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Can one have preroughening of vicinal surfaces?

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Abstract

We discuss the possibility that, besides roughening, a vicinal surface could display preroughening (PR), and consider the possible mechanisms for its promotion. Within the framework of a terrace–step–kink model, it turns out that a PR transition is possible, and could be induced by a short-range repulsion between parallel kinks along the same step or on adjacent steps, or even by some kind of extended range step–step repulsion. We discuss the possible relevance of this phenomenon to the anomalous roughening behaviour recently reported for Ag(115). © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The identification of a new thermodynamic surface phase is always of fundamental significance. Vicinal surfaces of metals, consisting of a regular array of low-index terraces separated by parallel steps, are of special interest because of their ubiquity, due to e.g. small miscut angles, and because of the expected rich interplay between steps and kinks. A vicinal surface typically has only two states: flat and rough, with a phase transition from flat to rough at a much lower temperature than that of a low-index face. The transition is generated by the proliferation of kinks in the steps, as first discussed by Villain et al. [1]. At roughening, steps develop kinks and start to meander freely, giving rise to divergent fluctuations in the position of the surface along the normal. At these relatively low temperatures, very neat STM observations of roughening are possible, as recently demonstrated for Ag(115) by Hoogeman et al. [2–4].

A more complex and interesting roughening behaviour could be anticipated if interactions between the kinks were important. Elasticity theory predicts a repulsive interaction between two kinks in the same direction along a step (parallel kinks) which asymptotically should decay as r^{-3} [5,6]. If this repulsion were strong enough, a new vicinal disordered flat (VDOF) phase, with long-range antiparallel order of kinks within a step, could perhaps be stabilized, in analogy with the stabilization on a low-index surface of a standard DOF phase [7] by elastic parallel step–step repulsion. [8]. Similarly, the effect of parallel kink–kink repulsion should be to shift vicinal roughening to a higher temperature, and this may uncover a

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vicinal preroughening (VPR) transition which, involving proliferation of correlated left–right kinks, remains unaffected.

We have identified a simplified model of a vicinal surface where precisely this scenario is realized. While we believe that our findings have a broader significance, we have specialized our modelling to mimic the situation of Ag(115), where we speculate VPR might take place.

2. Model and method

So long as temperature is far below melting, a good description of vicinal surface roughening is given by the terrace–step–kink (TSK) model (see e.g. Ref. [9]). It ignores the possibility of adatoms on terraces, so that the step positions are the only statistical variables in the problem. If a solid-on-solid condition is assumed all over the step length, then the position of a step with respect to $T=0$ can be encoded by a variable $u_m(y)$ (where m is the step label and y is an abscissa along the step). The TSK model further assumes a repulsive interaction between neighbouring steps and an energy cost for forming kinks on primary steps. In the celebrated model by Villain, Grempel, and Lapujoulade (VGL) [1], $u_m(y)$ is an integer variable and only unitary kinks are permitted (the energy cost for each being $W_1>0$). Moreover, an energy $U_1>0$ is to be paid when $\Delta u = u_{m+1}(y)-u_m(y)=-1$, nothing for $\Delta u>-1$, while $\Delta u<-1$ is not allowed. The VGL model is exactly solvable in the highly anisotropic, $W_1/U_1\to+\infty$ limit [1]. In particular, a Kosterlitz–Thouless phase transition is predicted to occur at a temperature T_R given by $U_1/(2k_BT_R)\exp[W_1/(k_BT_R)]=1$. This transition describes surface roughening since the correlation function $G(m)=\langle[u_m(y)-u_0(y)]^2\rangle$ is finite as m goes to infinity when $T<T_R$, while it diverges logarithmically when $T>T_R$.

We have modified the VGL Hamiltonian to include interactions between the kinks. These interactions generally arise from the mutual interference between the elastic strain fields determined by the individual kinks. In particular, we allow for a short-range repulsion (W_2) between parallel kinks in the same step, and also between parallel kinks in neighbouring steps (U_2). Moreover, the two-sublattice structure of fcc(115) is also taken into account (see Fig. 1).

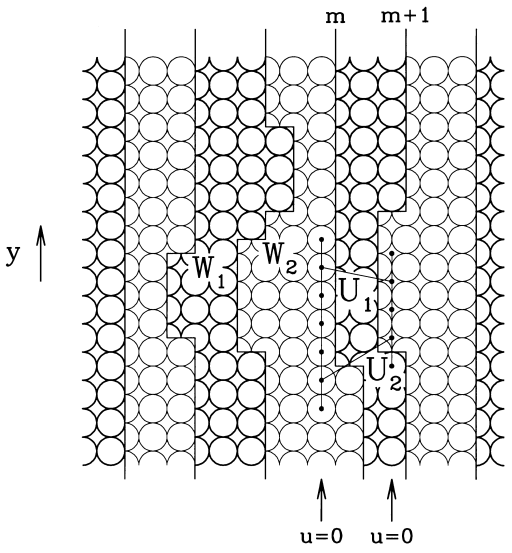

Fig. 1. Schematic view of the TSK vicinal surface, including excitations and their energy cost. Atomic positions along the step are all odd or all even, depending on which sublattice the terrace atoms on the left of the step belong to. The total energy of the pair of consecutive parallel kinks on the same step is $2W_1+W_2$, while the energy of the two nearby parallel kinks on the steps labelled m and $m+1$ is $2W_1+U_2$.

With these ingredients, we have applied standard Metropolis Monte Carlo or alternatively, mapping onto a 1D quantum spin chain to study the phase diagram as a function of temperature. The Monte Carlo lattices employed comprise an increasing number of steps, up to $N_x=24$, while the number N_y of step sites along the hard y direction is taken 60 times larger. We monitor usual quantities such as kink–kink correlations, heat capacity, VDOF order parameter $P=\langle(-1)^{u_m(y)}\rangle$, and the average square lateral excursion of a step $\delta u^2=\langle(u_m(y)-\overline{u_m})^2\rangle$. Strong anti-parallel VDOF correlations between consecutive kinks in a step will result into a vanishing P in the thermodynamic limit, with a finite δu^2 infinite-size extrapolation. In the ordered flat phase, conversely, P is finite, whereas in the disordered rough phase, δu^2 extrapolates to infinity.

3. Results

First, we prove the existence of a VDOF phase in the phase diagram of our model vicinal surface by Monte Carlo simulation. To this end, we observe that the most favourable situation for the VDOF is when U_2 and W_2 are both infinite. We take $W_1 = 20U_1$ and vary $\beta U_1 = U_1/k_B T$ from 0 to 0.18. We find that the rough phase is completely absent in this case and the high-temperature phase of the model is VDOF. In Fig. 2, a small part of the vicinal surface is shown at infinite temperature. A glance at this picture reveals the general structure of the VDOF phase in our model: kinks are very numerous along the steps but the correlation between two consecutive kinks is strictly antiparallel, so that the overall surface is flat and its slope well defined. The VDOF state in Fig. 2 is nearly ideal: each step strictly meanders between two positions with equal probability, whence $\delta u^2 \simeq 0.25$. On decreasing temperature, δu^2 shows a peak, centred at $\beta U_1 \simeq 0.08$, which is size dependent and allows one to locate the VPR [8] ($\delta u^2 = 0.473$, 0.580, 0.618 for $N_x = 8$, 16, 24, when $\beta U_1 = 0.08$; a $K \ln N$ fit of the data for $N_x = 16$ and 24 yields $K \approx 0.09$). At the VPR temperature, δu^2 grows logarithmically as a function of the surface size and the vicinal surface is thus rough at an isolated temperature point, while being flat both below and above. We conclude that, if the short-range repulsion between parallel kinks is strong enough, then generally three different surface phases will be thermodynamically stable, i.e. a low-temperature ordered flat phase, an intermediate VDOF phase, and a rough phase at sufficiently high T. A weaker repulsion between the kinks, in contrast, may not be sufficient to stabilize the VDOF phase, and in that case the standard flat–rough transition is recovered, as in the straight VGL model.

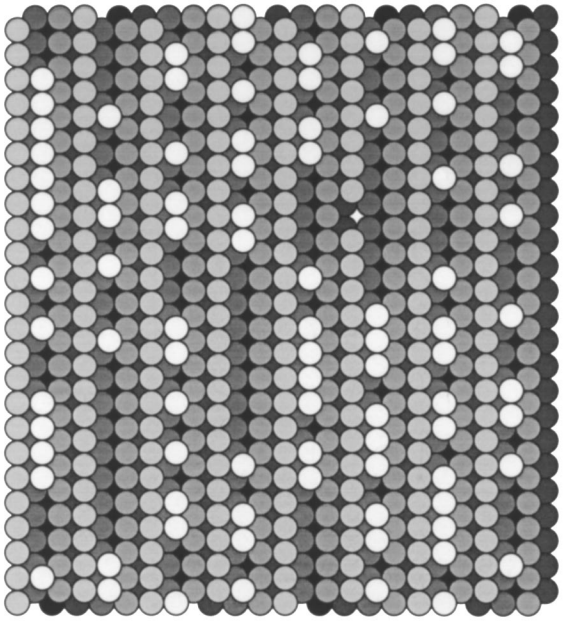

Fig. 2. A snapshot from the Monte Carlo simulation of the TSK model with $U_2 = W_2 = +\infty$. Here, the step number is 16 and $T = \infty$ (only a small part of the lattice with eight steps is shown). The viewpoint is from [115], and darker atoms are deeper than lighter atoms. Left and right kinks strictly alternate along the steps, leading to an extremely idealized realization of a VDOF surface (i.e. defect number and amount of correlation between the u values of adjacent steps both negligible).

Next, we consider the phase diagram for $W_2 = U_2 = 0$, but with an additional interaction similar to U_1 assumed between *second*-neighbour steps too. Precisely, we assume an energy cost U_1' whenever two second-neighbour steps get to the minimal distance $3a$, where a is the atomic diameter. This discourages meandering of the steps without affecting their kink–antikink zigzagging between two positions only. By mapping onto a 1D quantum model [1,10], we confirm that a VDOF phase can be generated by this second-neighbour step repulsion. While the precise value U_1' assumed is of course unrealistic since the repulsive force between two distant steps decay as r^{-2} with distance [5,6], this represents an interesting alternative mechanism to parallel kink repulsion to generate a VDOF phase.

4. Is there a VDOF phase on Ag(115)?

Having satisfied ourselves that VPR transitions and VDOF phases exist in a suitable vicinal model, it becomes of course of interest to ask whether they might actually be realized in a real system. Hoogeman et al. have carried out the first really extensive STM study of a vicinal surface, chosen

to be Ag(115) [2–4]. Their analysis indicates that, in the temperature range 400–500 K, the correlation function $G(m)$ of this surface is well represented by a law of the type $-K\ln(m^{-2}+X^{-2})+C$, which people use for standard surface roughening. Strikingly, however, X^{-1} extrapolates to zero at about 440 K, while K crosses the universal roughening value $1/\pi^2$ only at the much higher temperature of 490 K. In regular roughening, these two temperatures ought to coincide. It is tempting to hypothesize that the divergence of X could now indicate VPR at 440 K, so that a VDOF phase would be realized on Ag(115) in the temperature window 440–490 K.

What could be a realistic set of parameters to represent Ag(115)? Within the framework of the TSK model with interacting kinks, the problem of fitting the parameters to a realistic vicinal has no simple solution. For Ag(115), Hoogeman et al. have shown that the kink formation energy and the step repulsion can be extracted from STM data, thus providing values for W_1 and U_1 [1]. Moreover, even without a systematic study of kink–kink interactions, a value of 260 K was reported for the repulsion between kinks in neighbouring steps, which we take as the value of U_2. Finally, we have no information on W_2, but we believe it should be lower than U_2, and thus we tentatively set it to zero.

In Fig. 3, we show simulation data for three sizes, $N_x=12$, 18, and 24. Even though the statistics are insufficient, both these data and the behaviour of the u values during the run are suggestive of a VPR transition at about 380 K, while roughening would not occur before 390 K. Alternatively, the VDOF state which is occasionally observed during the simulation is in fact only metastable, and a single roughening transition actually occurs at about 375 K, as suggested by the thermal behaviour of $G(m)$. Summing up at this stage, we find that with this first choice of parameters there are hints of VPR and of a narrow DOF region. However, the evidence is quantitatively inconclusive. Further work is now in progress, using a different set of parameters. In particular, it is expected that the effect of a positive W_2 should be to shift roughening (and to a smaller extent also preroughening) further up in temperature, which goes qualitatively in the right direction. A more detailed account of ongoing calculations will be presented elsewhere. [10]

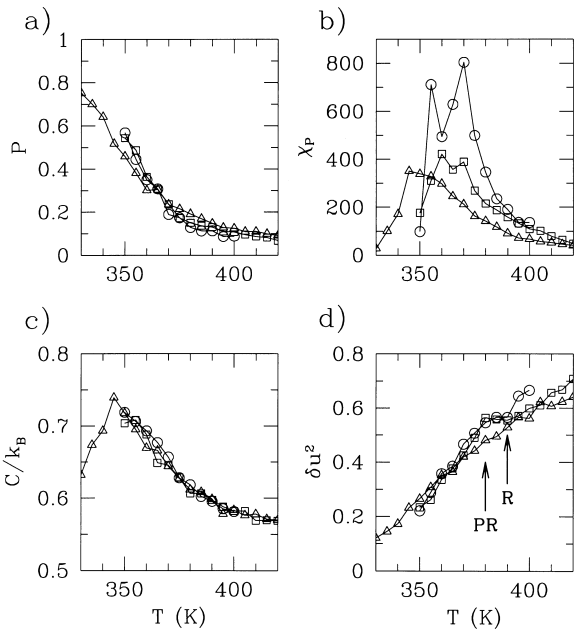

Fig. 3. MC results for the TSK model with $U_1=19$ K, $W_1=1183$ K, $U_2=260$ K, and $W_2=0$ (from 2 to 4 million MC sweeps were produced at each temperature point). Simulation data are plotted for three different sizes, $N_x=12$ (△), 18 (□), and 24 (○), with $N_y=60N_x$ in each case. Results are shown for (a) the DOF order parameter P, (b) its susceptibility χ_P, (c) the specific heat C/k_B, and (d) the average square lateral step excursion δu^2. In particular, the broad shoulder of δu^2 at 380 K appears to be the fingerprint of VPR, while roughening does not occur below 390 K. The order parameter and susceptibility are consistent with a size-limited critical transition near 380 K. The heat capacity is non-critical and size-independent, as expected for negative α.

[1] Owing to a misinterpretation, we erroneously attributed the kink density reported in Ref. [8] to $[\bar{1}10]$ secondary steps with only two positions allowed. In this case, the same mapping considered in Eq. (2.7) of Ref. [11] applies, with $v=\beta W_1/2$ and $L=0$, whence a kink density of $d=[1+\exp(\beta W_1)]^{-1}$ and a W_1 estimate of 1183 K. Actually, Hoogeman et al. were referring to an *unconstrained* meandering of the secondary step, leading to the correct result $d=2\exp(-\beta W_1)/[1+2\exp(-\beta W_1)]$ of Ref. [8]. Use of this W_1 (1323 K) instead of 1183 K will have the effect of shifting our roughening temperature upward. We thank J.W.M. Frenken for having drawn our attention to this error.

5. Conclusions

In conclusion, we have introduced a TSK model which generalizes the VGL description of vicinal surface roughening by including a short-range repulsion between parallel kinks on neighbouring steps as well as on the same step. If the strength of this repulsion is sufficient, a VDOF could be stabilized in a temperature window between the ordered flat and the disordered rough vicinal phases.

Recent STM data are speculatively interpreted to suggest that a possible realization of this new scenario could be found in Ag(115) between 440 and 490 K. A refinement of the STM data analysis, particularly concerning the short-distance correlations between kinks, is very desirable, as it could now confirm or deny this conjecture.

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