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Molecular dynamics study of homogeneous and inhomogeneous phase in charged colloids: The influence of surface charge density



OLLOIDS AN

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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Investigate the dynamic process of crystallization and voids formation in charged colloids.
- Influence of surface charge density on homogeneous to inhomogeneous phase transition.
- Finite size effects on the phase behavior of charged colloids.
- Show that Sogami and Ise theory cannot explain the reentrant transition of highly charged colloidal systems.

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ABSTRACT

Compared with previous Mote Carlo (MC) simulations with 432 particles, molecular dynamics (MD) simulations with much larger number of particles have been carried out to investigate the dynamic process of the structural ordering and voids formation in charge stabilized colloidal suspensions. Sogami and Ise (SI) potential which has a long-range attraction is used to represent the interaction between colloidal particles. As increasing the surface charge density on the colloidal particles, the data obtained from the simulations, such as the crystallization, bcc–fcc phase transition, homogeneous to inhomogeneous transition and the voids formation, are in agreement with previous observations of MC simulations and experiments. The effects of particle number used in the simulations are studied in detail. MD simulations in highly charged colloidal system with small sizes show very few crystallized particles, in accord with the results of MC simulations. However, the structure in the system with larger number of particles is always the voids coexisting crystallites instead of a glasslike or disordered inhomogeneous phase, indicating that the glasslike or disordered phase region obtained at very high charge density in small system is an artifact produced by very limited number of particles used in the simulations. Therefore, SI potential is not applicable for explaining the reentrant transition of highly charged colloidal systems.

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1. Introduction

Colloidal suspensions have been considered to model condensed matter systems, due to their structural ordering and related phase transitions [1-4]. Among the colloidal studies, 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 [4–6]. It has been believed for a long time that the interaction between charged colloidal particles can be described by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, in which the potential is predominantly screened Coulomb repulsion except the van der Waals attraction at very short distances [7]. For stable suspensions the van der Waals attraction is negligible so that the DLVO potential can be referred to the screened Coulomb repulsion only. DLVO theory has been used to explain some properties of homogeneous phases, e.g., the ordering in charged colloids. However,

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some experimental evidence has emerged such as the nonspace filling localized ordered structures coexisting with disordered regions observed by microscopy and scattering experiments, the existence of stable voids, vapor–liquid condensation and the reentrant phase transition, which suggest the existence of a long-range attraction between the charged colloids [8–14].

In order to explain the above-mentioned experimental results in charged colloids, Sogami and Ise (SI) have proposed an effective interaction model based on the Gibbs free energy of the interaction [15]. This model not only takes into account the large size difference between colloidal particles and small ions, but also relates the variation of macroion charge to the release of counterions. Based on this model, Tata and Ise have performed Monte Carlo (MC) simulations to observe the homogeneous and inhomogeneous structures in charged colloidal systems. Their results of MC simulations seem to be able to successfully explain some experimental observations, e.g. the formation of colloidal crystals, reentrant transitions, and the coexistence of voids with ordered and disordered regions [16–18]. For the past decades, a debate has been going on in colloidal science between the supporters of the classic DLVO theory and those who tend to accept the SI theory [19]. For instance, van Roij et al. used a volume term theory to explain some important feature of the phase diagram of charged suspensions at very low ionic strengths from the first principles, showing that there is no need to invoke longrange attraction between particles [20,21]. Moreover, it is difficult to quantitatively compare the results of previous MC simulations with those of experiments because MC steps are not real time. Until now, there are very few dynamics simulations for the study of inhomogeneous and homogeneous structures in charged colloidal systems with SI potential. On the other hand, the number of colloidal particles used in MC simulations by Tata and Ise is very small (typically N=432), possibly due to the computational cost. But, many earlier simulations have already shown that the system size has a large effect on the crystallization process [22–25]. Such small number of colloidal particles used in MC simulations may not be appropriate for the observations of structural ordering in the system, although the observed results in several different system sizes (up to N = 1024) are the same within statistical error [17,18].

In this work, we carry out molecular dynamics (MD) simulations in charged colloidal systems. Through simulations with different colloidal parameters, we can obtain inhomogeneous structures such as voids coexisting with ordered regions, and the homogeneous structures such as crystal structure without voids. The dynamic process of crystallization and the formation of voids is investigated in MD simulations. We mainly study the homogeneous and inhomogeneous phase as a function of surface charge density on the colloidal particles, keeping the other parameters fixed. The number of colloidal particles used in MD simulations (typically N = 10, 976) is sufficiently large to alleviate finite size effects.

2. Details of simulation

The interaction between the charged colloidal particles in the simulation box is SI pair potential [15], which has the following form,

$$U(r_{ij}) = B\left(\frac{A}{r_{ij}} - \kappa\right) \exp(-\kappa r_{ij}) \quad , \tag{1}$$

where r_{ij} is the pair distance between *i*th and *j*th particle, the inverse Debye screening length κ is given as

$$\kappa = \sqrt{\frac{e^2(n_p Z + C_s)}{\epsilon k_B T}} \quad , \tag{2}$$

and the parameters

$$A = 2 + \coth\left(\frac{\kappa d}{2}\right)$$

$$B = \frac{1}{2\pi\epsilon} \left[\frac{Ze\sinh(\kappa d/2)}{\kappa d}\right]^2 .$$
(3)

Ze is the charge on the particle (related to effective charge density by $Ze/\pi d^2$), C_s is the salt concentration, ϵ is the dielectric constant of water, and k_B is the Boltzmann constant. The temperature T is fixed at 298 K and the diameter of particles d is taken as 110 nm in simulations. SI potential has a minimum at the position R_m ,

$$R_m = \frac{A + \sqrt{A(A+4)}}{2\kappa} \quad . \tag{4}$$

For convenience, the reduced units are used in the simulation. The basic units are chosen as follows: energy units $k_B T$, the mass of colloidal particles m, and the relevant length scale $L_0 = \sqrt[3]{(6V/\pi N)}$, where N is the total number of particles and V is the volume of simulation box. In such reduced units, we can get $d = \sqrt[3]{\phi}$ (ϕ is the volume fraction of colloidal particles), and the average interparticle separation D_0 of homogeneous body-centered-cubic (bcc) or face-centered-cubic (fcc) crystal is constant (D_0 = 0.879 for bcc and D_0 = 0.904 for fcc, respectively).

The MD simulations are performed in *NVT* ensemble. The period boundary condition is applied. The simple truncation of interactions and the minimum image convention are used [26,27], where the cutoff distance is chosen as r_{cut} = 2.0 in reduced units. The equation of particles' motion is integrated using velocity Verlet algorithm with the time step δt = 0.0005 and the constant temperature is controlled via Berendsen thermostat [28]. Initially we place the particles randomly in a three-dimensional cubic simulation box. If a particle has an overlap with any other particles, it is rejected immediately and a new position will be generated randomly until no overlap happens. After a long enough period of MD time steps (typically $1.9 \times 10^6 \delta t$), the system can reach equilibrium and some parameters of the properties are calculated during another long runs ($10^5 \delta t$), in order for accurate average value obtained.

3. Results and discussion

According to Eqs. (1) and (2), the interaction between colloidal particles is determined by many factors, such as the salt concentration, surface charge density and volume fraction of the colloid, etc. Different values of those factors which influence the interactions will result in different phase behaviors of the system. In this research, we keep the diameter and the volume fraction of the colloid fixed, i.e, d = 110 nm and $\phi = 0.03$, while the salt concentration is taken as $C_s = 0$. Here the parameters chosen are the same to those of previous MC simulations in order for a convenient comparison [17]. Therefore, the research is only focused on the phase behaviors of the system as a function of the charge density σ . The charge density σ on the colloid plays an important role in determining the ordering of the charge stabilized suspensions as it alters the range and strength of the interaction. In the case of polystyrene colloids, a variation in σ is possible by controlling the concentration of charge determining salts during synthesis; In the case of charge stabilized silica colloids, σ can be varied by controlling the sodium hydroxide concentration [12].

When the charge density σ is small, the system exhibits a liquid state. Increasing the value of σ , colloidal particles begin to crystallize and a freezing transition occurs so that the structure ordering of the system takes place somehow. The colloidal particles' motion will be restricted to local regions after the crystallization is completed. The mean square displacement (MSD) measures the Download English Version:

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