

PHASE TRANSITIONS AND ORIENTATIONAL ORDER
IN A TWO DIMENSIONAL LENNARD-JONES SYSTEM

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It has long been suspected that the solid-fluid transition in two dimensions might be rather different than its 3-D counterpart, because of the lack of translational order in 2-D solids. Recently, a detailed theory of 2-D melting has been put forward by Halperin and Nelson.¹ This theory provides a picture of 2-D melting that is indeed very different from what is observed in the three dimensional world. In particular, Halperin and Nelson (henceforth referred to as HN) make the intriguing prediction that, if 2-D melting is not a first order transition, then two second order transitions are required to go from the solid to the isotropic fluid phase. The solid and isotropic fluid phases will be separated by a peculiar liquid crystal-like phase which exhibits short range translational order but long range "orientational" order.

Experiments on the melting of adsorbed monolayers^{2,3} strongly suggest that for some of the systems studied the solid-fluid transition is in fact continuous. Unfortunately, direct experimental verification of the predictions based on the HN theory is non trivial. This is so because the quantities that are probed most readily in experiments are expected to exhibit only subtle (and for all practical purposes, unobservable) changes at the phase transitions. On the other hand, physical properties which, according to the HN theory, should change markedly at the phase transitions, turn out to be very hard to measure experimentally.

In order to gain insight into the behavior of the different quantities that play a central role in the HN theory, we chose to perform a computer "experiment" (molecular Dynamics) on a collection of two dimensional Lennard-Jones (12-6) atoms. This particular system seemed a suitable candidate for detailed investigation

because the results of earlier calculations by Hanson and McTague⁴ indicated that the temperature dependence of the thermodynamic and structural properties of 2-D Lennard-Jonesium closely reproduce those of argon on graphite. This latter system appears to have a continuous melting transition. Although the 2-D Lennard-Jones system is quite similar to argon on graphite, it differs in some respects from the model for 2-D matter used in the HN theory. In the first place, the HN theory describes two dimensional matter as an elastic continuum with embedded dislocations, whereas the calculations are performed on a collection of interacting particles. Secondly, periodic boundary conditions are used in the MD calculations. As a consequence, all fluctuations with wavevector $k < 2\pi/L$ ($L = \text{boxlength}$) are excluded. In contrast, long wavelength fluctuations play an essential role in the HN renormalization group treatment of the two dimensional phase transitions. The box length used in the MD calculations is, however, of the same order of magnitude as the effective size of 2-D argon crystallites grown on exfoliated graphite surfaces.

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 10 to 15 τ . The $\rho^* = 0.8$ isochore was traversed in both directions to test for possible hysteresis effects that tend to accompany discontinuous phase transitions.

Fig. 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 contrast to what has been observed in 3-D, where freezing occurs through nucleation only upon significant under cooling.⁵ A two dimensional system that shows first order melting is, for instance, the registered phase of Kr on graphite. Results of computer simulations on this latter system⁶ are also shown in figure 1 for the sake of comparison. In this case the solid and fluid phases correspond to distinct branches in the E vs T plot. In contrast, the thermodynamic properties of the flat L.J. system appear to be continuous functions of temperature. 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 2 higher order phase transitions.

[†]In fact, the function plotted is $E^* - 2T^*$, i.e. the energy per particle minus the energy per particle in a harmonic lattice at the same temperature.

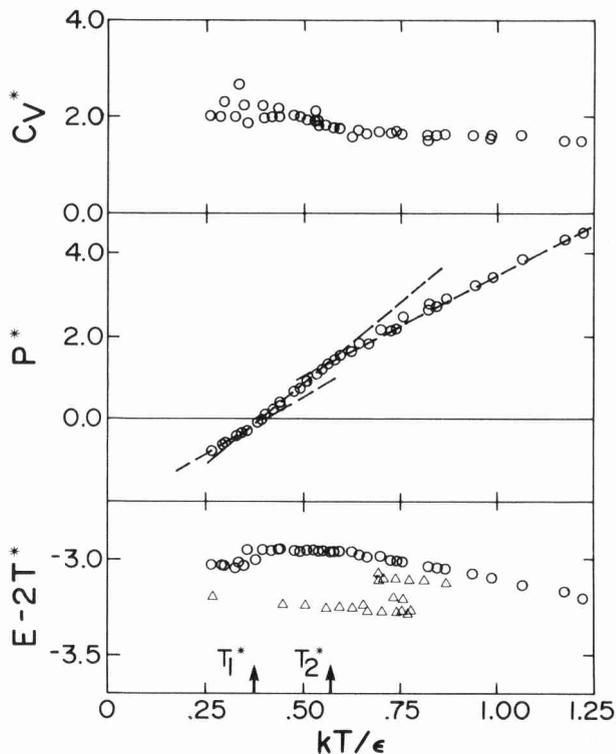


Figure 1. From top to bottom: Heat capacity, virial pressure and energy⁺ of a flat 2-D Lennard Jones system at $\rho^* = 0.8$ (\circ). T_1^* and T_2^* indicate the approximate temperatures where E and P change slope. To guide the eye, straight line segments have been drawn through the P vs T points; 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 figure (\triangle). The points correspond to "Kr on graphite" at $\rho^* = 0.825$ (from ref. 6).

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 non-negligible amount of free energy (this is in fact one of the reasons why hysteresis occurs in 3-D). The fact then, that no hysteresis is observed seems to indicate that, if the transition were first order, the free energy of inter-

face 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 2nd order phase transitions. The temperature dependence of the structure factor obtained from the machine calculations provides additional evidence that the melting transition is continuous. In particular, the width of the first Bragg peak is a smooth function of temperature. (The actual values agree almost quantitatively with the experimental data for argon on graphite.)

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:

$$\psi(\vec{r}) = \exp(6 i \theta(\vec{r})) \quad (1)$$

where $\theta(r)$ 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, $\theta(r)$ can be expressed in terms of the displacement field. Although no infinite range translational order exists even in a harmonic, infinite 2-D crystal, orientational order is long range, i.e., $\langle \psi^*(o) \psi(r) \rangle \rightarrow c \neq 0$ for $r \rightarrow \infty$.⁷ Halperin and Nelson predict that if melting in 2-D is not first order, $\langle \psi^*(o) \psi(r) \rangle$ will decay algebraically in the intermediate (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:

$$\psi_6(\vec{r}) = \frac{1}{N} \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \left\{ \frac{1}{6} \sum_{j=1}^6 \exp(6 i \theta_{ij}) \right\} \quad (2)$$

where $j = 1$ to 6 are the 6 nearest neighbors of atom i . Because $\psi_6(r)$ is only defined at the site of an atom, the correlation function $\langle \psi_6^*(o) \psi_6(r) \rangle = g_6(r)$ exhibits oscillations (see fig. 2). Partly this effect is due to oscillations in the radial distribution function, $g(r)$. 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 r_i and r_k are lattice sites, $\psi_6^*(r_i) \psi_6^*(r_k) = 1$ but if r_k is the site of an interstitial atom, $\psi_6^*(r_i)$

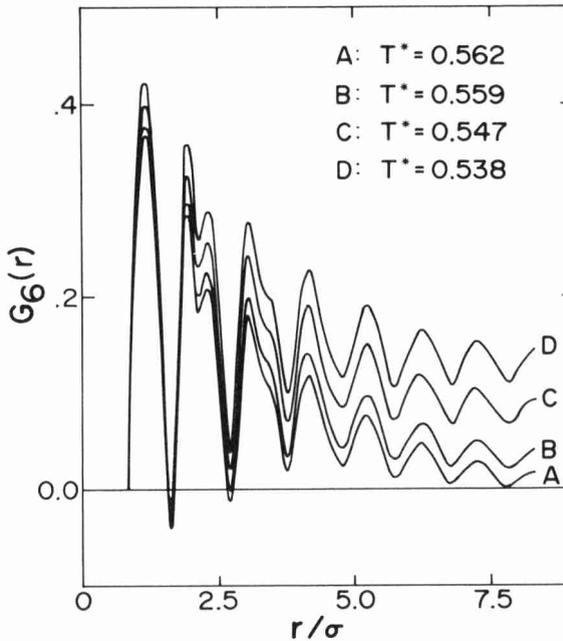


Figure 2. Correlation function of the orientational order parameter (as defined in text) in the vicinity of T_2^* . The function plotted is $\langle \psi_6^*(0) \psi_6(r) \rangle / g(r)$. Note that at the lower temperatures $g_6(r)$ does no longer die out within half a box length.

$\psi_6(r_k) = -1$. 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 $\xi_6(T)$. The HN theory predicts that this correlation length will diverge very strongly (in fact, as $\exp(b/(T - T_i)^{1/2})$) as the hexatic-isotropic fluid transition (T_i) is approached from above. The MD results for the temperature dependence of $\xi_6(T)$ are shown in fig. 3. Clearly, $\xi_6(T)$ increases dramatically around $T^* = T_2^*$, in sharp contrast to the rather un-spectacular behavior of the thermodynamic properties. We have not plotted $\xi_6(T)$ down to lower temperatures, because once $\xi_6(T)$ be-

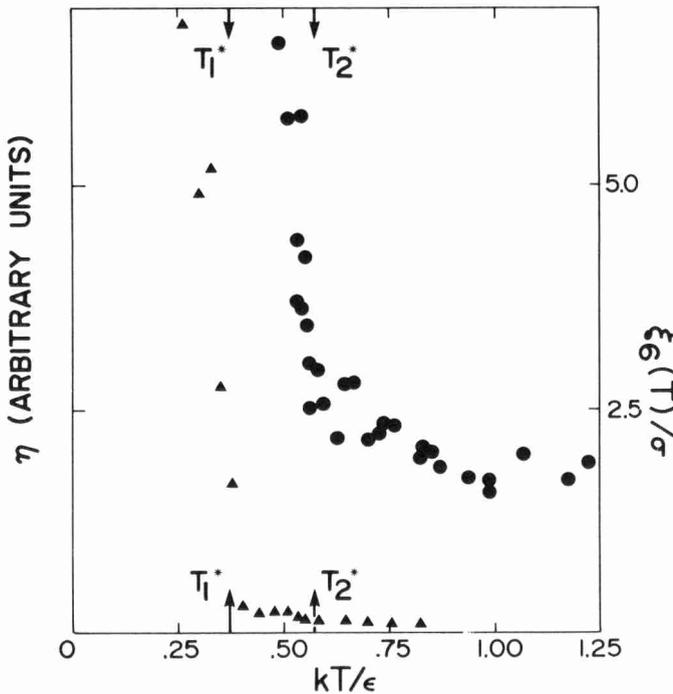


Figure 3. Correlation length of orientational order parameter vs. temperature (●). Shear viscosity, as obtained from the transverse current spectrum; (▲).

comes of the order of half a boxlength ($L/2 \approx 7.5\sigma$) the periodic boundary conditions start to dominate its behavior (see fig. 2). According to the HN theory, $g_6(r)$ will decay algebraically in the hexatic phase. We did not attempt to verify this prediction, let alone determine power law exponents, because the periodic boundary conditions will necessarily distort such slowly decaying correlation functions beyond recognition.

If we assume for the moment that the behavior of $\xi_6(T)$ indicates that there is indeed a hexatic-isotropic fluid transition around T_2^* , we should expect a solid-hexatic fluid transition at lower temperatures. Although the thermodynamic properties of the system are expected to be quite insensitive to this transition, the

HN theory predicts a rapid and dramatic drop in the resistance to shear as the system goes from the solid to the hexatic phase. The temperature dependence of the resistance to shear of the L.J. 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 $(k^2 \eta)^{-1}$. Fig. 3 shows the temperature dependence of η as obtained from $[k^2 G_T(k; 0)]^{-1}$ (after averaging over 3 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.

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 2-D melting. Of course, the earlier work of Cotterill and coworkers⁸ provides more direct qualitative evidence for the relation between dislocations in 2-D 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, T Monte-Carlo calculations (256 particles, $4 \cdot 10^6$ 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 2-phase behavior; in particular, the average density was found to be almost proportional to the pressure.

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REFERENCES

1. B. I. Halperin and D. R. Nelson, Phys. Rev. Lett., 41:121 (1978).
2. J. P. McTague, M. Nielsen and L. Passell, CRC Critical Reviews in Solid State and Materials Sciences, 8:125 (1979) and references therein.
3. T. T. Chung, unpublished, as quoted in ref. 4.
4. F. E. Hanson, M. J. Mandell and J. P. McTague, J. Phys. (PARIS), C-4:76 (1977).
5. M. J. Mandell, J. P. McTague and A. Rahman, J. Chem. Phys., 64:3699 (1976); 66:70 (1977).
6. F. E. Hanson and J. P. McTague, to be published.
7. N. D. Mermin, Phys. Rev., 176:250 (1968).
8. R. M. Cotterill, E. J. Jensen and W. D. Kristensen, in: "Anharmonic Lattices, Structural Transitions and Melting," Ed. T. Riste, Noordhoff, Leiden, 1974.
9. F. Tsien and J. P. Valleeau, Mol. Phys., 27:177 (1974).
10. S. Toxvaerd, preprint.
11. D. Henderson, Mol. Phys., 34:1 (1977).