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SURFACE RELAXATION MECHANISMS IN THE MORPHOLOGICAL EQUILIBRATION OF CRYSTAL SURFACES

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ABSTRACT

The phenomenology of surface relaxation below the roughening temperature T_R is shown via kinetic Monte Carlo simulation to exhibit extremely non-classical behavior depending on (1) initial morphology and (2) kinetic rate laws for atom motion. However, within the temperature and size scale of our simulations there are several different mechanisms that operate. The “pinch-off” mechanism is seen to be operative for ripple relaxation employing i -kinetics. For ripple relaxation employing Δi -kinetics, pinch-off is seen at short times. At long times, these particular surfaces spontaneously island, and then reduction of line tension drives relaxation. Reduction of line tension also drives relaxation of dimpled surfaces.

INTRODUCTION

Roughened crystalline surfaces above the surface roughening temperature T_R evolve to flatness in such a way that features of spatial frequency q decay in amplitude exponentially in time with time constant proportional to q^{-4} [1]. The behavior of surfaces in the technologically relevant temperature regime below T_R do not behave in this classical manner. The influence of discrete steps and terraces below T_R leads to different relaxation behavior that depends on (a) the initial morphology, (b) the kinetic laws that govern atom motion on the surface. We enumerate in this paper some of the different paths we have discovered surfaces to follow in relaxing to equilibrium below T_R . Such information is necessary for any proper interpretation of surface annealing behavior.

Our method is as follows. We examine “characteristic times.” These give universal scaling relations such that all amplitude vs. time curves should collapse onto some universal curve. That is, given some initial morphology with wavelength λ , often the amplitude $h_\lambda(t)$ evolves according to $h_\lambda(t) = f(t / \tau(\lambda))$. The quantity τ is a characteristic time in that plotting $h(t)$ vs. t / τ should give the same curve for all λ . Kinetic Monte Carlo (KMC) simulation of relaxing rippled and dimpled surfaces is used generate amplitude vs time curves with which the validity of one characteristic time versus another can be tested. Description of KMC can be found in a number of locations [2]. Previous to this work, only the Metropolis Monte Carlo technique, which is not guaranteed to yield proper time/dynamic information, had been used to study surface relaxation [4].

Our simulations were for solid-on-solid simple cubic (001) surfaces. The lateral bond energy of our system was ε , and the substrate bond energy was ε_B . In this way, the adatom concentration on terraces was equal to $C(T) = a^{-2} \exp(-2\varepsilon/k_B T)$ since 2ε is the

creation energy of an adatom, and the surface diffusivity is given by

$$D_s(T) = a^2 \frac{\nu_0}{4} \exp(-\varepsilon_B/k_B T), \text{ where } \nu_0 \text{ is a vibrational frequency. The simulation}$$

results presented here were performed in two sizes. For ripples of wavelength λ , we employed the “strip” geometry, in which the simulation field had dimensions $\lambda \times W$, where $W > 2048$. For dimples, a square field was used, with dimensions 256×256 or 512×512 . Periodic boundary conditions were used.

Two different rate laws for atomic motion on surfaces were studied, as shown in Figure 1. So-called i -kinetics have the physical analogy to a bond breaking model - an atom jumps over a barrier proportional to the number of bonds it currently has without any knowledge of its final configuration. In contrast, Δi -kinetics contain jump biases for adatoms so that they are more likely to move to low energy configurations.

Actually, both kinetic laws are somewhat artificial compared to what is certain to emerge from molecular dynamics or statics simulations are a table of barriers for elementary atomistic processes on the surface of any particular material. In Δi -kinetics, for instance, adatoms move as fast on steps as they do on terraces. In i -kinetics, atoms evaporate off steps onto terraces as frequently as they move along steps. Further discussion of these kinetic laws can be found in [3].

For i -kinetics,

$$k_i = \nu_0 \exp\left(\frac{-(\varepsilon_B + i\varepsilon)}{k_B T}\right). \quad (1)$$

whereas for Δi -kinetics,

$$k_{\Delta i} = \begin{cases} \nu_0 \exp\left(-\frac{\varepsilon_B}{k_B T}\right) & \Delta i < 0 \\ \nu_0 \exp\left(-\frac{\varepsilon_B}{k_B T}\right) \exp\left(-\frac{\Delta i \cdot \varepsilon}{k_B T}\right) & \Delta i > 0 \end{cases} \quad (2)$$

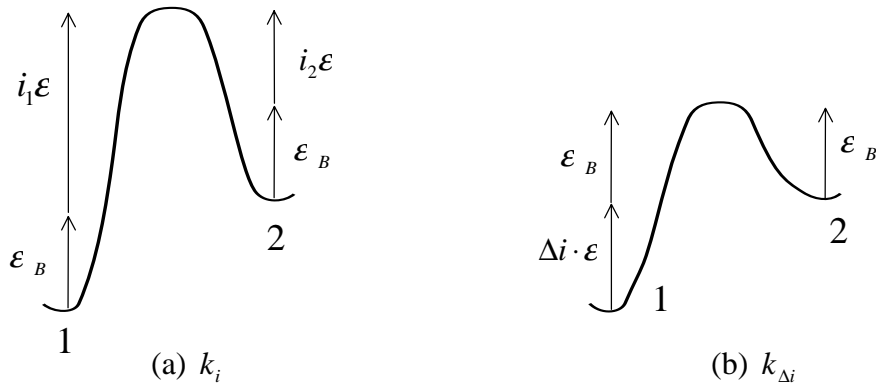


Figure 1. Activation barriers back and forth through a transition state using (a) i -kinetics, (b) Δi -kinetics.

RELAXATION OF DIFFERENT MORPHOLOGIES AT TEMPERATURES BELOW T_R

Sinusoids. The relaxation of sinusoids with [100] wave vector is found to exhibit different behavior than classical relaxation and also different behavior depending on the kinetic law used.

When using i -kinetics, the so-called pinch-off mechanism is found to always be operative. Figure 2 shows a series of simulation snapshots illustrating the idea, originally due to Rettori and Villain [5,6]. For each layer's dissolution, initially the steps bounding the topmost (bottom-most) terrace are essentially straight. These steps then fluctuate until they reach across the terrace and “pinch-off”, creating two extrema of very high step curvature. Once the pinch-off events begin forming, dissolution of the top (bottom) terrace is extremely quick due to evaporation (condensation) onto the terrace from steps of very positive (negative) curvature on the top (bottom) terrace. The rate limiting step in this process is the average time to create a pinch-off event. This dominates the scaling behavior.

To calculate the average time to pinch-off, we employ arguments [6] similar to Pimpinelli, et al. [7]. Assume that step fluctuations are caused by statistical fluctuations in the adatom flux off neighboring terraces. This flux is given by $J = (Ca) \left(\frac{4D_s}{a^2} \right) = (\#$ of atoms contributing to flux)(hopping rate). The number of atoms impinging on length l in time τ is $N(\tau) = Jl\tau = D_s Cl\tau / a$. Pinch-off requires a step fluctuation approximately of amplitude λ . The area of a step fluctuation of dimensions l by λ will be proportional to the variation in $N(\tau)$, i.e, $l\lambda \propto \sqrt{N(\tau)}$. Thus, $\tau \propto \frac{l\lambda^2}{D_s C}$. To relate l and λ we assume an equilibrium aspect ratio for the fluctuation, according to random walk theory. This introduces the resistance of a step to fluctuate from its mean orientation, the line stiffness, $\tilde{\beta}(T)$, and one finds $\lambda^2 \propto \frac{k_B T}{\tilde{\beta}(T)} l$ [8]. Plugging this into the previous expression yields the pinch-off scaling characteristic time

$$\tau_p^{-1} \propto \frac{(D_s C k_B T)}{\tilde{\beta}(T)} \lambda^{-4} \quad (3)$$

Mullins' classical theory of surface relaxation [1], valid above T_R , predicts a characteristic relaxation time given by

$$\tau_M^{-1} \propto \frac{D_s C}{k_B T} \lambda^{-4}. \quad (4)$$

Within the simulation model, the T and λ dependence of the characteristic times can be calculated from (3) and (4) without any adjustable parameters and compared to simulation. Figure 3 attempts a data collapse for i -kinetics using both characteristic times. It is seen that the classical model gives good data collapse at high temperatures (near T_R), but fails at low temperatures. The pinch-off model, on the other hand, gives good data collapse at temperatures well below T_R , but works less well near T_R .

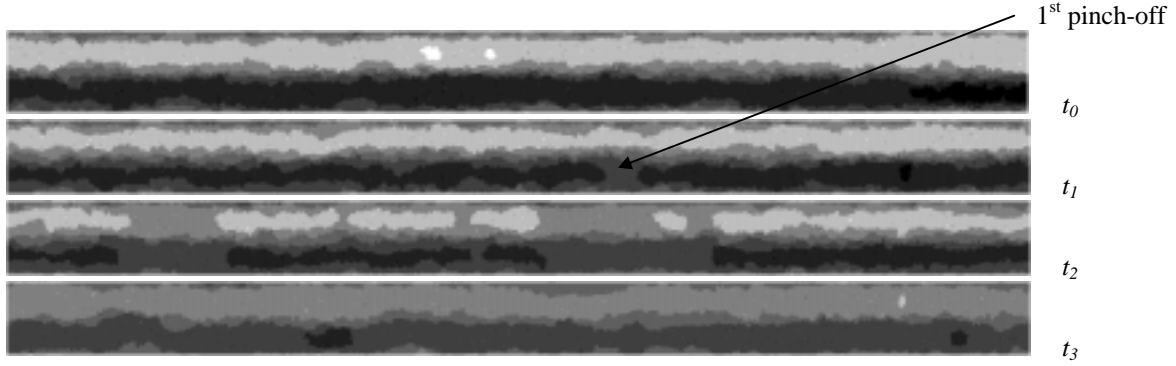


Figure 2. Snapshots of a surface obeying i -kinetics illustrating the pinch-off mechanism. $T = 0.56T_R$, $\lambda = 64a$. $t_0 v_0 = 1.75 \times 10^5$ (no pinch-off), $t_1 v_0 = 2.62 \times 10^5$ (first pinch-off), $t_2 v_0 = 3.78 \times 10^5$ (steady-state pinch-off), $t_3 v_0 = 5.24 \times 10^5$ (terrace dissolution virtually complete).

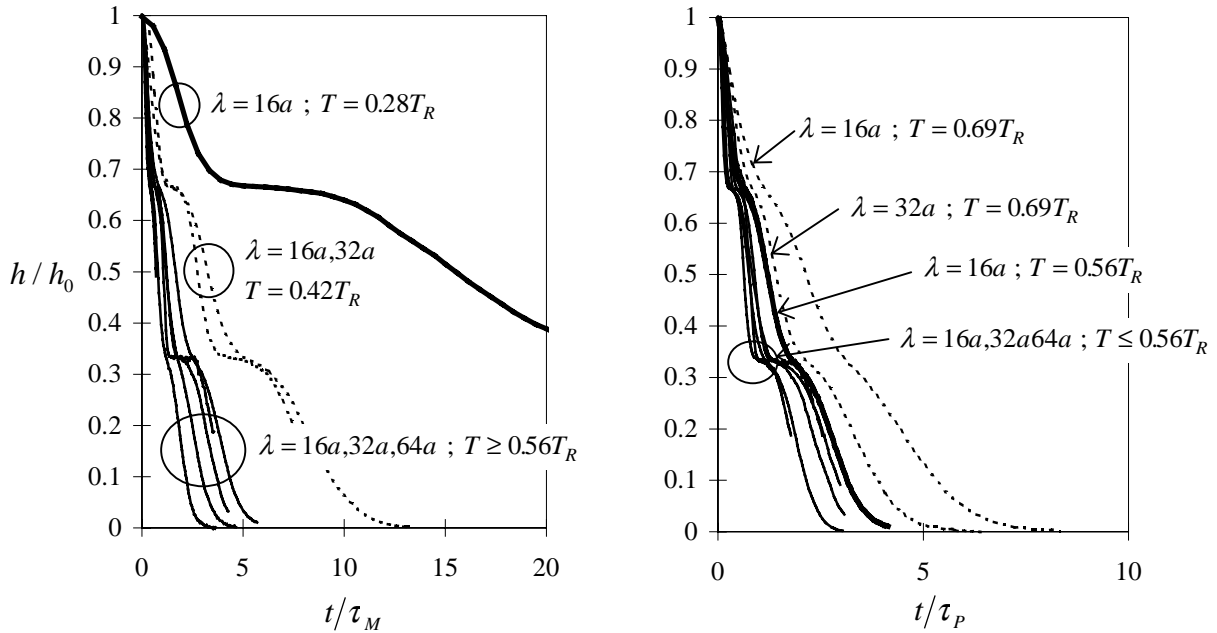


Figure 3. Attempts at collapse for relaxation of ripples, $0.28T_R \leq T \leq 0.69T_R$, $16a \leq \lambda \leq 64a$: (a) classical temperature dependence, $\tau_M^{-1} \propto (\exp(-\varepsilon^*/k_B T)/k_B T)\lambda^{-4}$, (b) pinch-off model, $\tau_P^{-1} \propto k_B T \exp(-\varepsilon^*/k_B T)/\tilde{\beta}(T)\lambda^{-4}$. In both cases, $\varepsilon^* = \varepsilon_B + 2\varepsilon$ and $h_0 = 3a$.

When using Δi -kinetics to relax a rippled surface, the pinch-off mechanism is observed to operate at short times. However as time progresses the simulated surfaces are seen to spontaneously island, as shown in Figure 4. The reason for this appears to be a kinetic preference to step-bunch in order to create many kink-kink-kink-etc. paths for atomic migration from the topmost to the bottom-most terraces. These paths are kinetically preferable because $\Delta i = 0$ along each step of the path; thus, there is essentially no barrier to migration along this route. Once islanded, the surfaces have a λ^3 scaling dependence, consistent with the typical behavior of dimple relaxation, discussed below.

Dimples. Bi-directional modulation, or dimples, can be thought of as artificially pinched-off surfaces. Seen in this way, the dimpled surface relaxes to equilibrium only through the driving force of reduction of line tension. Rettori and Villain[5] found that when only the reduction of line tension energy drives surface relaxation, the amplitude decay is *linear* with time, with characteristic time

$$\tau_B^{-1} = \frac{D_s C}{k_B T} \lambda^{-3}.$$

At low T and long λ , our simulations exhibit exactly this behavior, as shown in Ref [6].

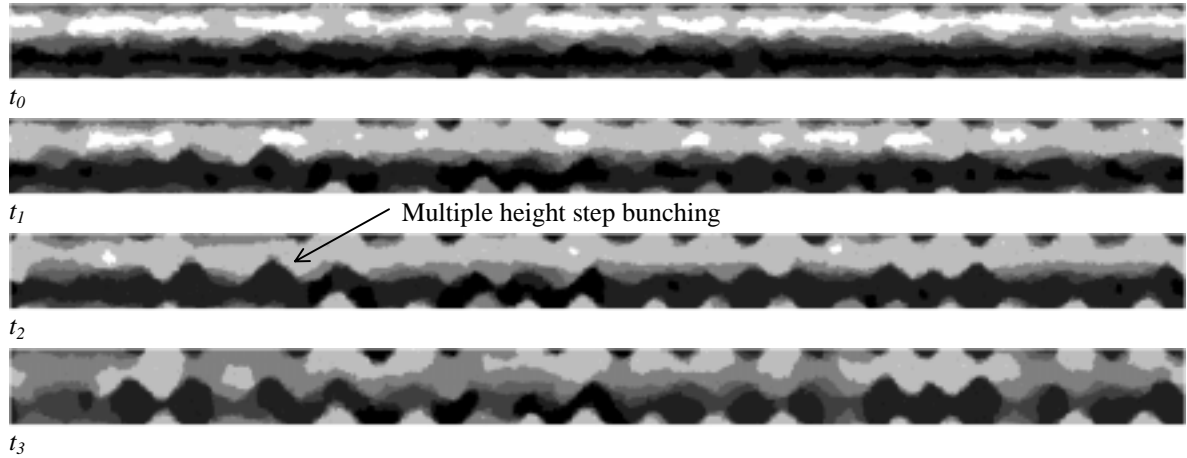


Figure 4. Snapshots of a surface obeying Δi -kinetics illustrating spontaneous islanding at low temperatures. $T = 0.42T_R$, $\lambda = 64a$. $t_0 v_0 = 4.31 \times 10^6$ (pinch-off mechanism operative), $t_1 v_0 = 6.7 \times 10^6$, $t_2 v_0 = 9.09 \times 10^6$, $t_3 v_0 = 1.87 \times 10^7$ (islanding apparent)

CONCLUSIONS

The phenomenology of surface relaxation below T_R has been shown via kinetic Monte Carlo simulation to exhibit extremely non-classical behavior depending on (1) morphology and (2) kinetic rate law for atom motion. However, within the temperature and size scale of our simulations there are only two mechanisms that operate. The pinch-off mechanism is seen to be operative for ripple relaxation for i -kinetics and Δi -kinetics at

short times. Reduction of line tension energy drives relaxation of dimpled surfaces and rippled surfaces obeying Δi -kinetics at long times.

It is cautioned that specific morphological considerations must be taken into account for any proper interpretation of experimentally measured $h(\lambda, T)$ curves below the roughening transition temperature.

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REFERENCES

1. W. W. Mullins, J. Appl. Phys. **28** (1957), 333; W. W. Mullins, J. Appl. Phys. **30** (1959), 77.
2. H. C. Kang, W. H. Weinberg, J. Chem. Phys. **90** (1989), 2824. A. M. Bowler, E. S. Hood, J. Chem. Phys. **94** (1991), 5162.
3. J. Erlebacher, proceedings of "Dynamics of Crystal Surfaces," edited by P. Duxbury, in press.
4. Z. Jiang, C. Ebner, Phys. Rev. B **40** (1989), 316. P. C. Searson, R. Li, K. Sieradzki, Phys. Rev. Lett. **74** (1995), 1395. M. V. Ramana Murty, B. H. Cooper, in press
5. A. Rettori, J. Villain, J. Phys. (Paris) **49** (1988), 257. W. Selke, T. Bieker, Surf. Sci. **281** (1993), 163.
6. J. Erlebacher, M. J. Aziz., accepted to Surface Science, 1996.
7. A. Pimpinelli, J. Villain, D. E. Wolf, J. J. Metois, J. C. Heyraud, I. Elkinani, G. Uimin, Surf. Sci. **295** (1993), 143.
8. E. D. Williams, R. J. Phaneuf, J. Wei, N. C. Bartelt, T. L. Einstein, Surf. Sci. **294** (1993), 219. E. D. Williams, R. J. Phaneuf, J. Wei, N. C. Bartelt, T. L. Einstein, Surf. Sci. **310** (1994), 451.
9. M. Ozdemir, A. Zangwill, Phys. Rev. B, **42** (1990), 5013.