Can random pinning change the melting scenario of two-dimensional core-softened potential system?

E. N. Tsiok,1 D.E. Dudalov,1 Yu. D. Fomin,1,2 and V. N. Ryzhov1,2

1 Institute for High Pressure Physics RAS, 142190 Kaluzhskoe shosse, 14, Troitsk, Moscow, Russia
2 Moscow Institute of Physics and Technology, 141700 Moscow, Russia

(Dated: December 21, 2015)

In experiments the two-dimensional systems are realized mainly on solid substrates which introduce quenched disorder due to some inherent defects. The defects of substrates influence the melting scenario of the systems and have to be taken into account in the interpretation of the experimental results. We present the results of the molecular dynamics simulations of the two dimensional system with the core-softened potential in which a small fraction of the particles is pinned, inducing quenched disorder. The potentials of this type are widely used for the qualitative description of the systems with the water-like anomalies. In our previous publications it was shown that the system demonstrates an anomalous melting scenario: at low densities the system melts through two continuous transition in accordance with the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory with the intermediate hexatic phase, while at high densities the conventional first order melting transition takes place. We find that the well-known disorder-induced widening of the hexatic phase occurs at low densities, while at high density part of the phase diagram random pinning transforms the first-order melting into two transitions: the continuous KTHNY-like solid-hexatic transition and first-order hexatic-isotropic liquid transition.

PACS numbers: 61.20.Gy, 61.20.Ne, 64.60.Kw

Despite almost forty years of investigations, the controversy about the microscopic nature of melting in two dimensions (2D) still lasts. In a crystal in contrast to an isotropic liquid two symmetries are broken: translational and rotational. These two symmetries are not independent, since a rotation of one part of an ideal crystal with respect to another part disrupts not only the orientational order but also the translational order. However, it is possible to imagine the state of matter with orientational order, but without the translational one. As it was shown by Mermin [1] in two dimensions the long-range translational order can not exist because of the thermal fluctuations and transforms to the quasi-long-range one. On the other hand, the real long range orientational order does exist in this case.

These ideas were used in the widely accepted KTHNY theory [2–5] where it was proposed that, in contrast to the 3D case where melting is the first-order transition, the 2D melting can occur through two continuous transitions. In the course of the first transition the bound dislocation pairs dissociate at some temperature \( T_m \) transforming the quasi-long range translational order into the short-range one, and long-range orientational order into the quasi-long range order. At this transition the decay of the translational correlation function will change from algebraic to exponential, and the orientational correlation function will obey the algebraic decrease. The new intermediate phase with the quasi-long range orientational order is called the hexatic phase. After consequent dissociation of the disclination pairs at some temperature \( T_i \) the hexatic phase transforms into the isotropic liquid with the exponential decay of the orientational correlations.

The KTHNY theory seems universal and applicable to all system, however, despite numerous experimental and simulation studies, it could not be consistently verified or refuted. The KTHNY scenario was unambiguously experimentally confirmed for superparamagnetic colloidal particles interacting via long-range dipolar interaction [6–10]. On the other hand, in 2D the first-order melting without hexatic phase is also possible [11, 12]. The possible mechanisms of the first-order melting are the formation of the grain boundaries [11] and the dissociation of the disclination quadrupoles [12]. It is now widely believed that the melting process strongly depends on the pair interaction of the system. Numerous experimental and simulation studies demonstrate that the systems with very short range or hard core potentials melt through weak first-order transition, while the melting scenarios for the soft repulsive particles favor the KTHNY theory. However, controversies still exist even for the same systems, like, for example, for hard spheres [13–23].

Recently, a number of papers have appeared where another melting scenario was proposed [24–30]. It was argued that the basic hard disk model demonstrates the two-stage melting transition with a continuous solid-hexatic transition but a first-order hexatic-liquid transition [24–26]. In Ref. [27] it was shown that in 2D Yukawa system there is a two-phase coexistence region between the stable hexatic phase and isotropic liquid. Kapfer and Krauth [28] have analyzed the effect of the potential softness on the melting scenarios. They have proposed that the soft sphere system with the potential of the form \( U(r) = (\sigma/r)^n \) melts in accordance with the KTHNY theory for \( n \leq 6 \), while for \( n > 6 \) the two-stage melting
transition takes place with the continuous solid-hexatic transition and the first-order hexatic-liquid one.

In experiment, planar confinement is typically realized by adsorption on solid substrates which introduce frozen-in (quenched) disorder due to some roughness or intrinsic defects. Quenched disorder can influence the crystallization/melting scenario of two-dimensional systems. As it was shown in Refs. 31, 32 (see also 33, 34), the KTHNY melting scenario persists in the presence of weak disorder. The temperature of the hexatic-isotropic liquid transition $T_\text{f}$ is almost unaffected by disorder, while the melting temperature $T_\text{m}$ drastically decreases with increasing disorder 31, 34, and the stability range of the hexatic phase widens. Recently these predictions have been tested by experiment and simulations of the behavior of the superparamagnetic colloidal particles 3, 10.

In this paper, we present a computer simulation study of 2D phase diagram of the previously introduced core softened potential system 35–40 in the presence of the quenched disorder. The core-softened potentials are widely used for the qualitative description of systems demonstrating the water-like anomalous behavior, including density, structural and diffusion anomalies, liquid-liquid phase transitions, glass transitions, melting of superparamagnetic colloidal particles 9, 10.

The system we study in the present simulations is described by the potential 35–40:

$$U(r) = \varepsilon \left( \frac{\sigma}{r} \right)^n + \frac{1}{2} \sigma \left( 1 - \tanh(k_1(r - \sigma_1)) \right).$$

where $n = 14$ and $k_1^2 \sigma = 10.0$. $\sigma$ is the hard-core diameter. We simulate the systems with the soft-core diameter $\sigma_1/\sigma = 1.35$. As it was shown in our previous publications 47, 50, the phase diagram of the system consists of three different crystal phases (see also similar picture in 10), one of them has square symmetry and the other two are the low density and high density triangular lattices (see, for example, Fig. 6 (a) in 49). Melting of the low density triangular phase is a continuous two-stage transition, with a narrow intermediate hexatic phase, in accordance with the KTHNY scenario. At high density part of the phase diagram, the square and triangular phases melt through one first order transition. At higher temperatures and high density there is one first order transition between triangular solid and isotropic liquid.

In the remainder of this paper we use the dimensionless quantities, which in 2D have the form: $\tilde{r} = r/\sigma$, $\tilde{P} = P \sigma^2/\varepsilon$, $\tilde{V} = V/N \sigma^2 \equiv 1/\tilde{\rho}$, $\tilde{T} = k_B T/\varepsilon$, $\tilde{\sigma}_1 = \sigma_1/\sigma$. In the rest of the article the tildes will be omitted.

We use the molecular dynamics simulations of the system in $NVT$ and $NVE$ ensembles (LAMMPS package 51) with the number of particles equal to 20000. Quenched disorder is introduced by pinning a randomly chosen subset of particles to the random positions and let them to be immobile for the entire simulation run. We make the simulations of 10 independent replicas of the system with different distributions of random pinned pattern and after that average the thermodynamic functions over replicas. We calculate the pressure $P$ versus density $\rho$ along the isotherms, and the correlation functions $G_6(r)$ and $G_T(r)$ of the bond orientational $\psi_6$ and translational $\psi_T$ order parameters (OPs), which characterize the overall orientational and translational order.

We define the translational order parameter $\psi_T$ (TOP), the orientational order parameter $\psi_6$ (OOP), the bond-orientational $G_6(r)$ (OCF) and translational $G_T(r)$ (TCF) correlation functions in the conventional way 3, 4, 16, 20, 22, 23, 31.

TOP can be written in the form

$$\psi_T = \frac{1}{N} \left\langle \left| \left\langle \sum_i e^{iG_{ri}} \right\rangle \right| \right\rangle_{rp},$$

where $r_i$ is the position vector of particle $i$ and $G$ is the reciprocal-lattice vector of the first shell of the crystal lattice. The translational correlation function can be computed in accordance with the definition 3, 4, 30:

$$G_T(r) = \left\langle \frac{\exp(iG\cdot(r_i - r_j))}{g(r)} \right\rangle_{rp},$$

where $r = |r_i - r_j|$ and $g(r) = < \delta(r_i) \delta(r_j) >$ is the pair distribution function. The second angular brackets $< ... >_{rp}$ correspond to the averaging over the random pinning. In the solid phase the long range behavior of $G_T(r)$ has the form $3, 4 \quad G_T(r) \sim r^{-\eta_T}$ with $\frac{1}{4} \leq \eta_T \leq \frac{1}{3}$.

To identify the existence the orientational order and the hexatic phase, we define the local order parameter, which measures the 6-fold orientational ordering, in the following way:

$$\Psi_6(r_i) = \frac{1}{n(i)} \sum_{j=1}^{n(i)} e^{i\theta_{ij}},$$

where $\theta_{ij}$ is the angle of the vector between particles $i$ and $j$ with respect to a reference axis and the sum over $j$ is counting $n(i)$ nearest-neighbors of $j$, found from the Voronoi construction. The global OOP is obtained as an average over all particles and random pinning:

$$\psi_6 = \frac{1}{N} \left\langle \left| \left\langle \sum_i \Psi_6(r_i) \right\rangle \right| \right\rangle_{rp}.$$

The orientational correlation function $G_6(r)$ (OCF) is given by the equation analogous to Eq. 8

$$G_6(r) = \left\langle \frac{\Psi_6(r)\Psi_6^*(0)}{g(r)} \right\rangle_{rp},$$

where $\Psi_6(r)$ is the local bond-orientational order parameter 4. In the hexatic phase there is a quasi-long range order with the algebraic decay of the orientational correlation function $G_6(r) \propto r^{-\eta_6}$ with $0 \leq \eta_6 \leq \frac{1}{4}$. 


Before to proceed with the study of the phase diagram of system \( G \) in the presence of the random pinning, let us consider the influence of disorder on the orientational and translational correlation functions. In accordance with the results of Nelson and coworkers [31, 32], we did not find any qualitative change in the behavior of \( G_q(r) \) (Eq. (6)) in the presence of pinning. In contrast with \( G_q(r) \), we found the qualitatively different behavior of the translational correlation function \( G_T(r) \) (Eq. (6)). In Fig. 1 we present \( G_T(r) \) for \( \rho = 0.48, T = 0.15 \) without pinning and for 3 different values of the concentration of pinning centers: 0.1%, 0.2%, 0.5% (Concentration 0.1% corresponds to 20 particles frozen-in in the random positions in the system). Density and temperature \( \rho = 0.48, T = 0.15 \) correspond to the point on the phase diagram deeply inside in the low density solid phase. Without pinning we have the conventional power law decay of TCF. In the case of pinning, the slope of the enveloping line increases at some crossover value \( r_0 \). The region \( r < r_0 \) corresponds to the local order unaffected by random impurities, while asymptotic behavior of TCF for \( r > r_0 \) is determined by the random pinning \( \eta \). From Fig. 1(b) one can see that, in accordance with the intuitive picture, \( r_0 \) decreases with increase of impurities concentration along with the increase of the slope of the enveloping line. Further we will consider the equality \( \eta_T = 1/3 \) for the long range asymptote of TCF as the solid-hexatic transition criterium. The hexatic-liquid transition occurs at \( \eta_3 = 1/4 \).

Let us first consider the effect of pinning on the low density part of the phase diagram where melting occurs in accordance with the KTHNY theory. Fig. 2 illustrates the behavior of OCF and TCF for different temperatures at \( \rho = 0.48 \) and the concentration of the pinning centers equal to 0.1%. Using equations \( \eta_T = 1/3 \) and \( \eta_3 = 1/4 \), we calculated the low-density phase diagram in the presence of random pinning. The phase diagram is shown in Fig. 3(a). One can see that random pinning leaves almost unaffected the line of the liquid-hexatic transition, while considerably changes the location of hexatic-solid transition. As a result, in the presence of random pinning the hexatic phase drastically widens in accordance with the theoretical predictions [31, 32] (see also [9, 10]).

The effect of random pinning on the first-order melting transition is shown in Fig. 3(b). The temperatures higher than 0.3 are considered. In this temperature range the transition in the pure system with the potential \( G \) is of first order [16–18]. The lines determined from the equations \( \eta_T = 1/3 \) and \( \eta_3 = 1/4 \) are denoted by the open symbols. One can see, that the line where \( G_q(r) \) decays algebraically with the exponent equal to 1/4 is located inside the two-phase region of the first-order melting transition of the system without pinning. At the same time, in the presence of random pinning the line of solid-hexatic transition obtained from condition \( \eta_T = 1/3 \) is shifted to higher densities. From this picture one can conclude that random pinning transforms the single first-order transition into two transition with rather wide hexatic phase. The solid-hexatic transition is continuous, while the nature of the transition from the hexatic phase
to the isotropic liquid is unclear. In order to elucidate this issue, we plot the isotherms of the system in Fig. 3 with and without random pinning. One can see, that the van der Waals loops which are characteristic of the first order transition are almost unchanged by impurities. This means that the hexatic phase transforms into isotropic liquid through first-order transition.

In conclusion, in this paper we present the computer simulation study of melting transition in 2D core softened system in the presence of random pinning. It is shown that at low densities, the system without pinning melts through two continuous transitions in accordance with the KTHNY scenario, random disorder does not change the character of the transition but drastically widens the range of the hexatic phase. At the same time, at high densities where the conventional first order transition takes place without random pinning, disorder drastically change the melting scenario. The single first-order transition transforms into two transitions, one of them (solid-hexatic) is the continuous KTHNY-like transition, while the hexatic to isotropic liquid transition probably occurs as the first order transition in accordance with the recently proposed scenarios [24–28]. The possible mechanism for this transition is the spontaneous proliferation of grain boundaries [11, 26, 27].

It should be noted, that the nature of the first-order liquid-hexatic transition is still puzzling. As it was shown in [14, 15, 50], using the Landau-type expansion one can see that the solid-liquid transition can be of first order in the case of small enough thermal fluctuations and continuous KT-like, when the singular fluctuations of the phase of the order parameter takes place. The choice between these two possibilities depends on the form of the potential and the thermodynamic parameters. In contrast, in the case of the liquid-hexatic transition one can show that both Landau expansion and KT mechanism lead to the continuous transition, however, simulations predict the first order transition. The strict theory like the KTHNY one is necessary for explaining this controversy. The results of this study can be useful for the qualitative understanding the behavior of water confined in the hydrophobic slit nanopores [52–54].

The authors are grateful to S.M. Stishov and V.V. Brazhkin for valuable discussions. We thank the Russian Scientific Center at Kurchatov Institute and Joint Supercomputing Center of Russian Academy of Science for computational facilities. The work was supported by the Russian Foundation For Basic Research (Grant No 14-02-00451).

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