spectrum.

In conclusion we have established the existence of twelve orthorhombic domains in NaCN. We have determined their relative orientation both to the pseudocubic phase and to each other.

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# Melting in Two Dimensions is First Order: An Isothermal-Isobaric Monte Carlo Study

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Isothermal-isobaric Monte Carlo computer experiments on melting in a two-dimensional Lennard-Jones system indicate that the transition is first order, in contrast to the two-stage, second-order melting behavior suggested as a possibility by Halperin and Nelson.

Expanding on the proposals by Kosterlitz and Thouless[1] and by Feynman,[2,3] Halperin and Nelson[4,5] have developed a detailed theory of dislocation-mediated melting for a two-dimensional "crystal." One important feature of the Halperin-Nelson theory is the possibility that the transition from two-dimensional solid to two-dimensional liquid takes place by *two second-order* transitions with increasing temperature. At some temperature $T_m$, dissociation of dislocation pairs gives rise to a second-order transition from a solid phase, with algebraic decay of translational order and long-range orientational order, to a "liquid-crystal" ("hexatic") phase, with exponential decay of translational order *but* algebraic decay of sixfold orientational order. At a higher temperature $T_i > T_m$, dissociation of dislocations into disclinations gives rise to another second-order phase transition from the hexatic phase to the isotropic fluid phase. Halperin and Nelson do emphasize that this particular melting mechanism is only one possibility. They cannot rule out the possibility of a first-order melting transition.

Direct experimental verification of the Halperin-Nelson theory for two-dimensional melting is difficult because several possible mechanisms are involved in real systems which might conceivably influence the apparent order of the transition; e.g., epitaxy, second-layer promotion, and heterogeneity, as well as the details of the adatom and substrate interactions.[5] In order to circumvent the uncertainties and limitations of current laboratory experiments, Frenkel and McTague[6] performed a "computer experiment" on the well-defined model system of Lennard-Jones (L-J) 12:6 atoms constrained to remain two dimensional. They chose the molecular-dynamics simulation method (with imposed periodic boundary conditions to simulate an infinite plane) to study the structure and thermodynamics of 256 L-J atoms at a reduced density $\rho^* = 0.80$ and reduced temperature range of $0.25 \leq T^* \leq 1.25$. From an analysis of their experimental data, Frenkel and McTague concluded that the L-J system loses its resistance to shear at a temperature $T_m^* \cong 0.36$, but has long-range "orientational" order up to a higher temperature $T_i^*$ 0.57; hence their molecular-dynamics experiments support the two-dimensional melting theory of Halperin and Nelson.

Attracted by the unusual predictions of the theory and the apparent confirmation by computer experiment, I decided to look more closely at the *thermodynamics* of the two-dimensional melting phenomenon by doing a different type of computer experiment: By employing the isothermal-isobaric Monte Carlo simulation method of classical statistical mechanics,[7,8] we may calculate the equilibrium *energy, enthalpy,* and *density* of the existing phase (whether solid, liquid, or hexatic) for a chosen *temperature* and *pressure.* Hence, by performing a series of experiments *at fixed pressure* and for a range of temperatures, we should observe (a) discontinuities in enthalpy and density at $T_m$ if the melting transition is first-order, or (b) discontinuities in the temperature derivatives of the enthalpy and density at $T_m$ and $T_i$ if the melting transitions are second order. Also, as pointed out by Frenkel and McTague, there should (should not) be hysteresis if the system passes back through the apparent melting temperature when the phase transition is first order (second order). I have performed such experiments and conclude that two-dimensional melting is a first-order phase transition.

The $(N, P, T)$ Monte Carlo calculations were performed on an $N = 256$ atom system with periodic boundary conditions to simulate the bulk. The interatomic force law was taken to be L-J 12:6 with $(\epsilon, \sigma)$ denoting the well-depth and size paremeters, respectively. In a typical simulation "experiment," the system was "equilibrated" through $10^6$ Monte Carlo moves with a 50% acceptance ratio. After equilibration, $10^6$ to $2\times10^6$ further moves were performed to obtain the enthalpy $H$, the average density $\rho$, the pair distribution function $g(r)$, and other quantities. Great care was practiced to determine that the system was in "local equilibrium" (stable or metastable) when taking the statistics for the quantities of interest.

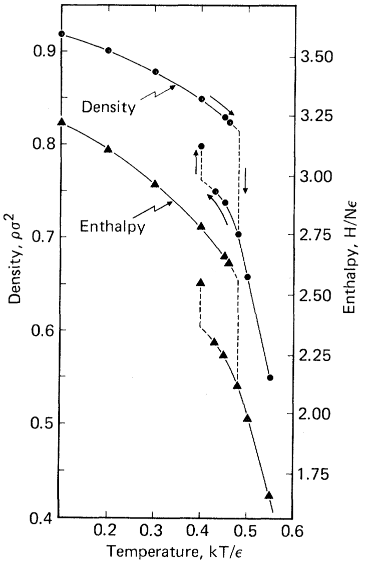

FIG. 1. The equilibrium density and enthalpy per atom as a function of temperature for the Lennard-Jones system at a fixed pressure $P\sigma^2/\epsilon = 0.05$.

In Fig. 1, I present the equilibrium density $\rho^* = \rho\sigma^2$ and the enthalpy per atom $h^* = H/N\epsilon$ for the L-J system as a function of temperature $T^* = kT/\epsilon$ and for a fixed pressure $P^* = P\sigma^2/\epsilon = 0.05$. The pressure was intentionally chosen to be low since Nelson and Halperin have speculated that the melting transition could be first order at high pressures but second order at low pressures,[4] and since it was suggested[4,6] that earlier studies[9-11] were examining a high-(temperature, density) regime where melting becomes first order.[12] Considering first the density behavior, note that the solid density decreases smoothly as I sequentially increase the temperature $T^* = 0.46$. At $T^* = 0.48$, the solid melts into a liquid with a dramatic decrease in equilibrium density $\rho_s^* - \rho_l^* = 0.11$. The pair distribution functions and "snap-shot" pictures of the atomic configurations (see Fig. 2) show the change from crystalline order to liquid disorder. At higher temperatures, the liquid density decreases smoothly. By sequential decrease of temperature and equilibration, the system passes through $T^* = 0.48$ and remains a liquid with smoothly increasing density down to a temperature $T^* = 0.43$ (again, the pair distribution functions reflect the fact that the undercooled states are liquid). This establishes hysteresis when passing back through the apparent melting temperature. At $T^* = 0.4$, the liquid solidifies with

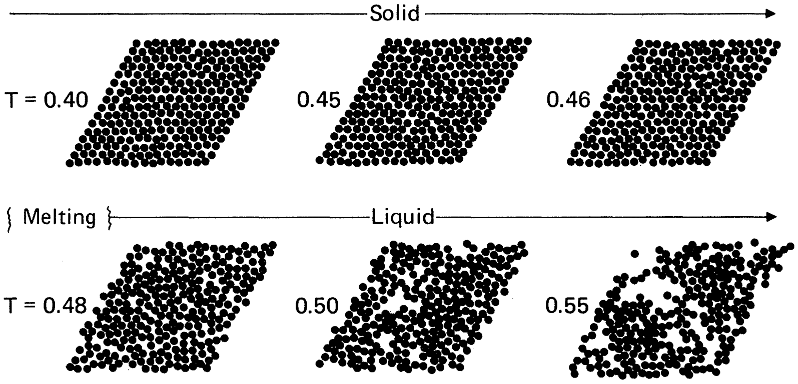

FIG. 2. Snapshot pictures of the 256-atom L-J system simulated by the isothermal-isobaric Monte Carlo method for the denoted temperatures and a fixed pressure of $P\sigma^2/\epsilon = 0.05$.

a sharp increase in density $\rho_s^* = 0.8$; however, this density is lower than the original solid at that temperature, $\rho_s^* = 0.85$. Examination of the atomic structure of this solid, which was nucleated from the liquid phase, revealed significant defect structure which accounts for the density difference for the two solid systems. Of course, it would be unlikely that the supercooled liquid would solidify directly into a defect-free crystal structure. The subsequent time for relaxation to a defect-free solid-state structure is too long to follow by computer simulation, and, in any case, this relaxation process is irrelevant to the conclusions of this study. The enthalpy of the system has the same behavior as the density and yields a latent heat of $\sim 0.44\epsilon$/atom.

The density discontinuity between solid and liquid, the evident latent heat, and the existence of metastability certainly demonstrate that melting of a two-dimensional solid is a first-order phase transition.

I conclude with the following comment. One should not be too concerned with the statement that the existence of the crystalline solid state in two dimensions is impossible.[13,14] I explain my viewpoint. At a nonzero temperature, the perfect translational order of the atoms in a classical crystal is destroyed because of the random thermal motion of the atoms about their equilibrium positions. Furthermore, in contrast to a 3-D (three-dimensional) crystal, the atomic equilibrium positions themselves in a 2-D crystal become uncorrelated at large separations.[13-15] A quantitative measure of the loss of long-range crystalline order is the difference $\delta$ between the average separation between two atoms and the distance corresponding to the proper number of lattice spacings. It is found that $\delta$ diverges slowly with $N$, the number of atoms in the 2-D system, the dependence on $N$ being only logarithmic. Using a relation found by Hoover, Ashurst, and Olness,[15] I estimate that to lose crystalline correlation equal to one lattice spacing ($\delta \sim 3$ Å) near the melting point, the area of the 2-D crystal should be $\sim 10^{27}$ cm$^2$, very large indeed. At the uppermost extreme, a crystal of dimension equal to the size of the universe ($\sim 10^{10}$ light-years) would have a correlation loss of $\sim 6$ Å![16] I can only conclude that for real situations, the crystalline solid state in two dimensions can exist. In reality, it will be the imperfectness of the material state (e.g., grain boundaries), and not a logarithmic divergence, that will prevent perfect translational order over macroscopic dimensions. The fact that "for practical purposes" the 2-D crystalline state exists suggests that Landau's argument that "transitions between bodies of different symmetry (in particular between a liquid and a crystal) cannot happen continuously"[14] may well be applicable in two dimensions.

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# Completion of the Phase Diagram for the Monolayer Regime of the Krypton-Graphite Adsorption System

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The results of a heat-capacity study of the region between one and two layers in the Kr/graphite (Grafoil) system are presented. Heat-capacity anomalies corresponding to the commensurable-incommensurable transition, the commensurable-fluid transition, and a previously unobserved incommensurable-fluid transition delimit the high-coverage extent of the registered phase. A phase diagram proposed on the basis of the heat-capacity data suggests the possibility of a new type of multicritical point.

Krypton physisorbed onto graphite has been the subject of a number of recent studies. Isotherm, low-energy electron diffraction, x-ray, and heat-capacity studies[1] have been used to map phase boundaries in the submonolayer and monolayer regimes. In particular, for coverages near one registered monolayer two higher-order transitions have been observed, a commensurable-incommensurable transition (CIT) at lower temperatures and a commensurable (registered) solid to a dense fluid transition (CFT). The phase diagram for the monolayer regime of the Kr/graphite system remains incomplete, however, since no transition delimiting the high-coverage extent of the registered solid has been observed. It has been conjectured[2] that the CIT and CFT join, enclosing the registered phase in a line of higher-order transitions and raising the interesting question of how the incommensurable solid melts. We have conducted a comprehensive heat-capacity survey of the regime between one and two layers. The results reported here map the boundaries of the registered phase and show that the CIT and CFT intersect at approximately 127 K and 1.5 layers. From this intersection a third line of heat-capacity anomalies emerges with increasing coverage. These anomalies constitute the first observation for the Kr/graphite system of the incommensurable-solid–dense-fluid transition (IFT), which appears to be higher order. The intersection of the CIT, CFT, and IFT suggests the possibility of a new type of multicrtical point.

In order to establish a detailed map of the phase boundaries, sixteen coverages (i.e., fixed total amount in the calorimeter) between 1.0 and 2.4 registered monolayers were studied. The results are summarized in Fig. 1, which shows the loci of heat-capacity anomalies in the temperature-coverage plane. For all coverages above the monolayer, desorption is significant and the amount adsorbed becomes a function of temperature. The heating paths for several representative coverages are also shown in Fig. 1. For coverages just above the monolayer, the heat capacity displays two anomalies [Figs. 2(a) and 2(b)]. With increasing coverage the lower temperature anomaly, at first ($A_1$, Fig. 1) broad and barely discernible, becomes larger and sharper, moving rapidly to higher temperature ($A_1A_2C_1$).