Dynamic Coarsening of Crystal Surfaces by Formation of Macrosteps

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Dynamic coarsening of crystal surfaces by formation of macrosteps is explained by an improved model for impurity absorption. It is related to interface propagation in random media. Some unusual recursive equations are encountered. The model is analyzed by various methods and exhibits some universal features. We find coarsening to proceed logarithmically with time in agreement with experiments.

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The growth of faceted crystals occurs by lateral propagation of surface steps, which typically are part of a surface spiral originating from a screw dislocation. Observations on nearly perfect surfaces show spirals with hundreds or thousands of turns ("steps").[1-3] The distance of a step from the spiral center is proportional to its average speed of propagation and time. The "unit height" of a step corresponds to the Burgers vector of the screw dislocation and is usually one or just a few lattice units. For reasons not completely understood, these steps often tend to form "bunches" by coalescing into macrosteps of dozens or hundreds of unit step heights. Since the resulting macroscopic roughness of the crystal surface affects the crystal quality, one looks for a better understanding of this process.

In addition to this concrete application there is an analogy to coarsening in "spinodal decomposition" if one regards the flat terraces as parts of phase A and the macrosteps as parts of phase B. Furthermore, there is a close relationship to the propagation of interfaces in random media, as briefly discussed at the end.

Our basic assumption is that a small concentration of impurities adsorbed on the "terraces" between surface steps may play an essential role in many coarsening phenomena, as supported by experiments.[1-3] Various models were previously defined starting from very similar ingredients,[4-7] but they lack some important cooperative effects. Some other models rely on rather arbitrary assumptions. We now introduce our basic model, then briefly discuss the linear stability analysis and present the results of a mean-field analysis of the resulting functional equation. Finally, we compare this with a computer simulation and experiments.

We assume that the substrate material, forming the growing crystal, impinges from the vapor or solution onto the terraces between steps, quickly reaches quasiequilibrium (in relation with the vapor), and finally crystallizes into a nearby step by surface diffusion. This advances the step. Impurities also impinge onto the terraces, where they remain immobile, also reaching quasiequilibrium exponentially with time,[7] but on a slower scale than the substrate material.[1] These random impurities hamper the rate of advancement of steps to an extent that depends on their concentration immediately in front of a step.[4-6] As the step advances the impurities are incorporated, leaving an essentially "clean" surface directly behind the step.

A particular position on the surface thus undergoes oscillations in impurity concentration as steps are passing by. Consequently, the velocity v_n of step n is basically a function of the time τ_n elapsed since the step ahead has passed the same position $y_n(t)$. More precisely, this is formulated as

$$y_n(t) = y_{n+1}(t - \tau_n), \tag{1a}$$

$$v_n(t) = V(\tau_n(t)), \tag{1b}$$

where n denotes a specific step and $n+1$ the step in front of it. Because of the exponential saturation of impurities with time, $V(\tau)$ asymptotically goes as $V_0 + \delta V \times \exp(-\lambda\tau)$ for large τ. For small exposure times τ_n the velocity v_n decreases with decreasing τ_n because of the lack of a supply of substrate material between densely spaced steps. The step velocity $V(\tau)$, therefore, first increases with τ, goes through a maximum at τ_m, then decreases towards V_0. This completes the basic one-dimensional model.

Our model turns out to be closer to experiments in formulation and results than previous theories,[4-7] which have not considered the collective effects produced by this natural "exposure time" formulation, and which lead to quite different results.[6]

Despite its simplicity the model (1) shows surprising features. Dynamics follow from our taking the time

derivative of (1a), using (1b) with $dy_n(t)/dt = v_n = V(\tau_n)$:

$$\frac{d\tau_n(t)}{dt} = 1 - \frac{V(\tau_n(t))}{V(\tau_{n+1}(t-\tau_n))}. \quad (2)$$

Innocent as it looks, this is a functional equation and, in addition, it is recursive! It has only a first time derivative but, in order to formulate initial conditions, one has to know the solution.[8] For long times, however, the distances between steps vary slowly in comparison with the typical exposure times, so that we may consistently replace $\tau_n V_{n+1}$ by $d_n = y_{n+1}(t) - y_n(t)$. This then gives an approximate set of differential equations for $d_n(t)$,[9] tractable by computer or by other methods discussed below.

Even for the full set (2) a linear stability analysis is readily performed. A constant velocity $V_{\rm av}$ ($V_m > V_{\rm av} > V_0$) for all steps corresponds to two exposure times $\tau_a < \tau_m$ and $\tau_b > \tau_m$. Making a small perturbation around τ_b, $\tau_n(t) = \tau_b + \varepsilon \exp(ikn + \Omega t)$, one arrives at

$$\Omega = (Q/\tau_b)[\exp(ik - \Omega\tau_b) - 1], \quad (3)$$

with $Q = d[\ln V(\tau)]/d(\ln\tau)$. Here k is the wave number of the perturbation. The system is unstable for $\tau_b > \tau_m$, meaning $Q < 0$, the maximal instability occurring at $k = \pi$. If we start with a nearly equidistant step train with $\tau \simeq \tau_b$, this means pairwise coalescence of steps. In other words, this coarsening process starts if the typical exposure times initially are around or larger than τ_m. (The singularity produced by the kinematic wave theory[5] for a continuum model depends sensitively on the initial distribution of steps, as already noticed by Frank, and hence differs substantially from the present result.) Note further that $V_{\rm av} = {\rm const}$ still allows for an enormous multiplicity of (dynamically) stationary states, as only the two exposure times then are fixed but not the actual distribution of steps. As can easily be deduced, the pairwise coalescence continues to hold also for macrosteps, i.e., bunches of steps (within which there is the short exposure time τ_a). This step doubling lives on the discrete nature of (2) and is lost in continuum approximations.[5,6]

In order to study the long-time behavior of this process we consider the distribution function $S(\tau,t)$ for exposure times τ at observation time t. Initially it may start as a unimodal function at $t = 0$. It is then quickly split into a bimodal structure, peaked around two values $\tau_a(t) < \tau_m$ and $\tau_b(t) > \tau_m$. Here τ_a corresponds to bunching of steps into macrosteps, while τ_b corresponds to the large terraces between macrosteps. According to the stability analysis (3) the distribution $S(\tau,t)$ is stable (contracting) around τ_a. This peak, therefore, serves as a "sink" for exposure times τ_n. Alternatively, the peak around τ_b represents the "source" and is decreasing during the coarsening process. The latter peak thus dominates the systems dynamics and accordingly can be viewed as a unimodal distribution. More pictorially, the dynamics of a macrostep is governed by the leading step of the bunch. The peak around τ_a then merely serves to maintain global conservation of steps.

This conservation law locally can be written as

$$\partial_t S(\tau,t) = -\partial_\tau[u(\tau,t)S(\tau,t)], \quad (4)$$

where u is the (drift) rate of change of τ values. Defining step distances $d_n = \tau_n V(\tau_{n+1})$ as above, we obtain

$$V(\tau_{n+1}) - V(\tau_n) = (\partial_t \tau_n)V(\tau_{n+1}) + \tau_n \partial_t V(\tau_{n+1}(t)). \quad (5)$$

We define a mean-field approximation by

$$V(\tau_{n+1}) \to \langle V(\tau)\rangle \equiv W(t) = \int d\tau\, V(\tau)S(\tau,t) / \int d\tau\, S(\tau,t), \quad (6)$$

stating that the velocity of step $n+1$ in front of step n be replaced by the average velocity $W(t)$ over all steps. Inserting (6) into (5) and identifying now $\partial_t \tau_n(t) = u(\tau,t)$, we obtain

$$u(\tau,t) = 1 - V(\tau)/W(t) - \tau\partial_t W(t)/W(t). \quad (7)$$

The set of equations (4), (6), and (7) defines the functional mean-field equation for the dynamics of the distribution function $S(\tau,t)$. To be precise, it only describes the dynamics of the peak near $\tau > \tau_m$. But for long times we shall observe $0 < \tau_a < \tau_m \ll \tau_b$, and so we may assume (4) to hold in the full range $\tau > 0$. The leakage out of $S(\tau,t)$ at $\tau = 0$ then contributes to the peak at τ_a (global conservation) which then need not be considered further.

A detailed analysis of this equation is obviously not an easy task. It turns out, however, that we may approximate $S(\tau,t)$ in the long-time limit by a Gaussian:

$$S(\tau,t) = m(t)\exp\{-[\tau - \tau_0(t)]^2/2\sigma(t)^2\}, \quad (8)$$

keeping amplitude $m(t)$, peak position $\tau_0(t)$, and width $\sigma(t)$ time dependent. The results are consistent to this order.[9]

With this approximation we can now derive[9,10] a set of three coupled ordinary nonlinear differential equations for m, τ_0, and σ, through use of the asymptotic $V(\tau)$ as given after (1a) and (1b). The width σ of the large-τ peak is predicted to go to a finite value, the amplitude to decay by a power law, and the peak position and thus the width of the large terraces to increase logarithmically with time:

$$\lambda\tau_0 = \ln t. \quad (9)$$

Because of this logarithm, the single experimental constant λ determines the results. It is the ratio of impurity atoms impinging on the surface per area and time to the equilibrium concentration at a flat surface. This scaling result is essentially a consequence of the exponential decay of $V(\tau)$. Thus it could be derived in a simpler way,[9] if one were to start with $\sigma(t)/\tau_0(t) = 0$ for long times as an assumption.

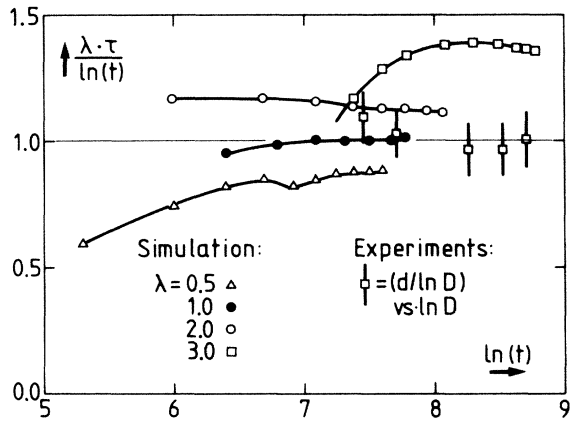

FIG. 1. Comparison of the prediced scaling relation (9) with computer simulations (Ref. 9) and experiments (Ref. 1). Since no experimental values for time scales τ were available we have taken experimental data for step spacing d and distance D from the spiral center. For long times all data converge towards the scaling relation.

A comparison [Fig. (1)] with direct computer simulations[9] shows agreement with the predicted asymptotic scaling (9) and with an analysis[9] of recent experimental data.[1] For small values of λ the convergence of the numerical data towards (9) of course is faster than for large ones. Other parameters like V_0, δV, τ_m, etc., affect the short-time behavior only. The agreement with experimental results[1] is also obvious. The plot shows d, the spacing between macrosteps, and D, the distance from the spiral center, both in arbitrary units. Previous attempts[6] suggesting a $t^{1/2}$ law on a more phenomenological basis, not explicitly considering impurities, are inconsistent with these experiments. However, we do not claim that the formation of macrosteps is always a consequence of the mechanism described here. The combined action of diffusion and kinetic coefficients was taken into account in an averaged way only, but in any case impurities even at small concentrations seem to play a central role in the kinetics of step movement. Furthermore, we have ignored fluctuations along the steps. As in the general problem of an interface moving in a random medium,[11] they presumably are significant in crystals with small anisotropy of the step free energy. A simple approximation can be made[9] to account for such fluctuations by the addition of a diffusion current into (4) in addition to the drift.

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