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Phase diagram of the system with the repulsive shoulder potential in two dimensions: Density functional approach

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HIGHLIGHTS

- Melting scenarios of two dimensional repulsive shoulder potential systems are studied.
- The phase diagram is calculated using the density functional theory of freezing.
- We show that at low densities the system melts though continuous transition.
- At high densities melting occurs through the first order transition.

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ABSTRACT

In the framework of the density functional theory of freezing proposed in our previous works, we calculate the phase diagram of two-dimensional system of particles interacting through the repulsive shoulder potential. This potential consists of the hard core and repulsive shoulder of the larger radius. It is shown that at low densities the system melts through the continuous transition in accordance with the Kosterlitz–Thouless–Halperin–Nelson–Young (KTHNY) scenario, while at high densities the conventional first order transition takes place.

A large number of papers studying the melting transition in two dimensions have been published during last decades. They include results of real experiments, computer simulations and various theoretical approaches. This is dictated by the growing interest to the behavior of the nanoconfined systems. Confining drastically changes the spatial distribution and the ways of dynamic rearrangement of the molecules in the system. The confined fluids microscopically relax and flow with characteristic times that differ from the bulk fluids. These effects play important role in the thermodynamic behavior of the confined systems and can considerably change the topology of the phase diagram. In general, the motivation for the study of the confined systems follows from the fact that there are a lot of real physical, chemical and biological processes which drastically depend on the properties of such systems [1–6].

It is not surprising that the spatial ordering of molecules depends on the dimensionality of the space to which it is confined. Mermin [7] has shown that in two dimensions (2D) the long-range crystalline order cannot exist because of the

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thermal fluctuations and transforms to the quasi-long-range order. On the other hand, the real long range bond orientational order does exist in this case. At high temperatures one can find the conventional isotropic fluid.

The melting scenario in two dimensions is a subject of long lasting controversy. Now it is widely believed that the Kosterlitz, Thouless, Halperin, Nelson, and Young theory (KTHNY theory) [8–11] correctly describes the melting transition in 2D. In the framework of the KTHNY theory the two-dimensional melting occurs in the way which is fundamentally different from the melting transition of three-dimensional systems. In 2D, the bound dislocation pairs dissociate at some temperature T_m transforming the quasi-long range translational order into the short-range one, and the long-range orientational order into the quasi-long range one. The new 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 system transforms into the isotropic liquid. Both transitions are continuous, in contrast with the conventional first order three dimensional melting.

The unambiguous confirmations of the KTHNY theory have been obtained, for example, from the recent experiments on the colloidal model system with repulsive magnetic dipole–dipole interaction [12–16]. On the other hand, the first-order melting in 2D is also possible [17–24]. In Refs. [23,24] it was shown that at low disclination core energy system can melt through one first-order transition as a result of the dissociation of the disclination quadrupoles.

KTHNY theory is independent on the pair potential of the system and seems universal, however, numerous experimental and simulation studies demonstrate the controversial results: 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 [2,25–50].

In Refs. [21,22] the phenomenological theory was proposed which explains on the qualitative level the possible interplay between the first-order and continuous melting transitions in 2D. Here we repeat some ideas from these works because they will be used in what follows. As it was mentioned above, in 2D the long range translational order cannot exist due to the thermal fluctuations. It is well known that in the 3D case the melting transition order parameters are given by the Fourier components $\rho_{\mathbf{G}}$ of the expansion of the one-particle distribution function in a Fourier series in reciprocal lattice vectors $\mathbf{G}$ (see, for example, reviews [51,52]).

In 2D, because of the thermal fluctuations, the order parameters $\rho_{\mathbf{G}}$ are no more the constants over the system and slowly vary at distances of the order of G^{-1}. In this case the order parameter can be written in the form $\rho_{\mathbf{G}}(\mathbf{r})$ and has the amplitude and the phase. Taking into account that in 2D the phase fluctuates most strongly, one can neglect the fluctuations of the amplitude and write the order parameter in the form:

$$\rho_{\mathbf{G}}(\mathbf{r}) = \rho_{\mathbf{G}} e^{i\mathbf{G}u(\mathbf{r})}. \tag{1}$$

Here $u(\mathbf{r})$ has the meaning of the displacement field, which, in general, can be decomposed into the smooth part corresponding to the phonon field, and singular part, which can be interpreted as the Kosterlitz–Thouless vortices [8] or dislocations.

Taking into account the long range fluctuations, one can write the phenomenological Ginzburg–Landau–Wilson expansion in the most general form:

$$\begin{aligned} \Delta F = {} & \frac{1}{2}\int d^2r \sum_{\mathbf{G}} \left[A|\mathbf{G}\times\nabla\rho_{\mathbf{G}}|^2 + B|\mathbf{G}\cdot\nabla\rho_{\mathbf{G}}|^2 + C|\rho_{\mathbf{G}}(\mathbf{G}\cdot\nabla)\rho_{\mathbf{G}}|\right] \\ & + \frac{1}{2}a_T\sum_{\mathbf{G}}|\rho_{\mathbf{G}}|^2 + b_T \sum_{\mathbf{G}_1+\mathbf{G}_2+\mathbf{G}_3=0} \rho_{\mathbf{G}_1}\rho_{\mathbf{G}_2}\rho_{\mathbf{G}_3} + O(\rho^4). \end{aligned} \tag{2}$$

ΔF is the difference of the free energies of crystal phase and isotropic liquid. The terms in the integrand in the expansion (2) correspond to all possible isotropic combinations which contain the gradients of the order parameter. This expansion was proposed in Ref. [53] in order to obtain the microscopic expressions for the Lame coefficients in the elastic energy. After substitution of Eq. (1) into (2), it may be shown that the first term in the expansion (2) is expressed in terms of the derivatives of $\partial u_i/\partial x_i$ and has the form of the free energy of a deformed solid [19,20,53] and can be used in the framework of the KTHNY theory [9–11] with the obtained microscopic expressions for the Lame coefficients. It should be noted, that the Lame coefficients are proportional to the squared modulus of the order parameter (1).

As it was discussed in detail in Refs. [21,22], with the help of Eq. (2), the 2D melting scenario can be described in the following way. The modulus of the order parameter becomes zero through the first-order phase transition at the mean-field temperature T_{MF}. On the other hand, if the order parameter modulus is nonzero, at temperature T_m the singular fluctuations of the phase of the order parameter (vortices), which corresponds to the free dislocations, appear in accordance with the standard Kosterlitz–Thouless paradigm, and the system melts through the continuous transition. So, there are two possibilities: (i) $T_m < T_{MF}$, and the system melts through the continuous Kosterlitz–Thouless transition; (ii) $T_m > T_{MF}$, the system melts through the first-order transition.

In our previous publications the density functional approach for the description of the 2D melting was proposed [19,20] and it was shown that the hard disk system melts through the first order phase transition, while in the 2D Coulomb system the melting transition occurs in accordance with the KTHNY scenario. In Refs. [21,22] the density functional calculations were used for the description of the melting transition in the 2D square-well system. It was shown that this system can demonstrate both first-order and continuous melting transitions depending on the width of the attractive well.