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Surface Science 377–379 (1997) 509–513

surface science

Disordered flat phase in a solid-on-solid model fcc (111) surface

Santi Prestipino [a,b,*], Erio Tosatti [a,b,c]

[a] *International School for Advanced Studies (SISSA-ISAS), I-34014 Trieste, Italy*
[b] *Istituto Nazionale di Fisica della Materia (INFM), Italy*
[c] *International Centre for Theoretical Physics (ICTP), I-34014 Trieste, Italy*

Received 1 August 1996; accepted for publication 15 October 1996

Abstract

We review results obtained with a restricted solid-on-solid model, the so-called FCSOS model, introduced to describe the thermal disordering of fcc (111) crystal surfaces. In the FCSOS, parallel surface steps repel each other, while antiparallel steps do not interact. The model shows a preroughening transition into a disordered flat (DOF) phase, where the outermost surface layer – exposing one of the three sublattices – is half-filled. It is found that a fairly extended parallel-step repulsion is essential to obtain a stable DOF phase. Static as well as dynamical properties obtained with the FCSOS model are reviewed. A close similarity emerges between roughening and preroughening, which is like roughening at a single temperature. The relevance of these results to observations on Ar(111) and other surfaces is briefly discussed.

Keywords: Surface dynamics, structure, morphology, roughness, and topography

1. Introduction

In a remarkable series of papers [1,2] den Nijs showed some years ago that thermal surface roughening, taking place at the roughening temperature $T = T_R$, can be preceded at a lower temperature T_{PR} by a critical disordering transition. Above this phase transition, called preroughening (PR), and below $T = T_R$ there is a proliferation of up–down correlated steps, and the crystal surface is disordered but smooth, or flat (DOF). This scenario was first described within a solid-on-solid (SOS) model of the surface, with interactions extending beyond first neighbors, and such as to allow for the existence of a reconstructed phase in the phase diagram. The DOF phase is in fact adjacent to the reconstructed phase, implicitly suggesting that reconstructive tendencies, either manifest or latent, might be an essential ingredient for its existence. Following similar ideas, studies were also carried out in our group, addressing the interplay of missing-row reconstruction, preroughening and roughening on fcc (110) noble metal surfaces [3]. While the validity of these results is unquestioned, the implicit message that reconstructive tendencies, either manifest or latent, might be always essential for preroughening is, as it turns out, denied by facts. Experimental evidence for PR is found, unexpectedly, on rare-gas fcc (111) surfaces, where reconstructions surely play no role. For these surfaces, adsorbtion isotherms indicate a clear loss of layering at an isolated temperature, followed by subsequent re-entrance of layering, which persists up to a much higher roughening temperature [4].

* Corresponding author.

PII S0039-6028(96)01433-1

As was noted early on [2], this is very much the scenario expected for preroughening. By contrast, the existence of preroughening originated by latent reconstructive tendencies on a well-defined metal surface is still unclear [5].

Stimulated by these facts, we have built a restricted SOS model fcc (111) crystal surface, the so-called FCSOS model, which has no reconstruction tendencies, but undergoes all the same PR, followed by a DOF region in the phase diagram. The results of this model, which we review here, indicate that parallel-step repulsion on an otherwise unreconstructed surface provides another route to PR, seemingly different from reconstruction. However, in order to have a stable DOF phase, the repulsion must be first of all strong enough and restricted to – or at least predominant among – parallel steps only. Secondly, its range must also be long enough [6].

In agreement with qualitative expectations, it was found that in the FCSOS model the single step free-energy vanishes critically at PR, turning non-zero again in the DOF phase and finally vanishing for good at roughening. Thus, PR constitutes an isolated point outside the rough phase where, as in all points inside the rough phase, all out-of-plane excitations are costless. In turn, this implies that the average interface width must become infinite strictly at $T=T_{\mathrm{PR}}$.

Our studies of surface structure and dynamics with the FCSOS model near PR were conducted mostly by Monte Carlo methods. The model Hamiltonian and its static properties are briefly recalled in Section 2, while dynamical properties are discussed in Section 3. Particularly interesting results are the finite linear growth rate, and the critical slowing-down of tracer surface diffusion, found at $T=T_{\mathrm{PR}}$.

2. The FCSOS model and its static properties

The model is built so as to embody realistic features of rare-gas (111) surfaces, including fcc bulk structure, with its three distinct triangular sublattices ($l=0,1,2$) and a repulsion between parallel steps, but no interaction between antiparallel steps [6]. With the provision that on the lth triangular sublattice heights are such that $h_i=l(\mathrm{mod}3)$ and $\Delta h=\pm 1,\ \pm 2$ for nearest-neighbor heights, the FCSOS Hamiltonian reads:

$$H=J\sum_{(2)}\delta(|h_i-h_j|-3)+K\sum_{(3)}\delta(|h_i-h_j|-4)+L\sum_{(4)}\delta(|h_i-h_j|-4), \tag{1}$$

where $\sum_{(n)}$ is shorthand for the sum over all pairs of nth neighbors in the triangular lattice and couplings J, K and L are taken as positive, so as to penalize the closest parallel steps.

From a preliminary transfer-matrix analysis of model (1) one learns that the minimal requirement for getting a stable DOF phase is to have non-zero K and L [5]. This means that the longer-range part of the parallel-step repulsion is crucial to obtain PR. For $L=0$ (JK model), or for $K=L=0$, there is no PR and no DOF phase. When instead $L>0$ and large, we find PR and a DOF phase, both for $K=0$ and for $K>0$. Clearly, inclusion of longer-ranged repulsion is favorable to PR.

We show in Fig. 1 the single step free-energy $\eta(1)$ in the FCSOS model along the $K=L=+\infty$, where parallel-step repulsion is the most effective (note that roughening is suppressed altogether with this choice of parameters). Similar behavior is also found for the free energy of a three-step excitation [5]. Results obtained with a different SOS model, called UV, are also reported for comparison (in this model, heights are defined on a single triangular lattice and $\Delta h=0,\ \pm 1$ for nearest-neighbor heights; U is the energy to be paid when $\Delta h=\pm 1$ at first-neighbor distance, while V is the cost when $\Delta h=\pm 2$ between second-neighbor heights). We see that in both cases $\eta(1)$ vanishes at a single temperature, which is the signal of PR. However, that happens only in the UV model and in the FCSOS model, either with non-zero K and L, or simply with large L, $K=0$ (JL model, data not shown). Conversely, the JK model, where $L=0$, was found to display no PR at all.

Monte Carlo (MC) simulations allow a better understanding of the structure of the DOF phase in the FCSOS model. An intriguing initial question was to guess precisely how the (111) surface would disorder with increasing temperature. With three

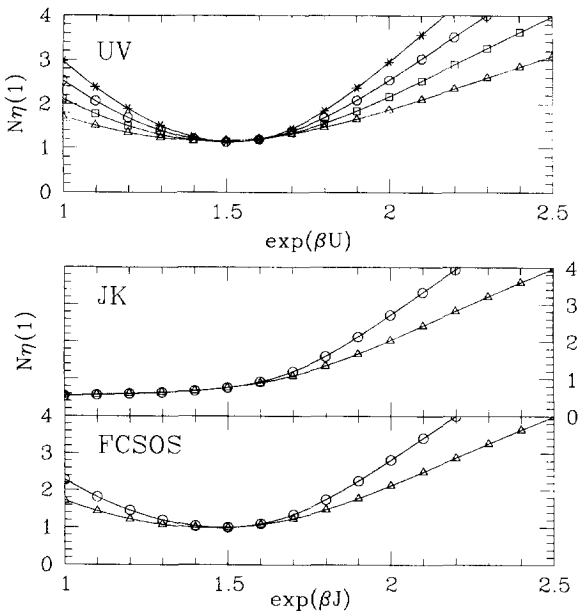

Fig. 1. Finite-size scaling behaviour of $\eta(1)$ for various SOS models (N is the size of the strip). Top: the UV model ($V=+\infty$, $N=3$ (△), 4 (□), 5 (○), and 6 (*)); center: the JK model ($K=+\infty$, $N=7$ (△), 10 (○)); bottom: the FCSOS model ($K=L=+\infty$, $N=7$ (△), 10 (○)). Notice that inclusion of a term like $M\,\Sigma_{\langle 4\rangle}\,\delta(|h_i-h_j|-5)$, with $M>0$, in the FCSOS Hamiltonian, Eq. (1), is simply redundant when $K=L=+\infty$, since in this case nearest-neighbor constraints effectively imply $M=+\infty$. The minimum (where present) signals the vanishing of $\eta(1)$ in the infinite-size limit as N^{-1}, namely preroughening. The JK model is the only model where $\eta(1)$ vanishes in a whole interval of J, $e^{\beta J}<1.5$, meaning that we are in the rough phase.

equivalent sublattices ($l=0$, 1, 2), disordering could involve in principle all of them at once, or it could involve only two at a time. It was found, eventually, that PR strongly involves only the two outermost layers. The DOF phase is itself threefold degenerate, exactly as the ordered phase. As in the two sublattice fcc (110) case [3], it is just this feature that makes PR a non-universal transition. A typical DOF configuration shows a (roughly) half-filled outermost surface layer, and thus a half-integer mean height. This feature permits, as in the other cases, one to identify the order parameter of the PR transition as Den Nijs' "parity" order parameter

$$P\propto\left\langle\sum_i(-1)^{h_i}\right\rangle, \qquad (2)$$

whose susceptibility diverges at T_{PR}. Upon weighting the height parities in Eq. (2) by a suitable "shadowing factor" (giving enhanced weight to the local surface maxima over all other configurations [3]), one can also build a quantity similar to the X-ray or atom scattering amplitude in antiphase conditions. It was found [6] that this weighted quantity vanishes at PR only, since odd and even surface maxima occur in equal amounts at T_{PR} [5], but is finite below and above. A dip in antiphase scattering is therefore the main static signature to be expected at PR.

3. Dynamical properties

The growth mode near PR is an interesting dynamical property which has hardly been addressed in the literature. One can use the FCSOS model to study it. The ordered flat surface grows layer-by-layer by classical nucleation. We expect that a DOF surface should also grow layer-by-layer, since the step free-energy is also non-zero there. Exactly at PR, which is the transition point between the two phases, continuous linear growth is more likely, since at this point the step free-energy vanishes, as on a rough surface.

Some clues about growth can be indirectly drawn from our equilibrium MC study. During the MC simulation one observes, due to finite size and thus especially in the smallest lattices, sudden diffusive events of the whole surface, in the form of relatively rapid jumps of the mean surface height $\bar{h}$ between quantized levels (see Fig. 2). These levels are integer in the smooth phase, but half-integer in the DOF phase; quantization clearly signifies stability for the full-or half-layers, respectively. At PR, which divides the two phases, there are non-quantized rapid fluctuations of $\bar{h}$, suggesting instead a non-activated growth process.

Non-equilibrium simulations of the FCSOS model at $\Delta\mu>0$ (where the solid grows at the expense of the vacuum) confirm these clues, and give a clear picture of the growth mode (see Fig. 3). Layer-by-layer behavior is confirmed both below and above PR. Near PR ($e^{\beta J}=1.5$, when $K=L=+\infty$), the surface growth velocity is orders of magnitude faster than either in the smooth surface

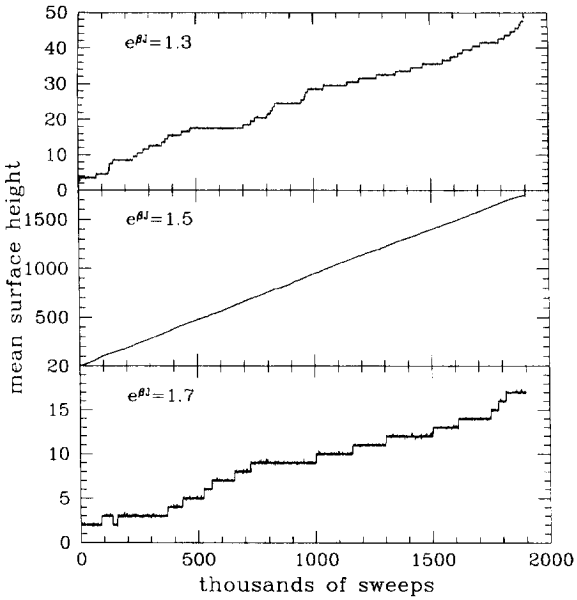

Fig. 2. FCSOS model at equilibrium (36×36 lattice and $K=L=+\infty$): mean surface height $\bar{h}$ as a function of time (measured in MC sweeps) at three different temperatures across the PR point. From top to bottom, DOF phase, PR and smooth phase. The jumps of $\bar{h}$ in the smooth and in the DOF phases qualify layer-by-layer growth (after Ref. [3]).

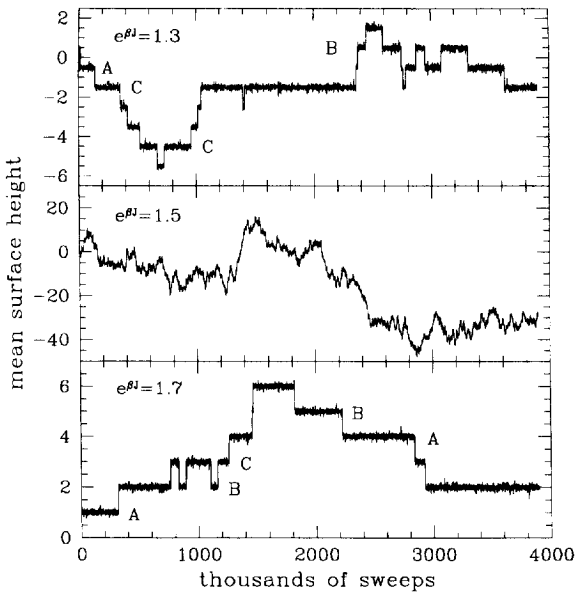

Fig. 3. FCSOS model out of equilibrium ($\Delta\mu=0.00333$, (36×36) lattice, and $K=L=+\infty$): mean surface height $\bar{h}$ as a function of time (measured in MC sweeps) at three different temperatures across the PR point. From top to bottom, DOF phase, PR and smooth phase. The $\Delta\mu$ term is small enough to remain in the linear response regime. We used simple Metropolis dynamics with the Hamiltonian $H'=H-\Delta\mu\,\Sigma_i\,h_i$ (after Ref. [3]).

below T_{PR}, or in the DOF phase above. This result can therefore be directly related to the experimental disappearance of layering observed near 69 K on Ar(111), and its re-entrance between $T_{PR}=69$ and $T_R=80$ K can thus be attributed to a DOF phase.

Another dynamical property is single-particle lateral surface diffusion. Separate MC simulations on the FCSOS model have been used to explore its behavior near PR. It is useful to work now under canonical conditions, where particles are neither created nor destroyed, but can jump horizontally from a surface site to another site a few lattice spacings away, via particle-conserving (Kawasaki-type) MC moves. From the general theory of dynamical criticality [7] we expect that a dynamical process such as diffusion could be affected by slowing-down at a continuous phase transition. If preroughening is no exception, we can expect the asymptotic lateral diffusion coefficient to exhibit a critical dip, and in fact to vanish at T_{PR}. MC results [6] confirm a dip of the asymptotic long-distance surface diffusion coefficient at T_{PR}. Its system size-dependence, although not strong, is at least compatible with a zero extrapolation at T_{PR} in the thermodynamic limit. Such a critical slowing-down of single-particle lateral diffusion at PR might in principle be observed experimentally, although obviously only as a long-distance diffusion anomaly.

4. Conclusions

The FCSOS model provides a useful theoretical workhorse for investigating various surface physics issues connected with the preroughening transition, particularly (but not exclusively) of fcc (111) surfaces. In particular, anomalies of antiphase scattering, surface growth and single-particle diffusion are predicted to occur.

This theoretical scenario ties in very well with the observed phenomenology of growth on Ar(111)

and other rare-gas surfaces. The fact that PR takes place in the FCSOS model only for a relatively long-range repulsion between surface steps suggests that elastic interactions should be a prime factor causing it to occur on these surfaces. Step energies and interactions calculated on the Lennard-Jones (111) surface [6] support, qualitatively, this conjecture, although the results (which are easily obtained only at $T=0$, and which of course yield power-law interactions not easily truncated) are not easily cast into effective FCSOS parameters. In particular, the PR temperature, which in the FCSOS is essentially fixed by J, is overestimated by a factor of about two by the $T=0$ step energy. It seems reasonable to attribute tentatively this disagreement to the neglect of vibrational and free-volume entropies, whose effective renormalization of the bare parameter values would undoubtedly reduce T_{PR}.

Extrapolating from FCSOS and rare-gas solid surfaces, we believe PR to be a more general phenomenon. Further experiments of the kind suggested in the present paper could help to identify PR in other surfaces, especially metals. Particle conservation, due to inefficient evaporation at metal surfaces, can also induce PR-related phase separation phenomena which we have recently studied, using a *canonical* version of the FCSOS model [8].

Acknowledgements

We acknowledge support from the EEC under contracts ERBCHRXCT930342 and ERBCHBGCT940636, and from CNR under project SUPALTEMP.

References

[1] M. den Nijs and K. Rommelse, Phys. Rev. B 40 (1989) 4709.
[2] M. den Nijs, in: Phase Transitions in Surface Films, Eds. H. Taub et al. (Plenum, New York, 1991) p. 247, and references therein.
[3] G. Mazzeo, G. Jug, A.C. Levi and E. Tosatti, Surf. Sci. 273 (1992) 237; Europhys. Lett. 22 (1993) 39; Phys. Rev. B 49 (1994) 7625, and references therein.
[4] H.S. Youn and G.B. Hess, Phys. Rev. Lett. 64 (1990) 918; P. Day, M. LaMadrid, M. Lysek and D. Goodstein, Phys. Rev. B 47 (1993) 7501; P. Day, M. Lysek, M. LaMadrid and D. Goodstein, Phys. Rev. B 47 (1993) 10716; H.S. Youn, X.F. Meng and G.B. Hess, Phys. Rev. B 48 (1993) 14556.
[5] A discussion is given by S. Prestipino and E. Tosatti, to be published.
[6] S. Prestipino, G. Santoro and E. Tosatti, Phys. Rev. Lett. 75 (1995) 4468; and to be published.
[7] S.-K. Ma, Modern Theory of Critical Phenomena (Benjamin, New York, 1976).
[8] S. Prestipino, C.S. Jayanthi, F. Ercolessi and E. Tosatti, to be published.