

Maximum Overheating and Partial Wetting of Nonmelting Solid Surfaces

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Surfaces which do not exhibit surface melting below the melting point (nonmelting surfaces) have been recently observed to sustain a very large amount of overheating. We present a theory which identifies a maximum overheating temperature, and relates it to other thermodynamical properties of the surface, in particular, to geometrical properties more readily accessible to experiment. These are the angle of partial wetting and the nonmelting-induced faceting angle. We also present molecular dynamics simulations of a liquid droplet deposited on Al(111), showing lack of spreading and partial wetting in good agreement with the theory.

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For a long time crystal overheating above the bulk melting temperature T_m has been believed to be impossible, at least in the presence of a free clean surface. The standard argument [1,2] is that surface premelting will always take place and act as a ubiquitous seed for the liquid to grow. The well-known surface melting of Pb(110) [3,4] provided first microscopic evidence of how liquid nucleation takes place on a solid below T_m . It was only a little later that simulations of Au(111) [5] and newer experiments on Pb(111) [6] and Al(111) [7] demonstrated microscopically that the opposite could also happen, namely, that certain surfaces may exhibit nonmelting up to and, in fact, even *above* the melting point [5,8]. A solid bounded by such surfaces can therefore be *overheated*, although in a metastable state, above T_m . Métois and Heyraud have first shown that small Pb particles with strictly (111) facets are easily overheated by a few degrees above T_m [9]. Even more strikingly, Herman and Elsayed-Ali found that a flat nonmelting Pb surface can be overheated by as much as 120 K above T_m [10]. This implies that the free energy of a crystal surface can have a local minimum for zero liquid thickness. As in other nucleation problems one should thus expect the metastable overheated state to survive up to some instability temperature $T_i > T_m$, where the barrier finally disappears (Fig. 1, inset). At present, however, there is no further available understanding of this phenomenon. In particular, there are no means to calculate T_i and possibly connect it with other quantities which are more readily measurable in a surface experiment. At a more microscopic level, it is very desirable to understand the different behavior of a nonmelting and of a melting surface, against nucleation of the liquid.

In this Letter, we introduce a simple theory of surface nonmelting which predicts the existence of a T_i , and connects its value with apparently unrelated geometrical quantities. These are the partial wetting angle θ_m which a drop of melt will form with that crystal surface at $T = T_m$, and the faceting angle θ_c of a vicinal surface. The angle θ_m has also been rather commonly measured in the past, a few early examples being the (0001) face of Cd [11] and the (100) faces of several alkali halides [12]. The nonmelting-

induced faceting [13,14] angle θ_c has been well characterized experimentally and theoretically for (111) vicinals of Au [13,15], Cu [16], and Pb [13,14,17,18]. The connection we find between θ_m , θ_c , and T_i offers new insight into nonmelting surfaces. At a microscopic level, we substantiate this connection with molecular dynamics (MD) simulations of Al(111), which demonstrate both the nonspreading of a liquid drop at T_m and the overheating of the flat face. The predicted relationship between θ_m , θ_c , and T_i is found to be in excellent agreement with the simulation results, as well as with experiments.

(i) *Theory.*—Consider a liquid film of thickness ℓ , sandwiched between semi-infinite solid and vapor, and let ℓ grow from zero (no liquid) to a finite value. The change in free energy per unit area takes the standard form [4]

$$\Delta F(\ell) = \rho L \ell (1 - T/T_m) + \Delta \gamma(\ell), \quad (1)$$

where ρ is the liquid density, L the latent heat of melting, and $\Delta \gamma(\ell)$ the difference between the overall free energy of the two interacting solid-liquid (SL) and liquid-vapor

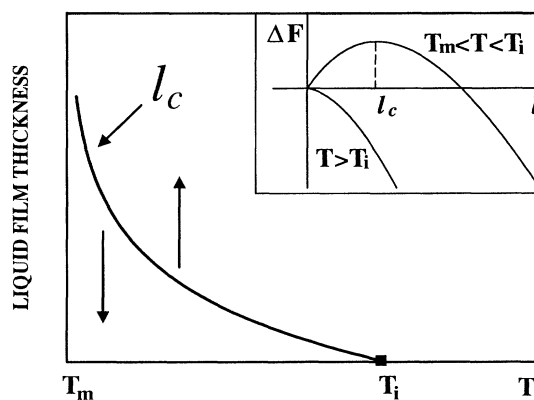


FIG. 1. Critical liquid thickness of a nonmelting surface vs temperature above T_m (schematic). A system with a liquid film thinner than the critical value will recrystallize for any T between T_m and T_i . One with a thicker film will melt completely. Inset: free energy change upon conversion of a film of thickness ℓ from solid to liquid. From T_m to T_i the solid surface is a local minimum.

(LV) interfaces separated by a distance ℓ , and the free energy of the solid-vapor (SV) interface. By definition, $\Delta\gamma(0) = 0$. Assuming short-range forces only, this term can be written phenomenologically as $\Delta\gamma(\ell) = \Delta\gamma_\infty[1 - \exp(-\ell/\xi)]$, where $\Delta\gamma_\infty \equiv \gamma_{SL} + \gamma_{LV} - \gamma_{SV}$ is the net free energy change upon conversion of the SV interface in two noninteracting SL and LV interfaces, and ξ is a correlation length in the liquid. For a melting surface $\Delta\gamma_\infty < 0$, and, for $T_w < T < T_m$, ΔF will have a minimum at $\ell_0(T) = \xi \ln[T_m |\Delta\gamma_\infty| / (T_m - T)L\rho\xi]$ which is the mean-field thickness of the melted film [4]. The wetting temperature defined by $\ell_0(T_w) = 0$ is $T_w = T_m(1 - |\Delta\gamma_\infty|/L\rho\xi)$.

For a *nonmelting surface* $\Delta\gamma_\infty > 0$, and we move over to $T > T_m$. Here, $\Delta F(\ell)$ will instead have a local minimum at $\ell = 0$, the absolute minimum for $\ell \rightarrow \infty$, and a *maximum* at a critical thickness

$$\ell_c(T) = \xi \ln \left[\frac{T_m \Delta\gamma_\infty}{(T - T_m)L\rho\xi} \right] \quad (2)$$

as shown in Fig. 1. The local minimum at $\ell = 0$ signifies metastability of the crystalline surface for $T < T_i$, the maximum overheating temperature. The minimum disappears when $\ell_c(T_i) = 0$, yielding

$$T_i = T_m \left(1 + \frac{\Delta\gamma_\infty}{L\rho\xi} \right). \quad (3)$$

Above T_i , the crystal surface will melt, no matter what its initial state is. In particular, a surface which is initially crystalline will wet itself with a liquid film, which will grow, and gradually melt the whole crystal. Hence T_i can be seen as a nonequilibrium wetting temperature, or, more accurately, as a *spinodal* point for the overheated solid surface. For $T_m < T < T_i$, the predicted behavior is that typical of a nucleation problem. If the surface is prepared initially with a melted film of thickness $\ell > \ell_c$ (upper vertical arrow in Fig. 1), then melting will proceed, and ℓ will grow to infinity, reaching full equilibrium. If, conversely, the starting thickness is less than ℓ_c , then the surface will recrystallize to reach the local metastable minimum at $\ell = 0$ (lower arrow in Fig. 1). This peculiar behavior was first found and described in detail in an early simulation of the nonmelting surface Au(111) [5].

We now show that there is a simple connection between T_i and the macroscopic nonwetting angle θ_m at $T = T_m$. Following Nozières [19], the angles θ_{LV} , θ_{SL} , formed by a drop of melt onto a nonwetting surface of the same material (Fig. 2), satisfy the equations

$$\gamma_{SV} = \gamma_{LV} \cos\theta_{LV} + \gamma_{SL} \cos\theta_{SL}, \quad (4)$$

$$R_{LV} \sin\theta_{LV} = R_{SL} \sin\theta_{SL}, \quad (5)$$

where R_{LV} , R_{SL} are the radii of, respectively, the LV and SL drop boundaries (supposedly spherical). Equation (4) is simply the balance of lateral forces, while Eq. (5) follows from simple geometry. Laplace's pressure equation $P = 2\gamma/R$ determines the shape ratio $x(T) \equiv R_{LV}/R_{SL} = \sin\theta_{SL}/\sin\theta_{LV} = [\gamma_{LV}P_{SL}(T)]/[\gamma_{SL}P_{LV}(T)]$. Since $P_{SL} \propto$

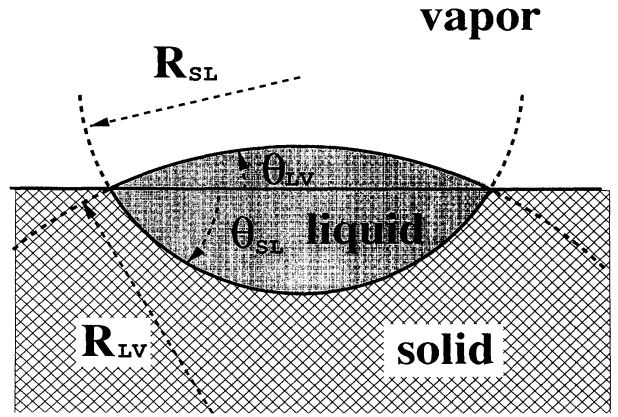


FIG. 2. Shape of a drop of melt onto a nonmelting solid surface of the same material. The two interfaces separating solid and liquid (SL), and liquid and vapor (LV) are assumed to be spherical, with radii R_{SL} and R_{LV} and contact angles θ_{SL} and θ_{LV} , respectively.

$(T - T_m)$ near T_m , we expect θ_{SL} to switch from negative for $T < T_m$ to positive for $T > T_m$. At $T = T_m$, $x = \theta_{SL} = 0$, $R_{LV} = \infty$, and $\theta_{LV} = \theta_m$, where

$$\cos\theta_m = 1 - \frac{\Delta\gamma_\infty}{\gamma_{LV}}. \quad (6)$$

A comparison of (6) with (3) shows that knowledge of $\Delta\gamma_\infty$ at $T = T_m$ determines *both* T_i and θ_m , which are monotonically related by

$$\frac{T_i}{T_m} = 1 + \frac{2\gamma_{LV}}{L\rho\xi} \sin^2 \frac{\theta_m}{2}. \quad (7)$$

For a nonmelting surface there is a second important angle θ_c , which is the nonmelting-induced faceting angle [13,14]. Consider vicinal faces tilted at an angle θ away from the nonmelting face. At $T = T_m$ there are two well-defined free energy minima (solid, $\ell = 0$ and liquid, $\ell = \infty$). We can thus draw [19] the two projected surface free energy branches $\sigma(\theta) = \gamma(\theta)/\cos\theta$ as a function of the step density $t = |\tan\theta|$. The two branches are approximately given by the standard expressions

$$\sigma_S(\theta) = \gamma_{SV} + \mu t + g t^3, \quad (8)$$

$$\sigma_L(\theta) = (\gamma_{LV} + \gamma_{SL})\sqrt{1 + t^2}, \quad (9)$$

where μ and g are the step free energy and the step-step repulsion on the solid surface. Here we have further assumed that γ_{SL} is approximately independent of θ . The faceting angle is given by $\theta_c = \arctan t_c$ which satisfies the double tangent construction: $c_0 + c_1 t_0 = \gamma_{SV} + \mu t_0 + g t_0^3$, $c_1 = \mu + 3g t_0^2$, and $c_0 + c_1 t_c = (\gamma_{LV} + \gamma_{SL})\sqrt{1 + t_c^2}$, $c_1 = (\gamma_{LV} + \gamma_{SL})t_c/\sqrt{1 + t_c^2}$. A particularly simple solution is obtained if the cubic (step-step repulsion) term $g t_0^3$ can be ignored, whence $t_0 = 0$, $c_0 = \gamma_{SV}$, $c_1 = [(\gamma_{LV} + \gamma_{SL})^2 - \gamma_{SV}^2]^{1/2}$ (note the nonanalyticity of σ_S

at $t = 0$), and $t_c = \{[(\gamma_{LV} + \gamma_{SL})/\gamma_{SV}]^2 - 1\}^{1/2}$. Even when this approximation cannot be made and t_0 is nonzero [as is the case for Pb(111) [14], where $\arctan t_0 \approx 2^\circ$], the above is still a pretty good approximation to the faceting angle, which is therefore simply related to $\Delta\gamma_\infty$,

$$\cos\theta_c \approx \left(1 + \frac{\Delta\gamma_\infty}{\gamma_{SV}}\right)^{-1}. \quad (10)$$

Equation (4) shows that θ_c is identical to *both* the droplet angles θ_{LV} , θ_{SL} at a single temperature $T_u > T_m$, satisfying $x(T_u) = R_{LV}/R_{SL} = 1$. We note that θ_c is slightly smaller than θ_m . The outer droplet angle θ_{LV} will therefore decrease from θ_m to θ_c to zero when T is raised from T_m to T_u to T_i . Finally, we observe that a physical upper bound for θ_m and θ_c is given by $\Delta\gamma_\infty \ll \gamma_{LV}$, whence $\theta_m \ll 90^\circ$, and $\theta_c \ll 60^\circ$, i.e., a melt must at least partially wet its own solid.

(ii) *MD simulations.*—Choosing Al(111) as our test case, we have simulated its behavior at and above T_m using the recent accurate glue potential of Ercolessi and Adams [20], derived by fitting to first-principles data. First, the approximate bulk melting point for this potential was determined using the phase coexistence technique [21] and found to be $T_m = 939 \pm 5$ K (against an experimental value of $T_m^{\text{exp}} = 933.6$ K). Then a 16-layer slab with three rigid bottom layers, one free surface, 224 atoms per layer, and x - y periodic boundary conditions was studied as a function of T . As T_m was reached and crossed, the surface remained crystalline (metastable) as expected, up to a large $T_i = 1088 \pm 18$ K $= T_m + (149 \pm 18)$ K, even for very long (2 ns) runs. On the basis of our theory, using the known values of $\rho = 0.0534 \text{ \AA}^{-3}$, $L = 105.4$ meV/atom [20], and an estimated $\xi = 2.6 \pm 0.3 \text{ \AA}$ [22], we extract from (3) $\Delta\gamma_\infty = 2.3 \pm 0.4$ meV \AA^{-2} . Inserting in Eq. (6), with an estimated value of $\gamma_{LV} = 46.6$ meV \AA^{-2} (obtained with a separate simulation of the free liquid surface at $T = T_m$), we finally predict $\theta_m = (18 \pm 2)^\circ$ and, with a value $\gamma_{SV} = 54.3$ meV \AA^{-2} [20], $\theta_c = (16 \pm 2)^\circ$.

To check this prediction, we have prepared an 861 Al atom cluster which is fully melted and forms a liquid drop already at 900 K [23]. By depositing this Al drop on any given Al surface, we can learn about its wetting habit. We deposit it first on the Al(110) face, which is prone to melting [7]. At $T = 930$ K (below T_m , but above T_w), the drop spreads out completely within 100 ps [Figs. 3(a)–3(c)]. However, when deposited on the nonmelting Al(111) face it does not diffuse away, but rather settles down as expected with well-defined exterior and interior angles whose azimuthal average $\langle\theta\rangle$ we can extract. By increasing temperature across T_m , from 930 to 945 K, we find that $\langle\theta_{LV}\rangle$ changes from $(24 \pm 3)^\circ$ to $(21 \pm 1)^\circ$, and $\langle\theta_{SV}\rangle$ from $-\langle\theta_{LV}\rangle$ (the droplet is essentially crystallized) to $(44 \pm 6)^\circ$. By interpolation we extract $\theta_m = (22 \pm 3)^\circ$, in fairly good agreement with the predicted value $(18 \pm 2)^\circ$. The approximate values of ξ and of γ_{LV} (about 20% lower than its experimental value,

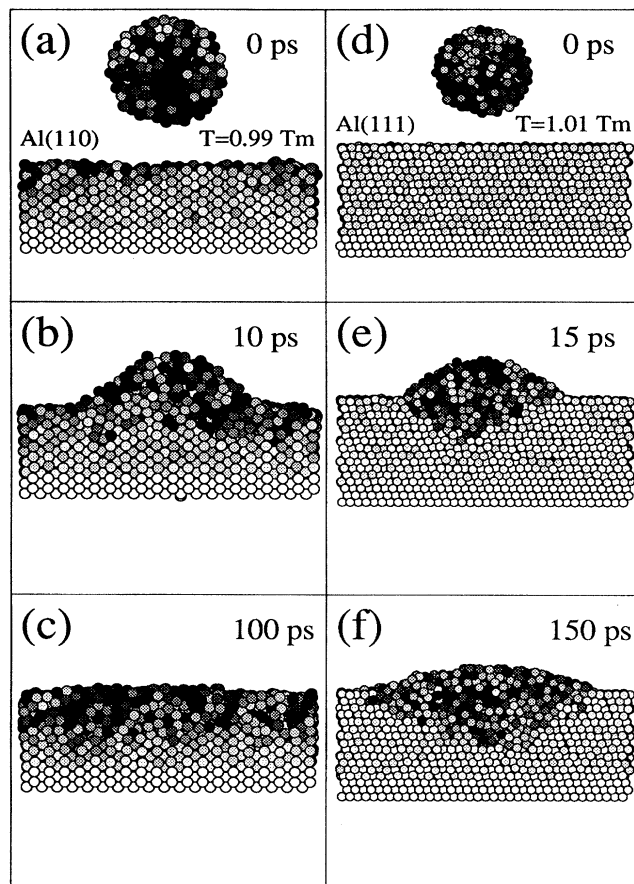


FIG. 3. Evolution of an 861-particle liquid drop of Al on a substrate of the same material. Left column: drop on a surface undergoing surface melting [Al(110) at $T = 0.99 T_m$]. (a) before contact; (b) after contact, the drop spreads readily; (c) the drop has been fully absorbed. Right column: drop on a nonmelting overheated surface [Al(111) at $T = 1.01 T_m$]. (d) before contact; (e) after contact: the drop settles, but does not spread; (f) final drop shape. Darkness of atoms is proportional to their square displacement in the run.

with our potential) constitute sources of error. Additional discrepancies are to be attributed to the macroscopic and phenomenological nature of the theory, which should, in principle, be improved to include fluctuations and finite-size effects. On the simulation side, one could consider in the future finite-size scaling as a possibility.

(iii) *Connection with experiments.*—We are not aware of measurements of θ_m , θ_c , or T_i on Al(111), for which we have thus a direct prediction. On Pb(111) van Pinxteren and Frenken [14] measured $\theta_c = (14.7 \pm 1.4)^\circ$, from where we are using Eq. (10), and for $\gamma_{SV} \approx 34$ meV \AA^{-2} we obtain $\Delta\gamma_\infty = 1.2 \pm 0.2$ meV \AA^{-2} . Furthermore, using $\rho = 0.033 \text{ \AA}^{-3}$, $L = 50$ meV/atom, and $\xi \approx 2.7 \text{ \AA}$ (averaging data from Ref. [24] as suggested in [14]), we obtain via Eq. (3) $T_i = T_m + (150 \pm 30)$ K. This is in rather good agreement with the experimental result,

$T_i^{\text{exp}} \approx T_m^{\text{exp}} + 120 \text{ K}$ [10]. From Eq. (6), using $\gamma_{LV} \approx 28 \text{ meV } \text{\AA}^{-2}$, we also predict $\theta_m = (16 \pm 1)^\circ$ for a droplet on Pb(111) at $T = T_m$. For Al(100), another nonmelting surface [25], we find by simulation $T_i = 1025 \pm 5 \text{ K}$, and assuming $\xi \approx 3 \text{ \AA}$ we predict $\theta_m \approx 15^\circ$ and $\theta_c \approx 13^\circ$. For Cd(0001), where $\theta_m = (37 \pm 1)^\circ$ [11], and using $\rho = 0.043 \text{ \AA}^{-3}$, $L = 64 \text{ meV/atom}$, $\gamma_{LV} = 40 \text{ meV } \text{\AA}^{-2}$, and again a guessed $\xi \approx 3 \text{ \AA}$, we get $T_i \approx T_m + 580 \text{ K}$, close to twice the melting temperature (594 K). Application of this scheme to Ge(111) or NaCl(111) appears instead problematic, due to the essential role of long-range forces in these cases. In fact, Ge(111) has a negative Hamaker constant, which is probably related to its nonmelting behavior [26], while long-range Coulomb forces are likely to be relevant to the nonmelting of NaCl(100). Finally, the present scheme is probably also inapplicable in its simplest form to surfaces such as Pb(100) or Au(100) which undergo *incomplete melting* [17,27–29].

In summary, we have described new results on the nonmelting crystal surfaces. A simple theory of nonmelting is given, which describes the metastable solid surface above T_m , up to a maximum overheating temperature T_i which acts as a spinodal point. This temperature is found to have a simple connection with the partial wetting angle of the surface by its own melt at $T \approx T_m$, and with the tilting angle of melted regions in vicinals undergoing nonmelting-induced faceting. Computer simulations on Al(111), as well as available data on Pb(111), are in good agreement with this theory.

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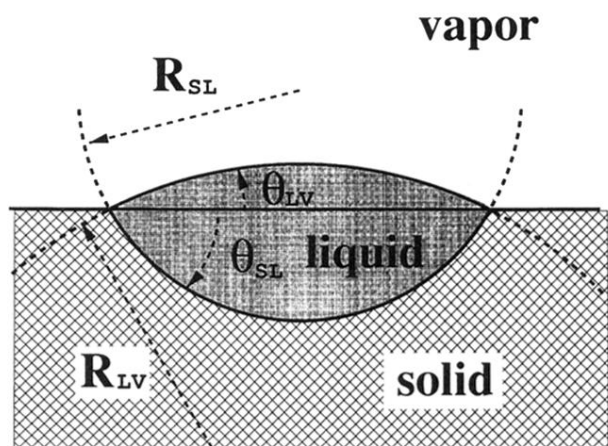


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