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The effect of kinetics in the surface evolution of thin crystalline films

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Abstract

The effect of kinetics on the faceting of crystal surfaces caused by strongly anisotropic surface free energies is shown by numerical simulations. We compare the evolution of a crystal towards its equilibrium shape by surface diffusion and surface diffusion with kinetics and observe a significant slow down of the dynamics. For quantitative studies of surface morphologies this effect is crucial, as kinetics are assumed to play a dominant role in the surface evolution of thin crystalline films.

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1. Introduction

We consider the evolution of a solid–vapour interface of a homogeneous crystalline film. An understanding of the morphology of such interfaces is crucial if films with specific properties have to be produced. Various effects are known which can lead to the development of small surface structures. Two prominent examples are the formation of quantum dots as a result of the release of elastic stresses caused by the lattice misfit between the film and the substrate and the thermal faceting of unstable surfaces caused by strong anisotropic surface energies. The resulting pyramidal structures on these surfaces, however, are always the result of an interplay of the two, and probably many more effects, which might result from kinetics. A detailed model which describes these interplay has recently introduced by Fried and Gurtin [1] in the framework of configurational forces. Here we will consider a different derivation based on more standard variational concepts and numerically demonstrate the effect of kinetics on the evolution of a crystal with strong surface anisotropy towards its equilibrium shape.

2. Model derivation

Let $\Gamma = \Gamma(t)$ be a surface separating a solid phase (labelled by "+") and a vapour phase (labelled by "−"), with a normal $\mathbf{n}$ pointing into the vapour phase. We define a surface free energy

$$E = \int_\Gamma \gamma + \frac{\alpha^2}{2} H^2 \,\mathrm{d}\Gamma \tag{1}$$

with $\gamma = \gamma(\mathbf{n})$ the surface free energy density, H the mean curvature. The last term in Eq. (1) is a penalization term, which smears out sharp corners on a length scale α. If γ is non-convex, which corresponds to a strong anisotropy, such corners develop for orientations for which the surface stiffness becomes negative. For these orientations the surface is unstable and undergoes a spinodal decomposition process to form stable orientations. With γ being non-convex and H being recognized as a gradient term the energy (1) can thus be understood as a geometric analog of a Ginzburg–Landau energy. Such an energy has been introduced for curves by DiCarlo et al. [2] and was later extended to surfaces by Gurtin and Jabbour [3] and Rätz and Voigt [4].

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Computing the variational derivative of E with respect to variations in Γ yields

$$\frac{\delta E}{\delta \Gamma} = H_\gamma - \alpha^2\left(\Delta_\Gamma H + H\left(\|S\|^2 - \frac{1}{2}H^2\right)\right), \tag{2}$$

with Δ_Γ the surface Laplacian, H_γ the weighted mean curvature defined as

$$H_\gamma = \sum_{i=1}^{d-1} \partial_{p_i p_i}\gamma(\mathbf{n})\kappa_i,$$

and S the shape operator, see e.g. Ref. [5]. Here $\partial_{p_i p_i}$ denotes the second derivative of the one-homogeneous extension of $\gamma : S^{d-1} \subset \mathbb{R}^d \to \mathbb{R}$ with respect to $\mathbf{n}$ in the ith principal direction, and κ_i, $i = 1, \ldots, d-1$ the principal curvatures. Our goal is now to define a thermodynamically consistent evolution law for the surface Γ. Without any contribution from the bulk phases we can define for the normal velocity V

$$bV = -\frac{\delta E}{\delta \Gamma} \tag{3}$$

with $b = b(\mathbf{n})$ a non-negative kinetic coefficient. This evolution defines a gradient flow and thus guarantees thermodynamic consistency. But the evolution of the surface is influenced from the bulk and we need to consider in addition to the contribution from the surface free energy the jump in the grand canonical potential of the bulk phases, see e.g. Ref. [6]. In the vapour, however, the grand canonical potential is negligible and what remains is the grand canonical potential in the solid $\Psi^+ - \rho\mu^+$, with Ψ^+ the free energy density in the solid, ρ the density in the solid and μ^+ the chemical potential in the solid. The surface evolution equation now reads

$$bV = -\frac{\delta E}{\delta \Gamma} - \Psi^+ + \rho\mu^+$$

and incorporates effects from the solid phase. Assuming the solid to be unconstrained, the limiting value of the chemical potential at the surface is equal to the surface chemical potential $\mu = \mu^+$.

A basic law we would also like to establish is mass conservation. To derive this we consider $\Sigma = \Sigma(t)$ to be an arbitrary subsurface of the $\Gamma(t)$, with geometric boundary $\partial\Sigma$. The atomic balance on the subsurface Σ requires that, if diffusion in the bulk is neglected, any change in mass is only due to a surface flux $\mathbf{q}$ across $\partial\Sigma$. We therefore have

$$\frac{\mathrm{d}}{\mathrm{d}t} m = -\int_{\partial\Sigma} \mathbf{q}\cdot\mathbf{m}\,\mathrm{d}s,$$

with $\mathbf{m}$ the conormal. Due to the movement of Σ we also have

$$\frac{\mathrm{d}}{\mathrm{d}t} m = \int_{\Sigma} \rho V\,\mathrm{d}\Gamma,$$

with ρ the bulk density in the solid and V the normal velocity of Σ. Together with the formula for integration by parts on Σ

$$\int_{\partial\Sigma} \mathbf{q}\cdot\mathbf{m}\,\mathrm{d}s = \int_{\Sigma} \nabla_\Gamma\cdot\mathbf{q}\,\mathrm{d}\Gamma,$$

we obtain the local mass balance

$$\rho V = -\nabla_\Gamma\cdot\mathbf{q}.$$

We now need to define constitutive equation for $\mathbf{q}$. We define

$$\mathbf{q} = -\nu\nabla_\Gamma\mu,$$

with $\nu = \nu(\mathbf{n})$ a non-negative coefficient, corresponding to surface diffusivity. We thus obtain a coupled system of equations for the evolution of Γ

$$\rho V = \nabla_\Gamma\cdot(\nu\nabla_\Gamma\mu), \tag{4}$$

$$bV = -\frac{\delta E}{\delta \Gamma} - \Psi^+ + \rho\mu. \tag{5}$$

It is a general model to describe the evolution of homogeneous crystalline surfaces, incorporating different mass transport mechanisms on the surface: surface diffusion as well as kinetic effects, which are due to the rearrangement of atoms on the surface. Furthermore, the evolution of the surface is effected by contributions from the bulk phases, here the free energy in the film. The last component has to be computed by solving additional equations in the bulk.

Eqs. (8) and (9) simplify and reduce to well-known geometric evolution equations if several terms are neglected. If we set $\Psi^+ = 0$ and $b = 0$ we obtain the model for surface diffusion

$$\rho V = \nabla_\Gamma\cdot(\nu\nabla_\Gamma\mu),$$
$$0 = -\frac{\delta E}{\delta \Gamma} + \rho\mu,$$

which can be combined to yield

$$\rho^2 V = \nabla_\Gamma\cdot(\nu\nabla_\Gamma(H_\gamma - \alpha^2\omega)),$$
$$\omega = \Delta_\Gamma H + H(\|S\|^2 - \tfrac{1}{2}H^2). \tag{6}$$

It was first derived in the isotropic setting ($\gamma = 1, \alpha = 0$) by Mullins [7] and describes mass transport by surface diffusion. If we set $\Psi^+ = 0$ we obtain a model for surface diffusion including kinetics

$$\rho V = \nabla_\Gamma\cdot(\nu\nabla_\Gamma\mu),$$
$$bV = -\frac{\delta E}{\delta \Gamma} + \rho\mu,$$

which can be combined to yield

$$\rho V = (\nabla_\Gamma\cdot\nu\nabla_\Gamma)\left(\nabla_\Gamma\cdot\nu\nabla_\Gamma - \frac{1}{b}\right)^{-1}\left(\frac{1}{b}(H_\gamma - \alpha^2\omega)\right),$$

$$\omega = \Delta_\Gamma H + H(\|S\|^2 - \tfrac{1}{2}H^2). \tag{7}$$

This model was first considered for weak anisotropies (γ convex, $\alpha = 0$) by Cahn and Taylor [8].

For the case of a convex anisotropy in γ and $\alpha = 0$ the resulting equations for surface diffusion (6) and surface diffusion with kinetics (7) are fourth order. If $\alpha>0$ the equations turn into sixth order equations. Numerical approaches for these higher order equations are only derived recently and are restricted to the case of surface diffusion. Haußer and Voigt [9] developed an algorithm for curves, which uses parametric finite elements. Burger [10] and Burger et al. [11] developed a numerical approach in a graph and a level-set formulation, respectively. Attempts to approximate the equations within a phase-field approach have been considered by Wise et al. [12,13] and Rätz et al. [14]. Here we will extend the algorithm in Ref. [11] to the surface diffusion model with kinetics and analyse the influence of the kinetic term on the dynamic evolution towards the Wulff shape.

3. Numerical approach

A level set approach is used to propagate the surface. The corresponding equations can be derived from an extended energy, which is defined for all level sets. In Ref. [11] the derivation and the numerical algorithm is described. Adaptive finite elements are used to discretize in space and a semi-implicit time discretization is used to obtain a linear system of equations, which yields stability of the scheme. The modifications necessary to deal with the additional terms in Eq. (7) are straightforward. The approach is implemented in AMDiS, an adaptive finite element toolbox for systems of partial differential equations, see e.g. Ref. [15].

4. Results

We will compare the simulation results for Eqs. (6) and (7) in various examples. Throughout the simulations we use the regularized anisotropy

$$\gamma(\mathbf{p}) = |\mathbf{p}| + a\sum_{k=1}^{d}\frac{p_k^4}{|p|}, \quad d = 2, 3,$$

with p_k denoting the kth spatial component of $\mathbf{p}$. Furthermore, in order to concentrate on the anisotropy in γ, we chose $v = 1$ and consider the kinetic coefficient b to be isotropic with $b = 0$ or 1. The strength of the anisotropy is given by $a = 1$, which leads to missing orientations and the regularization parameter is set to $\alpha = 0.1$.

Fig. 1 shows the evolution of a circle towards its Wulff-shape. It can be observed, that the time scale necessary to reach the equilibrium shape is different for Eqs. (6) and (7). Under the presence of the kinetic term the evolution slows down. In both cases the unstable orientations for 0, $\pi/2$, π

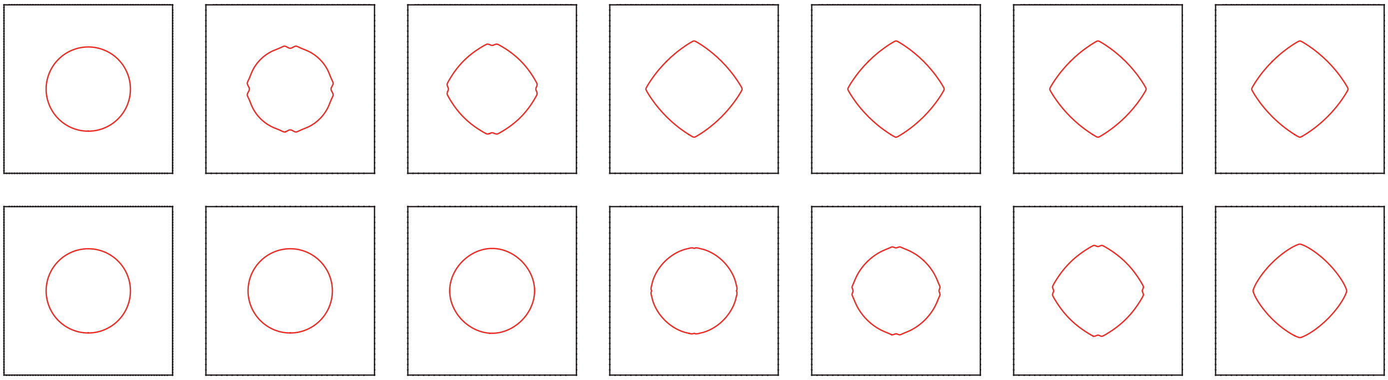

Fig. 1. 2-D case: (top row) evolution by surface diffusion, (bottom row) evolution by surface diffusion with kinetics. The times from left to right are 0.0, 0.0001, 0.002, 0.005, 0.01, 0.03, 0.042. For surface diffusion the Wulff shape is reached at $t = 0.002$.

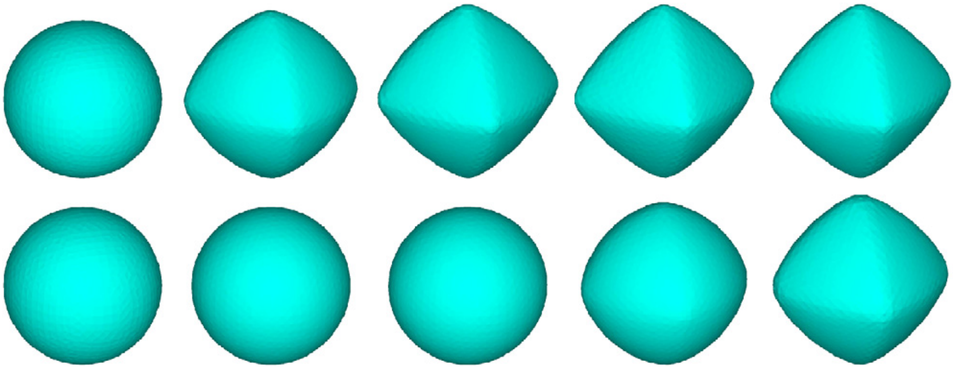

Fig. 2. 3-D case: (top row) evolution by surface diffusion, (bottom row) evolution by surface diffusion with kinetics. The times from left to right are 0.0, 0.001, 0.01, 0.02, 0.03. For surface diffusion the Wulff shape is reached at $t = 0.01$.

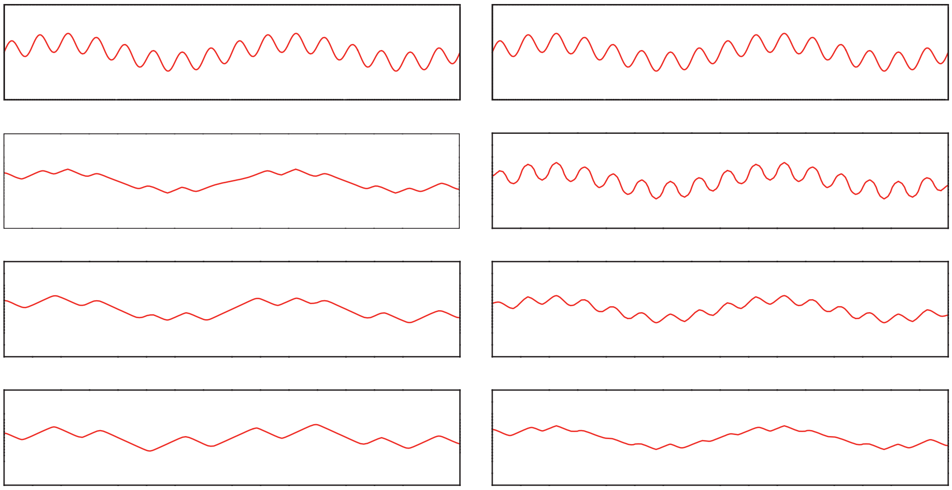

Fig. 3. (Left column) evolution by surface diffusion, (right column) evolution by surface diffusion with kinetics. The times from top to bottom are $0.0, 0.0001, 0.001, 0.01$.

and $3\pi/2$ lead to the formation of wrinkles with the allowed orientations, which subsequently coarsen.

Fig. 2 confirms the observation on the different time scale for the same example in three dimensions. Here the initial shape is a sphere. The winkling is not observed in this configuration, even for smaller grid sizes.

The second example shows the evolution of a perturbed straight line. The perturbation is a superposition of sines. The high frequencies are damped in both cases and a hill-valley pattern forms. After this initial stage, faceting and subsequent coarsening takes place, see Fig. 3. The difference between the two cases is again in the time scale. The damping is much faster for surface diffusion. The same is true for the coarsening process.

5. Conclusion

A detailed geometric model for the evolution of crystalline surfaces is derived. The numerical approach concentrates on specific aspects which are related to thermal faceting. The anisotropy in the surface free energy plays a crucial role in the faceting (spinodal decomposition) of thermodynamically unstable crystal surfaces. The strong anisotropy is regularized by an additional higher order term in the surface free energy, which depends on the mean curvature. The resulting evolution equations, defined as gradient flow for the surface free energy are higher order and highly nonlinear. We analyse by numerical simulations the influence of a kinetic term in the equations. The additional term accounts for the kinetics of rearrangements of atoms on the surface. In most classical models for surface evolution, based on Ref. [7] this term is not considered. However, the simulations indicate its importance if the dynamics of the surface is of interest. All simulations show the change in time scale, and a significant slowing down of the dynamics, if the term is included. Thus for quantitative studies the dissipative force $-bV$ should be considered. Even if b is small the effect might not by negligible as discussed in Ref. [1]. If we define

$$\mu_{\mathrm{eq}} = \frac{\delta E}{\delta \Gamma},$$

assume v and b to be constant and set $\rho = 1$, Eq. (7) can be written as

$$V = v\Delta_\Gamma \mu,$$

$$bV = -\mu_{\mathrm{eq}} + \mu,$$

which can be combined to yield

$$V - vb\Delta_\Gamma V = v\Delta_\Gamma \mu_{\mathrm{eq}}.$$

Thus, whether or not the kinetic term is important depends on the magnitude of the product vb and not only b.

Detailed coarsening studies within these models will be performed elsewhere [16]. As for curves, where the relation of the described geometric evolution laws to higher order Cahn–Hilliard-like equations for the surface slope, as considered in Ref. [17,18], follows from a long-wave approximation and where qualitatively similar but quantitatively different coarsening behaviour is obtained by numerical simulations in Ref. [19], comparisons with the coarsening dynamics of classical evolution equations for the height function of surfaces, see e.g. Ref. [20], will be given.

To quantitatively predict the coarsening of real surfaces additional effects have to be incorporated into the model. In a more general setting, where further contributions from the bulk phases are accounted for the arbitrary subsurface $\Sigma = \Sigma(t)$ used to derive the mass conservation equation has to be modified. Due to the interaction with the bulk phases it also has to have boundaries with the solid phase, namely Σ^+ and with the vapour phase Σ^-, see Fig. 4.

Now, the atomic balance on the subsurface Σ requires that any change in mass is only due to a surface flux $\mathbf{q}$ across $\partial\Sigma$, diffusion from the solid $\mathbf{j} \cdot \mathbf{n}$ across Σ^+ and

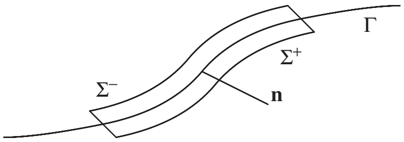

Fig. 4. Schematic of an interfacial pillbox along the interface, here shown as a curve. Let $\Sigma(t)$ be an evolving, i.e., time-dependent, subsurface of $\Gamma(t)$ whose geometric boundary consists of $\delta\Sigma$. Adapting the approach of Fried and Gurtin [1] to surfaces, we view the interfacial pillbox as encapsulating $\Sigma(t)$ and having an infinitesimal thickness. The pillbox boundary then consists of (i) two surfaces, one with unit normal $\mathbf{n(t)}$ and lying in the vapour phase $\Sigma^-(t)$, the other with unit normal $-\mathbf{n(t)}$ and lying within the film $\Sigma^+(t)$, and (ii) end faces which we identify with the boundary of $\Sigma(t)$.

supply from the vapour F across Σ^-. We therefore have

$$\frac{\mathrm{d}}{\mathrm{d}t}m = -\int_{\partial\Sigma} \mathbf{q}\cdot\mathbf{m}\,\mathrm{d}s + \int_{\Sigma} \mathbf{j}\cdot\mathbf{n}\,\mathrm{d}\Gamma + \int_{\Sigma} F\,\mathrm{d}\Gamma,$$

from which we obtain the local mass balance

$$\rho V = -\nabla_\Gamma\cdot\mathbf{q} + \mathbf{j}\cdot\mathbf{n} + F.$$

In addition to the constitutive equations for $\mathbf{q}$ we need to define an appropriate relation for F, which is

$$F = -k(\mu - \mu^-)$$

with $k = k(\mathbf{n})$ a non-negative coefficient, corresponding to attachment and μ^- the chemical potential in the vapour. We thus obtain a coupled system of equations for the evolution of Γ

$$\rho V = \nabla_\Gamma\cdot(v\nabla_\Gamma\mu) + \mathbf{j}\cdot\mathbf{n} - k(\mu - \mu^-), \qquad (8)$$

$$bV = -\frac{\delta E}{\delta\Gamma} - \Psi^+ + \rho\mu. \qquad (9)$$

This system coincides with the model derived in Ref. [1]. It is a general model to describe the evolution of homogeneous crystalline surfaces, incorporating different mass transport mechanisms on the surface: surface diffusion, evaporation and condensation as well as kinetic effects, which are due to the rearrangement of atoms on the surface. Furthermore, the evolution of the surface is affected by contributions from the bulk phases, here the free energy in the film, the material flux from the film and the chemical potential in the vapour phase are considered. The last three components have to be computed by solving additional equations in the bulk. The considered cases for surface diffusion and surface diffusion with kinetics follow by setting $\mathbf{j} = k = \Psi^+ = b = 0$ and $\mathbf{j} = k = \Psi^+ = 0$. If we instead set $\mathbf{j} = v = \Psi^+ = \mu^- = 0$ we obtain

$$\rho V = -k\mu,$$
$$bV = -\frac{\delta E}{\delta\Gamma} + \rho\mu,$$

which can be combined to yield

$$\left(b + \frac{\rho^2}{k}\right)V = -H_\gamma + \alpha^2\omega,$$
$$\omega = \Delta_\Gamma H + H(\|S\|^2 - \tfrac{1}{2}H^2). \qquad (10)$$

Only the kinetic coefficient is different compared to Eq. (3). In the isotropic case ($\gamma = 1, \alpha = 0, b + \rho^2/k = \mathrm{const}$) this model was first derived by Mullins [21]. If $\alpha > 0$ the equation is fourth order and has been considered numerically by parametric finite elements in Ref. [22]. The algorithm is applied to study coarsening of faceted structures in Ref. [23] and yields similar results as obtained in long-wave approximations of the equation, e.g. considered in Refs. [24–27].

The general case in which all mass transport mechanisms—surface diffusion, evaporation and condensation as well as kinetic effects—are accounted for has not been considered numerically, neither in the fully geometric setting as described here, nor in the long-wave approximation.

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