report that the mechanism of making voids in charged colloids is the long-range attractive interaction between particles. The present results are in good agreement with the experimental observations of stable voids in equilibrium with ordered structures, which may not be explained by repulsive potentials without a long-range attractive interaction such as the Derjaguin-Landau-Vervey-Overbeck potential. Our results are also in a good agreement with Monte Carlo simulation results. The voids have been reported with ordered structure in charged colloids by Brownian dynamics simulations.

PACS number(s): 82.70.Dd, 64.70.Pf

I. INTRODUCTION

Colloidal suspensions have been used with great success as model condensed matter systems [1] to study a variety of properties. Suspensions of charged colloidal spheres are ideal for model studies of crystallization because they are easily observed and their forces are readily manipulated by controlling the chemistry of the suspension medium. Recently, there has been some experimental evidence that there exists inhomogeneous phases such as stable voids, coexisting with ordered structure or disordered structures [2–6], which suggests the existence of a long-range attraction between particles. Direct measurements of pair potentials also show the attraction at large interparticle separation [7,8]. However, up to now, the purely repulsive potential Derjaguin-Landau-Vervey-Overbeck (DLVO) potential could be only used to explain homogeneous phases.

On the other hand, colloidal crystals have important technological uses as optical devices [9] and materials with photonic band gaps [10]. The phase diagram of charged colloidal suspensions has been constructed by experiments [11–13]. It was found that there exist crystalline, liquidlike, and glassy structural orderings in charged colloidal systems under certain conditions.

Compared with experimental work, more theoretical work and computer simulations to explain the existing experimental results and to understand the mechanism in the inhomogeneous phases of charged colloidals was strongly recommended. To our knowledge, there are only two types of potentials with long-range attraction in charged colloidal systems: one is the Sogami potential [14] and the other the Tokuyama potential [15]. The important result of Sogami's effective pair potential is that it has an attractive minimum at interparticle distances of thousands of angstroms, which is consistent with the experimental evidence mentioned above. The well depth and position strongly depend on the screening parameter κ. The Sogami potential has been applied to successfully explain the experimental structure factors of liquidlike ordered colloidal suspensions [16], reentrant transitions [17], the coexistence of voids with ordered and disordered regions [17,18], and recently the formation of fcc and bcc phases in charged colloidal systems [19].

Tata *et al.* [17,19] used the Sogami potential to simulate the homogeneous and inhomogeneous structures in charged colloidal systems by the Monte Carlo (MC) method. Their results can qualitatively explain some experimental observations. However, it is difficult to quantitively compare with experimental results because MC steps are not real time. Now it is very appropriate to develop dynamics simulations for the study of inhomogeneous and homogeneous structures in charged colloidal systems. Therefore, we did Brownian dynamics (BD) simulations in charged colloidal systems and obtained inhomogeneous structures such as voids with ordered regions and homogeneous structures such as crystalline ordered regions without voids. To our knowledge, this is the first time stable voids have been simulated with ordered regions and homogeneous phases in charged colloidal systems from BD simulations rather than MC simulations. This paves the way for the study of the dynamic properties of charged colloidal systems by computer simulations.

The outline of this paper is as follows. In Sec. II, we describe the model and details of the simulation. Section III is devoted to the results of our simulation. The concluding remarks and discussion are contained in Sec. IV.

II. MODEL AND DETAILS OF SIMULATIONS

We consider N identical spherical particles in a three-dimensional cubic box, and the interaction between particles is assumed via the Sogami pair potential [14]. The potential has the following form:

$$U(r)=2\frac{(Ze)^2}{\epsilon}\left(\frac{\sinh(\kappa d/2)}{\kappa d}\right)^2\left(\frac{A}{r}-\kappa\right)\exp(-\kappa r), \quad (1)$$

where $A=2+\kappa d\coth(\kappa d/2)$ and the inverse Debye screening length κ is given as

$$\kappa^2=4\pi e^2(n_pZ+C_s)/\epsilon k_BT. \quad (2)$$

r is the pair distance between particles, and d is the diameter of particle. Ze is the effective charge on the particle (related to the surface charge density by $\sigma=Ze/\pi d^2$), C_s is the salt

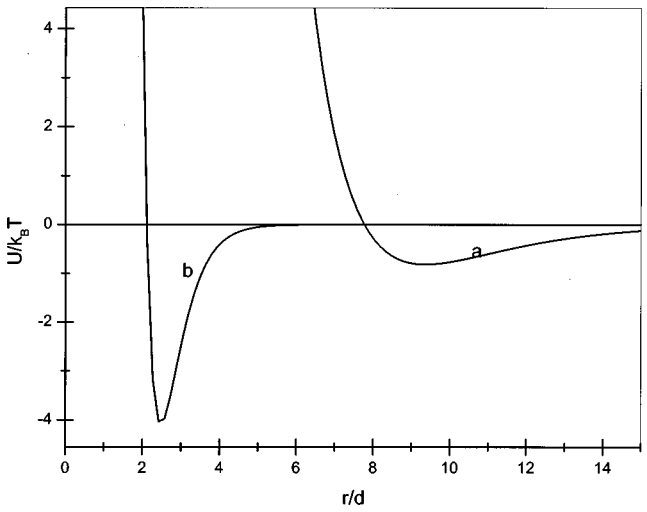

FIG. 1. The pair potential for different suspension parameters. Curves *a* and *b* correspond to the cases of $d=109\,\mathrm{nm}$, $Z=600$, $C_s=1.75\times10^{15}\,\mathrm{cm}^{-3}$, $\phi=0.0009$, and $d=110\,\mathrm{nm}$, $\sigma_s=0.35\,\mu\mathrm{C/cm}^2$, $C_s=2\,\mu\mathrm{M}$, $\phi=0.03$, respectively.

concentration, the temperature T is fixed at 298 K, ϵ is the dielectric constant of water, and k_B is the Boltzmann constant. The position of the potential minimum R_m is given as $R_m=\{A+[A(A+4)]^{1/2}\}/2\kappa$ and its depth by $U_m=U(R_m)$. Both R_m and U_m depend on σ and C_s. For the required volume fraction ϕ, the length L of the simulation cubic box is given as $L^3=N\pi d^3/6\phi$. Typical Sogami potentials for different parameters used in our simulations are presented in Fig. 1.

Following Ermak and Yeh [20], we use the finite-difference BD algorithm in which the hydrodynamic interactions are neglected and the stochastic Langevin equations of motion are integrated in a finite time interval Δt to update the particle position $\mathbf{r}_i(t)$:

$$\mathbf{r}_i(t+\Delta t)=\mathbf{r}_i(t)+\frac{D_0}{k_BT}\mathbf{F}_i(t)\Delta t+(\Delta\mathbf{r})_R+O((\Delta t)^2). \quad (3)$$

The random displacements $(\Delta\mathbf{r})_R$ are sampled from a Gaussian distribution with zero mean and variance $\langle(\Delta\mathbf{r})_R^2\rangle=6D_0\Delta t$. Here D_0 is the diffusion coefficient of the particle. $\mathbf{F}_i(t)$ is the force on particle i, which is from the derivative of the associated potential. However, in our simulations, the coordinates of particles and distance are scaled by the diameter d of the particle, and the time t and time interval Δt are scaled by the structural relaxation time $\tau_D=d^2/D_0$. Periodic boundary conditions are applied in our simulations.

We note the relation $D_0=k_BT/(3\pi\eta d)$, where η is the viscosity of solvent, and the choice of Δt should be such that the long-time behavior is reached in an optimum number of time steps. On the other hand, because of the error associated with the BD algorithm, a reasonable stability of the trajectory is ensured provided the integration time step Δt is chosen to be much smaller than the structural relaxation time τ_D but much larger than the velocity relaxation time $\tau_V=M/\xi$, where M is the particle mass and ξ is the macroscopic friction coefficient. Due to the above choice of $\Delta t\gg\tau_V$, the dynamics is coarsen grained, rendering the momentum variables absent in the BD.

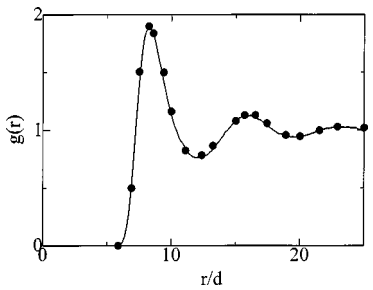

FIG. 2. Pair distribution function $g(r)$ vs r/d. The parameters and $d=109\,\mathrm{nm}$, $Z=600$, $C_s=1.75\times10^{15}\,\mathrm{cm}^{-3}$, $\phi=0.0009$. The solid line and solid circle correspond to our result of BD simulations and the BD result of Tata *et al.* [16], respectively.

In the case of $\phi=0.03$, suspensions of charged colloids are expected to order into a fcc or bcc crystalline order depending on the value of ϕ and other suspension parameters. In order to find out the truely ordered state, we carried out simulations with different initial configurations. We found that $\Delta t\leqslant10^{-3}\tau_D$ in the case of $\phi=0.03$ and $\Delta t\leqslant10^{-2}\tau_D$ in the case of a very dilute system ($\phi=0.0009$) are good enough to keep the integral of the stochastic Langevin equations of motion stable. In all the simulations, first the equilibrium run was performed for $500\tau_D$, and then the product run was performed. All results were taken in the product run. For our simulations, the number of particles was taken to be $N=343,432$ for different simulations. For $N=343$, the initial configuration of particles is the simple cubic lattice, and for $N=432$, the initial configuration of particles is the bcc structure.

III. RESULTS

As a check of our program, we have carried out BD simulations for the colloidal system ($d=109\,\mathrm{nm}$, $Z=600$, $C_s=1.75\times10^{15}\,\mathrm{cm}^{-3}$, $\phi=0.0009$), which has been studied by MC and BD simulations [16]. It should be noted that in this case, the system is in the state of homogeneous liquidlike ordering, and there is no void in the system. The potential $U(r)$ in this case is shown in Fig. 1. The number of particles is 343 in this simulation. As shown in Fig. 2, our results are in good agreement with the BD simulation result of Tata *et al.*, and we also tested the dynamic properties of the system.

We run the BD simulation in the charged colloidal system with the parameters $d=110\,\mathrm{nm}$, $\phi=0.03$, $C_s=2\,\mu\mathrm{M}$, and $\sigma=0.35\,\mu\mathrm{C/cm}^2$. The corresponding potential $U(r)$ is shown in Fig. 1. The number of particles is 432. The results of simulations for this case are shown in Figs. 3 and 4. From the position of the first peak in $g(r)$ of Fig. 3, the interparticle separation d_s is obtained to be $2.65d$. For the average interparticle separation d_0 for homogeneous bcc-like structure at $\phi=0.03$, $d_0=2.83d$, we can see that $d_s<d_0$, which suggests that the suspension could be inhomogeneous. The corresponding projection of the BD simulation cell in Fig. 4 also confirms this and shows two voids coexisting with a crystal-like ordered region. In a previous study of homogeneous nucleation, the coordination number of a particle was found to be the most reliable indicator of a solid phase [21]. With this motivation, we examine the coordination number

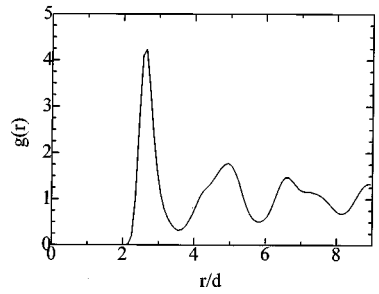

FIG. 3. Pair distribution function $g(r)$ vs r/d. The parameters are $d=110$ nm, $C_s=2$ μM, $\phi=0.03$, $\sigma=0.35$ μC/cm^2.

of particles, i.e., the number of nearest neighbors of every particle. In light of the nature of the potential and pair distribution function $g(r)$, a nearest neighbor of a given particle can be naturally defined as another particle whose distance from the given particle is smaller than or equal to $r_{\min}$, where $r_{\min}$ is the position of the first minimum of $g(r)$. We clearly see that the frequency of particles having 14 coordinated particles increases with simulation time. The number of 14 coordinated particles is the basis of the measure we seek, which suggests that the ordered region is bcc-like structure because the number of first and second near neighbors in the perfect bcc crystalline is 14.

The configuration in Fig. 4 is that of a two-dimensional projection of a three-dimensional BD simulation cell. It means that we did not plot the coordinate of the third dimension Z of all the particles in the BD simulation cell in Fig. 4. In the following, we call it the projection of particle coordinates in a BD cell. The projection in Fig. 4 is qualitatively similar to that of the MC configuration [19]. In the configuration in our BD simulation, there are two voids in the suspension rather than one void in the MC simulation, coexisting with a bcc-like ordered region. The reason for the small difference is not so clear yet. In fact, we did a very-long-time simulation and found that there exist two voids. The best guess is that if [19] the MC run of Tata *et al.* [19] were performed for longer MC steps, there may exist two voids rather than one void in their system because two voids and more than two voids are found in experimental systems [18].

The results for the case of $d=110$ nm, $\phi=0.03$, $C_s=0$, and $\sigma=0.35$ μC/cm^2 are shown in Figs. 5 and 6. In this case,

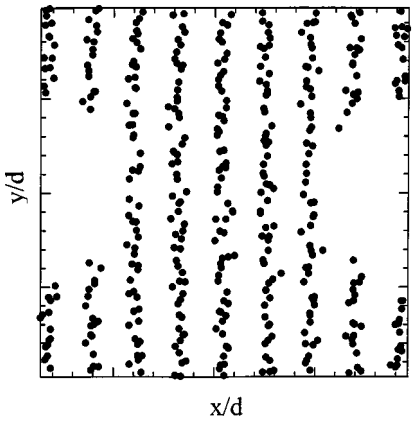

FIG. 4. Projection of the particle coordinates in the BD cell at $t=1284.1/\tau_D$. The parameters of suspension are the same as Fig. 3. The length of the cell is equivalent to L defined in the text.

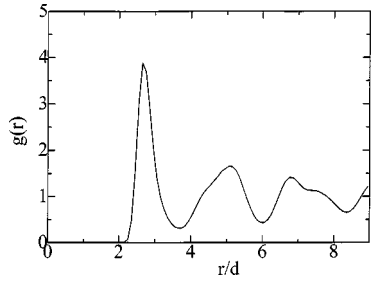

FIG. 5. Pair distribution function $g(r)$ vs r/d. The parameters are $d=110$ nm, $C_s=0$, $\phi=0.03$, $\sigma=0.35$ μC/cm^2.

the salt concentration is zero, which is only different from the above case. We chose the number of particles, $N=343$, so that it does not favor perfect fcc or perfect bcc structure. However, from the configuration of Fig. 6, we see that there is no void in the systems. From the calculation of the particle coordination number, it shows that the ordering has bcc-like structure. Thus the suspension is ordering into the homogeneous phase, which is also confirmed by MC simulations [19]. In this case, from our results of BD simulations, we conclude that when d_s is not very much different from d_0, a homogeneous bcc-like structure will be expected in charged colloidal suspensions, which is consistent with the result from MC simulations [19]. This also suggests that for the Sogami potential and parameters of the suspension defined in this case, the homogeneous bcc-like structure is stable because the number of particles in this simulation does not favor perfect bcc-like structures.

IV. CONCLUSIONS AND DISCUSSION

We have done BD simulations in charged colloidal suspensions for the cases of both very low and high volume fractions. From the calculation of the particle coordination number and configurations, it has been shown that in the case of a high volume fraction the suspension with slat orders into an inhomogeneous state and the suspension without salt into a homogeneous state. Thus our simulation results can explain the observation of experiments from the homogeneous state to the inhomogeneous state in charged colloidal suspensions. We conclude that the long-range attractive interaction be-

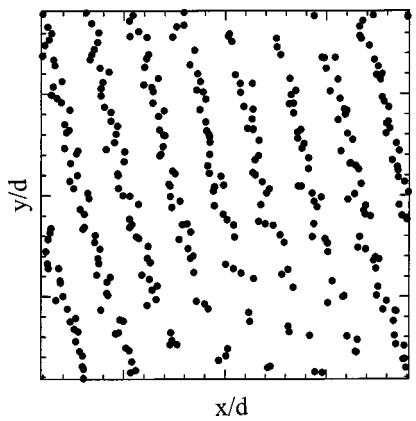

FIG. 6. Projection of the particle coordinates in the BD cell at $t=1329.5/\tau_D$. The parameters of suspension are the same as Fig. 5. The length of the cell is equivalent to L defined in the text.

tween particles is one of the important conditions for making voids in charged colloids, but it is not a sufficient condition. Our BD simulations shows that in the case of a charged colloidal suspension with salt, there are two voids with a bcc-like ordered region. However, in the case of a charged colloidal suspension without salt, there is no void. The long-range attractive interaction exists in the both cases.

It is deserving of mention that there exists a long-range attractive interaction in the Tokuyama potential [15]: however, the inhomogeneous state, i.e., voids with a ordered or disordered region under certain conditions, cannot be obtained by BD simulations [22], although in the Tokuyama potential parameters such as the radius of the particle and the charge of the particle and volume fraction can be adjusted to change the shapes of the potential [15]. Therefore, unless more detailed work is done with the Tokuyama potential, it cannot be used to explain ordering in charged colloidal suspensions. However, the Sogami potential has a reasonably attractive minimum even in the case of a high volume fraction, and the ordering phenomena in charged colloidal suspensions can be explained by the Sogami potential, which was confirmed by our BD simulations and the MC simulations of Tata *et al.*

From our BD simulations, it is clearly demonstrated that the Sogami potential captures the signature in charged colloidal suspensions. The significant importance of the long-range attractive term in the Sogami potential depends on κ, which is related to the volume fraction, charge, and salt concentration. Though this potential is successful in explaining experimental evidence, the exact mechanism of the long-range interaction is not fully understood yet. There exists a debate on the validity of the Sogami potential. After the Sogami potential [14] was proposed, Overbeek [23] made critical comments on the Sogami potential. However, the criticism turned out to be due to the violation of the Gibbs-Duhem equation in Overbeek's work [23], one of the fundamental relations for multicomponent systems, which was reviewed by Schmitz [24]. On the other hand, the Sogami potential may be derived from density-functional theory for colloidal suspensions from Roij *et al.* [25].

However, to my knowledge, this is the first time voids with ordered structure have been reported in charged colloids by BD simulations. Our BD simulations will motivate more dynamics simulations in charged colloidal systems. They will stimulate the quantitative comparison between experimental and simulation results. However, MC simulations can only qualitively compare with experiment. In our simulations, the mean-square displacement $\langle r^2/d^2 \rangle$ is calculated, and the diffusive behavior of the tendency towards saturation, which is a feature of the glassy and crystalline orders, is observed. Dynamic properties such as the mean-square displacement and others will be published elsewhere [22]. We also expect our results to stimulate experiments to study the interaction between particles in dilute colloidal suspensions so that we can understand the effective potential in the charged suspensions from experiment, computer simulation, and theory.

ACKNOWLEDGMENTS

I thank Professor T. Fukuda, Professor M. Tokuyama, and Professor M. Tashiro for the visit at Tohwa University. I acknowledge Professor N. Ise from the Central Laboratory in Rengo Co., Ltd., Osaka, Japan, Dr. A. V. Lyulin, University of Leeds, United Kingdom; Dr. I. Moriguchi, Tohwa University, Japan; and Dr. B. V. R. Tata, Indira Gandhi Center for Atomic Research, India for many discussions. Special thanks go to Dr. Tata for sending me reprints and the subroutine for the initial configuration. I am grateful to Dr. B. Düweg, Max-Planck Institute for Polymer Research, Mainz, Germany for his useful suggestions. I acknowledge the partial support of the Project Sponsored by the Scientific Foundation for Returned Overseas Chinese Scholars and Tohwa University.

[1] For a recent review, see *Ordering and Phase Transitions in Charged Colloids*, edited by A. K. Arora and B. V. R. Tata (VCH, New York, 1996).

[2] N. Ise, in *Ordering and Organization in Ionic Solutions*, edited by N. Ise and I. Sogami (World Scientific, Singapore, 1988), p. 624.

[3] B. V. R. Tata and B. Raj, Bull. Mater. Sci. **21**, 263 (1998).

[4] R. Kesavamoorthy, M. Rajalakshmi, and Babu Rao, J. Phys.: Condens. Matter **1**, 7149 (1989).

[5] S. Dosho *et al.*, Langmuir **9**, 394 (1993); K. Ito, H. Yoshida, and N. Ise, Science **263**, 66 (1994).

[6] H. Yoshida, N. Ise, and T. Hashimoto, J. Chem. Phys. **103**, 10146 (1995).

[7] G. M. Kepler and S. A. Fraden, Phys. Rev. Lett. **73**, 356 (1994); B. V. R. R. Tata and A. K. Arora, *ibid.* **75**, 3200 (1995).

[8] D. Grier *et al.*, Nature (London) **385**, 231 (1997); Phys. Rev. Lett. **77**, 1897 (1996).

[9] P. L. Flaugh, S. E. O'Donnell, and S. A. Asher, Appl. Spectrosc. **38**, 847 (1984); S. A. Asher, P. L. Plaugh, and G. Washinger, Spectroscopy **1**, 26 (1986); H. B. Sunkara, J. M. Jethmalani, and W. T. Ford, Chem. Mater. **6**, 362 (1994).

[10] I. I. Buhan and G. H. Watson, Phys. Rev. Lett. **76**, 315 (1996).

[11] A. P. Gast *et al.*, J. Colloid Interface Sci. **128**, 533 (1989).

[12] E. B. Sirota *et al.*, Phys. Rev. Lett. **62**, 1524 (1989).

[13] J. Yamanaka *et al.*, Phys. Rev. Lett. **80**, 5806 (1998); H. Yoshida *et al.*, Langmuir **15**, 2684 (1999).

[14] I. Sogami, Phys. Lett. **96A**, 199 (1983); I. Sogami and N. Ise, J. Chem. Phys. **81**, 6320 (1984).

[15] M. Tokuyama, Phys. Rev. E **59**, R2550 (1999).

[16] B. V. R. Tata and A. K. Sood, and R. Kesavamoothy, Pramana **34**, 23 (1990).

[17] B. V. R. Tata, A. K. Arora, and M. C. Valsakumar, Phys. Rev. E **47**, 3404 (1993); B. V. R. Tata and N. Ise, Phys. Rev. B **54**, 6050 (1996).

[18] B. V. R. Tata, E. Yamahara, P. V. Rajamani, and N. Ise, Phys. Rev. Lett. **78**, 2660 (1997).

[19] B. V. R. Tata and N. Ise, Phys. Rev. E **58**, 2237 (1998).

[20] D. L. Ermak and Y. Yeh, Chem. Phys. Lett. **24**, 243 (1974); D. L. Ermak, J. Chem. Phys. **62**, 4189 (1975); **62**, 4197 (1975).

[21] P. R. T. Wolde, M. J. Ruiz-Montero, and D. Frenkel, Faraday Discuss. **104**, 93 (1996).
[22] K. G. Wang (unpublished).
[23] J. T. Overbeek, J. Chem. Phys. **87**, 4406 (1987).
[24] K. S. Schmitz, *Macroions in Solution and Colloidal Suspension* (VCH, New York, 1993).
[25] R. V. Roij and J.-P. Hansen, Phys. Rev. Lett. **79**, 3082 (1997); R. V. Roij, M. Dijkstra, and J.-P. Hansen, Phys. Rev. E **59**, 2010 (1999).