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LETTER TO THE EDITOR

A model for the roughening of reconstructed surfaces: finite-size study and phase diagram

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Abstract. We present a novel solid-on-solid model loosely mimicking the structural properties of reconstructing FCC(110) solid-vapour interfaces. The model allows for the study of the interplay between the reconstruction and roughening phase transitions. A numerical finite-size transfer-matrix study of the model yields a phase diagram where roughening takes place above reconstruction, confirming the picture advocated by a related study of Villain and Vilfan for Au(110). The nature of both phase transitions is also investigated.

Recently, there has been considerable theoretical (Jayaprakash and Saam 1984, Trayanov *et al* 1989) and experimental interest in the roughening of unreconstructed FCC(110) metal surfaces, particularly in the cases of Cu (Mochrie 1987, Zeppenfeld *et al* 1989), Ag (Held *et al* 1987) and Pb (Prince *et al* 1988, Yang *et al* 1989). Less effort has been devoted to the problem of roughening in reconstructing noble-metal surfaces, e.g. Au (Campuzano *et al* 1985, Drube *et al* 1989), Ir (Hetterich and Heiland 1989) and Pt (Salmerón and Samorjai 1980, Robinson *et al* 1989), in particular to the question of whether the roughening transition coincides with or follows the order-disorder reconstruction transition much studied in these systems.

Different models have been proposed to date in order to provide a preliminary picture for the roughening of reconstructing surfaces. Villain and Vilfan (1988) have presented statistics for the defect lines and associated kinks, generated by thermal fluctuations within the 1×2 ground state configuration of Au(110). Their analysis yields indications for two transitions, both Ising-like, one corresponding to the order-disorder reconstruction at T_c, the other to the roughening at T_R, and with $T_R - T_c \approx$ 100 K in the specific case of Au. The second model, proposed by Levi and Touzani (1989), is stated in terms of an anisotropic six-vertex model plus an additional vertex-vertex interaction, which is solved numerically for the step free energy in order to establish the dependence of the roughening transition temperature on surface energy anisotropy. This model has the advantage of treating reconstructing and unreconstructing surfaces on the same footing.

In this letter we study a simplified version of a third model, proposed by two of the present authors in order to describe the dependence of both the roughening and reconstruction transition temperatures on surface anisotropy, as well as to elucidate the nature of the structural phase present below T_R. A preliminary analysis of the

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model (Jug and Tosatti 1989), to be described below, has shown that $T_R > T_c$, that roughening is of infinite-order (Kosterlitz-Thouless) whilst reconstruction is roughly speaking Ising-like, and that between the two transitions a sequence of disordered incommensurate phases is present as a precursor to true roughening. Here we present alternative results from a finite-size transfer-matrix study indicating that the above picture is essentially correct in predicting that $T_R > T_c$ for all reconstructing surfaces. Our analysis also yields the roughening temperature for surfaces that do not reconstruct.

The model can be written in terms of two sets of compenetrating rectangular lattice column heights, $\{h_{ij}\}$ and $\{l_{ij}\}$, each set being defined on the sublattice of one of the two inequivalent lattice layers of the semi-infinite FCC(110) crystal (see figure 1(*a*)). The Hamiltonian (in units of an effective atomic cohesion energy J) reads:

$$\mathcal{H} = \alpha \sum_{ij} [(h_{ij} - l_{ij})(l_{ij} - h_{i+1,j}) + (l_{ij} - h_{i+1,j})(h_{i+1,j} - l_{i+1,j})] + \sum_{ij} [(h_{ij} - l_{ij})(l_{ij} - h_{i,j+1}) + (l_{ij} - h_{i,j+1})(h_{i,j+1} - l_{i,j+1})] - \beta \sum_{ij} (h_{ij} - h_{i+1,j})^2 \tag{1}$$

where the sums run over the coordinates $\{i, j\}$ of a single sublattice and where the condition $s_{ij,i'j'} = h_{ij} - l_{i'j'} = \pm 1$ is imposed for the height differences between nearest-neighbour atomic columns. Since the $s_{ij,i'j'}$ can be interpreted as Ising variables, an alternative and yet exactly equivalent form for the Hamiltonian is:

$$\mathcal{H} = -\alpha \sum_{i \text{ even},j} s_{i,j} s_{i+1,j} - (\alpha - 2\beta) \sum_{i \text{ odd},j} s_{i,j} s_{i+1,j} - \sum_{i,j} s_{i,j} s_{i,j+1} \tag{2}$$

where the $\{i, j\}$ are now sites of the dual lattice of the combined $\{h\} \cup \{l\}$ lattice, and

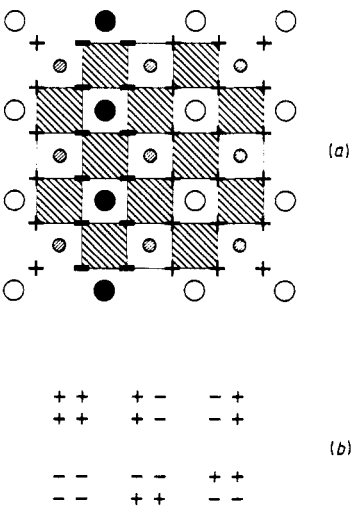

Figure 1. (*a*) Two-sublattice structure of the FCC(110) surface. Large circles indicate *h*-sublattice sites (empty ones at quote 0, filled ones at quote −2), smaller circles *l*-sublattice sites (all at quote −1); for simplicity, both sublattices are taken as square. In this way, the left-hand side represents the ordered 1×2 structure, the right-hand side the 1×1 structure. + or − signs refer to nearest-neighbour height differences ('spins'). (*b*) Spin configurations allowed in each elementary plaquette, owing to local height conservation.

with the additional constraint that not all spin configurations are allowed owing to local height conservation (ice-rule, figure 1(*b*)):

$$s_{i+1,j+1} - s_{i,j+1} + s_{i,j} - s_{i+1,j} = 0. \tag{3}$$

In terms of ground-state configurations, it is clear that the unreconstructed 1×1 surface is favoured for $\kappa = 4\beta - 2\alpha < 0$ (ferromagnetic 'spin' ground state), whilst the reconstructed 1×2 phase occurs for $\kappa > 0$($\langle ++--\rangle$ antiphase spin ground state). Hence, κJ can be thought of as proportional to the (110)/(111) surface energy anisotropy of any FCC metal. Notice however that contrary to real pure metal surfaces our Hamiltonian (1) contains an asymmetry between the h and l sites of the two inequivalent layers. Such an asymmetry would be present, for instance, on the surface of an ordered binary alloy (e.g. Cu_3Au) (Alvarado *et al* 1987). On the other hand we expect the essential physics of the model to hold also for pure reconstructing metal surfaces. Another way to visualise the effects of this asymmetry is to assimilate it to a weak external field making the h and l sites slightly inequivalent. We expect such a field to yield at most a rounding of some otherwise sharp phase transition. Another subtle feature which is realised on real metal surfaces but absent in Hamiltonians (1) and (2) is the presence of so-called 'deep' missing row reconstructions, which are replaced in our model by 'shallow' reconstructions. Otherwise, we believe that the main physics of coexisting roughening and reconstruction is quite well embodied in this model. For $\kappa < 0$ we expect the asymmetry to be unimportant, as there is no degeneracy in the 1×1 ground state. We emphasise that despite the unrealistic suppression of ground-state degeneracy for $\kappa > 0$, our model represents the first simple SOS Hamiltonian containing both reconstructed and unreconstructed ground states leading, at the same time, to roughening at high temperatures.

We have studied the phase behaviour of the model through the method of finite-size scaling (Nightingale 1981, Barber 1983) applied to the exact numerical evaluation of thermodynamic surface properties for infinite one-dimensional lattice strips. The transfer matrix (Domb 1960) for Hamiltonian (2) (which would be an alternate-coupling nearest-neighbour two-dimensional Ising model, were it not for the ice-rule constraint), is defined by

$$T_{(n)}(j, j+1) = \prod_{i=1}^{n} \exp(K_{ij,ij+1} s_{i,j} s_{i,j+1} + K_{ij,i+1j} s_{i,j} s_{i+1,j}) \tag{4}$$

where n is the finite strip width and $K_{ij,i'j'}$ are the nearest-neighbour couplings (in units of $J/k_B T$) appropriate for the chosen direction of transfer. In our case, convergence for increasing n is faster for a transfer in the diagonal direction and the full transfer matrix breaks down in the product of two matrices alternating in the direction of transfer due to the alternancy of the interactions. The height conservation constraint (3) is imposed in the determination of the matrix elements and eigenvalues. The height difference at column j between the two strip edges is given by

$$\Delta h_j = \sum_{i=1}^{n} (-1)^{i+1} s_{i,j} \tag{5}$$

so that the height conservation rule (3) automatically implies that $\Delta h_j = \Delta h_{j+1}$ for periodic boundary conditions in the direction orthogonal to the transfer. The full matrix is consequently of block-diagonal form, each block corresponding to a particular height difference (Lieb and Wu 1972, Baxter 1982). Thus, we evaluate the free energy

per site from the largest eigenvalue of the central block ($\Delta h = 0$),

$$f(\kappa, T) = -\frac{k_B T}{2n} \ln(\lambda_0) \tag{6}$$

whilst the free energy per column for step formation corresponds to

$$f_s(\kappa, T) = -\frac{k_B T}{2} \ln\left(\frac{\lambda_2}{\lambda_0}\right) \tag{7}$$

with λ_2 the dominant eigenvalue of the subcentral block ($\Delta h = 2$). The results obtained for the heat capacity per site are shown in figure 2 for strips of sizes $n = 4, 6, 8, 10$ as a function of temperature for $\kappa < 0$. Similar results are shown in figure 3 for $\kappa > 0$, although convergence suffers from parity effects owing to the symmetry of the 1×2 ground state. These results give indications reminiscent of rounded 2D Ising-like behaviour for sufficiently small values of $|\kappa|$. However, for larger values of $|\kappa|$ the heat capacity appears to be saturating with increasing n, perhaps an indication for the drifting of the related critical exponent towards the Kosterlitz-Thouless value $-\infty$. A possible explanation stems from the fact that while the energy of stepped defects is of order α, that of flat ones is of order $|\kappa|$. Hence, for $|\kappa| \ll \alpha$ reconstruction involves

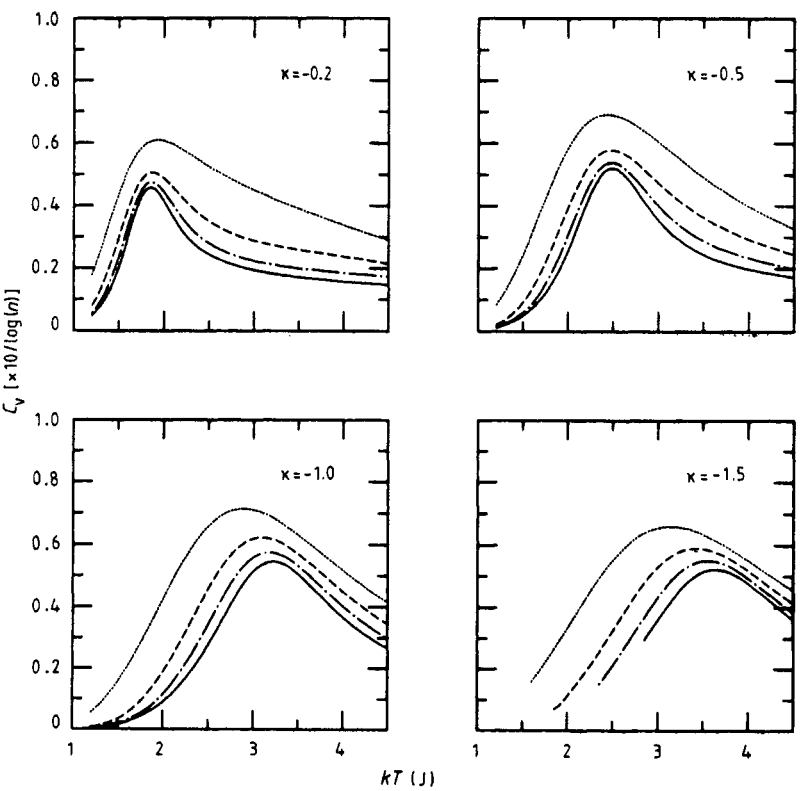

Figure 2. Finite-size and temperature dependence of the scaled heat capacity per site for unreconstructing surfaces (1×1). (· · ·) $n = 4$; (----) $n = 6$; (—·—·—) $n = 8$; (——) $n = 10$.

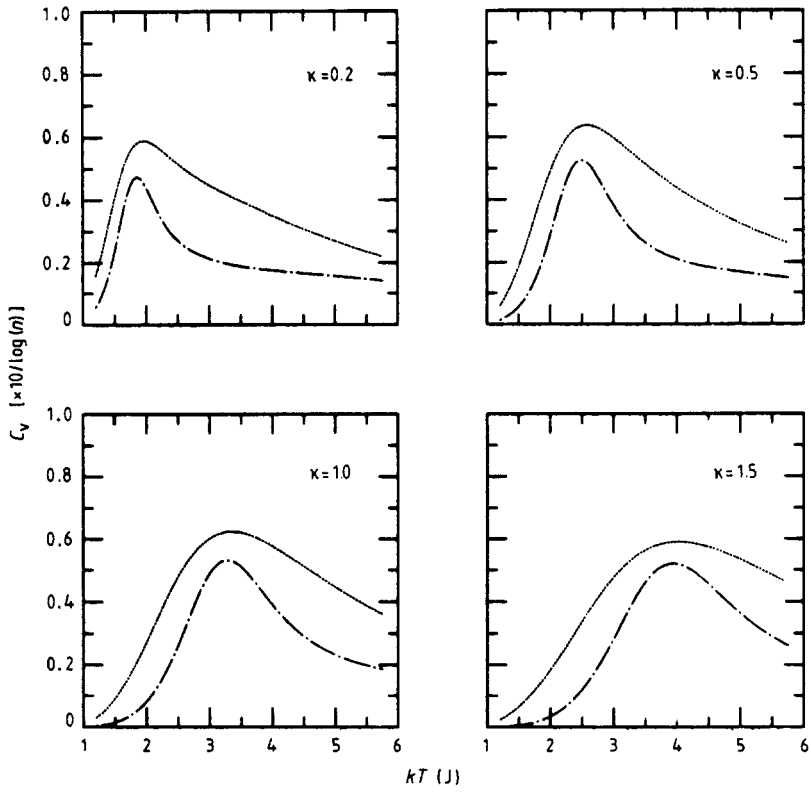

Figure 3. As in figure 2, but for reconstructing surfaces (1×2).

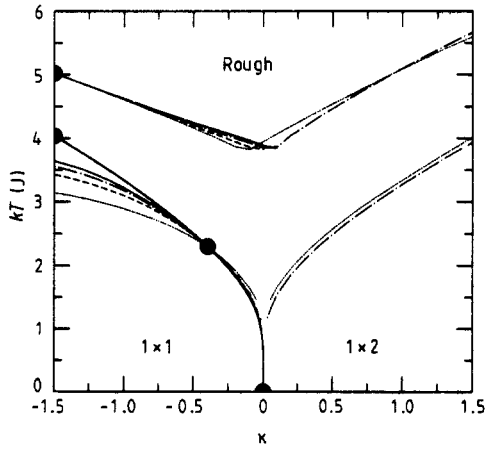

Figure 4. Suggested phase diagram for the present model. The upper curve is the smooth-rough transition; the lower curve represents the position of the roughening peak for $\kappa < 0$, and of the Ising-like order-disorder transition for $\kappa > 0$.

mostly in-plane degrees of freedom, whilst for larger $|\kappa|$s competition with off-plane degrees of freedom will modify the nature of the reconstruction transition for $\kappa > 0$. In figure 4 (lower curve) the position of the peak in the heat capacity is drawn as function of size n and anisotropy κ. For very small values of $|\kappa|$, severe finite-size effects come into play, as the system becomes strongly quasi-one-dimensional; however there is indication that the curves approach the origin with infinite slope. We identify the position T_c of the heat capacity peak with the order–disorder transition temperature for reconstructing surfaces $\kappa > 0$, transition that appears to be Ising-like for sufficiently small anisotropy. For $\kappa < 0$ the position of the peak (now presumably a precursor to anisotropic roughening) is determined with high accuracy for two special points (beside $\kappa = 0$, trivially). For $\kappa \simeq -0.4$ the position of the peak appears to be independent of size n (the finite-size corrections change sign at that point), thus its value is determined exactly to numerical precision. For $\kappa = -2\alpha$, the model becomes exactly isomorphic to an anisotropic BCSOS model, for which we know there is no second-order transition but instead an infinite-order transition preceded by a non-critical peak in the heat capacity, for which the position can be determined exactly. We point out that precisely for $\kappa = -2\alpha$ our model recovers symmetry between h and l inequivalent layer sites. Through the above exact points a fitting curve has been drawn in figure 4 in order to give a possible indication of the convergence of our finite-size evaluation.

The position of the roughening transition in our model for $\kappa = -2\alpha$ can also be determined numerically, by extrapolating the temperature dependence of the step free energy f_s to $n = \infty$ and determining the temperature T_R where f_s vanishes. Good agreement is obtained with the exact result for the BCSOS model, though this method is not very precise for determining the roughening temperature (Luck 1981). For $\kappa > -2\alpha$, a faster and more accurate convergence is obtained from the calculation of the following approximant to f_s

$$g_s(\kappa, T) = -\frac{k_B T}{2} \ln\left(\frac{\lambda_0'}{\lambda_2}\right) \tag{8}$$

where λ_0' represents the subdominant eigenvalue of the central block. g_s is an approximant to f_s in that λ_0 becomes degenerate with λ_0' precisely at T_R; however, g_s becomes negative for $T > T_R$, thus allowing for a more precise evaluation of T_R. The resulting curves are given in figure 4 (upper curve), which completes our phase diagram. As for the nature of the roughening transition, we point out that our model resembles that studied by Knops (1979), in which two anisotropic compenetrating SOS lattices are constrained precisely by the same $h_{ij} - l_{i'j'} = \pm 1$ condition on neighbouring columns. Knops proposes that, except for the isotropic case, the transition should be Ising-like. Here we see, from heat capacity studies, that by varying κ the thermal exponent can change almost continually indicating the possible existence of weak universality conditions (Suzuki 1974).

In conclusion, we have carried out a finite-size investigation of a model for the roughening of reconstructing surfaces. The resulting phase diagram confirms the proposal of Villain and Vilfan and of Jug and Tosatti that there should be two separate reconstruction and roughening transitions, for all surfaces having a 1×2 ground state. It is in fact interesting to point out that in a recent x-ray scattering experiment on Pt(110) (Robinson *et al* 1989) new evidence has been presented for an intermediate incommensurate phase (corresponding to a temperature-dependent shift of the diffraction peak) between T_c and (presumably) T_R. We hope that our model and findings will therefore stimulate further theoretical and numerical studies on the problem.

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