Phase transitions in two-dimensional colloidal particles at oil/water interfaces

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Enhanced digital video microscopy is applied to study the equilibrium structure of a two-dimensional charged sulfate-polystyrene particle (2 μm in diameter) monolayer at decane/water interfaces. When the surface density is decreased, a sequential phase transition, pure solid phase → pure hexatic phase → liquid-hexatic-coexisting phase → pure liquid phase, is observed. In addition, the transition between liquid and hexatic phases is first order, while the solid-hexatic phase transition is second order. The temperature effect on this two-dimensional melting transition is discussed by performing the experiments at three different temperatures. The Voronoi [J. Reine Angew. Math. 134, 198 (1908)] construction is applied to analyze the defect structure in the two-dimensional particle monolayer. The pair interaction potential of the two-dimensional colloidal particles is found to be a very long range repulsion and to decay with distance to the power of −3.


INTRODUCTION

It has been a wide interest in the behavior of particle monolayer at a fluid/liquid interface for several decades. In 1968, Sheppard and Tchereukdjian estimated the strength of steric barriers between stabilized spherical polymer particles at the air/water interface from the measurement of isotherms (surface pressure versus surface area) for particle monolayers. Aveyard et al. explored the capability of particles at interfaces to modify the stability of foams and emulsions. The aggregation of particles at the air/water interface as well as the aggregation morphology had also been reported. Due to the very long range repulsive forces between colloidal particles at oil/water interfaces, the charged particle system can form a highly ordered structure under the condition of a dilute density. The colloid-colloid interaction was experimentally determined by a laser tweezers method.

According to the Kosterlitz-Thouless-Halperin-Nelson theory, the melting process is mediated by topological defects in a two-dimensional solid. The KTHNY theory predicts that there is a sequential phase transition in the two-dimensional melting. That is, a transition from solid to hexatic phase and then followed by the other transition from hexatic to liquid phase. A special kind of order, called “bond orientational order,” is used to characterize these phases in the KTHNY theory.

Translational order $g(r)$ and bond orientation order $g_6(r)$ are used to characterize liquid phase, hexatic phase, and solid phase in the KTHNY theory. For the liquid phase, both $g(r)$ and $g_6(r)$ are short-range order and decay exponentially. For the hexatic phase, $g(r)$ is short-range order and decays exponentially, while $g_6(r)$ is quasi-long-range order and decays algebraically. For the solid phase, $g(r)$ is quasi-long-range order and decay algebraically while $g_6(r)$ is long-range order.

When bond orientational order is short range, it makes the structure factor an isotropic ring pattern. Quasi-long-range bond orientational order in the hexatic phase makes the structure factor becomes a sixfold pattern and long-range bond orientation order in the solid phase makes the diffraction pattern to be six clear spots.

Melting phenomenon in two-dimensional systems was examined by using many experimental systems, which can be classified into four categories: (1) layered liquid crystal phases, (2) electrons on the surface of liquid helium, (3) gases absorbed on graphite, and (4) a colloidal suspension of charged particles. X-ray measurement is usually applied to the former first three systems that can only provide indirect information of two-dimensional systems from the diffraction result. In 1987, Murray and Van Winkle first confined colloidal particles between two glass slides to study melting phenomena in two dimensions. The movement of colloidal particles can be observed directly and recorded by digital video microscopy method, and the structure factor, radial distribution function, and bond orientational function can then be evaluated by image analysis. The system has been frequently utilized to study phase transition phenomena in two dimensions. In addition, several kinds of colloidal particle have been applied to the system. Nevertheless there are some restrictions. The system confines colloidal particles between two glass slides. The gap of separation between two slides is about 1.2 times particle diameter. If the gap of separation is smaller than ~1.2 times particle diameter, the colloidal particles become immobile. Because of this limitation, the particle can still move along the vertical direction slightly. Therefore, this type of system is usually called the “quasi-two-dimensional system.” Since the separation is always slightly larger than the particle diameter, some three-dimensional effect may occur. Grier and Han also found that colloid-colloid interaction is related to the distance between confining walls. Further melting transition is also
related to the colloid-colloid interaction. The glass slides also cause some boundary effect, for example, wall drag effect. The experimental setup of the system is complicated and hard to assemble.

Colloidal particles usually stay at an interface in a form of monolayer. Aveyard et al. reported some properties about particle monolayer which was made of 2.6 μm charged polystyrene particles at oil/water interfaces. These authors also observed a solid-solid transition at relatively high density induced by lateral compression. In comparison with the quasi-two-dimensional system, there are several advantages in observing colloidal particles in two dimensions by trapping colloidal particles at oil/water interfaces. First of all, particles are trapped at the same plane and the vertical movement can be “almost” eliminated that ensures a two-dimensional system. It should be noted that the capillary boundary effects resulting from the walls in the quasi-two-dimensional system can be “almost” eliminated that ensures a two-dimensional system. It should be noted that the capillary wave fluctuations would permit the out-of-plane motion of a colloidal particle at oil/water interfaces. Since our oil/water system is far from its critical point, the amplitude of the capillary wave fluctuations is relatively small compared to the size of colloidal particles (2 μm in diameter). Second, particles suspend at oil/water interfaces which can avoid boundary effects resulting from the walls in the quasi-two-dimensional system.

Recently, we applied Langmuir trough as a platform to study the phase behavior of a charged polystyrene colloidal particle system in two dimensions at oil/water interfaces. A sequential phase transition, liquid phase → hexatic phase → solid phase, along with an increase in density, is observed. The purpose of this study is to explore the temperature effect on the phase behavior in the two-dimensional colloidal particle monolayers. Digital video microscopy method is used to capture the images of the configuration of particles. The pair distribution function \( g(r) \) and bond orientation correlation function \( g_2(r) \) of the system are evaluated by directly measuring particle locations in each frame of images. The phase behavior of the system can be further determined by calculating its structure factor \( S(k) \). Further defect analyze is accomplished by the Voronoi diagram to analysis the percentage of different kinds of coordinated particles. It is found that the pair interaction potential of the system is a very long range repulsion.

### EXPERIMENTAL DETAILS

Decane (99% purity) was purchased from Merck and used as received. Water was purified by double distillation and then followed by a purelab Maxima Series (ELGA, LabWater) purification system with the resistivity always better than 18.2 MΩ cm. The monodisperse polystyrene (PS) particles grafted with sulfate group with diameter of 2.000 ± 0.052 μm were supplied by Interfacial Dynamic Corp. (USA) as a surfactant-free aqueous dispersion (solid content: 8.1 g/100 ml). The surface charge density on the particles was 7.1 μC/cm². Isopropanol (IPA) (99% purity) was purchased from Merck and used as a spreading solvent. The spreading solution was prepared by mixing aqueous dispersions of particles (as supplied) with IPA at the volume ratio of 1:3 or 1:6.

The experimental setup is schematically illustrated in Fig. 1. The system of an oil/water interface was prepared in a glass vessel which was kept in a double-walled Pyrex vessel thermostated at a prescribed temperature by circulating water. The monolayer of particles at the oil/water interface was formed by injecting 0.5–6 μl spreading solution according to a prescribed surface density. The vessel was covered by a glass slide for better temperature stability and to prevent from contamination. An upward microscope (Olympus, BXFM) equipped with long working distance objectives with different magnifications (5×, 10×, 20×, and 50×) was set up on the vessel for in situ observation. The observation was performed in dark field method.

Systems of different surface densities could be obtained by carefully controlling the volume of the spreading solution injected onto the oil/water interface. The reduced surface density \( \rho^* \) was measured in units of particle number per frame area normalized by the cross-section area of particle,

\[
\rho^* = N \frac{\pi \sigma^2}{4A},
\]

where \( N \) is number of particles in each frame, \( \sigma \) is the particle diameter, and \( A \) is the surface area of each frame.

A long time observation was performed to examine the equilibration process of the system. After the spreading solution was injected into the interface, more than 50 frames of images every 1 h were recorded. There was no detectable change of structure factor after 1 h. That implies that the system would reach equilibrium in 1 h. Therefore, all the data in this study were collected after the system was left to equilibrate for at least 1 h.

The images were captured by a monochrome charged coupled device video camera (Sony Corporation) mounted on the microscope and grabbed by a frame grabber (NI-1409, National Instrument). All these images were recorded by a personal computer for further data analysis.

A standard image process was applied to extract the information about positions of particles. We closely followed...
the method used by Crocker and Grier. After the positions of particles are determined, the radial distribution function \(g(r)\) is then calculated by

\[
g(r) = \rho^{-2} \left( \sum_{i \neq j} \delta(r_i) \delta(r_j - r) \right),
\]

(2)

where \(\delta(r)\) is the delta function. The bond orientational correlation function is defined and evaluated by

\[
g_b(r) = \left( \sum_{i \neq j} \psi_{6i}(r_i) \psi_{6j}(r_j - r) \right),
\]

(3)

where

\[
\psi_{6i} = \frac{1}{n_i} \sum_{j \neq i} e^{i c \delta_{ij}},
\]

(4)

where \(n_i\) is the number of nearest neighbors of particle \(i\) and \(\delta_{ij}\) is the angle between two nearest neighbor bonds. The local bond correlation function measures the deviation of the structure near particle \(i\) from a perfect triangular lattice, for which \(\delta_{ij} = \pi/3\) and \(\psi_{6i} = 1\).

Once the radial distribution function is known, the structure factor \(S(k)\) can then be calculated by the Fourier transformation of the total correlation function, \(h(r) = g(r) - 1\).

\[
S(k) = \rho \int e^{-i \mathbf{k} \cdot \mathbf{r}} h(r) d\mathbf{r},
\]

(5)

where \(\mathbf{r}\) is the position vector in the real space and \(\mathbf{k}\) is the position vector in the reciprocal space.

Voronoi polyhedra is applied to analyze the defect structure in the two-dimensional particle monolayers. Note that there is no defect species besides \(k = 4, 5, 7,\) and \(8\) in our experimental results. The fraction of \(k\)-fold-coordinated particles, \(P_k\) (\(k = 4, 5, 6, 7,\) and \(8\)) is thus defined as

\[
P_k = \frac{n_k}{n_4 + n_5 + n_6 + n_7 + n_8},
\]

(6)

where \(n_k\) is the number of \(k\)-fold-coordinated particles.

In this study, digital video microscopy is also applied to directly probe colloidal interactions. When the radial distribution function is determined in the limit of infinite dilution, the pair interaction potential can be evaluated through the Boltzmann distribution

\[
U(r) = -k_B T \ln g(r).
\]

(7)

On the other hand, the radial distribution function under the condition of finite concentration also reflects neighboring particles’ influence, and the potential of mean forces with its structure can be evaluated via

\[
w(r) = -k_B T \ln g(r).
\]

(8)

Note that the potential of mean force can be identified with the system’s underlying pair potential only in the limit of infinite dilution,

\[
U(r) = \lim_{\rho \to 0} w(r),
\]

(9)

where \(\rho\) is the density of the system. Reliable approximations for \(U(r)\) can be obtained from \(w(r)\) using the Ornstein-Zernike integral equation with appropriate closure relations. In this study, the hypernetted chain approximation is applied to delineate the many-body effect to obtain the pair interaction potential \(U(r)\). The function \(c(r)\) is the direct correlation function defined by the Ornstein-Zernike equation.

RESULTS AND DISCUSSION

Optical micrographs of PS particle monolayers at the oil/water interface are shown in Fig. 2 at four different reduced surface densities, 0.004, 0.0155, 0.0257, and 0.0385, that correspond to four different states, a pure liquid phase, a liquid-hexatic-coexisting phase, a pure hexatic phase, and a pure solid phase, respectively, observed in this study. Based on the image analysis, the structure function, the angular dependence of the line shape of the two-dimensional structure function, the radial distribution function, and the bond orientational correlation function are calculated and applied to verify the phase behavior as a function of the surface density. The calculated results are also illustrated in Fig. 2 for four different states.

(1) The pure solid phase, \(\rho^* = 0.0385\). The diffraction pattern shown in Fig. 2(d) demonstrates a clearly developed sixfold angular pattern. The transverse line shape of the first peak in the static structure function is well described by a simple Lorentzian function, \(S(\theta_0) = \left[ g(\theta_0) - \chi^2 \right]^{-1/2}\), as shown in Fig. 2(d), indicating that the system falls in the solid phase. The symbol \(\theta_0\) is the angular position of the first peak in the static structure function, \(\chi\) is the in-plane angle that ranges from zero to \(2\pi\), and \(\kappa\) is the angular width of the simple Lorentzian function. The translational order \(g(r)\) is quasi-long-range and decays algebraically. The bond orientational order \(g_6(r)\) is long range.

(2) The pure hexatic phase, \(\rho^* = 0.0257\). The sixfold angular symmetry illustrated in Fig. 2(c) is a necessary but not sufficient condition to identify the phase behavior of the system to be hexatic. The line shape of the first peak of the structure function in Fig. 2(c) fits very well to a square-root Lorentzian function, \(S(\theta_0) = \left[ \left( \theta_0 - \chi \right)^2 + \kappa^2 \right]^{-1/2}\). Note that the square-root Lorentzian functional form of the line shape of the first peak of the structure function is well understood as a signature of hexatic order. The translational order \(g(r)\) is short range and decays exponentially. The bond orientational order \(g_6(r)\) is quasi-long-range and decays algebraically, in accord with the prediction of the KTHNY theory.

(3) The liquid-hexatic-coexisting phase, \(\rho^* = 0.0155\). Figure 2(b) demonstrates a liquid-hexatic-coexisting phase, which is identified by the superposition of isotropic background intensity (for the liquid phase) and a
(4) The pure liquid phase, $\rho^* = 0.004$. The diffraction pattern shows in Fig. 2(a) a pattern of ring. The angular dependence of the diffraction peak is almost constant.

Since there is no angular dependence, this sample is an isotropic liquid. Both the translational order $g(r)$ and the bond orientational order $g_6(r)$ are short range and decay exponentially.
It should be pointed out that a sequence of phase transitions, pure liquid phase $\rightarrow$ liquid-hexatic-coexisting phase $\rightarrow$ pure hexatic phase $\rightarrow$ pure solid phase, is observed along with an increase in density, in accord with the prediction of the KTHNY theory.\cite{12-16}

The Voronoi polyhedron analysis is performed to determine the fourfold-, fivefold-, sixfold-, sevenfold-, and eightfold-coordinated particles for each captured frame. A defect site is defined as its coordination number other than 6. By the Voronoi polyhedron analysis, coordination number of every particle can be obtained to further analyze the defect percentage.

Figure 3 shows the sample images at three different densities: (1) $\rho^*=0.0029$, the liquid phase [Fig. 3(a)]; (2) $\rho^*=0.0137$, the liquid-hexatic-coexisting phase [Fig. 3(b)]; and (3) $\rho^*=0.0407$, the solid phase [Fig. 3(c)], and their corresponding Voronoi diagrams. For clarity, in Fig. 3, all the sixfold-coordinated particles are marked by a blue dot. One can see in Fig. 3 that the fraction of sixfold-coordinated particles dramatically increases from the liquid phase to the solid phase.

One can see in Fig. 3(c) that there exist some defect sites in the solid phase. Note that these defect sites are limited to fivefold- and sevenfold-coordinated particles. In addition, any fivefold-coordinated particle is always accompanied by a sevenfold-coordinated particle, which is known as dislocation. The fractions of fivefold- and sevenfold-coordinated particles, $P_5$ and $P_7$, are also always smaller than 1.5% for the system in the solid phase. Voronoi construction for the system in the hexatic phase is similar to that in the solid phase, except that more dislocations appeared in the hexatic phase. There are almost no fourfold- and eightfold-coordinated particles appearing in the hexatic phase.

Figure 4 shows the fractions of $k$-fold-coordinated particles, $P_k$, as a function of density ($k=4, 5, 6, 7,$ and $8$) at three different temperatures: (A) 20 °C, (B) 30 °C, and (C) 40 °C. $P_4$ ( ), $P_5$ ( ), $P_6$ ( ), $P_7$ ( ), and $P_8$ ( )
obvious that the fraction of sixfold-coordinated particles increases along with the reduced density. Consider the system at 20 °C, as shown in Fig. 4(a). When \( \rho^* = 0.0013 \), the system falls in the liquid phase and \( P_6 = 0.397 \). That means almost 60% of particles are in defect structure. When the reduced density is increased to 0.0052, the system goes into the liquid-hexatic-coexisting region and \( P_6 = 0.580 \). The system reaches to the pure hexatic phase at \( \rho^* = 0.019 \). When the reduced density is further increased up to the region of the solid phase, the fraction of sixfold-coordinated particles \( P_6 \) levels off and asymptotically becomes constant.

The phase behavior at 20 °C, as shown in Fig. 4(a), can be classified into four regions: (1) \( \rho^* < 0.0045 \), the liquid phase; (2) \( 0.0045 < \rho^* < 0.0175 \), the liquid-hexatic-coexisting phase; (3) \( 0.0175 < \rho^* < 0.0208 \), the hexatic phase; and (4) \( 0.0208 < \rho^* \), the solid phase. It is obvious that the transition between the liquid and hexatic phases is first order due to the existence of a wide region of the liquid-hexatic-coexisting phase. On the other hand, the hexatic-solid-coexisting phase behavior is never observed in our system. Note that the density range of the hexatic phase is rather narrow. It is very likely that the transition between the solid and hexatic phases is second order. It should be noted that Marcus and Rice\(^{19,20} \) observed first order transition in both liquid-to-hexatic and hexatic-to-solid phase transitions in the quasi-two-dimensional system of sterically stabilized uncharged polymethylmethacrylate spheres. This finding is consistent with the prediction of the KTHNY theory.\(^{12-16} \) In addition, Bladon and Frenkel\(^{32} \) have reported the results of Monte Carlo simulations of a two-dimensional system of particles with a pairwise additive potential consisting of a hard core repulsion and a very narrow square well attraction. These authors predicted that the liquid-to-hexatic phase transition is first order while the hexatic-to-solid phase transition may be either first or second order.

Consider the transition from solid to hexatic phase based on the defect analysis shown in Fig. 4. While the fraction of fourfold- and eightfold-coordinated defects remain constant and almost zero, the fraction of fivefold- and sevenfold-coordinated defects start to increase right at the transition from solid to hexatic phase. This implies that the transition from solid to hexatic phase is induced by the substantial generation of fivefold- and sevenfold-coordinated defects. \( P_5 \) and \( P_7 \) keep increasing along with the further decrease in density, even when the system falls into the liquid-hexatic-coexisting region. Note that \( P_5 \) is always equal to \( P_7 \) in the regions of liquid-hexatic-coexisting, hexatic, and solid phases, since one fivefold-coordinated particle and one sevenfold-coordinated particle always appear together to form a dislocation. Once the system density is further decreased to enter the region of the pure liquid phase, \( P_5 \) becomes different from \( P_7 \), in accord with results of molecular simulation for quasi-two-dimensional system.\(^{31} \) In addition, the fractions of fourfold- and eightfold-coordinated defects start to increase substantially when the system enters the pure liquid region.

In addition to the system at 20 °C, we have carried out the experiments at another two temperatures, 30 and 40 °C, and the results are also shown in Figs. 4(b) and 4(c). Similar to the results at 20 °C, the phase behavior at 30 and 40 °C can also be classified into four regions as a function of density, as shown in Fig. 4. The phase boundaries for the system at three different temperatures are plotted in Fig. 5. Note that every phase boundary shifts to a higher density as the temperature increases. The density window of the hexatic phase remains quite narrow even at higher temperatures. On the other hand, the density window of the liquid-hexatic-coexisting phase enlarges along with rising temperature.

Consider a system of the solid phase at 20 °C, say, \( \rho^* = 0.025 \). The melting transition can be observed by simply increasing the temperature. Once the temperature is raised to 30 °C, the system would exhibit a transition from the solid to hexatic phase according to Fig. 5. If the temperature is further increased to 40 °C, the liquid phase would appear to coexist with the hexatic phase. However, it is hard to tell, based on the results shown in Fig. 5, whether the hexatic phase vanishes at high temperatures. It is still expected the hexatic phase would vanish at certain higher temperatures and the system would fall into the liquid phase due to the thermal fluctuations. To summarize the temperature effect on the two-dimensional solid melting, the system under the condition of a fixed density would demonstrate a sequential phase transition, pure solid phase → pure hexatic phase → liquid-hexatic-coexisting phase → pure liquid phase, by simply increasing the temperature. Similar phenomenon of the sequential phase transition has been also observed in two-dimensional paramagnetic colloidal particles by varying temperature.\(^{33} \)

It is interesting to point out that the solid phase occurs at extremely low densities \( \rho^* > 0.0208 \) in the system of 2 μm sulfate-polystyrene particles at 20 °C. In contrast to the results for the quasi-two-dimensional system of Rice and co-workers,\(^{19,20} \) the solid phase occurs at rather high densities, \( \rho^* > 0.874 \) for PMMA particles and \( \rho^* > 0.704 \) for silica particles. That is because of the existence of very long-range repulsive forces between particles at the oil/water interface. These strong repulsions between particles at the oil/water interface lead to highly ordered structure even at relatively low surface densities. This long-range colloid-colloid interaction at oil/water interfaces has been studied by using an optical tweezers method.\(^{10} \) In this work, we would like to
extract the pair interaction potential directly from the radial distribution function via the Boltzmann equation, Eq. (7). As mentioned above, the pair interaction potential can be evaluated through the Boltzmann equation, Eq. (7), in the limit of infinite dilution. Therefore, we performed the experiments at some low surface densities. The radial distribution function for the system of $\rho^* = 0.000\,13$ is shown in Fig. 6(a), and this result is inserted into Eq. (7) to calculate the pair interaction potential, as shown in Fig. 6(b). In addition, the pair interaction potential $U(r)/k_BT$ calculated from Eq. (7) for the system of $\rho^* = 0.000\,21$ is also illustrated in Fig. 6(b). Note that the plots of the $U(r)/k_BT$ versus distance resulting from two different densities coincide with each other perfectly. In addition, the hypernetted chain approximation, Eq. (10), is applied to eliminate the many-body effect at low densities and this correction is negligible, as illustrated in Fig. 6(b). It is thus believed that the surface density of the system ($\rho^* = 0.000\,21$) is low enough to be used to determine the pair interaction potential. It is interesting to note that the pair interaction potential decays with distance to the power of $-3$, as shown by the solid curve in Fig. 6(b), consistent with the finding of Aveyard et al.\(^\text{10}\) These authors applied an optical tweezers method to find out that the force between particles decays with distance to the power of $-4$, that implies that the pair interaction potential decays with distance to the power of $-3$. This long-range repulsion arises primarily from the presence of a small residual electric charge at the particle-oil interface.\(^\text{10}\)

In addition to the system at $20\,^\circ\text{C}$, we have carried out the experiments to calculate the pair interaction potential under the condition of low surface density ($\rho^* = 0.000\,13$) at other two temperatures, $30$ and $40\,^\circ\text{C}$. The pair interaction potentials, $U(r)/k_B$, as a function of distance $r$ for three different temperatures are shown in Fig. 7. The results of three different temperatures perfectly coincide with one another, as expected, to form a single curve. In addition, the hypernetted chain approximation, Eq. (10), is applied to eliminate the many-body effect at three different temperatures and this correction is negligible, as illustrated in Fig. 7. Note that this pair interaction potential also decays with distance to the power of $-3$.

**CONCLUSIONS**

The two-dimensional charged sulfate-polystyrene particle ($2\,\mu\text{m}$ in diameter) monolayer at decane/water interfaces is chosen to study the equilibrium structure by using an enhanced digital video microscopy. A sequential phase transition, pure solid phase $\rightarrow$ pure hexatic phase $\rightarrow$ liquid-hexatic-coexisting phase $\rightarrow$ pure liquid phase, is observed as decreasing surface density at three different temperatures: $20$, $30$, and $40\,^\circ\text{C}$. The density window of the liquid-hexatic-coexisting phase region enlarges as temperature is raised. The same sequential phase transition is also observed for the system of a fixed density by simply raising the temperature. In addition, the liquid-hexatic phase transition is first order, while the solid-hexatic phase transition is second order.

The Voronoi construction is applied to analyze the defect structure in the two-dimensional particle monolayers. The transition from solid to hexatic phase is induced by the sub-
stantial generation of fivefold- and sevenfold-coordinated defects. When the system density is decreased to enter the pure liquid region, the fraction of five-coordinated defects $P_5$ becomes different from that of sevenfold-coordinated defects $P_7$ and the fractions of fourfold- and eightfold-coordinated defects start to increase substantially. The pair interaction potential of the two-dimensional colloidal particles is found to be a very long range repulsion and to decay with distance to the power of −3, consistent with the result from the optical tweezers measurement.

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