Preroughening, Diffusion, and Growth of a fcc(111) Surface

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Preroughening of close-packed fcc(111) surfaces, found in rare gas solids, is an interesting but poorly characterized phase transition. We introduce a restricted solid-on-solid model, which describes it. Using mostly Monte Carlo, we study both statics, including critical behavior and scattering properties, and dynamics, including surface diffusion and growth. In antiphase scattering, it is shown that preroughening will generally show up at most as a dip. Surface growth is predicted to be continuous at preroughening, where surface self-diffusion should also drop. The physical mechanism leading to preroughening on rare gas surfaces is analyzed and identified in the step-step elastic repulsion.

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Thermal disordering in the height profile of a crystal surface will generally occur in two steps, as first shown by den Nijs. Using modified solid-on-solid (SOS) models [1,2], he found that regular roughening (temperature T_R) is preceded at some $T_c < T_R$ by a critical, preroughening (PR) transition. The intermediate disordered flat (DOF) phase presents a very special form of surface disorder with proliferation of up-down correlated steps, which causes the first layer to be only half occupied. Based on the concept that PR is driven by latent tendencies towards reconstruction [1,3], attempts at detecting PR focused mostly on metal surfaces, with uncertain results [4,5]. Surprisingly, the first convincing evidence of PR in unreconstructed surfaces came instead from rare gases [6,7]. The (111) faces of Ar, Kr, and Xe exhibit reentrant layering in adsorption isotherms above $T_c \approx 0.85T_m$ and below $T_R \approx 0.95T_m$ (T_m being the melting temperature), with a half-filled top layer between T_c and T_R. This is a clear indication of PR [8], and a simple hexagonal model can, in fact, be constructed which contains PR with good similarities with the experiment [9].

However, the driving force for PR on Ar(111) is certainly not reconstruction and remains to be understood. Moreover, the fcc(111) surface, with its three sublattices, has a richer content of degeneracy and symmetry than simple hexagonal, which needs to be addressed. At this stage, in fact, PR of fcc(111) surfaces is not well characterized at all. We need, in particular, to understand scattering-related quantities, such as order parameters and susceptibilities, as well as important dynamic properties like surface diffusion and growth. This need is made more urgent by the strong possibility that PR (and not roughening) might more generally constitute the true onset of surface melting, as will be suggested by our surface diffusion results.

We have constructed a restricted SOS model of fcc(111), which yields well-defined answers to these questions. We consider three triangular sublattices $l = 0, 1, 2$ with $ABCABC\cdots$ stacking. Heights in the lth sublattice are defined as integers $h_i = 3n_i + l$, $\forall n_i$. Nearest-neighbor height differences are constrained to be $\pm 1, \pm 2$ ("infinite" bond strength). A positive energy is associated with height differences departing from the value attained in the perfectly ordered fcc(111) surface (the ground state of the model). The Hamiltonian is

$$H = J\sum_{\langle 2\rangle}\delta(|h_i - h_j| - 3) + K\sum_{\langle 3\rangle}\delta(|h_i - h_j| - 4) + L\sum_{\langle 4\rangle}\delta(|h_i - h_j| - 4) + M\sum_{\langle 4\rangle}\delta(|h_i - h_j| - 5)\cdots, \quad (1)$$

where $\sum_{\langle n\rangle}$ is shorthand for a sum over all pairs of nth neighbors (distance measured in plane), and the couplings $J, K, L, M, \ldots$ are positive energy parameters. We call this the FCSOS model (Fig. 1). Anticipating the results,

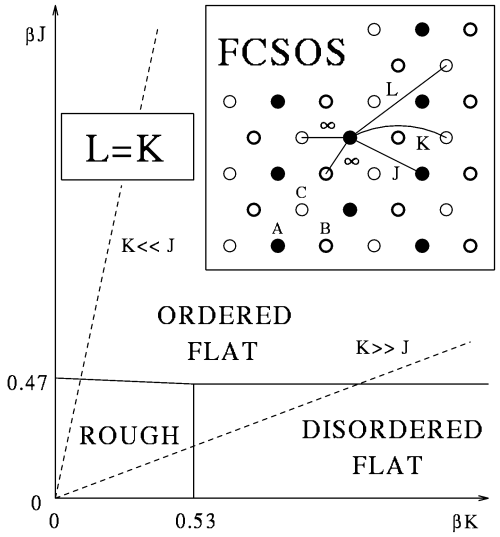

FIG. 1. Phase diagram of the FCSOS model (inset) for $L = K$. Thermal behavior of Ar(111) corresponds qualitatively to the line $K \gg J$.

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the minimal requirement in order to get a stable DOF phase into the model is to have at least nonzero K *and* L. Longer range interactions, including M and beyond, do not bring further changes. In this sense the FCSOS with $L \neq 0$ is generic.

We work out the essential features of the FCSOS phase diagram by the strip transfer-matrix method. Height parities $(-1)^{h_i}$ are chosen to represent the SOS configurations of a $N \times \infty$ strip [10]. The fairly long-range interaction L obliges to compute all possible states of *three* spin rows. Our maximum strip size is $N = 12$. We locate phase boundaries through the vanishing of the free energy of relevant interfaces [1]. Strictly *at* PR, we find that *all* off-plane excitations are costless. The step free energy vanishes at PR and remains zero inside the DOF phase (due to proliferation of steps), whereas the cost of two parallel steps is nonzero until roughening. Within the transfer matrix framework these quantities are evaluated by imposing suitable boundary conditions to the strip. Details of the calculation are reported elsewhere [11].

We list a number of results (all the couplings from M onward are put equal to zero). When the only nonzero coupling in the model is J, there is no PR and a simple roughening is found at $e^{\beta J} \simeq 1.6$. The situation remains unchanged when $K > 0$ but $L = 0$. In particular, roughening takes place at $e^{\beta J} \simeq 1.5$, when $K = +\infty$. Finally, a PR transition is found along the $K = L = +\infty$ line at $e^{\beta J} \simeq 1.5$. When $L = K$ and $J = 0$ the boundary between the DOF and the rough phase is found at $e^{\beta K} \approx 2$. The overall phase diagram is sketched in Fig. 1. It resembles that of Ref. [1] and is, in fact, more general (for positive couplings) as far as the nature of the phases it includes.

Monte Carlo (MC) simulations confirm the above findings. We use $N \times N$ cells of increasing size, ranging from $N = 24$ to 96, and a standard Metropolis algorithm. After equilibration, more than 2×10^6 MC sweeps are produced and average quantities such as the interfacial width $\langle \delta h^2 \rangle$, specific heat, and parity order parameter, $P = (3/N^2)\langle \sum_i (-1)^{h_i} \rangle$, are evaluated. In an ideal DOF configuration the average height is half integer, $\delta h^2 = 11/12$ due to half occupancy in the topmost layer, P should be zero, and its susceptibility χ_P should diverge at PR.

As Fig. 2 shows, on the $K = L = +\infty$ line, P indeed vanishes near $e^{\beta J} = 1.5$ and χ_P diverges. In the DOF phase, the average height is half integer (Fig. 3), and, correspondingly, the occupancy of the top layer is one-half. Moreover, both the specific heat and its derivative (not shown) remain finite at T_c, thus signaling a higher-order transition than Ising or three-state Potts. The ordered phase and the DOF phase have *the same degeneracy* (here threefold). As a consequence, PR is expected to be nonuniversal [1] unlike Ising or three-state Potts, where the degeneracy is fully removed above T_c.

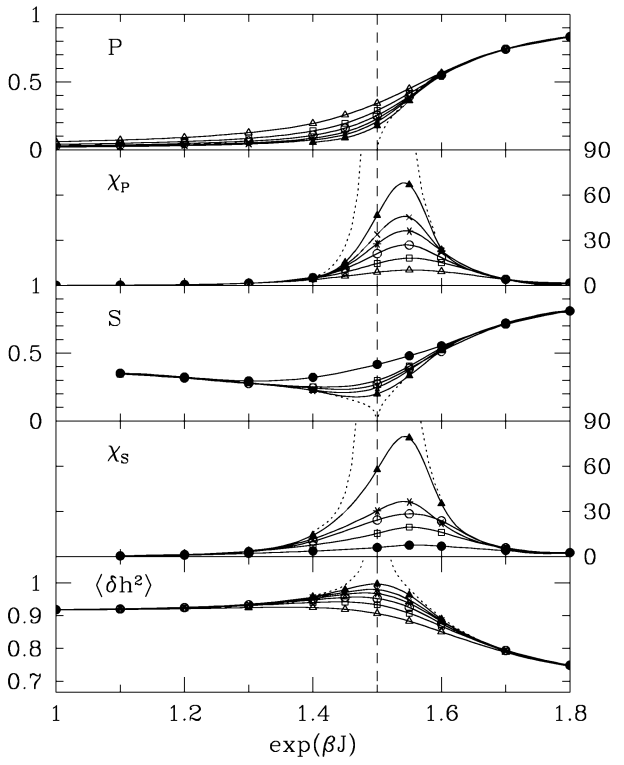

FIG. 2. Preroughening critical behavior of the FCSOS model obtained by Monte Carlo along the line $K = L = +\infty$. From top to bottom: parity order parameter P, susceptibility χ_P, Bragg scattering amplitude S, susceptibility χ_S, and interface width $\langle \delta h^2 \rangle = (1/N^2)\langle \sum_i (h_i - \bar{h})^2 \rangle$. Data for $N = 18$ (•), 24 (△), 36 (□), 48 (∘), 60 (∗), 72 (×), and 96 (▲) are shown. Dotted lines are guides to the eye.

Since the free energy of all step excitations is zero at PR, one expects the height fluctuations to diverge at T_c, $\langle \delta h^2 \rangle \sim 1/4\pi K_c \ln N$, but *not below or above* (until T_R). The MC results in Fig. 2 support this. Because of the Gaussian behavior at T_c, critical exponents along the PR line can be recovered in terms of one parameter only, namely, K_c [1,8]. At $K = L = +\infty$ and $e^{\beta J} = 1.5$ we estimate $K_c \approx 1.06$, whence $\eta = \pi/4K_c \approx 0.74$, $\nu = 2K_c/(4K_c - \pi) \approx 1.92$, $\alpha = 2 - 2\nu \approx -1.85$, $\beta = (\pi/4)/(4K_c - \pi) \approx 0.71$, and $\gamma = 2 - \alpha - 2\beta \approx 2.42$. At finite L and K, the PR line is nearly insensitive to L/K, while roughening (where $\langle \delta h^2 \rangle \sim \pi^{-2} \ln N$) shifts to higher βK as L/K drops. Hence the PR temperature is only controlled by the J value, which is then about 0.25 for argon ($T_c \approx 70$ K) [6], in units of the Lennard-Jones ϵ (120 K for Ar).

PR can be revealed in scattering experiments [1–3,12]. Antiphase elastic x-ray or atom scattering is given by

$$I\left(\mathbf{Q}, q_z = \frac{\pi}{a_z}\right) \propto S^2 \delta_{\mathbf{Q},\mathbf{G}} + \frac{k_B T}{N^2} \chi_S(\mathbf{Q}), \qquad (2)$$

where a_z is the vertical layer separation, and $\mathbf{Q}$ and q_z are the surface parallel and perpendicular momentum

transfer, respectively. Here $S = (3/N^2)\langle \sum_i \alpha_i (-1)^{h_i} \rangle$ contains a shadowing factor α_i [3], which may be taken, for example, to be 1 for local surface maxima and zero otherwise, and $\chi_S(\mathbf{Q})$ is the local susceptibility. We find (Fig. 2) that the Bragg amplitude S^2 has a dip and vanishes at PR. However, unlike P, it is nonzero on both sides of the transition point (Fig. 2). This experimental signature can be used to detect PR on surfaces, including metals.

Surface dynamics near PR is so far unexplored. We consider first surface growth. Continuous growth in the DOF phase is unlikely, since the free energy of two parallel steps is nonzero. This implies the existence of a free energy barrier for the formation of a stable growth nucleus, and a behavior $m \propto e^{-C/\Delta\mu}$ for the growth mobility, where $\Delta\mu$ is the overpressure (smaller than a threshold $\Delta\mu_c$) and C is proportional to the square of the cost of two parallel steps. At finite size, we can also learn indirectly about the surface mobility $m(N)$ from the behavior of the average surface height $\bar{h}(t)$ at equilibrium. The surface *as a whole* diffuses in the form $\langle [\bar{h}(t) - \bar{h}(0)]^2 \rangle \sim 2d(N)t$, with Einstein-like proportionality between $d(N)$ and $N^{-2}m(N)$. Figure 3 shows both the equilibrium evolution of $\bar{h}$ (left) and the growth behavior at finite $\Delta\mu$ (right). At equilibrium the surface behaves like a Stokes particle undergoing Brownian motion. The height is quantized, and is integer below T_c and half integer above T_c. At PR quantization disappears, and $d(N)$ is clearly much larger. This behavior is fully confirmed when $\Delta\mu > 0$. In both flat and DOF phases, growth is activated and occurs between quantized levels. At T_c the surface is rough, and m soars accordingly, indicating continuous growth.

The next dynamical issue is single-particle surface diffusion near the PR transition. On account of the critical slowing down affecting dynamical processes at a continuous transition, and of a finite coupling of a migrating particle to the DOF order parameter, we should expect a drop of the diffusion coefficient at PR [13]. Dynamic scaling hypothesis combined with the assumption of Gaussian spreading of density inhomogeneities out of criticality predicts that diffusion should vanish as $D \sim |t|^{\gamma(z-2)/(2-\eta)}$, where z is a dynamical critical exponent and $t = (T - T_c)/T_c \ll 1$. In the case of PR, the rugged landscape is expected to concur substantially to hinder particle hopping. The tracer diffusion $D = \langle \Delta r^2 \rangle / 4t$ is extracted from a particle-conserving (Kawasaki) MC simulation and displayed in Fig. 4. The size dependence is maximum near T_c, indicating a drop in the thermodynamic limit, as expected. A similar drop is found when approaching roughening from the DOF side (not shown).

We are now ready to make contact with real fcc(111) surfaces, such as Ar(111). Modeling Ar by a Lennard-Jones 12-6 potential ($\sigma = r_{\mathrm{NN}}/1.0933$, $\epsilon = 120$ K, cutoff at $r = 3.2\sigma$), we consider a variety of step geometries, and use simulated annealing to optimize the $T = 0$ geometry and energy. For both (100) and (111) single steps we find an energy (units of ϵ) $\simeq 0.58$ per unit length. This J value is about twice as large as that required for a PR transition at 70 K. This is not surprising at all, in view of the additional vibrational and free-volume reduction factors which must be applied to $T = 0$ step energies before using them near T_m. We further find that two adjacent steps cost 1.14 (at the shortest distance) if up-down, and 1.49, 1.35, 122, . . .,

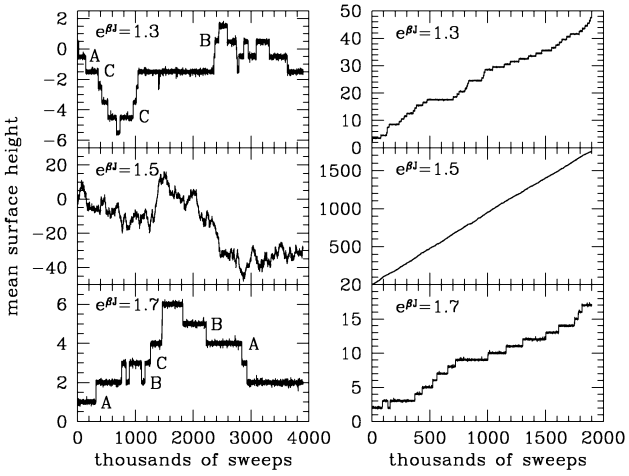

FIG. 3. Average surface height $\bar{h}$ during a MC run, for $N = 36$, at three different temperatures along the $K = L = +\infty$ line. Left: equilibrium ($\Delta\mu = 0$). Right: growth ($\Delta\mu = 0.0333$). From top to bottom, $e^{\beta J} = 1.3$ (DOF phase), 1.5 (PR), and 1.7 (ordered flat phase). Note the continuous growth at PR and the half-integer quantization in the DOF phase. Labels A, B, and C describe the top layer (half layer in DOF) sublattice.

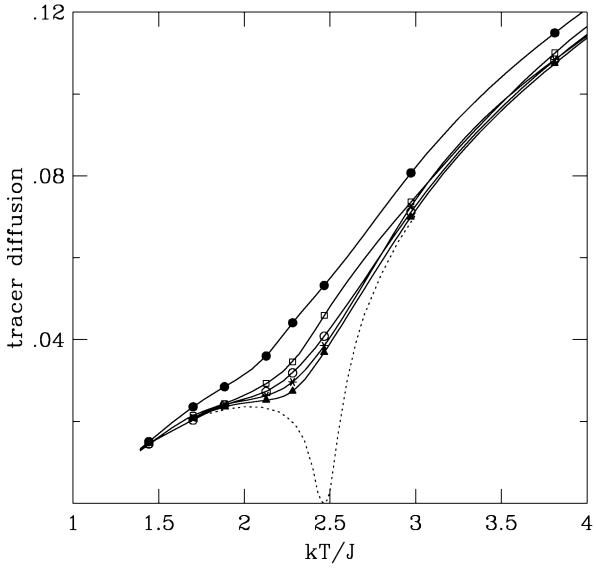

FIG. 4. Single-particle surface diffusion in FCSOS ($K = L = +\infty$). Data for $N = 18$ (•), 36 (□), 48 (∘), 60 (∗), and 96 (▲) are shown. Note the strong decrease with increasing size, suggesting a dip at PR. The dotted line is a guide to the eye.

$2 \times 0.58 + \alpha/(l - l_0)^2$ $(\alpha/r_{\mathrm{NN}}^2 \approx 1.0, l_0 \approx -0.5)$, if up-up at distances $1/2, 1, 2, \ldots, l$ lattice spacings, respectively. The lack of up-down interaction in FCSOS is thus justified. The relatively short-range up-up repulsion needs to be qualified. To do this we determine effective FCSOS K and L values (we take for simplicity $K = L$) so as to generate a probability distribution for the relative distance of two parallel steps which is closest to that generated by the true long-range repulsion, using a method similar to Bartelt, Einstein, and Williams [14]. For instance, when two parallel steps are, on average, $4, 4.5, 5$ lattice spacings apart, the long-range interaction $\alpha/(l - l_0)^2$ enhances K and L from bare values of ≈ 0.62 and ≈ 0.16, up to larger effective values $K = L = 2.0, 14.5, > 10^4$, respectively. With reference to Fig. 1, we conclude that long-range elastic up-up step repulsion is crucial in giving rise to PR. This has a very transparent physical interpretation. Without step-step interactions ($K = L = 0$), PR and roughening initially coincide. Parallel-step repulsion leaves PR unaffected, but not roughening which is pushed at higher temperature.

Now some experimental consequences. The reentrant behavior seen in rare-gas absorption isotherms, with half-filled layers above PR, agrees very well with our growth results (Fig. 3). Continuous growth strictly at T_c is found, a remarkable feature of this system. We, moreover, find that antiphase scattering, if feasible, should show the critical drop at T_c predicted for S^2, followed by a recovery in the DOF phase, as in Fig. 2. This finite value of S^2 is generic, so long as the shadowing factor $\alpha_i \neq 1$. Tracer diffusion along the surface, if measurable on a time scale short enough with respect to evaporation events, should also show a dip at T_c, providing evidence for entanglement with critical fluctuations at PR. Finally, since parallel-step elastic repulsion is universal, we can expect that PR should also be common. In fact, we surmise that the abrupt vacancy proliferation generally found at the early onset of surface melting [15] might be precisely related to PR. It is hoped that these results will stimulate newer experimental efforts.

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