Surface-Melting-Induced Preroughening

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Preroughening (PR) of a crystal surface can be induced by the tendency of the surface to melt. We show this analytically in a generalized solid-on-solid model and numerically by simulating the surface as an interface in the 3D N-state lattice Potts model, which for large enough N is shown to exhibit PR, roughening, and surface melting. The onset of PR is linked to the appearance of liquidlike signatures in the surface layer, and can be either continuous or first order. We suggest that this physics provides the natural explanation of the first-order PR of rare-gas-solid (111) surfaces.

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The surface of a solid can go through different stages in the process of disordering from the perfectly flat, zero-temperature configuration up to the melting temperature of the bulk material. Two well-characterized phenomena are surface melting (SM), where a very thin layer of the liquid wets the solid-gas interface, and roughening, implying divergent fluctuations in the position, or height, of the otherwise solid surface. Of these, the latter is a 2D phase transition taking place at a well definite temperature T_R, while the former is not generally associated with an independent phase transition. Simply, the liquid film grows critically as the bulk (first-order) melting temperature is approached. Recently, preroughening (PR) [1] has been identified as an additional 2D phase transition that may occur at surfaces. It is signaled by an abrupt jump in the mean position of the surface which passes from an integer value in the low-temperature, flat phase to a half-integer value in the high-temperature, so-called disordered flat (DOF) phase. The transition is driven by the entropy gain associated with the appearance of a roughly half-occupied top surface layer.

Theoretically, PR has been mostly studied within the so-called solid-on-solid (SOS) models, and is predicted to be a nonuniversal continuous phase transition [1], or less commonly a first-order one [2]. In these models, the possibility that PR might appear at some T_{PR} $(<T_R)$ is tied to the presence of some kind of further-neighbor interactions, which do not discourage step proliferation, while preventing roughening through the stabilization of the flat surface at large distances. Experimentally, evidence of PR has been evinced somewhat indirectly, from the reentrant layering of Ar(111) and other rare-gas multilayers on graphite [3–5]. Calorimetric measurements and the "zippering" structure of the adsorption phase diagram [2] support a first-order rather than a continuous phase transition of the free surface at T_{PR}. First-order PR is expected theoretically when $T_{PR} < T_R/4$ [2], but this is far from satisfied in Ar(111), where $T_R = 80$ K [3]. A possible source of this discrepancy could be the proximity of T_{PR} (69 K) to the bulk melting temperature T_m (84 K) in Ar introducing a mutual influence of these two phenomena. There is, in fact, clear simulation evidence indicating that first-layer mobility [6] and local melting [7] set in on Ar(111) precisely around $(0.8–0.85)T_m$, strongly suggesting an interplay with reentrant layering [7], and with PR [8,9]. However, lattice models studied so far lack precisely the continuous degrees of freedom permitting a description of free volume and of melting, and a clear statistical-mechanical understanding of the mechanism causing this interplay is still lacking.

In this Letter we report on models which show how the entropy gain associated with the appearance of a liquid layer between the solid and the gas can induce PR of the surface. First, we introduce a very simplified model which is of qualitative value, and has the advantage of being equivalent to a well-studied phenomenological description of PR. Subsequently, a 3D Hamiltonian description of the surface as an interface in the N-state Potts model is presented. The Potts interface undergoes both roughening and SM for all $N > 2$. Moreover, for large enough N it exhibits PR as well. In this model PR is, indeed, accompanied by "melting" of the first layer, whose associated entropy gain is capable of driving it first order.

The usual SOS description of a surface is in terms of discrete (integer) local heights that are functions of the position on the surface plane. Energy depends upon height differences between nearest and also next-nearest neighbors. Depending on the relative strength of the two terms, PR might occur, thus stabilizing the DOF phase in some temperature range, or not. We here consider an SOS model with only first-neighbor interactions, which in the lack of other ingredients is known to possess just roughening. The possibility of SM is included through the insertion, at the solid-gas interface, of an intervening liquid film between the solid and the gas. Since we intend to model the physics of SM at and very close to PR, where SM is only incipient, we can restrict the liquid film to a monolayer thickness. This limitation does not

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allow the system to proceed towards complete melting, but it provides in return a very neat characterization of the interplay of PR and SM.

We show in Fig. 1 two typical configurations of our surface. Shaded regions represent small (one-layer thick) liquid drops at the surface. The specific free energies of the "dry" and the "wet" interfaces are denoted as $f_D(T)$ and $f_W(T)$, respectively. Only those surface defects that are shown in Fig. 1 are permitted, with corresponding energies ε_1 and ε_2 ($<\varepsilon_1$). For simplicity, the wet-wet step energy has been set equal to the dry-dry step energy. If we identify the dry interface position with its integer height, and further describe the position of the wet interface by the exact middle height of the liquid layer (this by no means implies that the density of the liquid layer is half of that of the solid), we can formally write the following Hamiltonian for the system:

$$H = \sum_{\langle i,j\rangle} g(h_i - h_j) - \frac{1}{2}(f_W - f_D)\sum_i \cos(2\pi h_i) - y_4 \sum_i \cos(4\pi h_i), \qquad (1)$$

where $y_4 \rightarrow +\infty$, thus pinning the "height" h_i to either integer or half-integer values, and $g(x)$ is $0, \varepsilon_2, \varepsilon_1, +\infty$ for $|x| = 0$, $1/2$, 1, and >1, respectively. A Hamiltonian of the form (1) [with finite y_4 and $g(x) \propto x^2$] is commonly used to describe PR [1,2], which takes place at the temperature where the coefficient of $\cos(2\pi h)$ vanishes. Therefore, the existence of PR in our model will crucially depend on whether a temperature T_{PR} exists where the dry and the wet interfaces interchange their stability. While we shall see below how this can happen in a concrete model, let us just assume this to be the case. If $f_W > f_D$ at any T, integer values of h are deeper free-energy minima than half-integer ones, and only roughening will occur. The situation changes if f_W becomes smaller than f_D (suppose this happens above a temperature $T_{PR} < T_R$). In that case, half-integer h values become the relevant minima for $T > T_{PR}$. Exactly at T_{PR} integer and half-integer h values become degenerate and the Hamiltonian is now equivalent to one describing just roughening. Here, however, the step height is $1/2$ instead of 1, and its energy is ε_2. The roughening temperature of that problem is $\gamma\varepsilon_2$ with some constant γ. So if $T_{PR} < \gamma\varepsilon_2$ the system is not rough at T_{PR}, the correlation length remains finite, and PR is first order. In this case PR is signaled by an abrupt jump in the amount of liquid at the interface. We find that this jump is tiny for $T_{PR} \simeq \gamma\varepsilon_2$, but grows close to one monolayer for $T_{PR} \rightarrow 0$. In this limit PR simply resembles first layer melting. On the other hand, if $T_{PR} > \gamma\varepsilon_2$, the system is rough exactly at T_{PR}, PR is continuous with diverging height correlations, and the amount of liquid is expected to grow continuously at the transition.

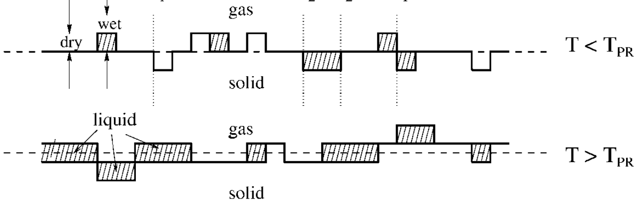

FIG. 1. Typical 1D configurations of the solid-gas interface in our model, below and above the PR temperature. Only two kinds ("wet" and "dry") of microscopic interface portions are considered. The energies ε_1 and ε_2 of the allowed defects at the surface are indicated. In both pictures, the dashed line signals the symmetry plane of the interface.

Having illustrated qualitatively how PR can be induced by SM, it remains to be shown that a microscopic model exists where the phenomenon is realized. In particular, the existence of two well defined wet and dry interfaces and the switch from the dry to the wet at some temperature T_{PR} are strong assumptions which need to be proven. This scenario is precisely realized by an interface in the N-state Potts model, for large enough N. Consider a variable $s_i = 1, 2, \ldots, N$ defined on the nodes of a 3D cubic lattice. An energy $-J$ ($J > 0$) is counted for any two equal spins on first-neighbor lattice sites. Periodic boundary conditions hold in the x and y directions, whereas the boundary condition on z interchanges states 1 and N. In this way, at zero temperature a (001) interface is created between one-half of the system in state 1 and the other in state N. These states are taken to represent the (ideal) solid and gas, respectively.

When $N = 2$ this is the Ising model, where a wall (our surface) undergoes roughening at $T \simeq 1.22J$ [10] (no SM, no PR). For $N > 2$ the bulk has three different phases, which represent the gas, the solid, and the liquid. The liquid corresponds to a phase where all the N states occur with equal probability, and thus its density is $(N - 1)/N$. The $N = 3$ case was studied in mean-field approximation by Jayanthi [11]. She found that, on approaching the triple point, a liquid layer grows at the solid-gas interface, describing SM. The growth is continuous as a function of temperature up to the bulk melting point. We reproduced this behavior in Monte Carlo simulations, and found a triple point temperature $T_m \simeq 1.82J$. We also found a roughening transition at $T_R = (1.17 \pm 0.03)J$ that is missed by the mean-field theory, where layers are assumed flat. There is, however, still no PR.

For $N > 3$, mean-field theory predicts a qualitatively different SM picture. At some temperature the minimum free-energy configuration of the system abruptly jumps from a state that is symmetric (upon interchanging states 1 and N) with respect to a plane located at an integer z, to another which is symmetric about a half-integer z. In Fig. 2 we report for $N = 20$ the two mean-field solutions that are equally stable at $T \simeq 0.93J$. These two states correspond to the dry and wet interfaces introduced earlier. If they survive beyond mean field, the change in the relative

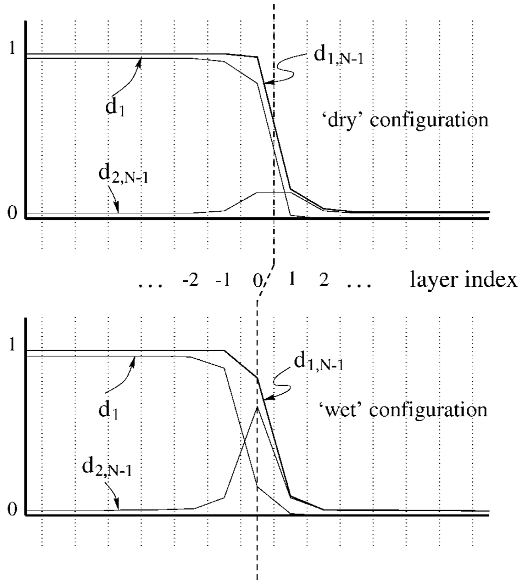

FIG. 2. Mean field density profiles for the 20-state Potts model across the solid-gas interface. The two configurations shown are of equal stability at $T \simeq 0.93J$ (they represent the competing dry and wet interfaces). d_1 is the density of state 1, $d_{2,N-1}$ is the overall density of states from 2 to $N - 1$, and $d_{1,N-1} = d_1 + d_{2,N-1}$. In both pictures the symmetry plane of the "symmetric density" $d_1 + \frac{1}{2}d_{2,N-1}$ is indicated by the dashed line.

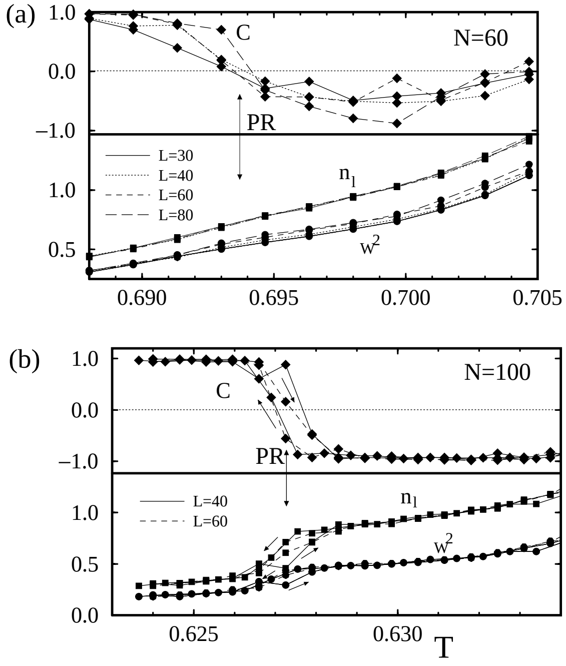

FIG. 3. Monte Carlo results for the Potts model in a slab of $L \times L \times 8$ sites. Values of the squared interface thickness W^2, the amount of liquid n_l, and the mean position of the interface [as expressed through the value of $C = \cos(2\pi\overline{h})$] are shown. (a) Continuous PR for $N = 60$. (b) First-order PR for $N = 100$ (heating and cooling paths are shown separately).

stability of the two will drive a PR transition. Note, however, that the liquid layer in the Potts model can now thicken as temperature rises, so we must check whether SM or roughening might possibly preempt PR, and cancel it.

We performed Monte Carlo simulations for lateral sizes up to 80×80 sites, and found that when $N \lesssim 50$ there is no PR, only a roughening transition very close to T_m (which in turn drops as N rises). For $N \gtrsim 50$ we unambiguously detected, prior to roughening and melting, a PR transition. It is continuous for $N \lesssim 80$, but it becomes first order for larger N. As an example, we show in Fig. 3 the results for $N = 60$ and 100. For increasing sizes, we plot the mean value of $C \equiv \cos(2\pi\overline{h})$ along the simulation, where $\overline{h}$ is the mean position of the interface defined [10] in terms of the "symmetric" density $\rho^{\text{sym}}(z) \equiv d_1(z) + \frac{1}{2}\sum_{n=2}^{N-1} d_n(z)$, where $d_n(z)$ is the fraction of sites in layer z with $s_i = n$. As in the simplified model of Eq. (1), this definition, assigning to a liquid layer a conventional value of h in the exact middle of the layer, allows a more precise, symmetry based, characterization of the transition, since in the thermodynamic limit C is exactly 1 (-1) in the flat (DOF) phase, and is 0 in the rough phase. We note, however, that the physical density is given instead by the same formula without the $1/2$ factor. In Fig. 3 the fluctuations of $\overline{h}$ are also plotted (expressed through $W^2 \equiv \langle\overline{h}^2\rangle - \langle\overline{h}\rangle^2$), as well as $n_l \equiv \sum_z \sum_{n=2}^{N-1} d_n(z)$, which is an indicator of the amount of liquid present at the interface.

For $N = 60$, PR is found at $T_{PR} = (0.694 \pm 0.002)J$ $(= 0.979T_m)$, where C switches sign from positive to negative. At this temperature W^2 shows a weak but monotonic increase as a function of size, whereas it saturates to a finite value both above and below T_{PR}. This is an indication of continuous, critical PR. On the contrary, for $N = 100$, W^2 shows no size dependence at $T_{PR} = (0.627 \pm 0.002)J$ $(= 0.984T_m)$, where it simply jumps, as does n_l. Moreover, hysteresis is found upon heating and cooling across the transition. Both are evidence of a first-order PR. At temperatures just above T_{PR}, there is a rapid increase of the liquid-layer thickness (as measured by n_l), typical of SM, foreshadowing a divergence on approaching bulk melting [$T_m = (0.709 \pm 0.001)J$ for $N = 60$ and $T_m = (0.637 \pm 0.001)J$ for $N = 100$]. There is also a size-dependent growth of W^2, signaling surface roughening. We cannot easily extract numerically T_R as distinguished from T_m, as the two temperatures appear to fall very close, but we expect quite generally T_R to be lower than T_m, since liquid surfaces are rough.

Our finding of a first-order PR in the $N = 100$ Potts model, taking place at a not much lower temperature than roughening and melting, is novel and gratifying, since it definitely resembles the phenomenology of the (111) surface of rare-gas solids. The entropy gain at PR brought about by the new degrees of freedom appears to effectively mimic the large configurational entropy of the true liquid. However, the large values of N necessary to get first-order PR ($N \gtrsim 80$) correspond to an entropy gain of roughly $4k_B$, which is far larger than what occurs in reality. This may be an indication that in real systems effective further-neighbor interactions are a stabilizing factor of flat surfaces, allowing first-order PR to occur for lower values of the entropy of melting. By properly extending the range of interactions in the Potts model, we have obtained first order PR at much lower values of N. In one simulation, we took third-neighbor interactions to be present, in such a way that an effective on-site parallel step repulsion is induced, thus stabilizing the DOF phase [12]. We took this interaction to be $-J_3 < 0$ for equal spins, $-J_3/2$ if the spins are different and at least one is in a "liquid" state (i.e., s_i in the range from 2 to $N - 1$), and zero otherwise. This choice was made in order to keep the PR temperature nearly constant. With this additional term, we have obtained, for $J_3 = J$, continuous PR for N as low as 8, and first-order PR starting from $N \simeq 20$ (where bulk melting entropy is $\simeq 2.7k_B$). For $N = 25$, we obtained $T_{PR} \simeq 0.89J$, $T_m \simeq 1.49J$, and a n_l jump at PR of $\delta n_l \simeq 0.1$.

The PR transition in the Potts model represents a symmetry change, very much as it does in the SOS models. In the Potts model, however, PR is accompanied by an N-dependent, nonuniversal jump of the surface height. Since the physical density ρ is given by $\rho = \rho^{\mathrm{sym}} + \frac{1}{2}n_l$, we can readily calculate predictions for the height jump at PR. We find that if PR is continuous the interface position has a jump across PR of exactly half a layer, again as in SOS models [12], but in this case not strictly between integer and half-integer values. When PR is first order, the jump is instead $1/2 - 1/2\delta n_l$. Since δn_l itself varies from ~ 1 when $T_{PR} \rightarrow 0$ to 0 when PR is nearly continuous (i.e., close to the tricritical point), the interface-height jump at PR can vary from ~ 0 in the strong first-order case, to half a layer in the tricritical case. Experimental [5] and simulation [9] suggestions of a height jump not far from half a layer could therefore signify that PR of Ar(111) is only weakly first order.

The models we have studied have a solid-vapor symmetry that allowed us to study the PR transition as a change of the symmetry plane of the interface from integer to half-integer values. In turn, this has permitted a clearer numerical study since, for instance, the jump of C from 1 to -1 at PR occurs only in models that have that symmetry. In real surfaces, symmetry-breaking terms would turn a continuous PR transition into a crossover, rounding all the features in this case. However, if these terms are small, first-order PR survives and can be observed experimentally.

It is interesting, in closing, to mention the possibility of SM-induced PR on surfaces other than rare gases. A semiconductor surface, such as Ge(111), undergoes an abrupt disordering transition at $0.86T_m$, which has been interpreted as the sharp onset of (incomplete) SM [13]. First principles simulations [14] indicated that this disordering should be accompanied by a distinct redistribution of atom population, so that the total first-layer population is reduced by as much as 50% relative to that of the second. That seems a likely scenario of SM-induced first-order PR. In metals, the incomplete melting of fcc(100) faces, such as those observed [15] and simulated [16] on Au(100) and on Pb(100) [17], provides good candidates for SM-induced PR, deserving further investigation, possibly by means of x-ray scattering, under growth conditions.

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