

Surface melting in a two-dimensional model

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(Received 16 December 1988)

We study surface melting in a two-dimensional lattice model which exhibits solid, liquid, and gas phases. Density and order-parameter profiles as well as interfacial free energies are calculated for both (10) and (11) solid-liquid and solid-gas interfaces by use of the cluster variational method. Both solid-gas interfaces begin to disorder slightly below one-half of the triple temperature, and undergo surface melting as this temperature is approached. The structural difference between the solid and the two fluids causes the solid interfacial free energies to be large compared to the liquid-gas tension.

The question of how a solid melts has been a long-standing one. It has been suspected for many years that melting could be initiated at the surface of the solid and then proceed inward,^{1,2} a process known as surface melting. Recently, the existence of this process has been reported in systems of Ar, Ne, CH₄, Pb, and H₂O.³⁻⁷ Of particular interest is the orientation dependence of the process. There is experimental agreement that the most-dense surface of Pb, the (111) surface, does not undergo surface melting. However, there is disagreement on whether the less-dense (110) surface does.^{5,6} In contrast to these observations on Pb is the result that the most dense surface of Ar does surface melt.³

The process of surface melting can be viewed as the wetting of the solid-gas interface by the liquid on approaching the solid-gas-liquid triple point, and is therefore a special case of complete wetting.² From this it follows that the solid-gas, solid-liquid, and liquid-gas surface free energies at the triple point are related by

$$\sigma_{sg} - \sigma_{sl} - \sigma_{lg} = 0 \quad (1)$$

and the manner in which this quantity vanishes as the triple point is approached is known.⁸

Surface melting has been simulated,⁹ but studied primarily by molecular dynamics.¹⁰⁻¹³ This approach is subject to various difficulties, however, which have been manifested by a positive value¹⁰ for the left-hand side of Eq. (1) which is not possible in equilibrium,² and a disagreement as to whether a system interacting with Lennard-Jones potentials undergoes surface melting.^{10,11}

Additional approaches would be desirable, but there is little analytic work on microscopic models. This is because there are few analytic methods which provide reasonable descriptions of all three bulk phases simultaneously, and are also capable of describing the interfaces between them. A first step toward such an approach was recently taken by Trayanov and Tosatti,¹⁴ who employed mean-field theory to study a form of three-dimensional lattice-gas model, which included the motion of atoms within each cell. The particles interacted via a Lennard-Jones potential. Among their interesting results was that both the (100) and (110) facets of the fcc solid surface melted. Their method was not applicable to the most-dense (111) face, however. Another result, not stressed

by them, was that the solid-liquid surface free energy was large compared to the liquid-gas free energy, much larger than that obtained by molecular dynamics.¹⁰ It is not clear how much of this result was due to the fact that the density of their liquid phase was only 0.6 of the solid, and that mean-field theory was employed. The latter, of course, ignores the correlations between densities which might be expected to be significant at solid-fluid interfaces. (It must also be noted that the surface free energies determined by molecular dynamics are also uncertain due to their sensitivity on the cutoff chosen for the Lennard-Jones potential.¹³)

We have studied surface melting in a lattice-gas system and, in order to ensure that the short-range correlations are treated accurately, have employed the cluster variational method (CVM).¹⁵ For simplicity, we have examined a two-dimensional model whose bulk phase diagram is known from transfer matrix methods¹⁶ and the CVM.¹⁷ The diagram shows a triple point at which the density of liquid is 0.77 of the simple square solid. We are able to study the possibility of surface melting of the solid at the surface of highest density, the (10), as well as for the (11) surface. We find that surface melting occurs for both of these orientations.

The model is defined on a two-dimensional square lattice, lattice constant c_0 , at each site of which there can be a particle. If site i is occupied, its first-, second-, and third-neighbor sites are excluded from being occupied. An attraction at the fourth-neighbor distance encourages the formation of a $\sqrt{5} \times \sqrt{5}$ square solid, and a competing attraction at the fifth-neighbor distance discourages it leading to the formation of a liquid. The Hamiltonian is

$$\mathcal{H} = -\varepsilon_4 \sum_{\langle ij \rangle} n_i n_j - \varepsilon_5 \sum_{\langle ij \rangle} n_i n_j - \mu \sum_i n_i, \quad (2)$$

where $n_i = 1$ if site i is occupied and is zero otherwise, μ is the chemical potential, and $-\varepsilon_4, -\varepsilon_5$ are the interaction energies of fourth- and fifth-neighbor pairs, respectively. The ratio of the former to the latter is 1.2:1. The first sum runs over all fourth-neighbor pairs, the second over all fifth-neighbor pairs, and the third over all sites.

The underlying lattice can be divided into five interpenetrating $\sqrt{5} \times \sqrt{5}$ square sublattices as shown in Fig. 1. In the solid phase, one of the five sublattices is occupied

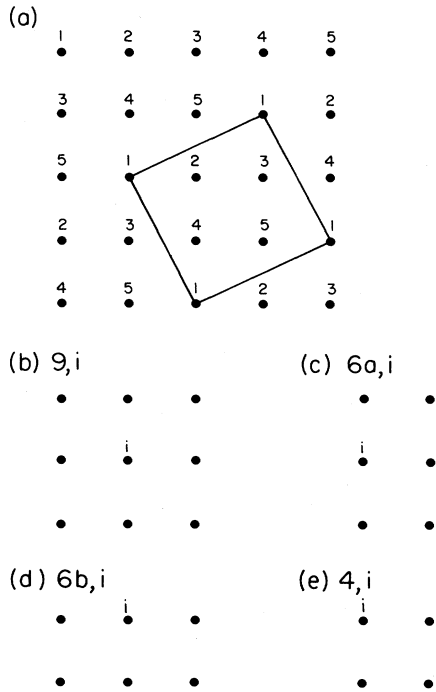


FIG. 1. Labeling of the five sublattices and the contributing clusters. The square shows the unit cell of the solid.

primarily, for instance, sublattice 1. For both liquid and gas phases, all five sublattices are occupied equally. Following Ref. 17, we choose the basic clusters of the CVM to be the 3×3 clusters as shown in Fig. 1. A given site i is labeled by two indices (m, l) , m the underlying lattice plane number, l the sublattice. The lattice plane number m of site i depends on the orientation of the interface, while the sublattice label l does not. Within this scheme,^{18,19} the CVM yields for the entropy of the whole system, including the interface, the approximation

$$S = \sum_{\alpha} a_{\alpha} S_{\alpha} = \sum_i S_{9,i} - \sum_i S_{6a,i} - \sum_i S_{6b,i} + \sum_i S_{4,i}, \quad (3)$$

where $S_{9,i} = -k_B T \text{Tr} \rho_{9,i} \ln \rho_{9,i}$, with k_B Boltzmann's constant, and $\rho_{9,i}$ the partial density matrix of the 3×3 cluster with site i at its center. The $S_{6a,i}$, $S_{6b,i}$, and $S_{4,i}$ are given by similar expressions; their associated clusters are depicted in Fig. 1. The internal energy is

$$E = -\varepsilon_4 \sum_{\langle ij \rangle} \text{Tr} \rho_{9,i} n_j - \varepsilon_5 \sum_{\langle ij \rangle} \text{Tr} \rho_{9,i} n_j, \quad (4)$$

where ρ_9 is the partial density matrix of any of the several 3×3 clusters which contains the ij pair. The grand potential is then

$$\Omega = E - TS - \mu \sum_i \text{Tr} \rho_{9,i} n_i. \quad (5)$$

This potential is minimized with Lagrange multipliers introduced to ensure the proper constraints among the partial-density matrices.²⁰ The equilibrium cluster probability (partial-density matrix) is found by solving a set of

nonlinear equations resulting from the minimization.

The bulk properties are those found earlier.^{16,17} In particular, there is a triple point at temperature $T_{\text{tr}} = 0.441 \varepsilon_5 / k_B$. The solid, liquid, and gas densities there are 0.199, 0.153, and 0.0116, respectively (in units of c_0^{-2} .) The density profile of an interface between two coexisting phases I and II is obtained from $\bar{n}_{m,l} = \text{Tr} \rho_{9,i} n_{m,l}$; the interfacial free energy is given by

$$\sigma_{\text{I,II}} = \lim_{L \rightarrow \infty} \lim_{A \rightarrow \infty} [\Omega_{\text{I,II}}(L) - \frac{1}{2} \Omega_{\text{I,I}}(L) - \frac{1}{2} \Omega_{\text{II,II}}(L)] / A. \quad (6)$$

$\Omega_{\text{I,II}}(L)$ is the grand potential of a finite strip of length A , width L with the $m=0$ row identical to one in bulk phase I, and row $m=L$ to one in bulk phase II; $\Omega_{\text{I,I}}(L)$, $\Omega_{\text{II,II}}(L)$ are similarly defined. In choosing L , one must make sure that the two ends ($m=0, m=L$) be physically identical if an ordered phase is imposed at both ends. Because the contributions to $\Omega_{\text{I,II}}(L)$, $\Omega_{\text{I,I}}(L)$, and $\Omega_{\text{II,II}}(L)$ from the ends at $m=0$ and $m=L$ cancel, they need not be included in the actual calculation of the interfacial free energy. Therefore, we can use

$$\sigma_{\text{I,II}} = \lim_{L \rightarrow \infty} \lim_{A \rightarrow \infty} [\Omega'_{\text{I,II}}(L) - \frac{1}{2} \Omega'_{\text{I,I}}(L) - \frac{1}{2} \Omega'_{\text{II,II}}(L)] / A, \quad (7)$$

where the prime denotes the same quantity calculated as if the strip were between semi-infinite bulk systems of the appropriate phase on either side. In calculating $\Omega'_{\text{I,II}}$, the cluster probabilities associated with planes $0 \leq m \leq L$ are varied to minimize the grand potential energy of Eq. (5). We start with L of 80, then increase it until the interfacial free energy converges to 0.1% (typically, $L \approx 150$).

The calculated density profiles of the solid(10)-gas interface at temperatures $T/T_{\text{tr}} = 0.45$ and 1.0 are shown in Figs. 2(a) and 2(b). The coordinate z perpendicular to the interface is measured in units of the lattice parameter of the solid $c_s = \sqrt{5}c_0$. Profiles for the solid(11)-gas interface are similar, but the interface is always somewhat wider at the same temperature than that of the more-dense solid(10). It can be seen that even at $0.45 T_{\text{tr}}$, the surface of the solid is significantly disordered. On approaching the triple point, the liquid phase intervenes between the solid (of either orientation) and gas. This can be seen by noting that the interface in Fig. 2(b) is a composite one consisting of a solid(10)-liquid interface [Fig. 3(a)] and a liquid-gas interface [Fig. 3(b)]. The thickness of the intervening liquid in our calculation is limited only by how accurately we can determine the triple temperature. At the triple point the interfacial free energies satisfy Eq. (1), within the numerical accuracy, for both (10) and (11) directions. Hence, we conclude that both orientations undergo surface melting.

The three surface free energies for each orientation are shown in Table I. Because of the underlying lattice in our model, the interfacial free energy between disordered liquid and gas phases depends on the direction of the interface between them. The effect is small, but serves as a measure of the anisotropy imposed by the lattice calculation. The anisotropy of the solid-liquid interfacial free energy is small, only a little more than 2%. That of the solid-gas interface follows from the other two anisotropies

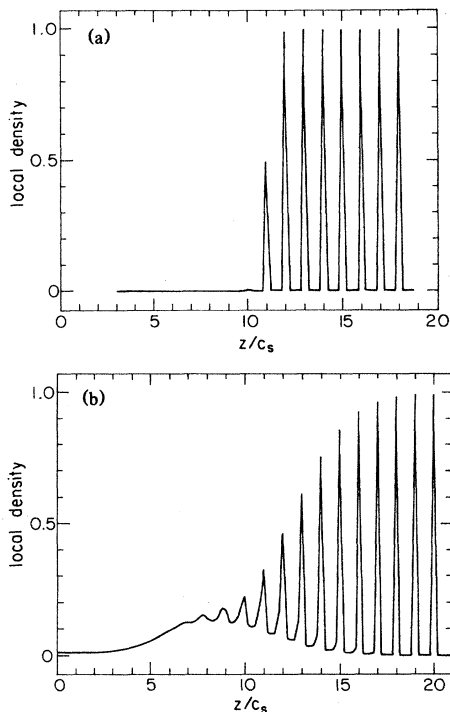


FIG. 2. The density profile of solid(10)-gas interface at (a) $T/T_{tr}=0.45$, and (b) $T/T_{tr}=1$.

and Eq. (1). The most notable result in Table I is that the solid-fluid free energies are much larger than the liquid-gas tension. Presumably, this is due to the short range of the interaction and the fact that the local density in the ordered solid changes rapidly with position, while that in the fluid does not. Thus the density-density correlation

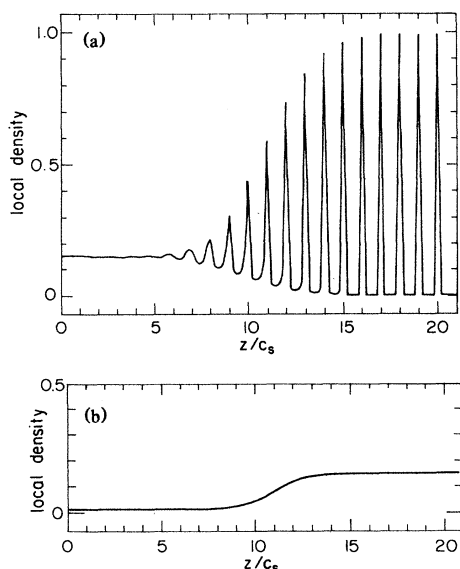


FIG. 3. Density profiles at T_{tr} of (a) solid(10)-liquid interface, and (b) liquid-gas interface.

TABLE I. Interfacial free energies at the triple point in units of ϵ_4/c_s .

Direction	σ_{lg}	σ_{sl}	σ_{sg}
(10)	0.0916 ± 0.0001	0.1721 ± 0.0001	0.2646 ± 0.0009
(11)	0.0924 ± 0.0001	0.1758 ± 0.0001	0.2683 ± 0.0009

functions, which enter into the interfacial free energy, are quite large at a solid-fluid interface even though the average densities may not be very different. Figure 4 shows the variation of density through the solid(10)-liquid interface as well as the variation of the solid order parameter. The latter is simply the average occupation of the solid sublattice minus the average occupation of the other four sublattices.

It seems reasonable that the relatively small liquid-gas tension and the occurrence of surface melting in this model are related. If the liquid layer were not permitted to intrude, the solid-gas interfacial free energy would be even larger than that of the solid-liquid because of the greater difference in the local densities. This large free energy is reduced by permitting the liquid to intrude. Even though there are now two interfaces, the solid-liquid and liquid-gas, the relatively small cost of the latter makes this process free energetically favorable.

Our calculation has been carried out on a two-dimensional system with short-range interactions. A similar calculation in three dimensions incorporating long-range interactions, while considerably more difficult, should be feasible. But even the two-dimensional calculation displays a result which we believe carries over to a three-dimensional, nonmetallic system such as Argon. This is that the anisotropy of the solid-liquid interfacial free energy is small at the triple temperature, which implies that one should expect that all surfaces will display the same surface melting behavior; either they will undergo it, or they will not. Thus, from the fact that Ar(111) undergoes surface melting,³ we would expect all directions to do so. This is an expectation, not a necessity. Should a system show a different behavior, then a surface melting (wetting) transition would be observed as a function of surface orientation.²¹

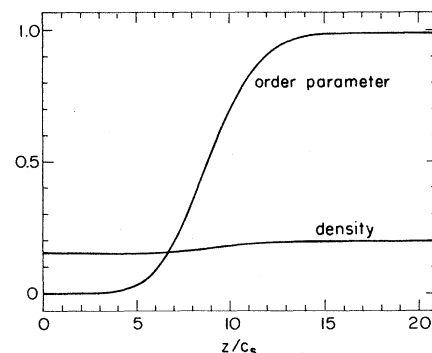


FIG. 4. Density and order-parameter profiles at the solid(10)-liquid interface.

It is a pleasure to thank J. G. Dash for his continued interest and support of this work, R. Kikuchi for his help in the numerical implementation of the CVM, G. Gompper for useful conversations, and M. Biehl for his assistance in the early stages of the calculation. The work was supported in part by the National Science Foundation under Grant No. DMR-8613598.

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