Crystallization in quasi-two-dimensional colloidal systems at an air-water interface

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The crystallization of colloidal particles at an air-water interface is investigated by computer simulations. We numerically clarify the bond-orientational order parameter Φ_6 with different particle concentrations. In addition, the profiles of the pair-correlation function $g(r)$, the orientational correlation function $g_B(r)$, and the static structure factor $S(\mathbf{q})$ of this system are calculated. We find the two-stage melting of the colloidal crystal and the existence of the hexatic phase at intermediate concentration. [S1063-651X(99)06212-1]

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I. INTRODUCTION

Charge-stabilized colloidal particles have received much attention in the field of statistical physics, polymer science, and chemical engineering [1]. Many experiments on colloidal suspensions using polystyrene latex have been performed, which display the wide range of structural behaviors. When the salt ions are added in an electrolyte solution, the repulsive force between charged colloidal particles is screened, and van der Waals attractive force dominates. In this case, colloidal particles coalesce each other and form colloidal aggregations. These phenomena have been described by a cluster-cluster aggregation model [2]. On the other hand, the repulsive interaction between colloidal particles becomes large when an aqueous solution is deionized, and the colloidal particles are suspended in a solvent. This is an ideal system for studying crystallization and the melting transition, because the changes are easily observed with optical techniques, and the forces between colloidal particles are readily manipulated by controlling the chemistry of an aqueous solution.

A three-dimensional (3D) colloidal system has been investigated to clarify its structure and thermodynamic properties [1,3–5]. The colloidal particles suspended in an aqueous solution acquire charges and interact via an electrostatic potential. As the screening effect is reduced, the repulsive range between colloidal particles increases and these particles form a *colloidal crystal*. On these systems, there is an order-disorder transition as a function of the particle concentration ϕ and the ionic strength in an aqueous solution. Robbins, Kremer, and Grest [3] have clarified the thermodynamic properties of charge-stabilized colloidal suspensions by molecular dynamics (MD) simulations. Monovoukas and Gast [4] have investigated the colloidal suspensions of highly charged polystyrene spheres, and compared their experimentally determined phase diagram with the MD simulations by Robbins, Kremer, and Grest [3]. These studies reveal that there is a face-centered-cubic (fcc) structure with high concentrations, and body-centered-cubic (bcc) structure with low concentrations in three-dimensional colloidal systems.

Understanding the properties of quasi-two-dimensional colloidal system is very attractive, because the phase behaviors of colloidal suspensions under confinement are expected to be drastically different from those in a 3D system [6–17].

Experimental works have been performed on these quasi-two-dimensional colloidal systems [6–9]. Pieranski [8] has studied polystyrene spheres trapped in a surface energy well at an air-water interface, and observed polymer particles forming a 2D triangular lattice. Murray and Van Winkle [9] have shown a melting transition in 2D colloidal suspensions of highly charged spheres confined between two flat glass plates. Zahn, Lenke, and Maret [16] have studied paramagnetic colloidal particles interacting via dipolar forces in two dimensions, which have different microscopic interactions in the experiment. It is predicted by the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory [1,18–21], that the nature of the melting transition in a 2D system is quite different from that in a 3D system: The first transition is from a *solid phase* with quasi-long-range positional order and long-range bond-orientational order to an *intermediate phase* with short-range positional order and quasi-long-range bond-orientational order. The second transition transforms such a bond-orientational ordered phase to a *fluid phase* in which both positional and bond-orientational order are short range. Different from 3D system, it is expected that there is such a characteristic bond-orientational ordered phase called the *hexatic phase*. However, the results of some experiments and computer simulations are inconsistent with regard to the above theoretical prediction. These studies raise the issue that the melting transition in a 2D system is not universal but depends on specific properties such as the interparticle potential [11,15]. The effect of the confinement of colloidal particles is not fully understood, and detailed investigations of the colloidal system with various interparticle potentials are required to understand the characteristics of 2D crystallization and the melting transition. Especially, numerical studies for interparticle potential with the realistic colloidal system are strongly needed.

In this paper, we perform computer simulations of quasi-two-dimensional colloidal suspensions trapped at an air-water interface. The bond-orientational order parameter Φ_6 is studied numerically with different particle concentration ϕ and the Debye screening length κ^{-1}. We calculate the pair-correlation function $g(r)$ and the orientational correlation function $g_B(r)$ to characterize the structural ordering of the colloidal system. We also clarify the profiles of the structure factor $S(\mathbf{q})$ with different particle concentrations. We observe two successive transitions from the solid phase to the fluid phase with an intermediate hexatic phase, in agreement
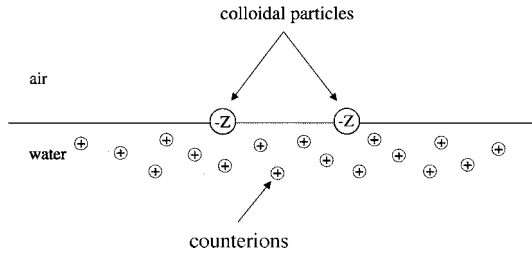
FIG. 1. Schematic diagram of the quasi-two-dimensional colloidal system. The colloidal particles are trapped at an air-water interface.

with Kosterlitz-Thouless-Halperin-Nelson-Young theory.

This paper is organized as follows. In Sec. II, we describe the model of colloidal particles at an air-water interface. In Sec. III, the numerical results on the bond-orientational order parameter, the pair-correlation function, and the orientational correlation function are displayed. We also show the results of the structure factor $S(\mathbf{q})$ on these system. Section IV is devoted to discussions and conclusions.

II. MODELS

In this section, we describe the model of quasi-two-dimensional charged colloidal particles. The electrostatic interactions between colloidal particles have been clarified by previous studies, which are derived from the linearized Poisson-Boltzmann equation [13,22]. Figure 1 shows the schematic diagram of charged colloidal particles at an air-water interface. In this case, the colloidal particles are trapped in a surface energy well at an air-water interface [8]. The pair-potential $V(r)$ between colloidal particles is given by [23,24]

$$V(r) = \begin{cases} \infty & \text{for } r < a, \\ \dfrac{Z^2 e^2}{4\pi\epsilon\epsilon_0} \dfrac{2}{r} \displaystyle\int_0^\infty dz \dfrac{z J_0(z)}{\{z^2 + (\kappa r)^2\}^{1/2} + z/\epsilon} & \text{for } r \geq a, \end{cases} \tag{1}$$

where Z, e, a, ϵ_0, and ϵ are the surface charge of the colloidal particles, the elementary charge, the diameter of the colloidal particle, the dielectric constant, and the relative dielectric constant of the solvent, respectively. Here $J_0(z)$ is the zeroth order Bessel function and κ is the inverse of the Debye screening length. In general, κ is a function of the concentration of microions in an aqueous solution. We have to mention that Eq. (1) includes an *ad hoc* approximation since it consists of the Debye-Hückel potential for pointlike particles, and the hardcore interactions for distances $r < a$ are incorporated. This pair potential $V(r)$ is dominated by exponential decay due to the screened Coulomb contribution at small r, and by algebraic decay from dipole-dipole contribution at large r [24].

III. COLLOIDAL CRYSTALLIZATION

We perform Monte Carlo simulation on the quasi-two-dimensional colloidal system described in Sec. II. At first, equilibrium configurations of colloidal particles are calculated under periodic boundary condition in the x and y direc-
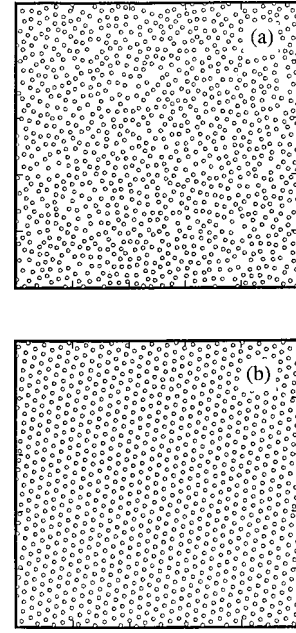

FIG. 2. Snapshots on the equilibrium state of colloidal particles at an air-water interface. The Debye screening length κ^{-1} is taken to be $\kappa^{-1} = 200$ nm. (a) Fluid phase ($\phi = 0.005$), (b) solid phase ($\phi = 0.02$).

tions. In the following, the temperature T and the relative dielectric constant of water ϵ in Eq. (1) are taken to be $T = 300$ K and $\epsilon = 80$, respectively. The surface charge of colloidal particles Z and the diameter of a particle a are taken as $Z = 500$ and $a = 100$ nm, respectively, which are realistic values for actual colloidal suspensions. To check the finite size effect, we perform calculations with different number of colloidal particles such as $N = 1024$ and 2048, treating a larger number of particles than previous studies [10,11,25,26]. The obtained results with different number of particles N show good agreement. We perform very long simulation runs to obtain true thermodynamic equilibrium states. The number of Monte Carlo steps (MCSs) is taken to be over 400 000 MCSs for each calculation. Figure 2 shows the snapshot of the colloidal particles trapped at an air-water interface. Figures 2(a) and 2(b) correspond to the system with the particle concentration $\phi = 0.005$ and $\phi = 0.02$, respectively. The Debye screening length κ^{-1} is taken to be $\kappa^{-1} = 200$ nm. In Fig. 2(a), the colloidal particles are randomly distributed, indicating that this system belongs to a fluid phase. On the contrary, the colloidal particles form a triangular lattice in Fig. 2(b). This is a typical example of a colloidal crystal formed on the quasi-two-dimensional system.

The bond-orientational order parameter Φ_6 was initially introduced by Nelson and Halperin to characterize the structural order in a two-dimensional system [27]. The value of Φ_6 is defined by [26]

$$\Phi_6 \equiv \left\langle \frac{1}{N} \sum_{m=1}^N \frac{1}{N_{\text{bond}}} \sum_{n=1}^{N_{\text{bond}}} \exp(6i\theta_{mn}) \right\rangle, \tag{2}$$

where the angular brackets indicate the configurational average and θ_{mn} is the angle between some fixed axis (e.g., x axis) and the bond joining the mth particle with another nth
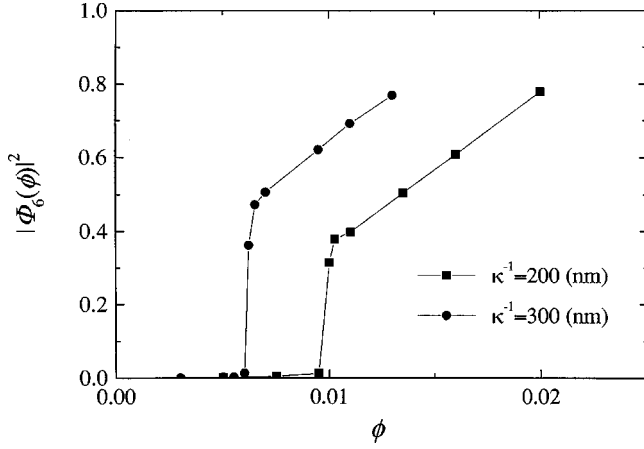
FIG. 3. The squared bond-orientational order-parameter $|\Phi_6|^2$ $=|\Phi_6(\phi)|^2$ of the colloidal particles at an air-water interface. Filled squares and filled circles denote the results for the screening length $\kappa^{-1}=200$ and 300 nm, respectively. Solid lines are only guides to the eye.

particle, lying within a radius $1/\sqrt{\rho_m}$, where ρ_m is the local density of colloidal particles at the neighbor of the particle m. Here N_{bond} denotes the number of the m-n bond. The quantity $|\Phi_6|^2$ is very sensitive to the structural order of the system. When the system belongs to a fluid phase and there is no structural order, the value of $|\Phi_6|^2$ becomes $|\Phi_6|^2 \ll 1$. On the other hand, $|\Phi_6|^2$ takes the value such as $|\Phi_6|^2 \sim 1$ when the colloidal particles form a crystal with the hexagonal order (triangular lattice).

From the obtained equilibrium states, we study the concentration dependence of the bond-orientational order parameter $\Phi_6 = \Phi_6(\phi)$. Figure 3 shows the concentration dependence of the squared bond-orientational order parameter $|\Phi_6|^2$ for the colloidal particles trapped at an air-water interface. The filled squares and circles show the results with the screening length $\kappa^{-1}=200$ and 300 nm, respectively. The solid lines are only guides to the eye. We can see that the value of $|\Phi_6|^2$ becomes zero at small particle concentration, indicating that the system belongs to a fluid phase. With increasing the particle concentration ϕ, the value of $|\Phi_6|^2$ becomes larger which shows that the colloidal particles self-assembly form a crystal lattice.

For further investigation on the structure and the physical properties of these system, the pair-correlation function $g(r)$ and the orientational correlation function $g_B(r)$ are investigated numerically [6,11]. The pair-correlation function $g(r)$ is defined as

$$g(r) \equiv \langle \delta(\mathbf{r}')\delta(\mathbf{r}'-\mathbf{r})\rangle = \left\langle \frac{1}{\phi^2} \sum_m^N \sum_{n \neq m}^N \delta(\mathbf{r}_m)\delta(\mathbf{r}_n - \mathbf{r}) \right\rangle, \tag{3}$$

where $\mathbf{r}_m$ is the positional vector of a particle m and the angle brackets imply the averaging over all angles ($r \equiv |\mathbf{r}|$) and different samples. The profile of $g(r)$ displays the existence (or nonexistence) of the translational order on the system. The orientational order parameter $g_B(r)$ is defined as

$$g_B(r) \equiv \frac{\langle \psi_6^*(\mathbf{r}')\psi_6(\mathbf{r}'-\mathbf{r})\rangle}{\langle \delta(\mathbf{r}')\delta(\mathbf{r}'-\mathbf{r})\rangle}, \tag{4}$$
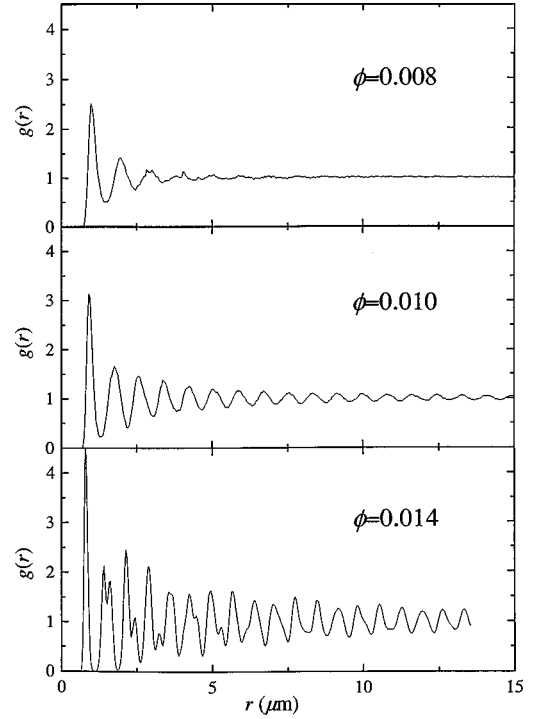

FIG. 4. The pair-correlation function $g(r)$ of the colloidal particles at an air-water interface. The surface charge of colloidal particles Z and the screening length κ^{-1} are taken to be $Z=500$ and $\kappa^{-1}=200$ nm, respectively. The particle concentration ϕ is taken as $\phi=0.008$, 0.01, and 0.014.

where the local bond-orientational order parameter $\psi_6(\mathbf{r})$ is given by

$$\psi_6(\mathbf{r}_m) \equiv \frac{1}{N_{bond}} \sum_{n=1}^{N_{bond}} \exp(6i\theta_{mn}). \tag{5}$$

Here the index n counts the mth particle's nearest neighbors. Figure 4 indicates the pair-correlation function $g(r)$ on the quasi-two-dimensional colloidal system at an air-water interface. The ordinate shows the value of $g(r)$, and the abscissa indicates the distance r in units of μm. In Fig. 4, we show the calculated results with the particle concentration $\phi=0.008$, 0.01, and 0.014, respectively. The Debye screening length κ^{-1} and the surface charge of the colloidal particles Z are taken to be $\kappa^{-1}=200$ nm and $Z=500$. We can see that the envelope of $g(r)$ with $\phi=0.008$ and $\phi=0.01$ decays exponentially. These results indicate that there is no translational order on the system. On the contrary, the calculated result of $g(r)$ with $\phi=0.014$ shows the (quasi-)long-range translational order and the crystallization of colloidal particles at an air-water interface. This feature qualitatively agrees well with the previous experiment on colloidal particles at an air-water interface [8].

Figure 5(a) shows the orientational correlation function $g_B(r)$ on the quasi-two-dimensional colloidal system. Figure 5(a) represents the calculated results of $g_B(r)$ with particle concentrations $\phi=0.008$, 0.01, and 0.014, respectively. At $\phi=0.008$, the envelope of $g_B(r)$ decays exponentially and becomes zero at $r \rightarrow \infty$, indicating that there is no bond-orientational order. It is striking that $g_B(r)$ at $\phi=0.01$ and $\phi=0.014$ in Fig. 5(a) take nonzero values at $r > 10 \, \mu$m. At
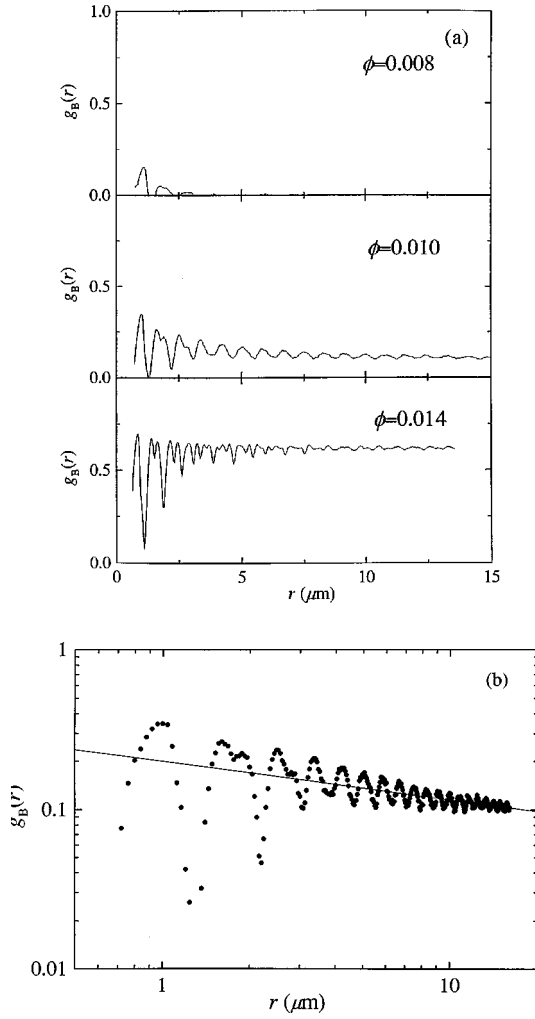
FIG. 5. (a) The orientational correlation function $g_B(r)$ of the colloidal particles at an air-water interface. The surface charge of colloidal particles Z and the screening length κ^{-1} are taken to be $Z = 500$ and $\kappa^{-1} = 200$ nm, respectively. The particle concentration ϕ is taken as $\phi = 0.008$, 0.01, and 0.014. (b) A logarithmic plot of the orientational correlation function $g_B(r)$ with $\phi = 0.01$. Straight line shows the power-law decay such as $\propto r^{-1/4}$.

$\phi = 0.014$, $g_B(r)$ takes a constant value at $r \to \infty$, which implies that there is a bond-orientational order with these system. Figure 5(b) shows a logarithmic plot of the orientational correlation function $g_B(r)$ with $\phi = 0.01$, where the straight line indicates a power-law decay such as $\propto r^{-1/4}$. From these results, we can see good agreement with the theoretical prediction [18–21].

The structure factor $S(\mathbf{q})$ is given by

$$S(\mathbf{q}) = \frac{1}{N} \sum_m \sum_n \exp\{i\mathbf{q} \cdot (\mathbf{r}_m - \mathbf{r}_n)\}, \qquad (6)$$

where $\mathbf{q} = (q_x, q_y)$ and $\mathbf{r}_m$ are the wave vector and the positional vector of the particle m, respectively. Figures 6(a), 6(b), and 6(c) correspond to the calculated results of the structure factor $S(\mathbf{q})$ with the concentration $\phi = 0.008$, 0.01, and 0.014, respectively. The screening length κ^{-1} is $\kappa^{-1} = 200$ nm, and the wave vector $\mathbf{q}$ in Eq. (6) are taken in the range of $0 \leq |q_x|$, $|q_y| < 4.0 \, \mu\mathrm{m}^{-1}$. Solid circles in Fig. 6
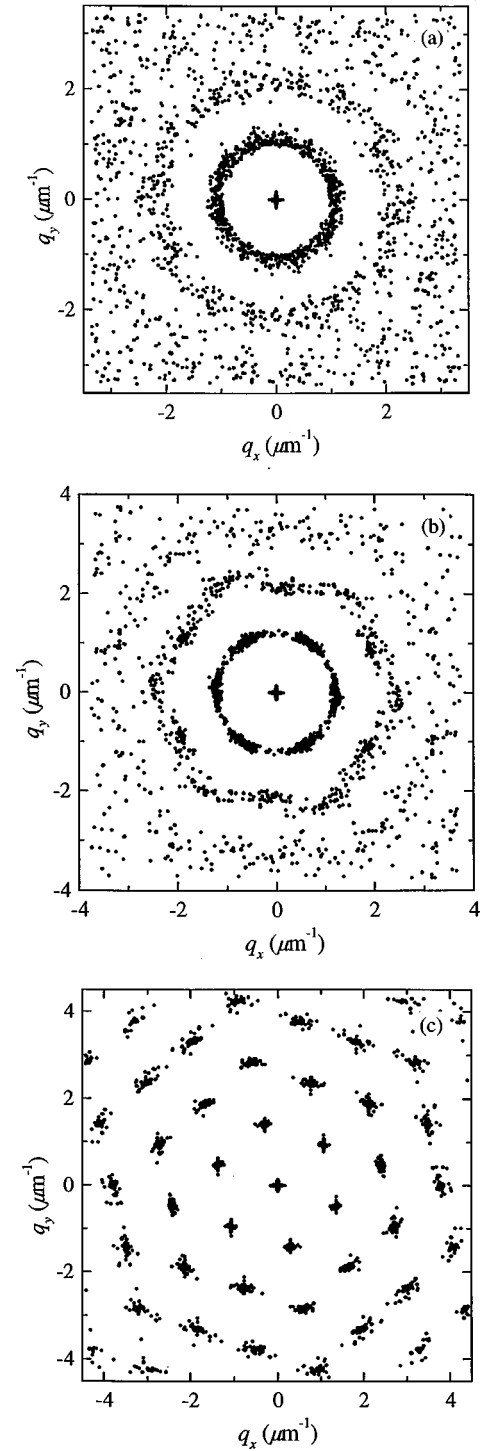

FIG. 6. The structure factor $S(\mathbf{q})$ of the colloidal system at an air-water interface. The screening length κ^{-1} is taken to be $\kappa^{-1} = 200$ nm. (a) Fluid phase ($\phi = 0.008$), (b) hexatic phase ($\phi = 0.01$), (c) solid phase ($\phi = 0.014$).

indicate the wave vector $\mathbf{q}$, where the value of $S(\mathbf{q})$ is larger than a threshold value. In Fig. 6(c), we can see the definite Bragg peaks with sixfold symmetry, reflecting the formation of the colloidal crystal. In contrast to Fig. 6(c), there is no sharp Bragg peak and the isotropic profile is observed in Fig. 6(a), indicating that the colloidal crystal is melting in this concentration (fluid phase). In Fig. 6(b), we can see the anisotropic profiles with sixfold symmetry, and no definite
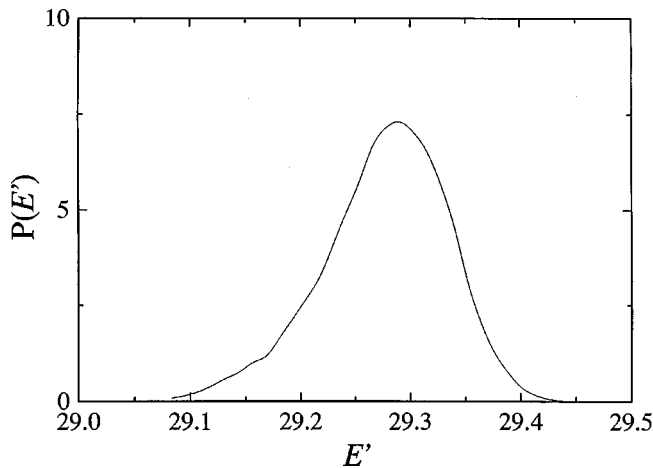
FIG. 7. The probability distribution $P(E')$ as a function of the renormalized total energy $E' \equiv E/Nk_B T$.

Bragg peak. Figure 6(b) displays that there is no translational order, but the orientational order still remains. These results coincide with the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory [1,18–21]. To our knowledge, this is the first calculation showing the hexatic phase of charged colloidal particles trapped at an air-water interface [Eq. (1)]. We also numerically study the probability distribution of the total energy $P(E)$ near the melting transition [28]. Figure 7 shows the profile of $P(E)$ at the concentration $\phi = 0.01$. It shows a single peak on the energy dependence of $P(E)$, which supports the theoretical prediction by KTNHY that these melting transitions are continuous.

IV. CONCLUSIONS

In this paper, we have performed computer simulations of quasi-two-dimensional colloidal suspensions at an air-water interface. The bond-orientational order parameter Φ_6 has been clarified numerically to characterize the structural order of these colloidal systems, with different particle concentration ϕ and the screening length κ^{-1}. The value of $|\Phi_6|^2$ becomes zero at small particle concentration ϕ, in a fluid phase. The value of $|\Phi_6|^2$ increases at larger concentration ϕ, reflecting the colloidal crystallization. In addition, we have clarified the pair-correlation function $g(r)$ and the orientational correlation function $g_B(r)$ on these colloidal systems. We have observed that both $g(r)$ and $g_B(r)$ decay exponentially for smaller concentration, where there is no translational or orientational order in these systems. For larger concentration, however, there is (quasi-)long-range translational order and bond-orientational order, which indicates crystallization on these systems. In the intermediate concentration, the orientational correlation function $g_B(r)$ shows a power-law decay such as $g_B(r) \propto r^{-1/4}$. We have also studied the structure factor $S(\mathbf{q})$ numerically. There is no sharp Bragg peak and the isotropic profile is observed for the fluid phase at smaller ϕ, which shows that the colloidal crystal is melting in this concentration. There are definite Bragg peaks for the solid phase at larger ϕ, which reflects the formation of the colloidal crystal. In the intermediate concentration, we observe anisotropic profiles with sixfold symmetry and no definite Bragg peak. These results demonstrate that the two-dimensional colloidal crystal at an air-water interface shows a two-stage melting, and there is a characteristic bond-orientational order called the hexatic phase at an intermediate concentration, in good agreement with the prediction by KTHNY theory [1,18–21].

We discuss the relationship between the calculated results of the bond-orientational order parameter $\Phi_6 = \Phi_6(\phi)$ and the two-stage melting transition described above. In Fig. 3, the value of $|\Phi_6|^2$ increases rapidly from zero at $\phi = \phi_1$, and increases slowly at $\phi = \phi_2 (> \phi_1)$. This corresponds to the fact that the two-stage melting occurs at the concentrations $\phi = \phi_1$ and $\phi = \phi_2$ (see Figs. 4–6), which implies that the bond-orientational order parameter $\Phi_6 = \Phi_6(\phi)$ is a useful quantity to observe the two-stage melting on these system. It is well known that there is a finite-size effect in actual computer simulations as well as experiments [21]. For understanding of two-dimensional melting transition, it is better to perform computer simulations with larger number of particles and this is a future problem. In Ref. [8] the fluid phase and the solid phase at an air-water interface have been studied in the experiment, but the existence of the intermediate hexatic phase has not been investigated yet. Experimental studies of the hexatic phase on the colloidal particles at an air-water interface are desired, to compare with our numerical results and obtain a deep understanding of colloidal system in aqueous solutions. These results give new insight into recent studies on colloidal crystallization in restricted geometries.

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