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# CONTINUUM DESCRIPTIONS OF CRYSTAL SURFACE EVOLUTION

Howard A. Stone[1] and Dionisios Margetis[2]
[1]*Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 01238, USA*
[2]*Department of Mathematics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

## 1. Morphological Evolution of Crystalline Materials

It is well known that liquid surfaces evolve in shape due to the effect of surface tension, which drives configurations towards lower energy. The break-up of an initially cylindrical fluid thread into spherical droplets, first quantified experimentally by Plateau and analyzed by Rayleigh, is a popular and illustrative example. Solid surfaces, in particular surfaces of crystals, also evolve according to the analogous principle of minimizing their surface energy. The evolution in this case, however, is more complicated to describe physically and mathematically than the analogous phenomena for fluid interfaces, because there is a richer variety of competing mechanisms that are available for the solid to change its shape. In addition, a solid supports strain, which leads to the surface energy depending on the slope of the crystal surface. In this article we summarize the basic physical ideas that underlie crystal surface evolution, introduce continuum descriptions in terms of continuum thermodynamics and partial differential equations (PDEs), and provide solutions to some analytically tractable prototypical problems.

A strong motivation for studying how crystal surfaces evolve is the need to better understand and harness properties of solid structures and electronic devices at the nanoscale. In most experimental, and technologically relevant, situations, such structures are not in thermodynamic equilibrium, and decay with a lifetime that varies appreciably with the temperature $T$ and, most importantly, scales as an integer power of the feature size; thus, smaller structures decay faster. Hence, there is a need for the quantitative understanding of the factors that affect surface evolution, such as formation and growth of islands



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and atom clusters. Other problems are related to crystal dissolution, the effects of catalysts, and surface functionalization (e.g., using physical chemistry techniques).

## 1.1. Mechanisms of Surface Evolution of Crystalline Materials

There are at least four primary mechanisms for solid surfaces to evolve: (i) Evaporation–condensation processes whereby atoms leave the surface or deposit on the surface from above. These processes are driven by differences between the chemical potential of the surface and the adjacent bulk phases (solid or vapor). (ii) Surface diffusion whereby movable atoms or point defects ("adatoms") perform random walks (Brownian motion) along the surface. (iii) Strain-driven rearrangements of atoms in the bulk of the material. (iv) Atomic motion driven by external electric fields, which is a phenomenon referred to as electromigration. Here we focus on mechanisms (i) and (ii).

These mechanisms, and especially their effects on the macroscopic surface features as well as their quantitative description, depend on the temperature and the surface orientation.

There are two distinct temperature regimes that mark different macroscopic behaviors of surfaces both at and away from equilibrium; these regimes are separated by the orientation-dependent roughening transition temperature $T_R$. For any fixed $T$, continuously curved portions of the surface are characterized by a roughening transition temperature $T_R < T$ whereas macroscopically flat regions of the surface known as "facets" have $T_R > T$ [1]. Below $T_R$ the surface consists of distinct steps bounding terraces whose size can vary from a few nanometers up to a few microns, as shown in Fig. 1a which also illustrates

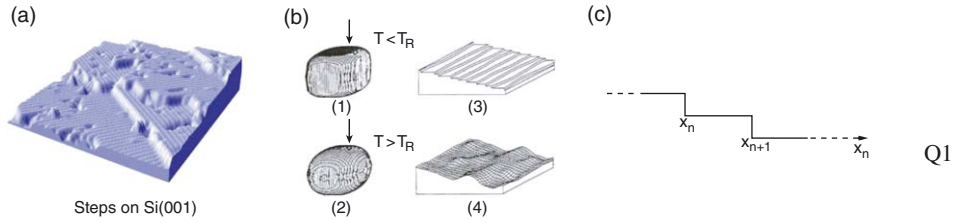


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*Figure 1.* (a) A STM (single tunneling microscopy) image of a stepped Si (001) surface, which illustrates kinks, voids, atom clusters, a step and a terrace. (Ref. B.S. Swartzentruber's website, Sandia National Laboratories). (b) The contrast between the shape of crystal surfaces above and below the roughening transition. For $T < T_R$ the equilibrium crystal shape has stable facets while for $T > T_R$ the surface is continuously rounded with no facets present (Ref. Fig. 7 from Ref. [3]). (c) The notation used for keeping track of the position of different steps with position $x_n(t)$.

kinks, clusters of atoms and voids. The increase of the temperature above $T_R$ causes the terraces to shrink as steps are spontaneously created everywhere, and the surface appears to be "rough," as shown in Fig. 1b. Accordingly, below $T_R$ the evolution is caused by the lateral motion of the atomic steps and is in principle more difficult to describe physically and mathematically. Moreover, the detailed description of these processes is impacted by kinetics at the step edges, especially those of extremal steps of opposite sign [2].

The physical picture described above implies that the energetics of the solid surface are different above and below $T_R$, which can be a few hundreds of degrees K below the melting temperature for solids; this description of surface evolution clearly has important differences from the case of liquid–liquid interfaces.

## 1.2. Theoretical Descriptions of Surface Evolution

The aim of most theoretical studies is to describe the surface morphology at macroscopic length scales by taking into account the motion of atoms or steps at smaller length scales. Historically, there have been two different theoretical approaches: (i) Approaches based on continuum thermodynamics and principles of continuum mechanics such as mass conservation, which lead to diffusion-like PDEs or variational principles (e.g., for a recent variational approach see Ref. [4]). (ii) Simulations of individual atoms or step motion by solving a large number of coupled equations; for example, the wandering of an individual step is studied by taking into account the local or nonlocal interactions with adjacent steps. This second approach often succeeds in providing detailed information about the surface morphology by accounting for motions over a wide range of length scales. Nevertheless, the merits of the first approach include its relative simplicity because it often enables analytical solutions and, therefore, allows for quantitative predictions for experiments. It is worthwhile mentioning that the differential equations that arise in this continuum approach vary in their form and properties of solutions, and are not generally so familiar to researchers. We take the first approach in the main body of this article.

There are many different types of problems that have emerged in the theoretical and experimental studies of morphological surface evolution, as determined mostly by the geometry and dimensionality of the surface configurations both above and below $T_R$. We mention here only four types of such problems. In particular, there have been studies of: (a) the relaxation or flattening of a surface with long-wavelength features, an example being a periodic corrugation with an initial sine in one or two rectilinear coordinates, (b) the relaxation of a surface morphology with an initial localized "bump," or structure of finite extent, (c) the evolution of the interface between two grain boundaries,

which is commonly referred to as *grooving*, and (d) the evolution of surfaces of revolution in three dimensions such as cones and cylinders (e.g., wires). Analytical solutions for representative versions of some of these problems are summarized in this paper.

## 1.3. Step-flow Models

The basic description of atomistic processes in the framework of step kinetics that underlies surface evolution was given by Burton *et al*. [5] and is referred to as BCF theory; for an overview see Ref. [3]. Figure 1c shows a cross-section of a 1D step configuration along $x$ with the position of the $n$th step denoted by $x_n(t)$, where the $n$th terrace is the region $x_n < x < x_{n+1}$. The starting point for step-flow models is the conservation of mass, which relates $x_n$ with the adatom surface current (atoms/time), $J_n(x)$, on the $n$th terrace by

$$\dot{x}_n(t) = \frac{\Omega}{a}\,[J_{n-1}(x_n, t) - J_n(x_n, t)], \quad \dot{x}_n(t) \equiv \frac{\mathrm{d}x_n}{\mathrm{d}t}, \tag{1}$$

where $\Omega$ is the atomic area and $a$ is the step height. The surface current is $J_n = -D_s(\partial c_n/\partial x)$, where $c_n = c_n(x, t)$ is the adatom concentration and $D_s$ is the diffusivity. The concentration $c_n(x, t)$ satisfies the diffusion equation, $D_s(\partial^2 c_n/\partial x^2) = \partial c_n/\partial t \approx 0$, where the time derivative is negligible in the quasistatic approximation. Thus, $c_n$ on each terrace is $c_n(x, t) = A_n(t)x + B_n(t)$, where the time $t$ enters implicitly through the boundary conditions. The requisite boundary conditions describe the attachment and detachment of atoms at the step edges,

$$-J_n(x_n, t) = k[c_n(x_n, t) - c_n^{\mathrm{eq}}], \quad J_n(x_{n+1}, t) = k[c_n(x_{n+1}, t) - c_{n+1}^{\mathrm{eq}}], \tag{2}$$

where $k$ is the attachment–detachment rate coefficient and the superscript "eq" denotes the equilibrium atom density at the step edge. Hence, $A_n$ and $B_n$ can be determined in terms of $c_n^{\mathrm{eq}}$, which is related to the step chemical potential, $\mu_n$, by

$$c_n^{\mathrm{eq}} = c^{\mathrm{eq}} \exp\left(\frac{\mu_n}{k_B T}\right) \approx c^{\mathrm{eq}}\left(1 + \frac{\mu_n}{k_B T}\right), \tag{3}$$

where we have also indicated the limit $|\mu_n| \ll k_B T$ [6]. Finally, $\mu_n$ is related to other step positions via the step interaction potential. In particular, for next-neighbor interactions described by the potential $V(x_n, x_{n+1})$, the step chemical potential is $\mu_n = \partial[V(x_n, x_{n+1}) + V(x_{n-1}, x_n)]/\partial x$. Hence, (1)–(3) define a system of coupled ODEs for the step positions which can be solved numerically with given initial conditions $x_n(0)$ to determine the evolution of a stepped surface.

## 2. Governing Equations for Continuum Descriptions

A basic ingredient of the continuum equations for surface evolution both above and below roughening is the chemical potential $\mu$ [7]. We restrict the majority of our discussion to the analysis of configurations in one independent space dimension where the height profile is denoted $h = h(x, t)$ and $h_x \equiv \partial h/\partial x$. The surface thermodynamics can be described in terms of either of two energies, the surface free energy per projected area of the high-symmetry plane, $G(h_x)$, or the perhaps more familiar surface free energy per area of the surface, $\gamma(\phi)$, where $\phi$ is the surface orientation, $\tan\phi = h_x$. The two energies are related by $G = \gamma\sqrt{1 + h_x^2}$. As above, we denote by $\Omega$ the atomic area.

The chemical potential $\mu$ is related to $G$ by $\mu - \mu_0 = -\Omega(\partial/\partial x)(\partial G/\partial h_x)$, as shown using a variational principle [8] in the Appendix. It then follows by elementary calculus that

$$\begin{aligned}\mu - \mu_0 &= -\Omega\frac{\partial}{\partial x}\frac{\partial G}{\partial h_x} = -h_{xx}\frac{\partial^2 G}{\partial h_x^2}\\ &= -\Omega h_{xx}\cos^2\phi\frac{\partial}{\partial\phi}\cos^2\phi\frac{\partial}{\partial\phi}\left(\frac{\gamma(\phi)}{\cos\phi}\right)\\ &= -\Omega\left(\gamma + \frac{\mathrm{d}^2\gamma}{\mathrm{d}\phi^2}\right)\underbrace{\frac{h_{xx}}{(1 + h_x^2)^{3/2}}}_{\kappa},\end{aligned} \tag{4}$$

where in the last step we used $\cos\phi = (1 + h_x^2)^{-1/2}$. Also, $\kappa$ denotes the curvature of the surface. The term $\mathrm{d}^2\gamma/\mathrm{d}\phi^2 \equiv \gamma_{\phi\phi}$ is *not* present when considering surface evolution of liquids. In the more general, 2D setting [8], we have $G = G(h_x, h_y)$ and use $\mu - \mu_0 = -\Omega_\mathrm{v}((\partial/\partial x)(\partial G/\partial h_x) + (\partial/\partial y)(\partial G/\partial h_y))$ where $\Omega_\mathrm{v}$ is the atomic volume. As a result, the chemical potential is $\mu - \mu_0 = -\Omega_\mathrm{v}(\gamma + \gamma_{\phi_1\phi_1})\kappa_1 - \Omega_\mathrm{v}(\gamma + \gamma_{\phi_2\phi_2})\kappa_2$, where $\kappa_1$ and $\kappa_2$ are the principal curvatures, and $\phi_1$ and $\phi_2$ are the corresponding angles (surface orientations) along the normals to these principal curvatures.

### 2.1. Surface Evolution by Evaporation–Condensation Above and Below $T_\mathrm{R}$

Perhaps the simplest case of surface dynamics is when the evolution occurs by displacement of atoms by evaporation from, or condensation on, the surface. The driving force for movement of the atoms is then the difference of chemical potentials between the surface and the vapor. Thus, with $v_n$ denoting the speed at which the surface is displaced in the normal direction,

$$v_n = -\zeta(\mu - \mu_0), \tag{5}$$

where $\zeta > 0$ is the product of a surface mobility [9] and the inverse of the step height.

It is necessary to distinguish two cases, $T > T_{\mathrm{R}}$ and $T < T_{\mathrm{R}}$, since below roughening the existence of steps and facets produces differences in the form of the relation between surface energy ($\gamma$) and surface orientation ($h_x$). In the classical case of evolution above roughening, $T > T_{\mathrm{R}}$, $\zeta$ and $\gamma$ are analytic in $h_x$. For the special case of constant properties, $\zeta_0$ and $\gamma_0$, Eq. (5) simplifies. Since $v_n = h_t/\sqrt{1+h_x^2}$ and the curvature is $\kappa = h_{xx}/\left(1+h_x^2\right)^{3/2}$, then (4) and (5) lead to

$$h_t = \Omega\zeta_0\gamma_0\frac{h_{xx}}{1+h_x^2} \quad (T > T_R). \tag{6}$$

In the small-slope limit, $|h_x| \ll 1$, we simply have the familiar linear diffusion equation. Some examples, for both the linear and nonlinear equations, are given below.

On the other hand, below the roughening transition, $T < T_{\mathrm{R}}$, the mobility may be dependent on the surface orientation, e.g., $\zeta = k_0|h_x|^\alpha$ with $\alpha = 0$ or 1 is common. Further, it is usual to consider small slopes and define the height function $h(x,t)$ relative to a crystallographic plane. In this case, $\gamma + \gamma_{\phi\phi} = \tilde{\gamma}\,|h_x|^\beta$, where $\beta = 1$ when the dominant physical effect at the nanoscale is that of step–step elastic interactions that decay inversely proportional to the square of the step distance [10], or $G = g_0 + g_1|h_x| + \frac{1}{3}g_3|h_x|^3$, where $2g_3 = \tilde{\gamma}$. For $\alpha = 1$ and $\beta = 1$ in particular, the surface evolves according to the non-linear equation

$$h_t = \Omega k_0\tilde{\gamma}\,h_x^2 h_{xx}. \tag{7}$$

A general discussion of the evaporation–condensation dynamics below roughening is given by Spohn [9]. Again, some examples are provided below.

## 2.2. Surface Evolution by Surface Diffusion Above and Below $T_{\mathrm{R}}$

As above, the surface evolves in the normal direction at a speed $v_n$ owing to variations in the flux of atoms along the surface. It is straightforward to give the development in two independent space dimensions here [11]. If we let $\mathbf{j}$ denote the number of atoms per unit length normal to a contour lying in the surface and $\Omega_{\mathrm{v}}$ the atomic volume as above, then mass conservation requires

$$v_n + \Omega_{\mathrm{v}}\nabla_s \cdot \mathbf{j} = 0. \tag{8}$$

For systems out of, but close to, equilibrium the surface flux $\mathbf{j}$ is proportional to the gradient of the surface chemical potential (or energy) for an

atom. The corresponding thermodynamic force on the atom is $-\nabla_s \mu$, and the flux of atoms then follows from a form of a Stokes–Einstein argument: $\mathbf{j} = -(D_s c_s / k_B T)\nabla_s \mu$, where $D_s$ is the surface diffusivity, $c_s$ is the adatom concentration (number/area; adatoms are those atoms free to diffuse at any time along the surface), $k_B$ is Boltzmann's constant and $T$ is the absolute temperature. Assuming all material parameters are constants, the surface evolves according to

$$v_n = \frac{D_s c_s \Omega_v}{k_B T} \nabla_s^2 \mu. \tag{9}$$

Above the roughening transition, the chemical potential change, $\mu - \mu_0$, is proportional to the surface curvature. Hence, (9) yields a fourth-order nonlinear PDE for the height $h$. In one dimension the PDE is

$$h_t = -\frac{D_s c_s \Omega^2 \gamma_0}{k_B T} \sqrt{1 + h_x^2}\, \frac{\partial^2}{\partial x^2} \left[ \frac{h_{xx}}{(1 + h_x^2)^{3/2}} \right]. \tag{10}$$

For small slopes, this equation is linearized to $h_t = -(D_s c_s \Omega^2 \gamma_0 / k_B T)\, h_{xxxx}$.

On the other hand, below the roughening transition, the surface energy depends on the surface orientation. Taking $\gamma + \gamma_{\phi\phi} = \tilde{\gamma}\,|h_x|$ in one dimension for small surface slopes, we obtain the nonlinear PDE

$$h_t = -\frac{D_s c_s \Omega^2 \tilde{\gamma}}{k_B T} (|h_x| h_{xx})_{xx}. \tag{11}$$

Some solutions of these equations for surface-diffusion-driven evolution above and below the roughening temperature are given below.

## 3. Solutions to Prototypical Problems: Surface Evolution by Evaporation–Condensation Processes, $T > T_R$

In these last sections we tersely summarize a number of problems that have been treated analytically, including both the familiar linear second and fourth order diffusion equations and the more intricate nonlinear equations. We treat in sequence evaporation–condensation and surface diffusion processes, first for conditions above, and then for conditions below, the roughening transition.

We begin with evaporation–condensation dynamics. Recall that (6) reduces to the diffusion equation for $|h_x| \ll 1$ so that $h_t = \Omega \zeta_0 \gamma_0\, h_{xx}$.

*Relaxation of periodically corrugated surfaces* [12]. For an initial periodic profile with wavelength $\lambda$, $h(x, 0) = A \sin(2\pi x/\lambda)$, the diffusion equation is solved by applying Fourier series in the form $h(x, t) = \sum_{n=1}^{\infty} a_n(t) \sin(2n\pi x/\lambda)$,

where the coefficients $a_n(t)$ satisfy the ODE $\dot{a}_n + \Omega\zeta_0\gamma_0(2\pi n/\lambda)^2 a_n = 0$ and the initial condition $a_n(0) = A$. Hence, the complete solution is

$$h(x,t) = A\sum_{n=1}^{\infty} e^{-\Omega\zeta_0\gamma_0\left(\frac{2\pi n}{\lambda}\right)^2 t}\ \sin\left(\frac{2n\pi x}{\lambda}\right). \tag{12}$$

For sufficiently long times, which corresponds to $t \gg \lambda^2/(4\pi^2\Omega\zeta_0\gamma_0)$, Eq. (12) simplifies to $h(x,t) \sim Ae^{-\Omega\zeta_0\gamma_0(2\pi)/(\lambda)^2 t}\ \sin(2\pi x/\lambda)$; thus, the lifetime of the periodic profile is proportional to $\lambda^2$.

*Decay of a localized mound of atoms*. Again, we restrict ourselves to the small-slope approximation. For an initial bump, $h(x,0) = f(x)$ where $f(x)$ is of finite extent, and the condition $h \to 0$ sufficiently fast as $|x| \to \infty$, $h(x,t)$ is determined analytically by applying the Laplace transform in $t$, $\tilde{h}(x,s) = \int_0^\infty \mathrm{d}t\, h(x,t)e^{-st}$. In particular, for $f(x) = \delta(x)$, we find $\tilde{h}^\delta(x,s) = e^{-\sqrt{s}|x|}/(2\sqrt{s})$ whose inversion gives the fundamental solution

$$h^\delta(x,t) = \frac{1}{\sqrt{\Omega\zeta_0\gamma_0 t}} e^{-\frac{x^2}{4\Omega\zeta_0\gamma_0 t}}. \tag{13}$$

Notice that this solution has the similarity form $t^{-1/2}H(\eta)$ where $\eta$ is the similarity variable $x/\sqrt{4\Omega\zeta_0\gamma_0 t}$. The solution for an arbitrary initial bump is obtained by superposition

$$h(x,t) = \int_{-\infty}^{\infty} \mathrm{d}x'\, h^\delta(x-x',t) f(x'). \tag{14}$$

*Grooving at a grain boundary* [13, 14]. Here we consider the evolution of a groove which forms at a grain boundary of an otherwise flat surface. It is thus necessary to solve (6) subject to the condition $h_x(0,t) = -(\cos\theta/\sin\theta)$, where $\theta$ is half the dihedral angle formed at the groove. This problem admits a similarity solution of the form $h(x,t) = (2\Omega\zeta_0\gamma_0 t)^{1/2}\, H\left(x/(2\Omega\zeta_0\gamma_0 t)^{1/2}\right)$ where $H(\eta)$ satisfies the ODE

$$\left(H - \eta H_\eta\right)\left(1 + H_\eta^2\right) = H_{\eta\eta}. \tag{15}$$

Thus, the grain deepens at a rate proportional to $t^{1/2}$. A numerical solution of (15) is in principle necessary and is straightforward to obtain by the usual shooting procedure of guessing $H(0)$ with a given $H_\eta(0)$ until $H(\eta \to \infty) \to 0$. For the special case of small surface slopes, $|H_\eta| \ll 1$, (15) can be linearized, and the resulting solution is $H(\eta) = -(\cos\theta/\sin\theta)(\eta\,\mathrm{erfc}(\eta/\sqrt{2}) - \sqrt{2/\pi}\,e^{-\eta^2/2})$.

## 4. Surface Evolution by Surface-Diffusion Processes, $T > T_R$

In the small-slope approximation, $|h_x| \ll 1$, Eq. (10) reads $h_t = -B\, h_{xxxx}$ where $B = (D_s c_s \Omega^2 \gamma_0 / k_B T) > 0$ is a material parameter with dimension (length)$^4$/time.

*Decay of periodic surface modulations*. For an initial periodic profile with wavelength $\lambda$, $h(x,0)=A\,\sin(2\pi x/\lambda)$, (10) is solved again by applying Fourier series; the coefficients $a_n(t)$ satisfy the ODE $\dot{a}_n + B(2\pi n/\lambda)^4 a_n = 0$ and the initial condition $a_n(0) = A$. Hence, the complete solution is

$$h(x,t) = A \sum_{n=1}^{\infty} e^{-B\left(\frac{2\pi n}{\lambda}\right)^4 t} \sin\left(\frac{2n\pi x}{\lambda}\right). \tag{16}$$

For sufficiently long times, $t \gg (2\pi)^{-4}\lambda^4/B$, this solution is approximated by $h(x,t) \sim A\, e^{-B(2\pi/\lambda)^4 t}\, \sin(2\pi x/\lambda)$; thus, the lifetime of the periodic profile is proportional to $\lambda^4$. This scaling with size should be contrasted with the case of evaporation-condensation for which the lifetime is proportional to $\lambda^2$.

*Decay of a localized mound of atoms*. In some circumstances there are initial conditions that correspond to a mound of material on an otherwise flat surface. The system proceeds to lower its energy by flattening and so it is of interest to quantify this decay process. For an initial bump, $h(x,0) = f(x)$, and the condition $h \to 0$ sufficiently fast as $|x| \to \infty$, $h(x,t)$ is again determined analytically by applying the Laplace transform of $h(x,t)$ in $t$. In particular, for $f(x) = \delta(x)$, we find $\tilde{h}^{\delta}(x,s) = 2^{-1} B^{-1/4} s^{-3/4}\, e^{-s^{1/4} B^{-1/4}|x|/\sqrt{2}}\, \sin(s^{1/4} 2^{-1/2} B^{-1/4}|x| + \pi/4)$ whose inversion gives the real solution

$$h^{\delta}(x,t) = \frac{1}{2\pi \mathrm{i}} \frac{1}{2(Bt)^{1/4}} \int_{-\mathrm{i}\infty}^{\mathrm{i}\infty} \mathrm{d}\sigma\, \sigma^{-3/4}\, \sin\left(\eta \sigma^{1/4} + \frac{\pi}{4}\right), \tag{17}$$

where $\eta = |x|/(4Bt)^{1/4}$. The solution has the similarity form $t^{-1/4} H(\eta)$, which, for long times, could have been deduced immediately. The solution for an arbitrary bump is given by (14); for sufficiently long times this solution also obtains a similarity structure. It is inferred that for long times the bump has a lifetime proportional to the fourth power of its linear size.

## 5. Surface Evolution by Evaporation–Condensation Processes, $T < T_R$

*Decay of a localized mound of atoms in one space dimension*. Here we consider Eq. (7). The material parameter $\Omega k_0 \tilde{\gamma}$ has the units of diffusivity, (length)$^2$/time. If we consider an arbitrary initial distribution of atoms confined

to a region $|x| \le X(t)$, then global mass conservation requires $2\int_0^{X(t)} h(x,t)\,\mathrm{d}x = M = \text{constant}$. For this problem there is a similarity solution that describes the long-time behavior of a bump, and a wide class of initial distributions are expected to evolve to the profile predicted by the similarity solution for times $t \gg \ell^2/(\Omega k_0 \tilde{\gamma})$, where $\ell$ is a length scale characteristic of the initial distribution. The similarity solution has the form

$$h(x,t) = \left(\frac{M^4}{96\Omega k_0 \tilde{\gamma}}\right)^{1/6} t^{-1/6}\, H(\eta), \quad \text{where} \quad \eta = \frac{x}{(3\Omega k_0 \tilde{\gamma} M^2/2)^{1/6} t^{1/6}}, \tag{18}$$

and the function $H(\eta)$ thus satisfies the fourth-order ODE $-(H\eta)_\eta = {H_\eta}^2 H_{\eta\eta}$. Conservation of the total mass becomes $\int_0^{\eta_\mathrm{e}} H(\eta)\mathrm{d}\eta = 1$, where $X_\mathrm{e}(t) = \eta_\mathrm{e}\left(3\Omega k_0 \tilde{\gamma} M^2/2\right)^{(1/6)} t^{(1/6)}$ is the finite extent of the evolving surface; the constant $\eta_\mathrm{e}$ remains to be determined. The ODE for $H(\eta)$ can be integrated twice; using the symmetry condition $H_\eta(0) = 0$ along with the definition of the leading edge $\eta_\mathrm{e}$ as $H(\eta_\mathrm{e}) = 0$ we obtain

$$H(\eta) = \left(\frac{3}{8}\right)^{1/2} \eta_\mathrm{e}^2 \left[1 - \left(\frac{\eta}{\eta_\mathrm{e}}\right)^{4/3}\right]^{3/2}, \tag{19}$$

which is the form given by Spohn [9]. The parameter $\eta_\mathrm{e}$ is determined from total mass conservation; we find

$$\eta_\mathrm{e}^3 \left(\frac{3}{8}\right)^{1/2} \int_0^1 (1-\eta^{4/3})^{3/2}\,\mathrm{d}\eta = 1 \quad \text{or} \quad \eta_\mathrm{e} = \left(\frac{2}{6\pi}\right)^{1/6} \left[\frac{\Gamma(1/4)}{\Gamma(3/4)}\right]^{1/6}, \tag{20}$$

where $\Gamma(s)$ is the Gamma function.

*Decay of an axisymmetric bump in two dimensions* ([9]). For axisymmetric shapes $h = h(r,t)$ where $r = \sqrt{x^2+y^2}$. We take [10]

$$G = g_0 + g_1|\nabla h| + \tfrac{1}{3} g_3 |\nabla h|^3, \tag{21}$$

and $\mu - \mu_0 = -\Omega_\mathrm{v}((\partial/\partial x)(\partial G/\partial h_x) + (\partial/\partial y)(\partial G/\partial h_y))$. The resulting PDE for small slopes, $|\nabla h| \ll 1$, and $h_r < 0$ follows from (5) and (21) with $\zeta = k_0|\nabla h|$ to be

$$h_t = A\frac{h_r}{r}\left[1 + \frac{g_3}{g_1}\frac{\partial}{\partial r}(r h_r^2)\right] \quad \text{where} \quad A = \Omega_\mathrm{v} k_0 g_1, \tag{22}$$

with the initial condition $h(r,0) = \mathcal{H}(r)$. Neglecting the $g_3/g_1$ term in the PDE and applying the method of characteristics we obtain $h(r,t) \approx \mathcal{H}\left(\sqrt{2At + r^2}\right)$. This solution describes how the initial bump shrinks to zero at long times, while corrections due to the $g_3/g_1$ term then are relatively small and can be obtained via simple iterations.

## 6. Surface Evolution by Surface–Diffusion Processes, $T < T_R$

*Evolution of a periodic profile in one dimension*. Kinetic simulations [15, 16] based on a step-flow model with elastic step–step interactions have indicated that the height of periodic profiles in one dimension may evolve as $h(x,t) = \Lambda(x)\Theta(t)$, i.e., $h$ has a separable form. From the continuum viewpoint the surface evolution can be described by (11), $h_t = -B\,(|h_x|h_{xx})_{xx}$ where $B = (D_s c_s \Omega^2 \tilde{\gamma}\,/\,k_B T)$. Assuming $h_x > 0$, $\Lambda$ and $\Theta$ thus satisfy $-\dot{\Theta}/\Theta^2 = C = \text{const.} > 0$ and $(\Lambda_x \Lambda_{xx})_{xx} = C\Lambda(x)$. Hence, $\Theta(t) = (Ct + K)^{-1} \approx C^{-1}t^{-1}$ for long times, while the ODE for $\Lambda$ can only be solved numerically. The set of boundary conditions that would yield a unique solution to this PDE is a topic of discussion in the literature (e.g. Ref. [2]).

*Evolution of an axisymmetric shape in two dimensions* ([17]). Here we consider the surface-diffusion-driven change in shape of an initially conical surface (see Fig. 2a). Using (21) and the equation for $\mu - \mu_0$ in terms of $G$ along with (9), we obtain a PDE for $h(x, y, t)$ in two dimensions. For axisymmetric shapes, $h = h(r, t)$, with a growing facet of radius $w(t)$, as shown in Fig. 2a, the PDE for the slope profile $F = -h_r$ is

$$\frac{\partial F}{\partial t} = \frac{3B}{r^4} - B\,\frac{g_3}{g_1}\,\frac{\partial}{\partial r}\,\nabla^2\left[\frac{1}{r}\,\frac{\partial}{\partial r}\left(rF^2\right)\right], \tag{23}$$

where $B = (D_s c_s \Omega_v^2 \gamma_0 / k_B T)$. This equation can be studied using a combination of free-boundary (the facet width $w(t)$ changes in time) and boundary-layer ideas (there is a region of rapid variation associated with the highest-derivative

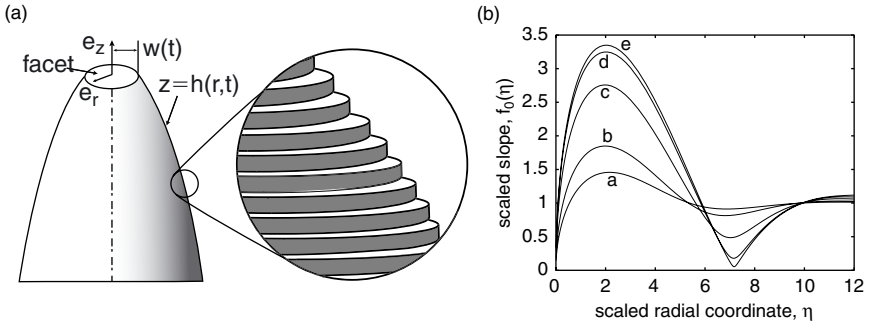


*Figure 2.* (a) Schematic of an axisymmetric shape with an indication of the step structure on the atomic scale. (b) Surface slope profiles as a function of a similarity variable. The different profiles correspond to different values of $g_3/g_1$ as described in Ref. [17].

term in Eq. (23). For $g_3/g_1 < O(1)$ singular perturbation theory suggests that the solution $F$ varies rapidly inside a boundary layer of width $\delta^b$ near the facet. Taking $F \approx a(t) f_0(\eta)$ for long times where $\eta = [r - w(t)]/\delta^b$ we obtain $\delta^b = O(\epsilon^{1/3})$ and a universal ODE for $f_0$, $(f_0^2)''' = f_0 - 1$. This equation can only be solved numerically assuming slope continuity, $f_0(0) = 0$. Solutions are obtained by the routine shooting procedure of starting with $f_0(\eta^*) \approx c_1(\eta^*)^{1/2} + c_3(\eta^*)^{3/2}$ for $\eta^* \ll 1$ and finding the coefficients $c_1$ and $c_3$ so that $f_0(\eta \to \infty) = 1$, as dictated by asymptotic matching at $\eta = \infty$ with the "outer solution" for $g_3/g_1 = 0$. Different numerical solutions of the ODE are shown in Fig. 2b. There is excellent agreement (not shown here) between the theoretical predictions and the results from kinetic simulations.

## 7. Outlook

The development of continuum descriptions for the time evolution of the shape of crystalline materials leads to a number of different partial differential equations. The distinction of the driving forces for surface evolution above and below the roughening temperature is significant and it is only in fairly recent years that attention has focussed on the below roughening case. The use of step-flow models, and the understanding gained from these systems, is also important for probing kinetic, and other, features of the basic continuum models. Further advances and comparison of these ideas with experiment will lead to progress in future years.

## Appendix A

Here we derive the first line of equation (4), which relates the chemical potential $\mu$ to the surface energy paramter $G(h_x)$. The total surface free energy in 1 D is $G^{\mathrm{t}} = \int \mathrm{d}x\, G(h_x)$. Close to equilibrium this energy is minimized under the constraint of fixed total mass, $\Omega^{-1} \int \mathrm{d}x\, h(x,t) = \text{const}$. Taking the first variation with respect to $h$ of $G^{\mathrm{t}} - \int \mathrm{d}x\, \tilde{\lambda}\, h$ to be *zero* for $h$ fixed at the endpoints, where $\tilde{\lambda}$ is the change of the chemical potential, or a Lagrange multiplier, we find

$$0 = \int \mathrm{d}x \left( \frac{\partial G}{\partial h_x} \delta h_x - \Omega^{-1} \tilde{\lambda} \delta h] \right) = - \int \mathrm{d}x \left( \frac{\partial}{\partial x} \frac{\partial G}{\partial h_x} + \Omega^{-1} \tilde{\lambda} \right) \delta h \ , \quad \text{(A1)}$$

By definition of the chemical potential, $\mu - \mu_0 = \tilde{\lambda}$ and the initial starting point in equation (4) is obtained.

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## Author Query

1. Figure 1 in color.