Phase Transitions in a Two-Dimensional System

Søren Toxvaerd
Institute for Chemistry, University of Copenhagen, DK-2200 Copenhagen N, Denmark
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Molecular-dynamics calculations on melting and evaporation in a two-dimensional (2D) Lennard-Jones system show a nonuniform particle distribution in the temperature and density intervals where the phase transitions take place. The behavior of the system agrees qualitatively with the behavior of a corresponding 3D system with a liquid-gas critical point and first-order phase transitions. No evidence is found for the two-stage melting behavior which has recently been predicted.

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Recently a detailed theory of melting in two dimensions (2D) has been put forward by Halperin and Nelson (HN).[1] The theory is based on the basic assumption that if the melting in a 2D system is not a first-order phase transition, then two second-order transitions are required to make the transition from the solid phase to the isotropic fluid phase. The solid and fluid phases will then be separated by an intermediate phase with short-range translational order and long-range orientational order. In the case of melting from the triangular lattice the so-called "hexatic" phase will have a sixfold anisotropy. This prediction has been supported by a molecular-dynamics (MD) calculation[2] on a 2D Lennard-Jones system, which seems to show a behavior at low temperatures compatible with the predictions by HN. In this Letter I will show that the MD result is compatible with traditional first-order melting.

The molecular-dynamics calculations are performed for a fixed number (N) of particles in a box with periodic boundaries and the temperature (T) and pressure (p) are then obtained from the kinetic energy and the virial, respectively. Thus, the MD calculations are often presented as isochores in a p-T diagram. In Fig. 1 are sketched isochores in a p-T phase diagram; also shown in the figure is the location of the area where HN predicted the hexatic phase. When the solid-state system is heated the pressure increases until it reaches the melting pressure. If the melting is first-order the system will break up and form coexisting solid and fluid phases, and the pressure will follow the melting-pressure line until the solid is melted completely. However, if the melting consists of the two second-order phase transitions, the isochore might be very similar in fashion to the isochore for a first-order transition, as indicated in Fig. 1, and it is not possible from the isochores themselves, obtained from a discrete set of MD data, to decide about the nature of the melting, as also pointed out in Ref. 2. However, Frenkel and McTague (FM) stated that their MD system did not show hysteresis, that the system lost its resistance to shear above $kT_1/\epsilon = 0.36$, and finally that the interphase exhibited sixfold anisotropy. From these three observations they concluded that the melting was compatible with the HN theory with the intermediate phase located in the temperature interval $kT/\epsilon \in [0.36, 0.57]$ for the density $\rho\sigma^2 = 0.8$. Below 0.36 the system should then be in the solid state with a triangular lattice structure. However, this is not the case as can be seen from following facts:

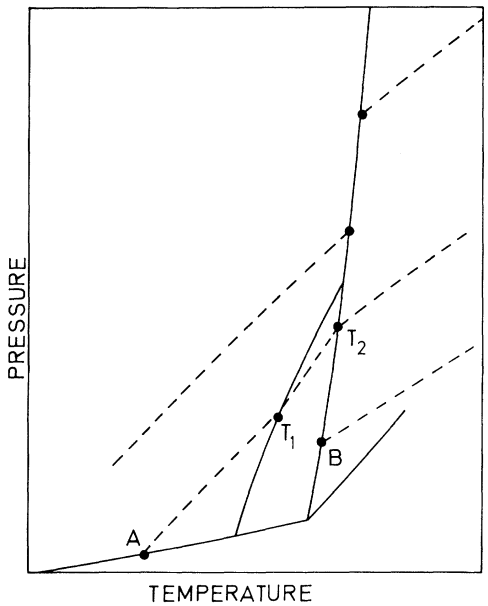

FIG. 1. Schematic p-T diagram for the 2D system with the phase transition lines (full lines). The triangle near the triple point is the area where Halperin and Nelson predict the hexatic phase. The dotted lines are isochores.

The density in FM's simulation is $\rho\sigma^2 = 0.8$. This is considerably less than the density at zero temperature, $\rho_0\sigma^2 \gtrsim 2^{2/3}3^{-1/2} = 0.9165$, which means that when a macroscopic solid system is cooled down it will break up into two phases (solid and gas) at A in Fig. 1. A finite system which is constrained by the periodical boundaries will have a tendency to cross the point A and continue in a uniform state with negative pressure and when it tries to break up into a more dense solid and the coexisting gas (vacuum), the system will end in an unphysical situation, since the periodical boundaries only match with a triangular lattice with $\rho\sigma^2 = 0.8$.[3] In accordance with this fact FM find a *negative* pressure at $T \lesssim 0.36$ [Ref. 2, Fig. 1(b)]. I have performed MD calculations for the same isochore as FM's. In Fig. 2 are shown the particle trajectories for $kT/\epsilon = 0.36$ and for 1000 time steps.[4] The state is created by starting the system with the particles in a triangular lattice and adjusting the temperature to 0.36 (and the torque to zero). The system has an initial pressure $p\sigma^2/\epsilon \approx -1$, but it breaks up into a two-phase system after few hundred time steps. Figure 2 is obtained after 5400 time steps. The pressure of the two-phase system behaves as in Ref. 2, Fig. 1(b), with negative pressures for $kT/\epsilon \lesssim 0.36$ due to the constraints from the periodical boundaries on the "coexisting" solid phase.

The triple-point values of T, ρ_s, and ρ_l for the MD system are estimated to be[5] $kT/\epsilon = 0.41$, $\rho_s\sigma^2 = 0.81$–0.82, and $\rho_l\sigma^2 < 0.80$. If these values are correct a macroscopic fluid system with $\rho\sigma^2 = 0.80$ will break up into coexisting solid and fluid at B (Fig. 1) and continue in two-phase states under further cooling provided that the phase transitions are of first order. I have performed MD calculations which show that the system behaves in this manner. In Fig. 3 are shown the trajectories over 2000 time steps for the 256 particles within a quadratic box[6] and at a temperature $kT/\epsilon = 0.50$. The state is generated in the same way as FM's by cooling the system slowly down from a fluid state. From the figure it can be seen that even at this "high" temperature and for a quadratic box the system is nonuniform with a region with the particles arranged in a triangular lattice. At a lower temperature the "triangular" coexisting solid phase is increased as one should expect. The system is followed for 16 000 time steps and Fig. 3 shows the movements of the particles in the middle of the time interval. During the time interval the shape of the coexisting phases changes, which means that the interfacial excess free energy is relative small.

From these observations I conclude that the dynamic behavior of the (finite) MD system is compatible with first-order phase transitions, and the sixfold anisotropy found by FM is explained by the anisotropy of the solid coexisting phase. The discontinuous change in the slope of p at $kT/\epsilon \approx 0.57$ is due to the fact that the system goes from fluid states to coexisting solid-fluid states, and the corresponding change in the slope at $kT/\epsilon \approx 0.36$ is due to the constraints from the periodical boundaries which force the system into negative pressures at $kT/\epsilon \lesssim 0.36$. The system will now show hysteresis at $kT/\epsilon \approx 0.36$ since it is

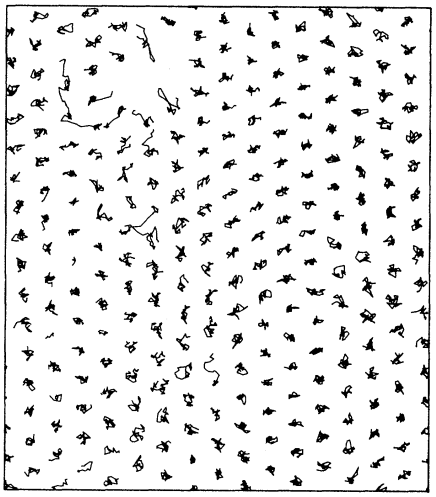

FIG. 2. Trajectories of the particles obtained from 1000 time steps and at $kT/\epsilon = 0.36$ and $\rho\sigma^2 = 0.80$.

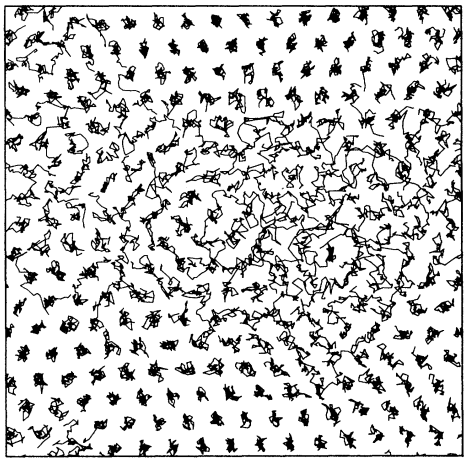

FIG. 3. Trajectories of the particle center obtained from 2000 time steps at $kT/\epsilon = 0.50$ and $\rho\sigma^2 = 0.80$.

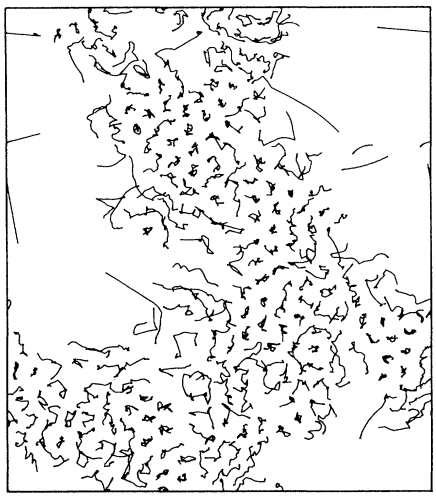

FIG. 4. Trajectories of the particle center obtained from 800 time steps and at $kT/\epsilon = 0.50$ and $\rho\sigma^2 = 0.357$.

found that no points on the isochore correspond to a uniform solid.

In the end of their Letter FM stated that they have tried to reproduce some Monte Carlo calculations[7,8] that seemed to suggest a first-order liquid-gas transition at lower densities, but apart from the observation that the system was very sluggish and showed large density fluctuations, they failed to find evidence for a two-phase system. The present calculations confirm this behavior. However, a particle diagram (Fig. 4) shows a nonuniform liquid-gas system. The figure is for $kT/\epsilon = 0.50$ and $\rho\sigma^2 = 0.357$ and for 800 time steps and represents a typical particle distribution although the shape of the liquid phase changes during the calculation. This behavior can be explained by the fact that the excess free energy is relatively small, which will be the case near the critical point, where—on the other hand—the fluctuations are large and the 256-particle system might be too small. However, a test run on a 576-particle system showed the same phase separation, and if the system was forced into a uniform particle distribution by constraints,[9] the pressure exhibited a van der Waals loop. Again the (dynamic) behavior of the finite system indicates the existence of a first-order liquid-gas transition below the critical temperature $T_c \approx 0.56$.[8]

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[1]B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. 41, 121 (1978).

[2]D. Frenkel and J. P. McTague, Phys. Rev. Lett. 42, 1632 (1979).

[3]The periodical boundaries must fit into the triangular lattice, e.g., by having a rectangular box with the ratio $\sqrt{3}/2$ between the sides.

[4]One time step is equal to $0.005(m/\epsilon)^{1/2}2^{1/6}\sigma$.

[5]S. Toxvaerd, J. Chem. Phys. 69, 4750 (1978).

[6]Since a rectangular box with the ratio $\sqrt{3}/2$ between the sides might force the system into a triangular lattice when the correlation length is of the order of a half box-side.

[7]F. Tsien and J. P. Valleau, Mol. Phys. 27, 177 (1974).

[8]D. Henderson, Mol. Phys. 34, 301 (1977).

[9]J. P. Hansen and L. Verlet, Phys. Rev. 184, 151 (1969).