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Two-dimensional melting, solid-state stability, and the Kosterlitz-Thouless-Feynman criterion

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The melting transition for simple atomic, two-dimensional solids occurs in the Monte Carlo computer experiments at the Kosterlitz-Thouless-Feynman instability temperature and with first-order behavior, in contradiction with renormalization-group arguments. It is pointed out that this melting temperature is not the thermodynamic melting temperature but an upper limit for the stability of the metastable solid.

I recently presented an isothermal-isobaric Monte Carlo computer simulation study on melting for a two-dimensional Lennard-Jones system[1,2] and concluded that the melting transition is first order, in contrast to the two-stage, second-order melting behavior suggested as a possibility by Halperin and Nelson.[3–6] In this present paper, I demonstrate that the Kosterlitz-Thouless-Feynman[7,8] instability criterion for a two-dimensional solid is satisfied at the observed *first-order* melting transition for my Monte Carlo experiments. This is consistent with the recent computer simulation[9] and laboratory experiment[10] for the melting of the two-dimensional electron solid where the order of the transition has not been established but is inconsistent with renormalized-group arguments that the transition should be continuous. This also supports my interpretation of the Frenkel-McTague[11] and Tobochnick-Chester[12] computer experiments; i.e., they were simulating a *constant-density, first-order* melting transition for the two-dimensional Lennard-Jones solid.[2] Finally, the suggestion that my computer experiments may have missed the hexatic phase because of "critical slowing down" of the relaxation processes near the alleged second-order melting transition (e.g., see Ref. 6) is not supported by my findings, since my observed melting temperature equals the Kosterlitz-Thouless-Feynman instablility temperature and this instability temperature is significantly greater than the thermodynamic melting temperature.

Kosterlitz and Thouless,[7] and independently Feynman,[8] pioneered the application of the dislocation model of melting for a two-dimensional solid. From this theory of melting, the Kosterlitz-Thouless-Feynman (KTF) criterion for the stability of a solid phase against the formation of isolated dislocations was found to be

$$K=\frac{4a^2}{kT_m}\frac{\mu(\mu+\lambda)}{(2\mu+\lambda)}=16\pi \ , \qquad (1)$$

where T_m is the melting transition temperature, a is the lattice constant, and μ, λ are the Lamé elastic coefficients. Hence, the parameter K shows a universal discontinuity of 16π at the instability temperature which Kosterlitz-Thouless and Halperin-Nelson identify with the thermodynamic melting temperature. The point of view argued here is that the metastable solid does indeed become unstable at this temperature, but that this bears no relation to the thermodynamic melting transition; the dislocation-unbinding instability provides a path by which the system reaches the stable (liquid) phase which becomes the thermodynamically stable phase at a lower temperature.

I have extended my previous studies[1,2] on two-dimensional melting of a Lennard-Jones solid by calculating numerically the Lamé coefficients as a function of temperature and density. Expanding on my earliest study,[1] I have performd isobaric-isothermal Monte Carlo calculations for Lennard-Jones 256- and 529-atom systems to study melting at two low pressures near the triple-point pressure ($P\sigma^2/\epsilon=0.01$ and 0.05) and at one high pressure ($P\sigma^2/\epsilon=1$).[2] The constants (ϵ, σ) denotes the well depth and size parameters of the Lennard-Jones 6-12 interatomic potential. For the 529-atom system, approximately 11 million configurations were generated for each temperature and pressure. By monitoring the various thermodynamic and structural measurements in the configurational averaging, I carefully established that the system was not continually relaxing to some unachieved state near the melting transition ($\sim 10^6$ configurations were needed for equilibration); i.e., there was no peculiar behavior in the convergence to equilibrium, such as a "critical slowing down" of the system (see Ref. 2). In all cases, the melting transition was found to be first order.[1,2] In Fig. 1(a), I present the equilibrium density $\rho\sigma^2$ for the Lennard-Jones system of 529 atoms as a function of temperature kT/ϵ and for fixed pressure $P\sigma^2/\epsilon=0.05$. At $kT/\epsilon=0.45$, the solid melts into a liquid after $\sim 5\times10^6$ configurations with a dramatic decrease in equilibrium density. The details of the Monte Carlo method, the thermodynamic and structural properties

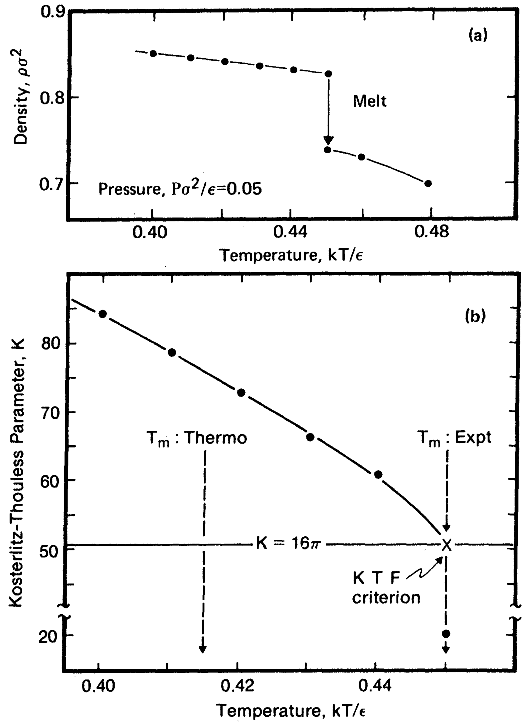
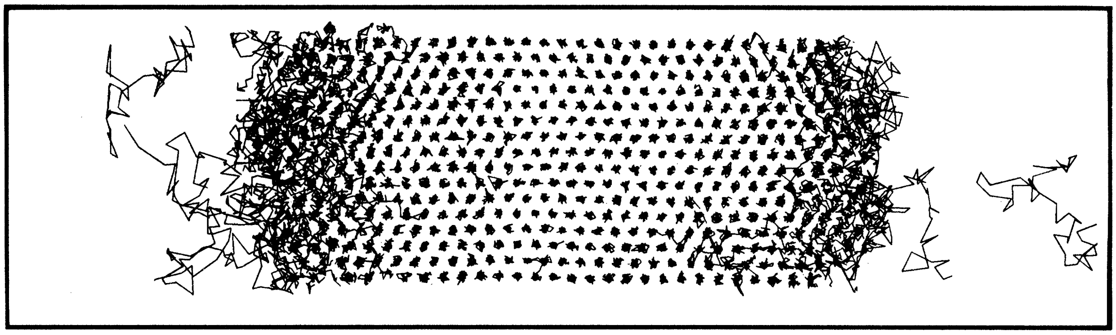


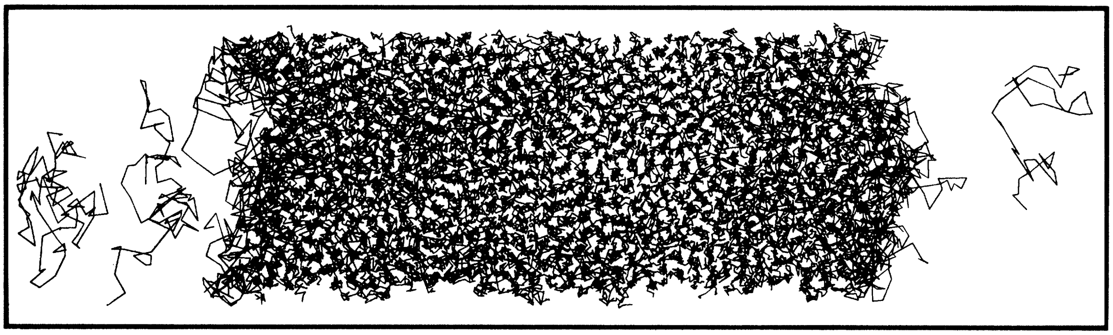
FIG. 1. (a) Equilibrium density as a function of temperature for the Lennard-Jones 529-atom system at a fixed pressure $P\sigma^2/\epsilon=0.05$ near the triple point pressure. (b) The Kosterlitz-Thouless parameter K as a function of temperature for the Lennard-Jones 529-atom system at fixed temperature and density corresponding to an average pressure of $P\sigma^2/\epsilon=0.05$.

of the two-dimensional condensed phases, and the melting process may be found in Refs. 1 and 2. For the Lennard-Jones 529-atom system at fixed temperatures and densities corresponding to an average pressure of $P\sigma^2/\epsilon=0.05$, I have now calculated the Lamé coefficients using the exact expressions originally derived by Squire, Holt, and Hoover.[13] From the measured Lamé coefficients and Eq. (1), the Kosterlitz-Thouless parameter K was obtained and is presented as a function of temperature in Fig. 1(b). We note that at the observed instability temperature $kT_m/\epsilon=0.45$, K has approached, by extrapolation, the approximate value of 16π, while at the neighboring temperature of 0.44 the K of the solid is significantly above 16π. Using my experimental elastic constants data for temperatures below 0.45, I estimate that the instability temperature based on the Kosterlitz-Thouless criterion is 0.45 ± 0.005.[14] The measured value of K at the observed melting temperature is significantly lower than 16π because of defect formation in the solid constrained to remain at a solid density. I conclude that my experimentally observed melting temperature[2] is consistent with the Kosterlitz-Thouless-Feynman instabiltiy criterion and that the transition at this temperature is consistent with a first-order phase change. The first-order behavior contradicts the prediction based on the application of renormalization-group arguments to the dislocation model for melting where it is predicted that the two-dimensional melting transition is continuous.

A detailed free energy analysis yielding the phase diagram of the two-dimensional Lennard-Jones system finds that the *thermodynamic melting temperature is approximately 0.415.*[15] This is in sharp contrast to my finding that computer experiment and the Kosterlitz-Thouless-Feynman theory give a melting temperature of ~0.45. However, this may be resolved by the following argument. The dislocation theory of melting only describes the stability of the solid state in terms of the improbable existence of solid-state defects (e.g., dislocations, disclinations) in its equilibrium solid structure. At the Kosterlitz-Thouless-Feynman instability temperature, a dilute concentration of defects becomes likely and the solid may then readily transform to the lowest free energy phase, the liquid state. Certainly, the defect solid with a low concentration of dislocations is not a proper model for a liquid and must be in a higher free energy state relative to the equilibrium liquid state. However, the defect solid state is an effective *precursor* for melting to the liquid state. In the laboratory, atomic solids do not melt at this stability limit to defect formation, but melt at, or very near to, their thermodynamic melting temperature. This is because of the necessary existence of a solid surface. In Fig. 2, this is demonstrated by Monte Carlo simulations of a two-dimensional strip of 512 Lennard-Jones atoms at a temperature (0.40) slightly below and at a temperature (0.42) slightly above the thermodynamic melting temperature of 0.415 and initialized at the appropriate low-pressure, solid-state densities for the respective temperatures. Periodic boundary conditions exist at the strip's horizontal boundaries, while the two vertical boundaries are free surfaces in contact with a vapor phase region (see Ref. 16 for additional technical details). The trajectory plots are generated from 5×10^6 consecutive configurations and are typical of the equilibrium atomic behavior of the strip over a continuous simulation of $\sim 50 \times 10^6$ configurations for each temperature. The simulations clearly demonstrate a stable crystal phase with premelted surfaces at $kT/\epsilon=0.40$ [Fig. 2(a)] and a stable liquid phase at $kT/\epsilon=0.42$ [Fig. 2(b)]. Surface premelting of a *three-dimensional* crystal has also been established by computer simulation.[17] The results in Fig. 2 also provided nice confirmation that the earlier estimate of the thermodynamic melting temperature[15] is valid. In the computer experiments, it is easy (actually, too easy) to exclude the presence of surfaces by imposing periodic conditions at all boundaries of the computational cell and to effective-



(a) $kT/\epsilon = 0.40$



(b) $kT/\epsilon = 0.42$

FIG. 2. Atomic trajectory pictures of a two-dimensional Lennard-Jones system with two free surfaces for a temperature slightly below (a) and slightly above (b) the thermodynamic melting point of 0.415.

ly constrain the solid to superheat well beyond the thermodynamic melting temperature.

We may imagine other types of fluctuations that may result in a different stability limit for the "surfaceless" atomic solid. For example, in a heterophase fluctuation,[18] we would consider a local crystal region of a few tens of atoms which would "premelt" (i.e., a liquid cluster embedded in the crystal matrix). However, because of the density difference between the liquid and solid states and because of liquid layering neighboring a crystal boundary,[19] the energetics would be prohibitive, and this heterophase precursor to melting would be very unlikely. I conclude that the dislocation-dissociation mechanism is the most efficient precursor to bulk melting of the metastable solid.

In summary, the dislocation-unbinding model for two-dimensional melting leads to a theoretical instability temperature that is consistent with the experimentally observed instability temperature of the solid phase. However, this melting temperature is not the *thermodynamic* melting temperature, this being much lower; it is a temperature corresponding to an upper limit for the stability of the *metastable,* two-dimensional solid. Also, the renormalization-group arguments applied to the Kosterlitz-Thouless-Feynman model predict that the melting transition is continuous, in sharp contrast to the first-order character observed in my numerical experiments. I conclude that the dislocation-unbinding theory for melting does not give a correct thermodynamic theory of melting. The *thermodynamic* melting temperature is significantly lower than the temperature for which the solid becomes unstable to dislocation pair dissociation (the Kosterlitz-Thouless-Feynman temperature), and the thermodynamic phase transition is first order.

It seems likely that my findings and conclusions for the melting of a two-dimensional atomic solid are also valid for three dimensions.

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