

Lattice Theory of Crystal Surface Melting

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We have developed a lattice theory capable of providing, within certain mean-field restrictions, a realistic description of the surface-initiated melting taking place at a low-index crystal-vapor interface near the bulk triple-point temperature T_M . Direct application is presented to the (100) and (110) surfaces of an fcc Lennard-Jones crystal. A quasiliquid layer of thickness growing like $(T_m - T)^{-1/3}$ is found, in good qualitative agreement with recent experiments on Ar films.

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The idea that when a liquid wets the surface of its own solid phase then crystal melting might be a surface-initiated process is very old,¹ and much macroscopic evidence has been accumulated over the years by the chemical physicists.² Recent microscopic studies indicate the formation very close to the triple-point temperature T_M of what is plausibly a "quasiliquid" layer.³⁻⁵ By that, we mean a very thin film, inside which the single-particle density and surface corrugation may still be influenced by the underlying bulk crystal, but where the average density ρ , the pair correlation function, and the diffusion coefficient are essentially those of the unperturbed bulk liquid, as it would appear just above T_M . While phenomenological and other simplified descriptions of this phenomenon are available,⁶⁻¹⁰ it is hard to tackle it theoretically, both by conventional microscopic theory and by simulation (whose results are still somewhat controversial^{11,12}). Some aspects of surface melting are common to the simpler problem of wetting of a hard

wall, whose theory is discussed.⁷ However, it is not really clear how to extend these theories, and a fresh microscopic start seems necessary. Microscopically, one needs for a start a simple and accurate bulk theory. It should account for the phase diagram including solid, liquid, and vapor phases, the triple point, and the critical point of a true substance. The theory should then be generalized to describe the solid-gas interface near T_M . This program has never been implemented so far. None of the existing approaches calculates a surface free energy, or a density profile across the surface, or the propagation of crystalline ordering across the quasiliquid film. The gradual evolution from a compact, flat, warm crystal surface with just a few vacancies to a quasiliquid film remains to be understood in all details. In this Letter we present a new attack to this problem, capable of providing a first answer to at least some of these questions.

We divide the volume V of a system of N atoms into K cells of a simple regular lattice ($N < K$). The grand partition function is

$$Q = \sum_{\{p_i\}} \int_{v_0} \cdots \int_{v_0} \exp \left[-\beta \left(\frac{1}{2} \sum_{ij} p_i p_j U(\mathbf{r}_i, \mathbf{r}_j) - \mu N \right) \right] d^3 r_1 \cdots d^3 r_N,$$

where $U(\mathbf{r}_i, \mathbf{r}_j)$ is a pairwise interaction, $\beta = (k_B T)^{-1}$ is the inverse temperature, μ is the chemical potential, and p_i is zero if the site is empty and unity otherwise. If the volume $v_0 = V/K$ of each cell is small, we can neglect the possibility of multiple occupancy of a cell. The summation $\sum_{\{p_i\}}$ is taken over all possible configurations of N atoms on K sites. In the free-volume approximation¹³ Q is replaced by the product of a discrete Ising-type lattice model term Z and a free-volume term Ω ,

$$Q_0 = \left(\prod_{k=1}^N \frac{v_k^f}{v_0} \right) \left\{ \sum_{\{p_i\}} \exp \left[-\beta \left(\frac{1}{2} \sum_{ij} p_i p_j U_{ij} - \mu N \right) \right] \right\} = \Omega Z,$$

where v_k^f defines a "free volume" for atom k , $U_{ij} = U(\mathbf{R}_i, \mathbf{R}_j)$, and \mathbf{R}_i denotes a cell site. Our reference lattice consists of two fcc sublattices, labeled 0 and 1. By our choosing the cell size to be $1/\sqrt{2}$ times the optimal interparticle separation, one of the sublattices is nearly filled in the solid phase, and the other nearly empty. We call the imbalance $c = (\langle p_0 \rangle - \langle p_1 \rangle) / (\langle p_0 \rangle + \langle p_1 \rangle)$ the "crystallinity" order parameter. In the liquid and in the gas phases both sublattices are equally populated

($c=0$). Mori, Okamoto, and Isa¹⁴ have applied this scheme to bulk melting by treating the Ising system in mean-field approximation and crudely setting $\Omega=1$. In spite of its crudeness this scheme describes fairly well the triple-point behavior of the Lennard-Jones (LJ) system.¹⁴ We have modified this procedure for an inhomogeneous situation, like the solid-vapor interface. Our system consists of a simple cubic reference lattice, whose

layers, labeled l , are parallel to the interface. Within mean-field theory (no fluctuations) each layer has a constant density ρ_l , as well as a constant crystallinity c_l . Both Z and Ω are functional of $\{\rho_l, c_l\}$.

For the inhomogeneous Ising problem we take the mean-field evaluation

$$Z = g \exp \left[-\beta \left(\frac{1}{2} \sum \langle p_{il} p_{jl'} \rangle U_{ij} - \mu N \right) \right],$$

$$Z = g \exp \left\{ \beta \left[\mu N - \frac{1}{2} N_0 v_0^2 \sum_{lm} \rho_l \rho_{l+m} \sum_{k=2}^{\infty} [1 + (-1)^k c_l c_{l+m}] z_m(k) U_k \right] \right\},$$

where $z_m(k)$ is the number of k th neighbor sites (interactions U_k) for a given site m layers away, N_0 is the number of the lattice sites in every layer, and $N = v_0 N_0 \sum_l \rho_l$. The combinatorial factor g , calculated by extension of Takagi's method,¹⁵ is

$$\ln g = \frac{1}{2} N_0 \sum_{v=0}^1 \sum_{lm} \{ [z_m(1) - 1] [h(\langle p_l^v \rangle) + h(1 - \langle p_l^v \rangle)] - z_m(1) [h(\langle p_l^v \rangle) + \delta_{0,v} h(1 - \langle p_l^v \rangle - \langle p_{l+m}^{v+1} \rangle)] \},$$

where $h(x) \equiv x \ln(x)$.

Next, we need to express the free-volume term Ω as a functional of $\{\rho_l, c_l\}$. The formal definition Q/Z is not useful for that, and we have adopted the following procedure. We start by assuming a local dependence, i.e., $v_l^f = v^f(\rho_l, c_l)$, which we further take to be the same function $v^f(\rho, c)$ which applies for a bulk with homogeneous $\rho = \rho_l$ and $c = c_l$. Calculating the free volume v_c^f of an atom in the crystal ($c \approx 1$) we approximate

$$v_c^f \approx \int_{v_0} \exp \left[-\beta \rho v_0 \sum_n [U(\mathbf{r}, \mathbf{R}_n) - U_n] \right] d^3 r$$

$$D^{-2} = 8C(1-C) - 1 + \sum_m \left\{ \frac{[z_m(1) - 1] \rho v_0}{1 - \rho v_0} - \frac{v_0 \rho}{k_B T} \sum_{k=2}^{\infty} (-1)^k z_m(k) U_k \right\},$$

where C (a function of ρ and T)¹⁶ is the Fourier transform of the direct correlation function of the liquid at $2\pi\sqrt{3}/a$, and a is the lattice constant. The Gaussian falls off for increasing c , and crosses v_c^f at some $c_0 < 1$, at which point we believe v_c^f to be more accurate. In conclusion we have

$$v^f = \max[v_0(1 - \rho v_{\text{core}}) \exp(-c^2/2D^2), v_c^f].$$

Our final free-energy expression is

$$G = -k_B T \left[N_0 v_0 \sum_l \rho_l \ln(v_l^f/v_0) + \ln Z \right].$$

Minimization with respect to c_l, ρ_l yields $2M$ equations for M layers, to be solved self-consistently.

We have applied this scheme to a LJ crystal. Lattice sums are extended to infinity, first as true sums, and then as integrals, to allow for the effect of the tail of the van der Waals potential. First, we study the bulk phase diagram and find a triple point at $T_M = 1.0662\epsilon/k_B$, and critical point at $T_c = 1.229\epsilon/k_B$. (The LJ potential has a depth ϵ and core radius σ .) With consideration of the crudeness of the lattice model assumed, the agreement

where p_{il} denotes the occupancy of site i in layer l and $g \equiv g\{\rho_l, c_l\}$ is a combinatorial factor which accounts for the multiplicity of the saddle-point configuration. We take $\langle p_{il}^v p_{jl'}^v \rangle = 0$ if il is first neighbor of jl' or equal to $\langle p_l^v \rangle \langle p_{l'}^v \rangle$ for second and further neighbors. Moreover, $\langle p_l^v \rangle = v_0 \rho_l [1 + (-1)^v c_l]$, with $v=0$ denoting one sublattice, and $v=1$ the other. Occupancy of nearest-neighbor sites is extremely unlikely and is excluded.

Finally,

(here n spans only the occupied sublattice). Near T_M , v_c^f might be called the "Lindemann volume." For $c=0$ (gas and liquid), we can expect v^f to be given roughly by $v_0(1 - \rho v_{\text{core}})$, where $v_{\text{core}}(T, \rho)$ is the effective hard-core atomic volume.¹⁶ For intermediate c , we evaluate $v^f(\rho, c)$ by calculating the free-energy difference due to a single-shell crystalline order parameter by the method of Ramakrishnan and Yussouff.¹⁷ The final result is rather cumbersome, but we find it to be extremely well approximated by a simple Gaussian, whose width is

with the true values $T_M = 0.7\epsilon/k_B$, and $T_c = 1.26\epsilon/k_B$ is quite acceptable.

When applying this model to surface melting, we note that the neglect of fluctuations makes it inapplicable to high-index surfaces, where step fluctuations should be important. Then we consider the three low-index crystal surfaces. Of these, the (111) surface is discarded, because within our two-sublattice model a (111) layer is either totally filled or totally empty, and this does not allow for intralayer communal entropy to develop. We are left with the (100) and (110) surfaces and both of them have been studied. For a typical number of layers M of order 400, we have solved the $2M$ minima equations for $\{\rho_l, c_l\}$, when (μ, T) lie on the coexistence line. The boundary conditions were solid on one side of the slab, gas on the other side. An initial guess for $\{\rho_l, c_l\}$ was taken, and brought to self-consistency by successive iterations. For T well below T_M , convergence was fast (≈ 100 iterations). On approach to T_M , convergence became progressively poorer; for example, for $t = 1 - T/T_M \approx 10^{-5}$, about 10^5 iterations were needed.

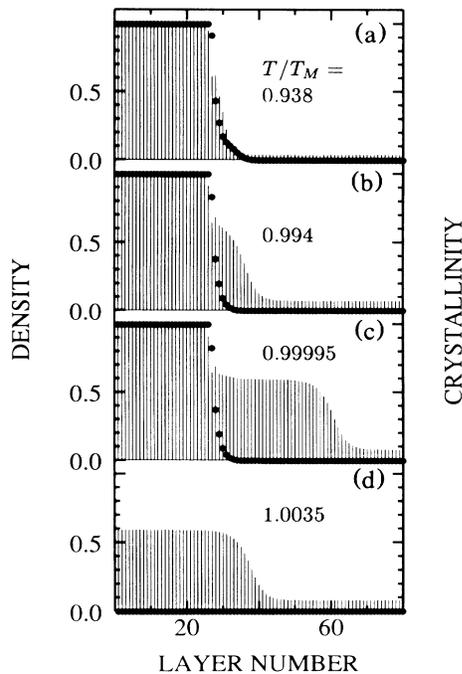


FIG. 1. Density (units of σ^{-3} , vertical lines) and crystalline-order (dots) profiles of the LJ (110): (a),(b),(c) solid-gas and (d) liquid-gas interfaces at coexistence.

Our main result is displayed in Fig. 1, for the (110) surface [the (100) results differ only numerically]. Surface melting is clearly taking place, with a quasiliquid layer growing critically near T_M . There appears to be no singularities below T_M . The surface free energy, expressed as $\gamma = (PV + G)/\text{area}$, is directly calculable (P is the pressure at coexistence), and, as Fig. 2 shows, it is continuous. This does not at all rule out the possibility that in reality a first-layer melting transition,¹⁰ and/or a roughening transition,⁹ might occur below T_M . Simply, the associated fluctuations are not permitted in our treatment. In spite of this, we believe that no previous theory of comparable quality exists, particularly very near T_M . Before leaving surface free energies, we note the strong tendency of (110) and (100) results to merge already for t as large as 10%. This thermal decrease of surface anisotropy has been well-known experimentally,¹⁸ and was also found by computer simulations,¹¹ but not described theoretically before.

According to phenomenological theories,⁶⁻⁸ the quasiliquid layer grows critically as T_M is approached. While growth like $|\ln t|$ is expected for short-range forces,⁶⁻⁸ a power-law growth $t^{-1/3}$ is predicted^{7,19} for r^{-6} van der Waals forces. Both types of behavior have been reported in recent experiments.³⁻⁵ We can extract from our calculation the thickness of the liquid layer (arbitrarily defined as the numbers of layers between $c_l = \frac{1}{2}$ and $p_l = 90\%$ of the bulk liquid density). The growth behav-

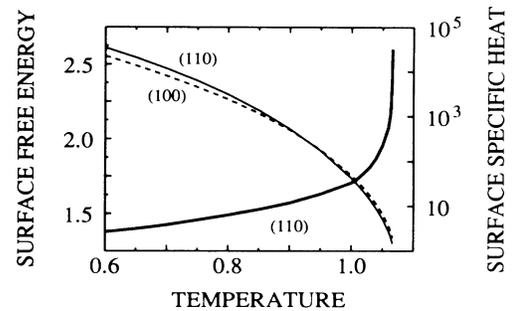


FIG. 2. Calculated LJ surface free energies γ (units of ϵ/σ^2) and (110) surface specific heat $C_s = -T(\partial^2\gamma/\partial T^2)$ (thicker solid line, units of k_B/σ^2). Note singularities due to surface melting at $T_M = 1.0662\epsilon/k_B$.

ior seems indeed to tend asymptotically to $t^{-1/3}$, although with strong deviations for large t . The calculated behavior of Fig. 3 parallels remarkably the experimental points for Ar on graphite,⁴ although the numerical agreement is merely a coincidence, since the experimental surface was very likely not (110). We have further tried cutting off the long-range attractive tail (at $r \approx 3.2\sigma$), and also reversing its sign into a weak repulsive tail, to see whether the quasiliquid film growth was altered, as expected. The result of Fig. 3 provides a remarkable confirmation. In the short-range case the growth is indeed logarithmic, similar to the reported behavior for Pb(110)³ and oxygen.⁵ In the repulsive case the film thickness does not diverge any more, but rather levels off at some finite value. This "blocked" surface melting agrees well with a prediction of Levi and Tosatti.⁸ It may be related to the behavior found in the computer simulations of Au(111)²⁰ and also to that seen experimentally on Ge(111).²¹ Lastly, we have calculated the value of crystallinity at the gas-quasiliquid-layer interface $c(0)$, and find $c(0) \sim \exp(-At^{-B})$, with $A \approx 0.9$

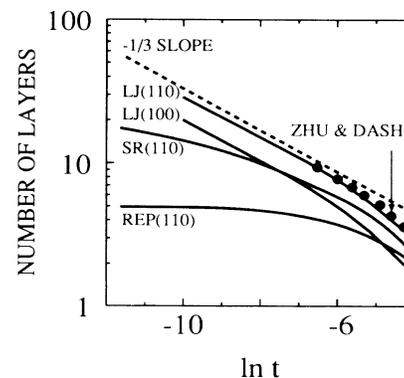


FIG. 3. Dependence of the quasiliquid layer thickness upon the reduced temperature. Note the change of behavior from long-range attraction (LJ) to short-range (SR) to long-range repulsion (REP). Experimental points from Ref. 4.

and $B \approx \frac{1}{3}$ in the long-range case, but $c(0) \sim t^{1.6}$ in the short-range case. This quantity is in principle measurable by surface diffraction.

In summary, we have developed a lattice theory which describes surface melting. It contains approximations, but it is basically "ab initio," and has no adjustable parameters. The growth of a quasiliquid layer at a warm low-index LJ crystal surface is demonstrated and parallels closely that found in very recent experiments.

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