

Evidence for an Orientationally Ordered Two-Dimensional Fluid Phase from Molecular-Dynamics Calculations

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Results of molecular-dynamics calculations on melting in a two-dimensional (2D) Lennard-Jones system are presented. We find that this system loses its resistance to shear at a temperature T_1 (≈ 0.36). However, long-range "orientational" order persists up to a higher temperature T_2 (≈ 0.57). These observations are compatible with the existence of a liquid-crystal-like phase with sixfold anisotropy separated from both the solid and the isotropic-fluid phase by second-order phase transitions. Such two-stage melting behavior in 2D has been predicted by Halperin and Nelson.

There is growing experimental evidence that melting in two dimensions (2D) may be qualitatively different from the corresponding phenomenon in 3D. Neutron scattering experiments¹ and heat capacity measurements² on adsorbed monolayers seem to indicate that for some systems regions in the phase diagrams exist where the transition from solid to fluid is actually continuous.

A detailed theory of melting in 2D has been put forward by Halperin and Nelson (HN).³ These authors make a startling prediction, namely, that, if melting in 2D is not a first-order transition, then in fact *two* second-order transitions are required to make the transition from the solid phase to the isotropic fluid. The solid and isotropic-fluid phases will then be separated by a peculiar intermediate phase that exhibits short-range (exponential decay) translational order, but relatively long-range (algebraic decay) "orientational" order. They propose the name "hexatic" for this phase which has the property of a two-dimensional liquid crystal with sixfold anisotropy.

Direct experimental verification of the more striking predictions of the HN theory is complicated by the fact that those quantities that are most readily observed experimentally are expected to exhibit only subtle changes at the phase transitions. Conversely, properties that are predicted to change in a more dramatic way are very hard to probe experimentally. It is for this reason that we decided to perform a computer (molecular-dynamics) "experiment" on a well-defined model system in order to study the temperature dependence of some of the quantities that play a central role in the HN theory.

The system we chose to study was a collection of two-dimensional Lennard-Jones (12-6 potential)

particles. The reason for selecting this particular system was that earlier calculations on the same system⁴ had been quite successful in modeling the behavior of certain real systems (in particular argon on graphite) that appear to have a continuous melting transition. One should note that, strictly speaking, the system studied in the computer experiments cannot be described by a model Hamiltonian of the type used by HN, for two reasons. First of all, in the HN theory two-dimensional matter is described as a continuum with embedded dislocations, whereas the systems studied by molecular dynamics (MD) are, of course, particulate. More serious is the fact that in MD calculations on finite systems one is forced to use periodic boundary conditions, thereby excluding all fluctuations with wave vector $k < 2\pi/L$ (L is the box length). In contrast, long-wavelength fluctuations necessarily play an essential role in the HN renormalization-group treatment of the phase transitions.

Molecular-dynamics calculations were performed on a 256-particle Lennard-Jones system at a reduced density $\rho^* = \rho\sigma^2 = 0.8$ and at reduced temperatures ranging from $T^* = kT/\epsilon = 0.25$ to 1.25. The duration of most runs was approximately 100τ [$\tau = \sigma(m/\epsilon)^{1/2}$; $100\tau = 20\,000$ time steps], though runs at least twice as long were done to obtain transverse current correlation functions. Each run was preceded by an equilibration period of 10τ to 15τ . The $\rho^* = 0.8$ isochore was traversed in both directions to test for possible hysteresis effects that tend to accompany discontinuous phase transitions.

Figure 1 shows the temperature dependence of the energy, pressure, and heat capacity along the $\rho^* = 0.8$ isochore. The important thing to note about Fig. 1 is that hysteresis seems to be virtually absent. This behavior is in marked con-

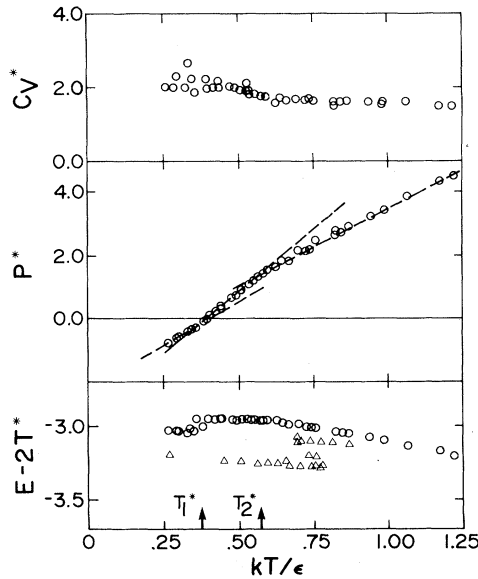


FIG. 1. From top to bottom: Heat capacity, and virial pressure and energy of a flat 2D Lennard-Jones system at $\rho^* = 0.8$ (open circles). T_1^* and T_2^* indicate the approximate temperatures where E and P change slope. To guide the eye, straight-line segments have been drawn through the P vs T points; these line segments do not, however, have any theoretical significance. In particular, no discontinuous changes in slope of P at T_1^* and T_2^* are implied. Typical first-order behavior is shown in the lower panel (open triangles). The points correspond to "Kr on graphite" at $\rho^* = 0.825$ (from Ref. 6). In the figure $2T^*$, i.e., the energy per particle in a harmonic lattice, has been subtracted from all energies.

trast to what has been observed in 3D, where freezing occurs through nucleation only upon significant undercooling.⁵ For the sake of comparison, results of machine calculations on the melting of the registered phase of Lennard Jones (LJ) "krypton on graphite,"⁶ a transition that is (weakly) first order, are also shown in Fig. 1. Closer inspection of Fig. 1. shows that both E and P change slope around $T_1^* \approx 0.36$ and $T_2^* \approx 0.57$. This fact, in itself, is no indication of the occurrence of two higher-order phase transitions. In fact, in an infinite system, one would expect to observe something similar if a first-order phase transition at constant density is pressure broadened; the region $T_1^* < T^* < T_2^*$ would then be a two-phase region. In a finite system, however, the creation of interfaces in general requires a nonnegligible amount of free energy (this is, in fact, one of the reasons why hysteresis occurs in 3D). The fact, then, that

no hysteresis is observed seems to indicate that, if the transition were first order, the free energy of interface formation is negligible. But that is equivalent to the statement that the system shows critical behavior. The MD calculations therefore seem compatible with the interpretation of T_1^* and T_2^* as second-order phase transitions, although a more conclusive answer would require a study of the system-size dependence.

An intriguing prediction of the HN theory concerns the temperature dependence of the correlation function of the orientational order parameter. The orientational order parameter that has the symmetry properties of a triangular lattice is defined as

$$\Psi(\vec{r}) = \exp[6i\theta(\vec{r})], \quad (1)$$

where $\theta(\vec{r})$ is the angle between some fixed axis and the line joining the centers of mass of two neighboring atoms. In the continuum description used by HN, $\theta(\vec{r})$ can be expressed in terms of the displacement field. Although no infinite-range translational order exists even in a harmonic, infinite 2D crystal, orientational order is long ranged, i.e., $\langle \Psi^*(0)\Psi(r) \rangle \rightarrow c \neq 0$ for $r \rightarrow \infty$.⁷ Halperin and Nelson predict that if melting in 2D is not first order, $\langle \Psi^*(0)\Psi(r) \rangle$ will decay algebraically in the hexatic phase and exponentially in the high-temperature isotropic-fluid phase. For computational purposes it is more convenient to define the orientational order parameter in the following way:

$$\Psi_6(\vec{r}) = N^{-1} \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \frac{1}{6} \sum_{j=1}^6 \exp(6i\theta_{ij}), \quad (2)$$

where $j = 1-6$ are the six nearest neighbors of atom i . Because $\Psi_6(r)$ is only defined at the site of an atom, the correlation function $\langle \Psi_6^*(0)\Psi_6(r) \rangle \equiv g_6(r)$ exhibits oscillations (see Fig. 2). This effect is partly due to oscillations in the radial distribution function, $g_6(r)$. But even after dividing $g_6(r)$ by $g(r)$ (which has been done in Fig. 2), oscillations remain. These oscillations can be understood by considering a regular triangular lattice with a few interstitial atoms. If both \vec{r}_i and \vec{r}_k are lattice sites, $\Psi_6^*(\vec{r}_i)\Psi_6(\vec{r}_k) = 1$; but if \vec{r}_k is the site of an interstitial atom, $\Psi_6^*(\vec{r}_i)\Psi_6(\vec{r}_k) = -1$. For comparison with the continuum theory it is only meaningful to speak about the envelope of $g_6(r)$. In the high-temperature fluid phase this envelope is found to be very nearly exponential for all but the shortest distances. We denote the correlation length of this exponential by $\xi_6(T)$. Figure 3 shows the temperature dependence of

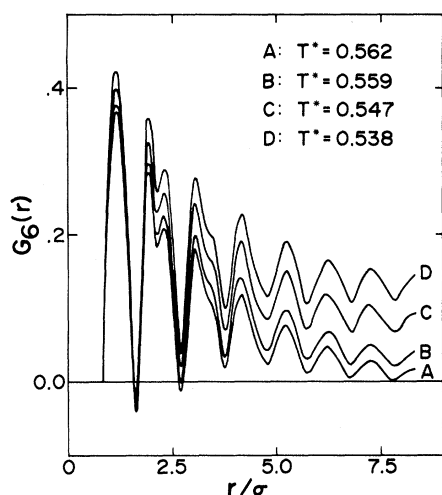


FIG. 2. Correlation function of the orientational order parameter (as defined in text) in the vicinity of T_2^* . The function plotted is $\langle \Psi_6^*(0) \Psi_6(r) \rangle / g(r)$. Note that at the lower temperatures $g_6(r)$ does no longer die out within half a box length.

$\xi_6(T)$. Around $T^* = T_2^*$ $\xi_6(T)$ shows a dramatic increase; the HN theory predicts that $\xi_6(T)$ diverges as the hexatic phase is approached from above. We have not plotted $\xi_6(T)$ at lower temperatures because once $\xi_6(T)$ becomes of the order of $\frac{1}{2}L (\approx 7.5\sigma)$, the periodic boundary conditions will start to dominate its behavior (see Fig. 2). Of course, algebraically decaying correlation functions will always be distorted beyond recognition by periodic boundary conditions; to look for power-law decays below T_2^* would be meaningless.

According to the HN theory, a 2D system will lose its resistance to shear upon going from the solid to the hexatic phase. The temperature dependence of the resistance to shear of the LJ system is followed most conveniently by studying the decay of transverse current fluctuations. In the hydrodynamic limit, transverse currents decay as $\exp(-k^2\eta t/\rho m)$; hence the total area under the transverse current correlation function [i.e., the $\omega=0$ component of the power spectrum $G_T(k; \omega)$] is proportional to $(k^2\eta)^{-1}$. Figure 3 shows the temperature dependence of η as obtained from $[k^2 G_T(k; 0)]^{-1}$ (after averaging over three long-wavelength transverse phonons). Clearly there is a very dramatic drop in viscosity around $T^* = T_1^*$. Close to T_2^* the viscosity decreases by about 50%. At higher temperatures the viscosity appears to be more or less constant.

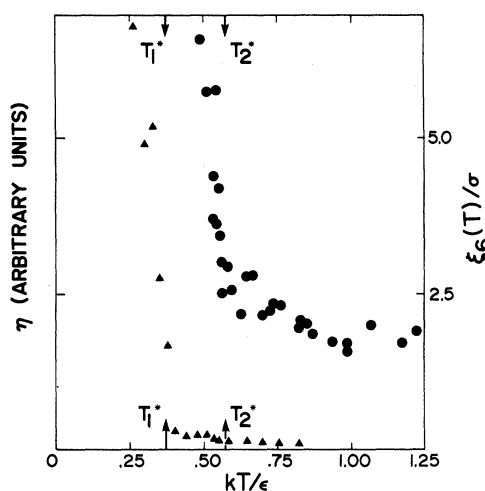


FIG. 3. Correlation length of orientational order parameter vs temperature (filled circles). Shear viscosity, as obtained from the transverse current spectrum, (filled triangles).

In summary, it then appears that, to the extent to which our calculations can be compared with the continuum theory, they seem to support its predictions. We tentatively identify the phase between T_1^* and T_2^* as a hexatic liquid bordered at lower and higher temperatures, respectively, by a solid and an isotropic-fluid phase. It should be noted that in the HN theory the melting transition is driven by the dissociation of dislocation pairs. Our results therefore reaffirm indirectly the importance of dislocations in 2D melting. Of course, the earlier work of Cotterill, Jensen, and Kristensen⁸ provides more direct qualitative evidence for the relation between dislocations and 2D melting. It is not possible to construct a phase diagram on basis of the limited data available at present. It appears that the solid-fluid transition becomes first order at higher temperatures and densities.^{9,10} Several authors have reported results of machine calculations that seemed to suggest a first-order liquid-gas transition at lower densities.^{9,11} We have tried to reproduce those results by performing constant- N , $-P$, and $-T$ Monte Carlo calculations (256 particles, $\sim 4 \times 10^6$ configurations/run) in the relevant region of the phase diagram ($T^* = 0.5$, $P^* = 0.05$ to 0.1). Apart from the observation that the system is very sluggish and shows large density fluctuations, we failed to find any evidence for two-phase behavior; in particular, the average density was found to be almost proportional to the pressure.

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Direct Observation of Charge-Density Waves by Molecular-Beam Diffraction

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Using molecular-beam diffraction we have observed surface corrugation effects due to charge-density waves in TaS₂. Satellite peaks have about the same intensity as Bragg peaks, contrary to results obtained from electron, neutron, and x-ray diffraction.

The question this paper wants to address is the following: Do charge-density waves (CDW) propagate up to the topmost layer of a crystal? If so, will the set of satellite wave vectors be the same as those observed in the bulk? Low-energy electron diffraction (LEED) experiments¹ on 1T-TaS₂ suggest indeed that the surface structure of this layered compound is almost identical to that of the bulk. A LEED beam directed into a crystal penetrates a small but finite number of atomic layers so that we can say that a LEED diffraction pattern reflects the average structure over, say, the first four or five atomic layers.

If a beam of neutral atoms, instead of slow electrons, is used in a diffraction experiment, only the very first atomic layer is involved in the scattering process, and a diffraction pattern obtained in these conditions reflects the corrugation of the surface, on the atomic scale, resulting from the crystalline periodic potential.²

While x-ray, neutron, or electron diffraction patterns reflect oscillations of the potential in the bulk, even though in the case of LEED by "bulk" we mean a crystal slice four or five atomic layers thick, a molecular-beam diffraction pattern can be interpreted strictly in terms of scattering from a hard corrugated surface, whose shape z

$= f(x, y)$ can be obtained from the intensities of the diffraction peaks.³

We selected 1T-TaS₂ as a crystal suitable for this experiment because the various superstructures at different temperatures are well known,⁴ and, given the good results obtained on graphite,⁵ it was expected that a layered compound would in general give good diffraction patterns with molecular beams after cleavage in air along the layer planes.

The experiment was done using a He beam with $K_0 = 2\pi/\lambda = 11.05 \text{ \AA}^{-1}$. The experimental setup has been described in detail elsewhere.⁶ A 1T-TaS₂ crystal, previously checked with x rays to really be the 1T polytype, was fastened with Aquadag⁷ to a sample holder that could be heated up to high temperature in order to clean the surface in vacuum. The sample holder could be rotated around the normal to its surface by means of an external manipulator. Good vacuum was obtained by cryopumping with liquid helium in proximity of the crystal.

Care was taken to avoid heating the crystal above 450°K, at which temperature the 1T polytype transforms irreversibly to 2H, which does not exhibit any superstructure at 80°K.⁸ All experiments were done with the crystal at about 80°K.