Melting Scenario of the Two-Dimensional Core-Softened System: First-Order or Continuous Transition?

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Abstract. We present a computer simulation study of the phase behavior of two-dimensional classical particles repelling each other through an isotropic core-softened potential. As in the analogous three dimensional case, a reentrant-melting transition occurs upon compression for not too high pressures. However, in two dimensions in the low density part of the phase diagram melting is a continuous two-stage transition, with an intermediate hexatic phase. All available evidence supports the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) scenario for this melting transition. On the other hand, at high density part of the phase diagram one first-order transition takes place. We expect that such a phenomenology can be checked in confined monolayers of charge-stabilized colloids with a softened core and water confined between two hydrophobic plates.

Despite the long history of investigations, the melting transition of most materials in two dimensions 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. Moreover, the defects reducing the translational order of the crystal are expected to play a major role. In their pioneering works, Halperin, Nelson, and Young [1, 2, 3], using the Kosterlitz-Thouless ideas [4], 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. The shear modulus of the hexatic phase $\mu$ is equal to zero. The properties of the hexatic phase are similar to those of a nematic liquid crystal, except that triangular lattices melt into a phase with persistent sixfold, rather than twofold order. 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 [5, 6, 7] and computer simulations of the 2D electron systems [8, 9]. An experimental confirmation for the KTHNY theory for crystal melting in 2D has been found with the colloidal model system with...
repulsive magnetic dipole-dipole interaction \[10, 11, 12\]. However, a conventional first-order transition between a two-dimensional solid and an isotropic liquid is also a possibility (see, for example, \[13, 14, 15, 16, 17\]).

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 \[18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35\]. The problems are understandable since correlation times and lengths (translational and orientational) can be extremely long near the phase transition. Particularly severe is the situation for hard-core particles, where enormous samples and huge simulation times are required in order to discriminate between the various transition scenarios, while the state sampling may be less demanding for systems of soft particles whose steric constraints are less pronounced. 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. 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 behavior with the range and the softness of the potential \[33, 34, 35\].

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 water-like anomalies in fluids that interact through spherically symmetric core-softening potentials with two length scales. A lot of different core-softened potentials were introduced \[36, 37\].

In this work we study a two-dimensional system with a potential with a hard core followed by a smooth shoulder. In three dimensions it does exhibit the density, the diffusion, and the structural anomalies observed in water. We present a simulation study of two-dimensional melting transition in the purely repulsive core-softened system introduced in our previous publications \[38, 39, 40, 41, 42, 43, 44, 45, 46, 47\].

The general form of the potential is written as

\[
U(r) = \varepsilon \left( \frac{\sigma}{r} \right)^{14} + \frac{1}{2} \varepsilon (1 - \tanh(k_1(r - \sigma_1))).
\]

Here \(k_1 = 10.0\), and \(\sigma_1 = 1.35\). The potential (1) is plotted in Fig. 1. It should be noted that potential (1) is very similar to the Fermi-Jagla potential suggested recently in Ref. \[48\], where the Fermi distribution function is used instead of the hyperbolic tangent in Eq. (1) in order to describe the smoothed step \[46\].

In the remainder of this paper we use the dimensionless quantities: \(\tilde{r} \equiv r / \sigma\), \(\tilde{P} \equiv P \sigma^2 / \varepsilon\), \(\tilde{V} \equiv V / N \sigma^2 \equiv 1 / \tilde{\rho}\), \(\tilde{T} \equiv k_B T / \varepsilon\). Since we will use only these reduced variables, the tildes will be omitted.

In three dimensions particles interacting through a purely repulsive potential given by Eq. (1) exhibit reentrant melting, a maximum melting temperature, superfragile glass behavior, and
thermodynamic anomalies similar to the ones found in water and silica [38, 39, 40, 41, 42, 43, 44, 45, 46, 47].

As it was discussed before [49, 50], there are two characteristic temperatures for the melting transition in two dimensions: the dislocation unbinding temperature \( T_m \) and the first-order transition temperature \( T_{MF} \). The modulus of the order parameter vanishes at the temperature \( T_{MF} \) which can be obtained from the double-tangent construction for the free energies of liquid and solid phases. There are two possibilities [49, 50]: 1: \( T_m < T_{MF} \). In this case the system melts via two continuous transitions of the Kosterlitz-Thouless type with the unbinding of dislocation pairs. 2: \( T_m > T_{MF} \). The system melts via a first-order transition because of the existence of third-order terms in the Landau expansion as in the ordinary three-dimensional case [49, 50]. 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 [52]). 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 [51]:

\[
\frac{F(\rho)-F_\infty(\rho)}{k_B T} = \frac{1}{k_B T} \int_0^\rho P(\rho') - \rho' k_B T d\rho' - \rho^2 k_B T.
\]

Free energies of different crystal phases were determined by the method of coupling to the Einstein crystal [51]. The phase diagram calculated in this way corresponds to the first-order transition scenario.

In Fig. 2, we plot 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 isostructural 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 three dimensions was discussed in details in our previous publications [38, 39]. It is important to note that there is a region of the phase diagram where we have not found any stable crystal
Figure 2. (a) Phase diagram of the system with the potential (1) 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.

Figure 3. The low-temperature (a) and high-temperature (b) sets of isotherms.

phase. The results of three dimensional simulations [38, 46] suggest that a glass transition can occur in this region.

To disentangle first-order from continuous melting, we used the criteria described in the Ref. [31]. In Fig. 3 we present the low-temperature (Fig. 3(a)) and high-temperature (Fig. 3(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 [31] 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. 3 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 consider two different order parameters (OP), which are separately sensitive to the overall translational and orientational order, with their respective
correlation functions. The translational OP is taken to be

$$\psi_T = \frac{1}{N} \left\langle \sum_i \left| e^{i G r_i} \right| \right\rangle,$$

(2)

where the sum is over the particle labels and \( G \) is any first shell reciprocal-lattice vector of the crystal. From its very definition, it follows that \( \psi_T \) is sizeable only in a solid that is oriented in a way consistent with the length and direction of \( G \). Hence, \( \psi_T \) is only measured on heating, where memory of the original crystal orientation is preserved as long as the system is large and remains solid. A sharp drop of \( \psi_T \) signals the melting of the solid into a fluid, be it hexatic or normal.

At regular intervals during the simulation, we identify the \( n_c(i) \) nearest neighbors (NN) of each particle \( i \), together with the orientation \( \theta_{iNN} \) of each neighbor bond with respect to a reference axis. Whence, the orientational OP follows as

$$\psi_6 = \frac{1}{N} \left\langle \sum_i \frac{1}{n_c(i)} \sum_{NN(i)} e^{i \theta_{iNN}} \right\rangle = \frac{1}{N} \left\langle \sum_i \Psi_6(r_i) \right\rangle.$$

(3)

The local bond-angular OP \( \Psi_6(r_i) \) enters the definition of the orientational correlation function (OCF):

$$G_6(r) = \rho^{-2} \left\langle \sum_{i,j} \delta(r_i - R) \delta(r_i - R') \Psi_6(r_i) \Psi_6^*(r_j) \right\rangle,$$

(4)

where the prime over the sum excludes \( i = j \), and \( r = |R - R'| \). The KTHNY theory predicts an algebraic \( r^{-\eta(T)} \) large-distance decay of the OCF in the hexatic phase, which should be contrasted with the exponential asymptotic vanishing of angular correlations in a normal fluid. Another prediction of the theory is \( \eta = 1/4 \) at the hexatic-to-normal fluid transition point.

In Fig. 4, 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. 5, we plot the two OPs 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. 6, the phase transition lines of the solid-hexatic and hexatic-liquid transitions are shown in comparison with the solid-liquid transition line (see Fig. 2). 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. The errors in calculation of the OOP \( \psi_6 \) are less than 1%, while the errors of the translational order parameter \( \psi_T \) do not exceed 5%.

A more direct evidence of the hexatic phase emerges from the large-distance behavior of the OCF. We plot this function in Fig. 7 at various densities across the hexatic phase for \( T = 0.12 \). It appears that the OCF decays algebraically in a \( \rho \) region of limited extent, which roughly corresponds to the middle of the bridging region in Fig. 6.

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.
Figure 4. Orientational order parameter as a function of density for different temperatures.

Figure 5. OPs $\psi_T$ and $\psi_6$ as functions of temperature for $\rho = 0.56$. It is clearly the narrow hexatic phase.
Figure 6. The low-density part of the phase diagram (Fig. 2(a)) along with the lines of solid-hexatic and hexatic-liquid transitions.

It should be noted, that the scaling analysis made in accordance with the algorithm in Refs. [21, 31] also supports the melting scenario described above. For the OOP we used a system of 102400 particles which was divided in subboxes. The subbox size parameter $M_b$ is equal to the number of subboxes along the edge of the total system and varies in our simulations from 1 to 16. As expected (see [21, 31]), the bond-orientational order parameter does not change in the ordered region while it increases with increasing the number of the subboxes in the liquid phase. At the same time, we observe an increase of OOP susceptibility without the change of the locations of the peaks maxima.

In conclusion, we have provided the first unambiguous evidence of the occurrence of two-stage continuous reentrant melting via a hexatic phase in the 2D core-softening model at low densities, while at high densities the melting occurs through the conventional first-order phase transition. We have validated a number of KTHNY predictions. This kind of behavior can be understood from the consideration of the potential (1) (see Fig. 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 the 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. The thermodynamic anomalies which does exist in this system will be considered in the forthcoming publications [53]. The present discovery of reentrant-hexatic behavior in the core-softening potential is relevant for many soft-matter systems. For instance, one can engineer colloidal particles interacting through a temperature modulated softened repulsion, which will likely exhibit reentrant melting in a range of packing fractions well below the density at which hard-core crystallization occurs. These results may be also useful for the qualitative understanding the behavior of confined monolayers of charge-stabilized colloids with a softened core and water confined between two hydrophobic plates [54, 55, 56].
Figure 7. Log-log plots of the orientational correlation function $G_6(r)$ at selected densities across the hexatic region for $T = 0.12$. (a) Upon increasing $\rho$ from 0.41 to 0.45 there is a qualitative change in the large-distance behavior of $G_6(r)$, from constant (solid) to power-law decay (hexatic fluid), up to exponential decay (normal fluid). (b) Note that, consistently with the KTHNY theory, the decay exponent $\eta$ is less than $1/4$ for $\rho > 0.43$.

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[1] Nelson DR and Halperin BI 1978 Phys. Rev. Lett. 41 121
[2] Nelson DR and Halperin BI 1979 Phys. Rev. B 19 2457
[3] Young AP 1979 Phys. Rev. B 19 1855
[4] Kosterlitz M and Thouless DJ 1973 J. Phys. C 6 1181
[5] Grimes CC and Adams G 1979 Phys. Rev. Lett. 42 795
[6] Mehrotra R, Guenin BM, and Dahm AJ 1982 Phys. Rev. Lett. 48 641
[7] Stan MA and Dahm AJ 1989 Phys. Rev. B 40 8995
[8] Morf RH 1979 Phys. Rev. Lett. 43 931
[9] Strandburg KJ 1988 Rev. Mod. Phys. 60 161
[10] Gasser Urs, Eisenmann C, Maret G, and Keim P 2010 ChemPhysChem 11 963
[11] Zahn K and Maret G 2000 Phys. Rev. Lett. 85 3656
[12] Keim P, Maret G, and von Grunberg HH 2007 Phys. Rev. E 75 031402
[13] Chui ST 1983 Phys. Rev. B 28 178
[14] Kleinert H 1983 Phys. Lett. A 95 381
[15] Janke W and Kleinert H 1990 Phys. Rev. B 41 6848
[16] Ryzhov VN 1991 THEORETICAL AND MATHEMATICAL PHYSICS 88 990 (DOI: 10.1007/BF01027701)
[17] Ryzhov VN 1991 ZHURNAL EKSPERIMENTALNOI I TEORETICHESKOI FIZIKI 100, 1627
[18] Alder BJ and Wainright TE 1962 Phys. Rev. 127, 359
[19] Hoover WG and Ree FH 1968 J. Chem. Phys. 49 3609
[20] Lee J and Strandburg KJ 1992 Phys. Rev. B 46 11190
[21] Weber H, Marx D and Binder K 1995 Phys. Rev. B 51 14636
[22] Mak CH 2006 Phys. Rev. E 73 065104
[23] Jaster A 1999 Phys. Rev. E 59 2594
[24] A. Jaster, Europhys. Lett., 42, 277 (1998).
[25] Bagchi K, Andersen HC, and Swope W 1996 Phys. Rev. Lett. 76 255
[26] Lozovik YE and Farztdinov VM 1985 Solid State Commun. 54 725
[27] Ryzhov VN and Tareyeva EE 1995 Phys. Rev. B 51 8789
[28] Ryzhov VN and Tareyeva EE 1995 ZHURNAL EKSPERIMENTALNOI I TEORETICHESKOI FIZIKI 108, 2044
[29] Bernard EP and Krauth W 2011 Phys. Rev. Lett. 107 155704
[30] Engel M, Anderson JA, Glotzer SC, Isobe M, Bernard EP, and Krauth W 2013 Phys. Rev. E 87 042134
[31] Binder K, Sengupta S, and Nielaba P 2002 J. Phys.: Condens. Matter 14 2323
[32] Bladon P and Frenkel D 1995 Phys. Rev. Lett. 74 2519
[33] Lee SI and Lee SJ 2008 Phys. Rev. E 78 041504
[34] Prestipino S, Saija F, and Giaquinta PV 2011 Phys. Rev. Lett. 106 235701
[35] Prestipino S, Saija F, and Giaquinta PV 2012 J. Chem. Phys. 137 104503
[36] Buldyrev SV, Malescio G, Angell CA, Giovambattista N, Prestipino S, Saija F, Stanley HE, and Xu L 2009 J. Phys.: Condens. Matter 21 504106
[37] Vilaseca P and Franzese G 2011 Journal of Non-Crystalline Solids 357 419
[38] Fomin YD, Gribova NV, Ryzhov VN, Stishov SM, and Frenkel D 2008 J. Chem. Phys. 129 064512
[39] Gribova NV, Fomin YD, Frenkel Daan, and Ryzhov VN 2009 Phys. Rev. E 79 051202
[40] Fomin YD, Ryzhov VN, Gribova NV 2010 Phys. Rev. E 81 061201
[41] Fomin YD, TsioEn, and Ryzhov VN 2011 J. Chem. Phys. 134 044523
[42] Fomin YD and Ryzhov VN 2011 Phys. Lett. A 375 2181
[43] Fomin YD, TsioEn, and Ryzhov VN 2011 J. Chem. Phys. 135 124512
[44] Fomin YD, TsioEn, and Ryzhov VN 2011 J. Chem. Phys. 135 234502
[45] Fomin YD, TsioEn, and Ryzhov VN 2013 European Physical Journal - Special Topics 216 165
[46] Ryltsev RE, Chcthelkatchev NM, and Ryzhov VN 2013 Phys. Rev. Lett. 110 025701
[47] Fomin YD, TsioEn, and Ryzhov VN 2013 Phys. Rev. E 87 042122
[48] Abraham JA, Buldyrev SV, and Giovambattista N 2011 J. Phys. Chem. B 115, 14229
[49] Ryzhov V N and Tareyeva E E 2002 Physica A 314 396
[50] Ryzhov V N and Tareyeva E E 2002 THEORETICAL AND MATHEMATICAL PHYSICS 130 101 (DOI: 10.1023/A:1013884616321)
[51] Frenkel Daan and Smit Berend 2002 Understanding molecular simulation (From Algorithms to Applications), 2nd Edition (Academic Press)
[52] http://lammps.sandia.gov/
[53] D.E. Dudalov, Yu.D. Fomin, E.N. TsioEn, and V.N. Ryzhov, arXiv:1311.7534.
[54] Rice SA 2009 Chem. Phys. Lett. 479 1
[55] Krott LB and Barbosa MC 2013 J. Chem. Phys. 138 084505
[56] Almudallal AM, Buldyrev SV, and Saika-Voivod I 2012 J. Chem. Phys. 137 034507