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, named FCSOS, 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 analysed, and identified in the step-step elastic repulsion.

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,\cite{denNijs} he found that regular roughening (temperature \( T \)) 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 disordering, 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,\cite{denNijs} attempts at detecting PR focused mostly on metal surfaces, with uncertain results.\cite{denNijs} Surprisingly, the first convincing evidence of PR in unreconstructed surfaces came instead from rare gases.\cite{denNijs}

The (111) faces of Ar, Kr, and Xe, exhibit re-entrant layering in adsorption isotherms above a \( T_R \approx 0.95T_m \) \((T_m\) being the melting temperature), with a half-filled top layer between \( T_c \) and \( T_R \). This is a clear indication of PR,\cite{denNijs} and a simple hexagonal model can in fact be constructed which contains PR with good similarities with the experiment.\cite{denNijs}

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 contents 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 \( ABCABC \ldots \) stacking. Heights in the \( l \)-th 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:

\[
H = J \sum_{\langle i,j \rangle} \delta(|h_i - h_j| - 3) + K \sum_{\langle 3 \rangle} \delta(|h_i - h_j| - 4) \\
+ L \sum_{\langle 4 \rangle} \delta(|h_i - h_j| - 4) + M \sum_{\langle 4 \rangle} \delta(|h_i - h_j| - 5) \ldots \tag{1}
\]

where \( \sum_{\langle n \rangle} \) is shorthand for sum over all pairs of \( n \)-th 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, the minimal requirement in order to get a stable DOF phase into the model is to have at least non-zero \( K \) 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.\cite{denNijs} 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.\cite{denNijs} 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 non-zero 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.

We list a number of results (all the couplings from $M$ onward are put equal to zero). When the only non-zero coupling in the model is $J$, there is no PR, and a simple roughening is found at $e^{3J} \approx 1.6$. The situation remains unchanged when $K > 0$ but $L = 0$. In particular, roughening takes place at $e^{3J} \approx 1.5$, when $K = +\infty$. Finally, a PR transition is found along the $K = L = +\infty$ line at $e^{3J} \approx 1.5$. 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 $N = 96$, and a standard Metropolis algorithm. After equilibration, more than two million 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 $\chi_P$ should diverge at PR.

As Fig. 2 shows, on the $K = L = +\infty$ line, $P$ indeed vanishes near $e^{3J} = 1.5$ and $\chi_P$ 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 signalling a higher-order transition than Ising, or 3-state Potts. The ordered phase and the DOF phase have the same degeneracy (here 3-fold). As a consequence, PR is expected to be non-universal [8] unlike Ising or 3-state Potts, where the degeneracy is fully removed above $T_c$.

Since the free energy of all step excitations is zero at PR, one expects the height fluctuations to diverge at $T_c$, $\langle \delta h^2 \rangle \sim \frac{1}{4\pi K_c} \ln N$, 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][9] At $K = L = +\infty$ and $e^{3J} = 1.5$ we estimate $K_c \approx 1.06$, whence $\eta = \frac{2K_c}{K_c - \pi} \approx 0.74$, $\nu = \frac{2K_c}{K_c - \pi} \approx 1.92$, $\alpha = 2 - 2\nu \approx -1.85$, $\beta = \frac{\nu}{\nu - 1} \approx 0.71$, 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 $\beta K$ 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), in units of the Lennard-Jones $\epsilon$ (120 K for Ar).

PR can be revealed in scattering experiments. Antiphase elastic X-ray or atom scattering is given by

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

where $a_z$ is the vertical layer separation, $Q$ and $q_z$ are the surface parallel and perpendicular momentum transfer, respectively. Here $S = (3/N^2)\langle \sum_i (-1)^{h_i} \rangle$ contains a shadowing factor $\alpha_i$, which may be taken, for example, to be one for local surface maxima and zero otherwise, and $\chi_S(Q)$ 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 non-zero 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 non-zero. This implies 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 $N^{-2}m(N)$. Fig. 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. [1][3] Dynamic scaling hypothesis combined with the assumption of Gaussian spreading of density inhomogeneities out of criticality predicts that diffusion should vanish as $D \sim |t|^{-\frac{z}{z-\alpha-2}}$, where $z$ is a dynamical critical exponent and $t = T - T_c$ is extracted from a particle-conserving (Kawasaki) MC
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, 1.22, . . . , 2 · 0.58 = $\alpha/(l - l_0)^2$ ($\alpha/\epsilon_{NN} \approx 1.0, l_0 \approx -0.5$), if up-up at distances 1/2, 1, 2, . . . , $l$ 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 FC-SOS $K$ 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 et al. [4]. 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 $\approx 0.62$ and $\approx 0.16$, 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 re-entrant 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 [12] might be precisely related to PR. It is hoped that these results will stimulate newer experimental efforts.

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Figure Captions

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

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 \( \chi_P \), Bragg scattering amplitude \( S \), susceptibility \( \chi_S \), and interface width \( \langle \delta h^2 \rangle = (1/N^2) \langle \sum_i (h_i - \bar{h})^2 \rangle \). Data for \( N = 18(\bullet), 24(\triangle), 36(\square), 48(\bigcirc), 60(\ast), 72(\times), 96(\text{solid } \triangle) \) are shown. Dotted lines are guides to the eye.

Fig. 3  Average surface height \( \bar{h} \) during a MC run, for \( N = 36 \), at three different temperatures along the line \( K = L = +\infty \). Left: equilibrium (\( \Delta \mu = 0 \)). Right: growth (\( \Delta \mu = 0.0333 \)). From top to bottom, \( e^{3J} = 1.3 \) (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, C describe the top layer (half-layer in DOF) sublattice.

Fig. 4  Single-particle surface diffusion in FCSOS (\( K = L = +\infty \)). Data for \( N = 18(\bullet), 36(\square), 48(\bigcirc), 60(\ast), 96(\text{solid } \triangle) \) are shown. Note the strong decrease with increasing size, suggesting a dip at PR. The dotted line is a guide to the eye.
