

A Simulational Study of a Simple Fluid Monolayer on a Smooth Solid Surface

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A Lennard-Jones fluid layer adsorbed on a smooth solid surface was studied at coverages $\theta \approx 0.8$ to 1.8 on an isotherm by performing intensive grand canonical Monte Carlo simulations. The results clearly show a picture of two-step melting process which used to be observed in recent thermodynamic measurements of argon monolayer melting on graphite. The observed melting process consists of an abrupt density change followed by a gradual transition. Snapshots of monolayer configurations indicate that the creation and dissociation of a dislocation pair are involved in the melting mechanism. Taking the effect of system size into account, it is suggested that, while the abrupt density change may be not related to the theory of Kosterlitz, Thouless, Halperin, Nelson, and Young (KTHNY), the second gradual transition is probably a KTHNY-type melting transition.

$\theta \approx 0.8$ 1.8

Lennard-Jones

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Halperin, Nelson, and Young (KTHNY)
KTHNY

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Kosterlitz, Thouless,

Key words : Phase transition, Adsorption, Monolayer, Monte Carlo

INTRODUCTION

The transition between two-dimensional (2D) phases adsorbed on solid surfaces is of considerable theoretical and experimental interest. The dislocation-unbinding model of Kosterlitz, Thouless, Halperin, Nelson, and Young[1-4] (KTHNY) suggests that the melting of such a two-dimensional system could be continuous. A detailed theory of dislocation-mediated melting in two dimensional systems on a smooth substrate by Halperin and Nelson[2,3] predicts that a liquid-crystal phase, called the hexatic, would exist between solid and liquid in a portion of the phase diagram. Melting takes place via two consecutive continuous transitions. The unbinding of dislocation pairs first drives a transition from the solid phase to the hexatic phase, characterized by sixfold bond-orientational order, and the unbinding of disclination drives the second transition into a liquid phase. Halperin and Nelson also argued that dislocation unbinding should describe melting of an incommensurate solid adsorbed on periodic substrates into a fluid phase. While there have been intensive searches for confirmative evidence of such novel features by experiments and simulations, results are sometimes contradictory and fail to provide unambiguous evidence.

Over the last few years, argon monolayer melting on graphite has been the subject of controversy. Precision heat-capacity measurements by Migone *et al.* [5] detected an additional small sharp peak on the low-temperature side of the previously observed broad heat-capacity anomaly [6]. The small sharp peak was interpreted as a sign of a *weakly first-order* melting transition. In contrast, subsequent high-resolution x-ray studies by Nielsen *et al.* [7] and D'Amico *et al.* [8] reported a single continuous melting transition. High-resolution vapor-pressure iso-

therms by Zhang and Larese [9] revealed, however, that there exists an intermediate solidlike phase and the melting occurs via a two-stage process. In recent precision heat-capacity measurements, Day *et al.* [10] observed a small sharp peak prior to the monolayer melting, in a high temperature region. They proposed that this peak might represent a commensurate-incommensurate transition. However, a most recent neutron diffraction study by Johnson *et al.* [11] revealed that no commensurate phases exist in the portion of the phase diagram suggested by Day *et al.* Here we note that the above thermodynamic measurements reported a consistent picture of a two-step melting process, no matter what temperature regions were investigated. In this Letter, we present the first simulational evidence of such a picture.

Simulational studies of 2D melting can be done by 2D or 3D simulations. Most of them have been 2D simulations. In 2D simulations of idealized 2D systems, it appears that the melting transition might be a first order [12-14]. Recently, however, Chen *et al.* [15] reported that they observed a metastable hexatic phase from large scale molecular dynamics simulations. In a 3D simulation study of argon submonolayer melting on graphite, Abraham [16] reported that his finding of a continuous transition is consistent with the experiment of McTague *et al.* [6]. However, 3D simulations of 2D melting at coverages near monolayer completion have been superficial so far. In this work, we performed 3D grand canonical ensemble Monte Carlo (GCEMC) simulations for argon layers on a continuum graphite at coverages $\theta \sim 0.8$ to 1.8 on an isotherm. The results clearly show that the argon monolayer melts (and freezes) via two-step process. There exists a stable intermediate phase with a solidlike short-range spatial order between solid and liquid phases. Such a picture has never been observed in previous simulations.

RESULTS and DISCUSSION

In the simulations we used simplest potential models for the argon on a continuum graphite which had been used by Rowley *et al.* [17,18]. They are a Lennard-Jones 12-6 potential

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

and a 9-3 potential

$$V'(r) = \frac{3^{3/2}}{2} \epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

for the adsorbate-adsorbate interactions and the adsorbent-adsorbate interactions, respectively. The parameters ϵ' and σ' are typical of the graphite-argon system ($\epsilon'/\epsilon=9.240$, $\sigma'/\sigma=0.5621$). The computational box had a plane rectangular surface with sides $7 \times 21\sigma$ and $4\sqrt{3} \times 21\sigma$, on which 56 triangular lattice points with a nearest-neighbour distance of 21σ can reside. Periodic boundary conditions were imposed at the four faces of the computational cell. A

reflecting wall was placed at the top of the computational box at a 14σ height. The adsorbate-adsorbate potential was cut off at $r = 2\sqrt{3} \times 21\sigma$. Moves, creations, and destructions of a particle are selected at random, with equal probability. Maximum displacement length of 0.03σ was used in moves. The overall acceptance ratio then being about 27 per cent.

Series of simulations, mimicking the experimental procedures for adsorption and desorption, along the $0.67\epsilon/k$ ($\sim 80.4\text{K}$) isotherm have been performed (here k represents the Boltzmann constant). A series of simulations for adsorption were done first by increasing the activity, $Z \equiv (2\pi\hbar^2/mkT)^{-3/2} \exp(\mu/kT)$, of the argon gas from 0.1×10^{-4} to 0.55×10^{-3} . Secondly, in order to check hysteresis, two independent series of simulations for desorption were performed at activities spanning the transition regimes detected from the first series of simulations. For every state, preliminary runs of generating 5×10^6 configurations were performed for the thermal

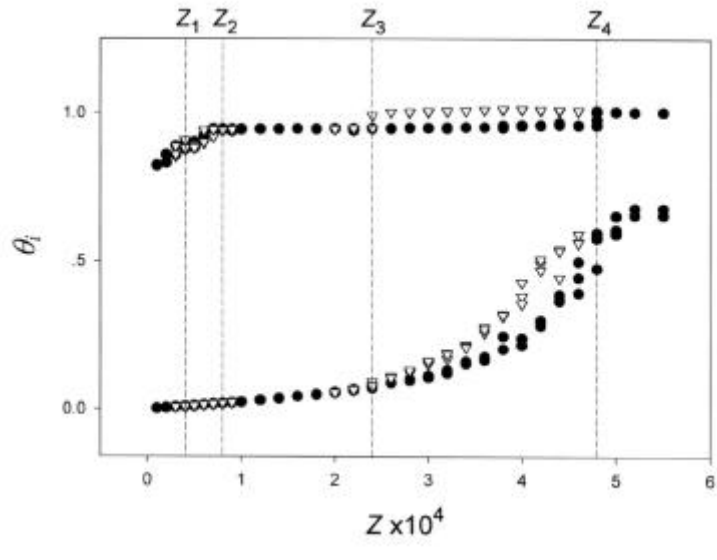


Fig. 1. Plot of the coverages of the first layer, θ_1 , and the second layer, θ_2 , versus activity for the results of simulations for adsorption (●) and desorption (▽).

equilibration of the system. Two to four consecutive runs of generating 5×10^6 configurations performed additionally and ensemble averages were calculated in each run.

In Figs. 1-3 are presented our computational results which clearly indicate that the monolayer melting (and freezing) take place in two steps and an intermediate phase exists. The coverages of the first and the second layers, θ_1 and θ_2 , as functions of activity are presented in Fig. 1 ($\theta_i \equiv \langle N_i \rangle / 56$, with $\langle N_i \rangle$ representing the ensemble average of the number of atoms in the i -th layer). It appears that the layers in intermediate phase have almost a constant coverage of $\theta_1 \sim 0.946$ ($\langle N_1 \rangle \sim 53$). While we note that the transition from the fluid phase to the intermediate phase and the reverse occur gradually at a same region, $Z_1 (= 0.04 \times 10^{-4}) < Z < Z_2 (= 0.08 \times 10^{-4})$, the transition from the intermediate phase to the solid phase and the reverse occur abruptly at different activities, $Z = Z_3 (= 0.48 \times 10^{-4})$ and $Z_4 (= 0.24 \times 10^{-4})$, respectively, which establishes hysteresis. In Fig. 2 is presented the

energy fluctuation per atom as a function of activity. The smallness of energy fluctuation over the region of $Z_2 < Z < Z_3$ where exists a single intermediate phase only, implies that the intermediate phase is very stable. The peaks at $Z_1 < Z < Z_2$ and $Z = Z_3$ are signs of phase transitions of the first layer. However, the larger fluctuations in $Z > Z_3$ is caused by the condensation of the second layer. Since the first layers are in a stable solid or intermediate phase, the origin of such large fluctuation of energy over the $Z > Z_3$ region is the fluctuation of coverage of the second layer (see Fig. 1). The sign of the transition from the intermediate phase to the solid phase at $Z = Z_4$ is screened off. In order to see the structural property of the monolayer, the in-plane cylindrical pair distribution, $g(\rho)$, was calculated in each run of simulation. The results from final runs for nominal activities along the desorption branch are presented in Fig. 3, a perspective plot of $g_2(\rho)$ as a function of activity. Looking at the figure, we see that a long-range translational order is transformed into a short-range solidlike

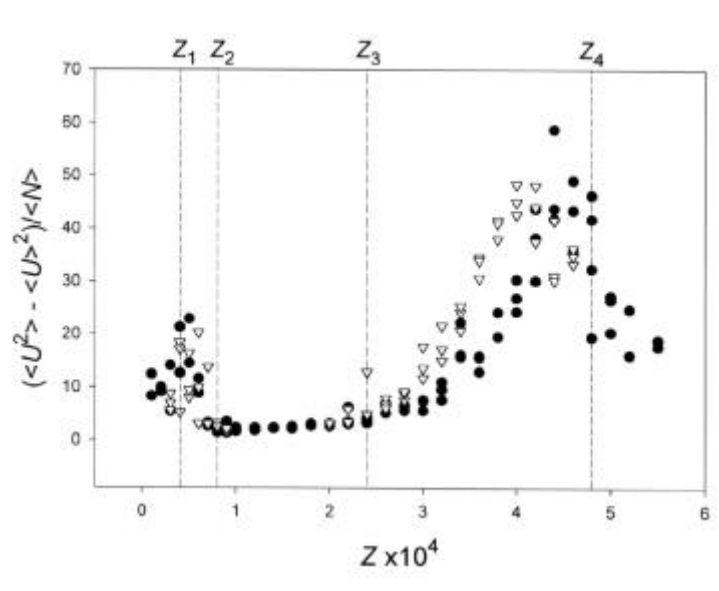


Fig. 2. Plot of the energy fluctuation per atom versus activity for the results of simulations for adsorption (●) and desorption (▽).

structural order upon the transition out of the solid phase, and liquid and intermediate phases coexist during their transition.

The features shown in Figs. 1-3 were not observed in the earlier GCEMC simulations on an isotherm ($T = 0.668\epsilon/k$) done by Rowley *et al.* [17,18] who used the identical potentials of Eqs. (1) and (2). What they observed is a single transition from a fluid phase with $\theta < 0.93$ to a solidlike phase with $\theta \sim 1.0$. One should note, however, that a small square periodic surface, which does not fit a triangular lattice with a nearest-neighbour distance of $2l/6$ was used in the previous work [19]. In order to verify the reliability of our computer code, we have used identical periodic cell dimensions and temperature, and reproduced the results of the previous work. It appears that the contradictory results of the previous work against this work is due to the artifact imposed by dimensions of the periodic surface; no solid phase with long-range translational order can be observed but solidlike and fluid phases.

Let us now turn to the question of if our observed two-step melting process is a kind of the KTHNY model. Can we rule out the possibility of a KTHNY-type melting process,

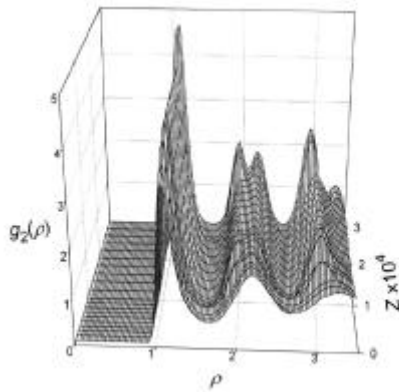


Fig. 3. Perspective plot of the in-plane cylindrical pair distribution, $g_2(\rho)$, of the monolayer as a function of activity.

since a hysteresis is observed in transition between solid and intermediate phases? Then, what is the origin of the two-step melting behavior, as shown in Figs. 1-3? It is impossible to see if the intermediate phase is a hexatic phase, because our system size is too small to check the long-range orientational order. Instead, we examined snapshots of final configurations of monolayers for nominal activities between $Z1$ and $Z3$. It appears that the creation and dissociation of dislocation pair are involved in the melting mechanism. The snapshots at $Z = Z3$, $Z2$ and $Z1$ are presented in Figs. 4(a), (c) and (d), respectively. In the range of $Z2 < Z \leq Z3$ most of the examined have structures with an uncertain dislocation pair like shown in Fig. 4(a). We note that such

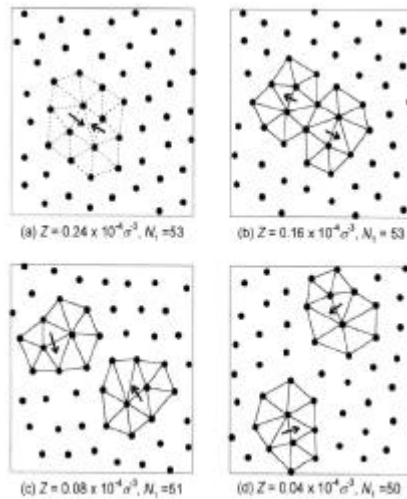


Fig. 4. Snapshots of the monolayers showing appearances of a dislocation pair at (a) $Z = Z3$, (b) an activity in $Z2 < Z < Z3$, (c) $Z = Z2$ and (d) $Z = Z1$. These indicate that the creation and unbinding of a dislocation pair are involved in the melting mechanism. The arrows represent Burger's vectors of dislocations. In (a) dotted lines are used to represent an uncertain appearance of a dislocation pair.

structures are so flexible and distorted that a dislocation pair can appear. In order to show an instance of clear appearance of a dislocation pair, Fig. 4(b) is given. Figures 4(a) and (b) suggest that the transition at $Z = Z3$ may be caused by the creation of a dislocation pair in which an effect of system size are involved; for systems with a finite surface, it might be much more energy consumable to create a dislocation pair with persisting a long-range translational order than to change the density, so that the system is transformed into an intermediate phase with flexible structures in which the creation of a dislocation pair is easier. For the larger system, the smaller density change is expected. Figure 4(c) strongly suggests that the gradual transition at $Z1 \leq Z \leq Z2$ is initiated by the unbinding of dislocation pair which plays a key role in the KTHNY theory. Figure 4(d) indicates that the unbinding of dislocation pair is involved all through the transition.

Based on data from this work, we interpret our findings as follows. For the melting process, the transition with an abrupt density change may be not related to the KTHNY theory but caused by the creation of a dislocation pair and the effect of system size. The intermediate phase may be not a hexatic phase but a solidlike phase with a bound dislocation pair. However, the second gradual transition probably represents a dislocation-unbinding transition of the KTHNY theory. The dislocation-unbinding transition might be eliminated or altered by the effect of system size. For the infinite system, the absence of the transition at $Z = Z3$ is expected. What is more, assuming the relevance of the KTHNY theory, a melting process consisting of two consecutive continuous transitions could be expected at $Z1 \leq Z \leq Z2$. It is very interesting that our GCEMC simulations which used a *smooth* substrate give a picture of two-step melting process observed in previous experiments [5,9,10]. This means that the influence of the simulational surface size on the monolayer

melting properties in simulations is very similar to that of the substrate structure in real which misfits the argon film structure. So, it is possible to make a similar interpretation for observations of two-step melting picture in real. This would resolve a number of discrepancies between previous experimental measurements of argon monolayer melting on graphite.

Summary

In summary, the results of GCEMC simulations for argon layers on a continuum graphite clearly show that the monolayer melts via a two-step process which consists of an abrupt density change followed by a gradual transition. The snapshots of monolayer configurations show that the creation and dissociation of a dislocation pair are involved in the melting mechanism. Taking account of the effect of system size, it is suggested that, while the transition with an abrupt density change may be not related to the KTHNY theory, the second gradual transition is probably a KTHNY-type melting transition. We expect that the argon monolayer melting on the infinite continuum substrate would be an example of a KTHNY melting process. Our simulational findings may give a clue to resolving discrepancies between experimental measurements.

It would be better to confess that we did not initiate this work expecting such a new result. Frankly speaking, our GCEMC simulations were originally intended for providing reference data that will be used in developing a new isochoric Monte Carlo technique suitable for simulating solid-gas interfaces. This is why we used such simple potentials and such a small system. The new technique will be presented in other place.

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19. In fact, Rowley et al. have also used the same dimensions of this work for the periodic surface, but generated just three data points only so that they could not have observed our findings.