Anomalous Melting Scenario of the Two-Dimensional Core-Softened System

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We consider the phase behavior of two-dimensional (2D) system of particles with an isotropic core-softened potential introduced in our previous publications. As one can expect from the qualitative consideration for the three dimensional case, the system demonstrates a reentrant-melting transition at low densities along with waterlike anomalies in the fluid phase near the melting maximum. In contrast with the three dimensional case, in two dimensions melting is a continuous two-stage transition in the low density part of the phase diagram with an intermediate hexatic phase corresponding to the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) scenario. At the same time, at high densities the system melts through one first-order transition. We also show, that the order of the region of anomalous diffusion and the regions of density and structural anomalies are inverted in comparison with the 3D case and have silicalike sequence.

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In recent years, a growing attention has been paid to investigation of melting/freezing phenomena of confined fluids in relation with the different fields of modern technology such as fabrication of nanomaterials, nanotribology, adhesion, and nanotechnology [1, 2]. The fundamental question is how the properties of a system change as the dimensionality changes from three dimensions (3D) to two dimensions (2D). The most interesting topics concern the existence of the specific 2D phase, hexatic phase, that interpolates between the fluid and ordered solid phases, and the dependence of the nature of 2D phase transition on the character of the interparticle interaction. In 3D, systems melt through the first-order transition due to the third-order term in the Landau expansion. However, in 2D the singular fluctuations of the order parameter (dislocations and disclinations) may cause the qualitative differences between 2D and 3D behavior of matter [2, 3].

Despite the long history of investigations, the melting transition of most materials in 2D is not well understood, because theories explaining the transition on a microscopic scale are not available. Furthermore, the mechanism of melting depends on the details of the interactions between the particles forming the crystal lattice. In their pioneering works, Halperin, Nelson, and Young [1], using the Kosterlitz-Thouless ideas [8], proposed the scenario of two-dimensional melting which is fundamentally different from the melting scenario of conventional three-dimensional systems. It has been shown that the transition between a crystal and an isotropic liquid can occur by means of two continuous transitions which correspond to dissociation of bound dislocation and disclination pairs, respectively. The low-temperature solid phase is characterized by quasi-long-range translational order and long-range bond-orientational order. Dislocations unbinding at some temperature $T_m$ leads to a phase with short-range translational order, but with quasi-long-range bond-orientational order. This intermediate phase is called a hexatic phase. Paired disclinations in the hexatic phase ultimately unbind themselves, driving a second transition at a higher temperature $T_i$ into an isotropic liquid.

This theory has strong support from experiments with electrons on helium [9] and computer simulations of the 2D electron systems [10]. An experimental confirmation for the KTHNY theory for crystal melting in 2D has been found in the colloidal model system with repulsive magnetic dipole-dipole interaction [11, 13]. However, a conventional first-order transition between a two-dimensional solid and an isotropic liquid is also a possibility (see, for example, [14, 17]).

It should be noted that the KTHNY theory is phenomenological and seems universal. It is not clear from this theory whether the melting scenario depends on the shape of an intermolecular potential. Actually, the natural way to analyze this dependence is to use computer simulations. However, simulations are not reliable enough in the case of two-dimensional melting: it is interesting to note that the similar simulation methods have led to contradictory conclusions even when applied to the same systems [15, 28]. The problems are understandable since correlation times and lengths (translational and orientational) can be extremely long near the phase transition. A lot of efforts were made on computational studies of two-dimensional melting of hard-core potential systems including hard disks or Lennard-Jones potentials [18, 24]. Simulation results on these systems tend to favor a first-order transition scenario for melting, although some conflicting results also exist. In spite of all these efforts, a satisfactory answer has not been obtained yet for one of the most important questions in two-dimensional melting, which is as follows: what condition determines the existence of a hexatic phase and the nature of the melting transition? It seems natural to relate this be-
behavior with the range and the softness of the potential [26, 28].

It is well known that some liquids demonstrate anomalous behavior in some regions of thermodynamic parameters. The most common and well known example is water. The water phase diagrams have regions where a thermal expansion coefficient is negative (density anomaly), self-diffusivity increases upon compression (diffusion anomaly), and the structural order of the system decreases with increasing pressure (structural anomaly). Later on it was discovered that many other substances also demonstrate similar behavior. Some typical examples are silica, silicon, phosphorus, and many others. It is reasonable to relate this kind of behavior to the orientational anisotropy of the potentials, however, a number of studies demonstrate waterlike anomalies in fluids that interact through spherically symmetric core-softened potentials with two length scales. A lot of different core-softened potentials were introduced (see, for example, reviews [29, 30]). However, it should be noted that in general the existence of two length scales is not enough to mark the occurrence of the anomalies. For example, reviews [29, 30]. It is reasonable to relate this kind of behavior to the orientational anisotropy of the potentials, however, a number of studies demonstrate waterlike anomalies in fluids that interact through spherically symmetric core-softened potentials with two length scales.

FIG. 1: (a) Phase diagram of the system with the potential $U(r)$ in $\rho - T$ plane, where the Triangular (T) and Square (S) phases are shown. (b) Phase diagram of the same system in the $P - T$ plane.

Landau expansion as in the ordinary three-dimensional case [5, 6]. The phase diagram corresponding to $T_{MF}$, gives the limit of the thermodynamic stability of the solid phase. In order to conclude whether the melting occurs through the KTHNY scenario, the additional analysis is necessary.

We simulate the system in $NVT$ and $NVE$ ensembles using the molecular dynamics (LAMMPS package [39]). The number of particles in the simulation varied between 3200 and 102400. In order to find the transition points we carry out the free energy calculations for different phases and construct a common tangent to them. For the purely repulsive potentials we computed the free energy of the liquid by integrating the equation of state along an isotherm [38]:

$$F_\rho - F_{id} = \frac{1}{k_B T} \int_0^{\rho} \frac{P(\rho')}{\rho^2} \left( \rho'^2 k_B T \right) d\rho'.$$

Free energies of different crystal phases were determined by the method of coupling to the Einstein crystal [38]. The phase diagram calculated in this way corresponds to the first-order transitions scenario.

We plot in Fig. 1 the phase diagram of the system in $\rho - T$ and $P - T$ coordinates. There is a clear maximum in the melting curve at low densities. The phase diagram consists of two isostuctural triangular crystal domains (T) corresponding to close packing of the small and large disks separated by a structural phase transition and square lattice (S). Similar phase diagram in 3D was discussed in details in our previous publications [32, 33]. It is important to note that there is a region of the phase diagram where we have not found any stable crystal phase. The results of 3D simulations [32, 33] suggest that a glass transition can occur in this region.

To distinguish the first-order melting scenario from the continuous one, we used the criteria described in the Ref. [24]. In Fig. 2 we present the low-temperature (Fig. 2(a)) and high-temperature (Fig. 2(b)) sets of isotherms. One can see that at low temperatures there are four regions on the isotherms corresponding to the phase transitions (see Fig. 2(a)), the low density ones being smooth as in the case of liquid-hexatic-solid transition [24] and the high densities part containing the Van der Waals loops characteristic of the first order phase transition. At high temperatures (see Fig. 2(b)) there is only one liquid-triangular lattice first-order transition. From Fig. 2 one
can guess that the melting of the low-density and high-density parts of the phase diagram occurs with different scenarios: at low densities the KTHNY scenario is probable, while the high density phase melts through the first-order phase transition. As we are going to show in the following, the intermediate region between the solid and the (normal) fluid can be qualified as hexatic.

To confirm this guess, let us define the translational order parameter \( \psi_T \) (TOP), the orientational order parameter \( \Psi_n \) (OOP), and the bond-orientational correlation function \( G_n(r) \) (OCF) in the conventional way:

\[
\psi_T = \frac{1}{N} \left\langle \sum_i e^{i G r_i} \right\rangle .
\]

(2)

where \( r_i \) is the position vector of particle \( i \) and \( G \) is the first reciprocal-lattice vector. It may be easily seen that \( \psi_T \) is nonzero if a solid the orientation corresponding to the length and direction of \( G \). In the simulation, melting of the crystal phase into hexatic phase or isotropic liquid is determined by the sharp decrease of \( \psi_T \) on heating.

The orientational order and the hexatic phase may be studied with the help of the local order parameter, which can be used for measuring the \( n \)-fold orientational ordering:

\[
\Psi_n(r_i) = \frac{1}{n(i)} \sum_{j=1}^{n(i)} e^{i \theta_{ij}},
\]

(3)

where \( \theta_{ij} \) is the angle of the bond joining the particles \( i \) and \( j \) with respect to a reference axis and the sum over \( j \) is over all \( n(i) \) nearest-neighbors of \( i \). The Voronoi construction is used to obtain \( n(i) \). An average over all particles gives the global OOP:

\[
\psi_n = \frac{1}{N} \left\langle \left| \sum_i \Psi_n(r_i) \right|^2 \right\rangle .
\]

(4)

It should be noted that \( n = 6 \) corresponds to the triangular solid and \( n = 4 \) - to square solid. In a perfect triangular solid \( n(i) = 6, \theta_{ij} = \pi/3 \) and \( \psi_6 = 1 \).

The bond-orientational correlation function \( G_n(r) \) (OCF) is given by the equation:

\[
G_n(r) = \langle \Psi_n(r)\Psi_n^*(0) \rangle ,
\]

(5)

where \( \Psi_n(r) \) is the local bond-orientational order parameter \( 6 \).

In the isotropic fluid phase and in the hexatic phase, \( \psi_n \to 0 \) as \( L \to \infty \), where \( L \) is the linear size of the system, but the behaviors of \( G_n(r) \) are different in hexatic and isotropic phases. In the framework of the KTHNY theory, an algebraic large-distance decay of the OCF is predicted for the hexatic phase, in contrast with the exponential asymptotic decay of angular correlations in a normal isotropic fluid:

\[
G_n(r) = e^{-r/\xi}, r \to \infty, \rho < \rho_f, \quad \xi = \eta(T), r \to \infty, \rho_f < \rho < \rho_s, \quad \eta = 1/4.
\]

(6)

Here \( \xi \) is the correlation length of the bond orientational order, which diverges as \( \rho_f \) is approached. Another prediction of the theory is \( \psi_n(r) \) as a function of density for different temperatures.

\[
\chi_n = \frac{1}{N} \left\langle \left| \sum_i \Psi_n(r_i) \right|^2 \right\rangle - N\psi_n^2.
\]

(8)

shows a peak. Location of the peak estimates the transition point.

In Fig. \( 3 \) (a), we represent the orientational order parameter (OOP) as a function of density for a set of temperatures. We see, that at the low density part of the phase diagram OOP behaves smoothly while at high densities one can see the abrupt change of OOP. This kind of behavior suggests again that the melting at low densities is continuous in accordance with the KTHNY scenario, and at high densities melting transition is of the first order. In Fig. \( 3 \) (b), the corresponding susceptibility is shown as a function of density for several temperatures. One can see, that at low densities, \( \chi_6 \) demonstrates the sharp peaks characteristic for the continuous transition, while at high densities the peaks are much smaller, as in the case of the first-order phase transition.

In Fig. \( 4 \) (a), we plot the two OOPs for \( \rho = 0.56 \) as a function of temperature (an analogous behavior was observed for all the other densities). We see that \( \psi_T \) vanishes at a slightly smaller temperature than \( \psi_6 \), which
implies that the hexatic phase is confined to an narrow T interval. In Fig. 3(b), the phase transition line of the solid-hexatic and hexatic-liquid transitions are shown in comparison with the solid-liquid transition line (see Fig. 1). One can see that the transitions are mainly inside the solid region, obtained in the framework of the free-energy calculations. This fact also supports the idea that the melting in this region occurs through two continuous transitions. It is necessary to note, that in the case of the conventional first-order phase transition, the density change at the melting line maximum is equal to zero. We see, that the hexatic phase becomes narrower in the vicinity of the maximum, however, our calculations can not answer whether the width of hexatic region tends to zero at the maximum point.

In order to get another evidence of the hexatic phase existence can be obtained from the large-distance behavior of the OCF. It is shown in Fig. 4 for several densities for $T = 0.12$. One can see that the OCF decays algebraically in a $\rho$ region, approximately corresponding to the hexatic phase region in Fig. 3(b).

It should be noted, that the scaling analysis also supports the melting scenario described above. The similar analysis was made for the melting of the square lattice region of the phase diagram, and it was shown that the square lattice melts through the first-order phase transition.

It was shown that the mentioned above anomalous behavior also exists in 2D 10, 14, 19. The core-softened systems, described by the potential 14, demonstrate the anomalous behavior in three dimensions 53, 57. In 2D, we found the same anomalies (see Fig. 4); however, the order of the region of anomalous diffusion and the regions of density and structural anomalies are inverted in comparison with the 3D case and have silicallike sequence 33, 37, 44. It should be noted, that the similar sequence of anomalies was found in Ref. 28 for extremely soft po-

\[ \psi(r) = \psi_0 - \frac{\eta}{\xi} r^{\eta} \]
tential, however, the authors of Ref. [28] did not compare the 2D and 3D cases.

In conclusion, we show that at low densities the core softened system defined by the potential Eq. [1] demonstrates a two-stage continuous reentrant melting via a hexatic phase. At the same time, at high densities the system melts through the conventional first-order phase transition. The low density melting corresponds to the KTHNY scenario [7]. This kind of behavior can be understood from the consideration of the potential [1]. It is widely believed that the 2D melting transition scenario corresponds to the KTHNY one for the softer potentials, however, the systems with hard potentials melt through first-order transition. The behavior of the system described by the potential [1] is determined by the soft long-range part of the potential at low densities. At the same time, the hard core of the potential plays the main role at the high densities. It seems that this is the reason of the observed peculiarities of the phase diagram. It was also shown, that the order of the region of anomalous diffusion and the regions of density and structural anomalies are inverted in comparison with the 3D case and have silicalike sequence. These results may be also useful for the qualitative understanding the behavior of confined monolayers of water confined between two hydrophobic plates [1, 2, 41, 42].

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