Phase transitions at the early stages of surface melting

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Abstract

We show that the early stage of surface melting can be associated with a well defined phase transition, of the pre-roughening type. The problem is modeled by simulating the surface as an interface in the three-dimensional large N-state lattice Potts model, which is shown to exhibit pre-roughening, roughening, and a lattice version of surface melting. The lowest transition is pre-roughening, but it is in fact linked to the appearance of liquid-like signatures in the first surface layer, and thus represents the phase transition where surface melting starts. We suggest that this physics is realized on rare-gas-solid (111) surfaces and possibly also on other semiconductor and metal surfaces. © 2000 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Surface melting (SM) is the phenomenon by which, close to the bulk melting temperature T_m of a solid, the equilibrium solid–vapor interface becomes wetted by a thin liquid film, whose thickness grows critically as the triple point is approached. The initial stages of SM have been simulated many times, but never really been well characterized from a statistical mechanics viewpoint. There is no well defined model showing, for example, whether the onset of massive diffusivity on the solid surface should always be a gradual crossover as temperature increases, or whether it could instead be a sharp phase transition, at least in some case.

In a different context, there is evidence, on rare gas solid surfaces, of a sharp phase transition-like phenomenon, namely re-entrant layering, which occurs in multilayer adsorbtion on a substrate [1–4]. What is found is that the adsorbtion isotherms display the usual layering steps for increasing chemical potential (as expected for a flat rare gas surface), up to some temperature T_{PR} (~ 0.83 T_m). Here, the steps temporarily disappear, only to reappear slightly above T_{PR} displaced by an amount of approximately half a layer relative to the low-temperature side. Calorimetric measurements have suggested that this phenomenon must be associated to a first order transition that occurs in the free standing film.

The phenomenon has been theoretically interpreted in terms of a pre-roughening (PR) transition [5–10]. This kind of phase transition is signaled by an abrupt jump in the mean position of the surface measured along the normal (also referred to as coverage) which passes from an integer value in the low-temperature, flat phase to a half-integer

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value in the high-temperature, so-called disordered flat (DOF) phase. In the original models [5,6] PR is driven by the meandering entropy gain associated with the appearance of a correlated step network in the roughly half-covered surface above T_{PR}, over that of the step-free ordered fully-covered surface below T_{PR}. In these models (mainly of SOS type), PR is further tied to the presence of some kind of further-neighbor height–height interaction, particularly one that does not discourage step proliferation, while preventing roughening through the stabilization of the flat surface at large distances. Moreover, for Ar(111) the PR scenario predicts a non-universal *continuous* phase transition [5,6], contrary to the apparent first order seen experimentally.

It seems plausible that a source for this discrepancy could be the onset of surface mobility and premelting, as suggested by the proximity of T_{PR} (69 K) to T_m (84 K), and by Lennard–Jones simulation evidence indicating that first-layer diffusivity [11–13] and local melting [14–16] set in on Ar(111) ca. 0.8–$0.85 T_m$, strongly suggesting some interplay with reentrant layering [14–16], and with PR [17].

We have studied, as a simple three-dimensional lattice model for the surface, an interface in the three-dimensional N-state lattice Potts model, and found that the entropy gain associated with the appearance of a 'liquid layer' between the solid and the gas is associated with the PR of the surface. The coverage and the symmetry jump associated with PR transform the otherwise gradual onset of surface disorder into a sharp phase transition. The entropy gain associated with top layer melting, on the other hand, appears precisely to be the factor which lowers the PR temperature, turning it, at least in the rare gas surfaces, first order.

2. Model and results for $N=2$ and $N=3$

We consider a variable $s_i = 1, 2, \ldots, N$ defined on the nodes of a three-dimensional 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 sharp (001) interface is created between one half of the system in state 1 and the other in state N. These two states are taken to represent the (ideal) solid and the gas, respectively.

When $N=2$ we recover the Ising model, where a wall (our surface) undergoes just roughening at $T=1.22J$ [18] (no SM, no PR). For $N>2$ the bulk Potts model has three different phases, which may now represent the gas, 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 the mean field approximation by Jayanthi [19], who found that, on approaching the triple point, a liquid layer grows at the solid-gas interface, providing an idealized lattice description of SM. The liquid thickness is continuous as a function of temperature. We reproduced this behavior by Monte Carlo simulations, and found a triple point temperature $T_m = 1.82J$. We also found a roughening transition at $T_R = 1.17 \pm 0.03J$, present for $N=3$, but missed by the mean-field theory, where the layers were assumed flat. However there was still no PR, and the onset of SM is gradual and uneventful.

3. Larger values of N and preroughening

For $N>3$, mean-field theory predicts a qualitatively different picture. At some temperature T^*, 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. If this effect survives beyond mean field, the change in the relative stability of these two states will drive a transition, which can be seen as a combination of PR and first layer melting. Note, however, that the liquid layer in the Potts model can become rough as temperature rises, so we must check whether roughening might possibly pre-empt PR, and cancel it.

We performed numerical Monte Carlo simulations for sizes up to $80 \times 80 \times 8$ sites, and found that when $N < 50$ there is no PR, only a roughening

transition very close to T_m. For $N > 50$ we unambiguously detected, prior to roughening and melting, a PR transition. It is continuous for $N < 80$, but it becomes first-order for larger N. As an example, we show in Fig. 1 the results for $N = 60$ and $N = 100$. For increasing sizes, we plot the mean value of $C \equiv \cos(2\pi\bar{h})$ along the simulation, where $\bar{h}$ is the mean position of the interface defined [18] in terms of the 'symmetric' density $\rho^{sym}(z) \equiv d_1(z) + \frac{1}{2}\sum_{n=2}^{N-1} d_n(z)$, where $d_n(z)$ is the fraction of sites in layer z with $s_i = n$. This definition, assigning 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, whereas it vanishes 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. 1 the fluctuations of $\bar{h}$ are also plotted (expressed through $W^2 \equiv \langle \bar{h}^2 \rangle - \langle \bar{h} \rangle^2$), 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.

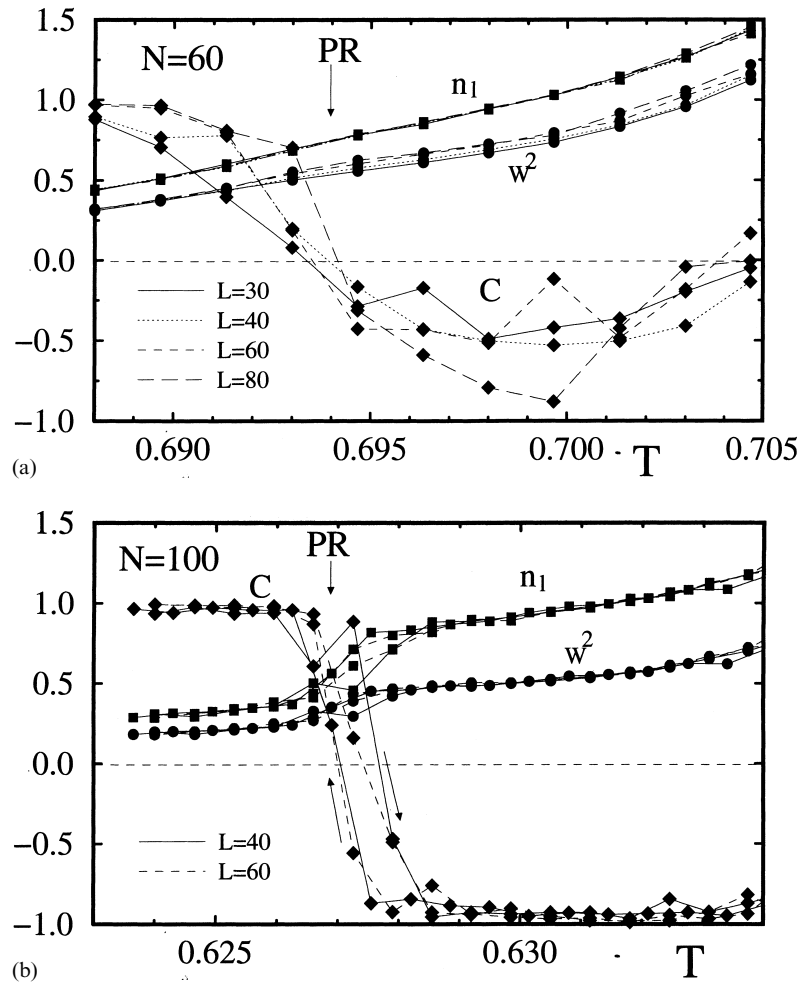For $N = 60$, PR was found at $T_{PR} = 0.694 \pm$

Fig. 1. Monte Carlo results for the 60- and 100-state 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 $C = \cos(2\pi\bar{h})$] are shown. PR is continuous for $N = 60$ and first-order for $N = 100$ (for the latter, heating and cooling paths are shown separately).
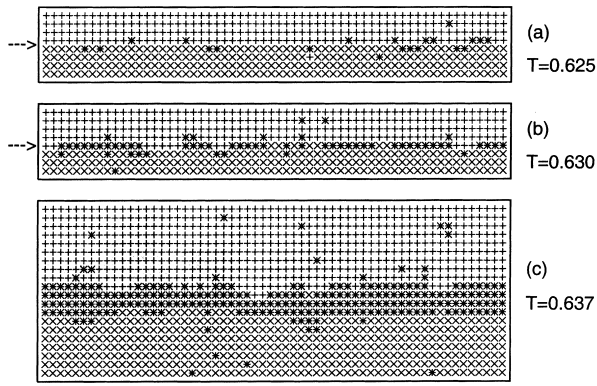
Fig. 2. Snapshots of the configurations of the spins for a slice of system perpendicular to the interface, for $N=100$, in the flat (a), DOF(b), and (presumably) rough phase, very close to bulk melting (c). System size is $60 \times 60 \times 8$ in (a) and (b), and $60 \times 60 \times 20$ in (c). $+$ and $\times$ represent the 'gas' and 'solid' states, whereas $*$ represent any other ('liquid') configurations of the spins. In (a) and (b) the (average) symmetry plane of the interface is indicated by the arrows.

$0.002 \ (=0.979 T_m)$, 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 — for the largest sizes — 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 $T_{PR}=0.627 \pm 0.002 \ (=0.984 T_m)$, where it simply jumps, as does n_l. Moreover, hysteresis is found upon heating and cooling across the transition. Both are evidences 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 ($T_m=0.709 \pm 0.001$ for $N=60$ and $T_m=0.637 \pm 0.001$ 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. We know quite generally that SM at T_m implies roughening at some $T_R < T_m$. This is because liquid surfaces are rough, and the step free energy of the melt-covered solid surface drops very fast for increasing melt thickness [20] In Fig. 2 we show for the $N=100$ case, typical snapshots of the states of spins at the interface, below and above the PR

transition, and very close to bulk melting. Note the change in the symmetry plane of the interface across the PR transition.

4. Discussion and conclusions

Our finding in the $N=100$ Potts model of a first-order SM-induced PR taking place at a temperature just below those of roughening and of melting definitely resembles the phenomenology of the (111) surface of rare-gas solids. The PR transition from the ordered flat to the DOF surface still represents a symmetry jump, very much as it did in the SOS models, but here it is accompanied by a non-universal jump of the surface height (and therefore, also of the amount of liquid present at the surface). Since the physical density ρ is given by $\rho = \rho^{sym} + \frac{1}{2} n_l$, we can readily calculate predictions for the height jump at PR. We find that in the continuous case, the interface position has a jump of exactly half a layer, as in SOS models [10], but unlike there, not strictly between integer and half-integer values. When it is first-order, the jump is instead $1/2 - 1/2 \, \delta n_l$, where δn_l is the jump in n_l, and goes from ~ 0 in the strong first-order case, to half a layer at the tricritical point. Experimental [4] and simulation suggestions of a height jump not far from half a layer could therefore signify that SM-induced PR of Ar(111) is only weakly first-order.

The large number (>80) of Potts states in the model appears to require an entropy jump at bulk 'melting' of 3–4 k_B atom^{-1} which is too large, effectively exceeding by at least a factor 2 the configurational entropy of melting (ca. 1.7 k_B atom^{-1}) of the true rare gas. It seems plausible that next nearest neighbors interaction, producing an effective step–step repulsion [10], may still be a stabilizing factor of flat phases in real surfaces. In fact, preliminary numerical results show that these terms are certainly capable of producing first order PR at values of N compatible with the known entropy of melting of rare gases [21] It is also expected that the features of the layering phase diagram (when growing a film in the presence of a substrate potential) are qualitatively reproduced by our model as well.

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 [22]. First principles simulations [23] 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 [24] and simulated [25] on Au(100) and on Pb(100) [26,27] are good candidates, deserving further investigation, possibly by means of X-ray scattering, under growth conditions. A more detailed report of the present work will appear elsewhere [21].

Acknowledgements

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