A variationnal model for equilibrium shapes of hetero–epitaxial films

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Abstract

We study shape instabilities of heteroepitaxial crystalline films resulting from lattice misfits between the substrate and the film. Equilibrium shapes of the film are defined variationnally, as those that minimize a free energy functional, which combines elastic bulk energy and surface energy. We describe a functional framework where the variationnal problem is well-posed and we show how equilibrium states can be approximated using a phase field model.

1 Stress driven shape instabilities

The production of high–quality high–performance hetero–epitaxial systems (such as e.g. Si/Ge films) is faced with a challenging technical problem: the control of shape instabilities in the growth process. When a film is grown on a flat substrate, its free surface remains flat until a critical value of the thickness is reached, when the free surface becomes corrugated. Atomic-force microscopy images show ripples and islands of pyramidal shapes. Those shapes may or may not be desirable, depending on the applications.

The mechanism that explains these instabilities (sometimes called Grinfeld instabilities or stress driven instabilities) is the following. As atoms of the film are deposited, elastic strains are induced in the film because of lattice misfit between substrate and film. To relax some of the associated bulk elastic energy, the film atoms can move along the free surface and rearrange themselves into a configuration which is energetically more economical.

This behavior can be modeled as the competition between two forms of energy : surface energy and bulk elastic energy. The former prefers a flat configuration, that minimizes the area of the free surface. An asymptotic calculation of M. Grinfeld [4] shows that the latter favors corrugated configurations.

In most of the litterature on such instabilities (for a review see [3]) the system is described by a PDE that governs the shape of the free surface. It expresses the fact that the surface flux of film atoms is proportional to the gradient of a diffusion potential, the form of which is derived from the thermodynamics of stressed solids [5]. This potential is a sum of a (local) surface strain energy density and a term of surface energy, equal to the surface tension times the curvature of the free surface in the reference state. The film/substrate interaction is modeled by an induced misfit strain in the film. In the simplest setting, the substrate is assumed to be infinitely rigid, and the misfit is replaced by a linear Dirichlet boundary condition for the

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tangential displacement. The free surface is described by a function $h(x,y,t)$ and one ends up with a nonlinear evolution equation which involves 4-th order derivatives of h [8], of the form

$$V_n = D\frac{\partial^2}{\partial s^2}\left(\gamma\kappa + \frac{1}{2}\,\sigma : e(u)_{/\Gamma}\right), \tag{1}$$

where V_n denotes the normal velocity of the free surface Γ, D is a diffusion constant, γ, the surface tension, κ, the surface curvature, and where σ and $e(u)$ are respectively the (linearized) stress and deformation tensors.

At equilibrium, this equation reduces to the following relation between the strain energy density along the free surface and the curvature

$$\gamma\kappa + \frac{1}{2}\,\sigma : e(u)_{/\Gamma} = \text{constant}. \tag{2}$$

We notice that writing the above equation requires a lot of smoothness on the free surface and on the displacement.

Linear stability around a uniform profile has been addressed for the steady-state and time-dependent problems in various configurations: when the film is modeled as a semi-infinite region, when the interaction between film and substrate (rigid or non-rigid) is taken into account. The stabilizing influence of kinetic (deposition) effects has also been studied with this model and a similar model has been investigated in the context of alloy thin films. See [4, 5, 11–16] and the references therein.

Rather than studying an equilibrium equation of the form (2), we are interested in another, variational, approach. There, equilibrium shapes are defined as absolute minimizers of a free energy functional $E(\Omega, u)$ that depends on the domain Ω occupied by the film and on the elastic displacement u. The free energy is the sum of the bulk elastic energy and of a surface energy, proportionnal to the area of the free surface. The advantage of this formulation is that very little smoothness is required *a–priori* on the domain. In particular, it allows free surfaces with vertical slopes or with cracks.

The minimization of the energy is performed under several constraints. First, we assume that the shape of the film is adjusted instantaneously, thus, the minimization is performed at fixed volume. Physically, it means that inertia effects due to deposition of atoms are neglected.

Second, the contact between the film and the substrate is modeled as a Dirichlet boundary condition, reflecting the conditions of a film growing on an infinitely rigid substrate. Finally, the shape of the film is supposed to be periodic, an assumption that merely serves to simplify the analysis and which reflects the atomic–force microscopy pictures.

In [2], a simpler model that contains these ingredients is analyzed. There, the bulk elastic energy only involves one component of the displacement (in a 2 dimensionnal setting). When the interface is a smooth positive function, the free energy takes the form

$$I(h,u) = K\int_0^1 h(x)\,|u'(x)|^2 + \int_0^1 \sqrt{1+[h'(x)]^2}.$$

When the parameter K (which depends on the scalings and the surface tension of the film) is large, the global minimizer can be characterized analytically: the optimal shape consists of arcs of circle, separated by vertical cracks down to the level of the substrate. Noticeably, it is not a smooth function.

For a more general 2 or 3–dimensionnal situation, the above results lead to the following questions: What is a proper functional setting for the energy minimization ? What are the qualitative properties of the optimal shapes ? How to compute equilibrium shapes ? In the sequel, we present some answers to these questions, the detailed proofs of which will appear in [1].

2 Functionnal setting in 2 dimensions

In view of the pictures from Physics [7], we assume that admissible shapes are graphs. Let Q denote the x–periodic cylinder $\mathbf{R}/\mathbf{Z}\times\mathbf{R}$. The analysis of [2] shows that admissible shapes should be allowed to have vertical cracks. To this end, let $\mathcal{G}$ denote the set of subgraphs of positice lower semi–continuous functions defined on the torus $\mathbf{R}/\mathbf{Z}$

$$\Omega\ \in\ \mathcal{G}\quad\Leftrightarrow\quad \Omega=\{(x,y)\in Q\ /\ \ y=h(x)\ \}\,,$$
$$h\ \text{l.s.c.},\qquad h\geq 0,\qquad \int_0^1 h=1.$$

For $\Omega\in\mathcal{G}$, we let $\Omega^+=\Omega\cap\{y>0\}$ and we define a set $X(\Omega)$ of admissible displacement by

$$X(\Omega)\quad=\quad\left\{\begin{array}{l} u\in L^2_{loc}(\Omega)\quad e(u)\in L^2_{loc}(\Omega)\\ u(x,y)\ =\ (x,0)\quad \text{for } y<0\\ u-(x,0)\ \text{ is } 1\text{–}x\text{–periodic}\end{array}\right\}.$$

Tthe set $\mathcal{G}$ is equipped with the following topology : a sequence $(\Omega_n)\subset\mathcal{G}$ converges to a set Ω, if the Hausdorff distance between the complements (Ω_n^c) and Ω^c tends to 0. In this topology, $\mathcal{G}$ is the closure of the set of Lipschitz graphs.

To define the free energy, let $\Omega\subset\mathcal{G}$. There exists 2 l.s.c. functions h and $\overline{h}$, such that

$$\Omega=\{(x,y)\in Q,\ \ y<h(x)\}\qquad \overline{\Omega}=\{(x,y)\in Q,\ \ y<\overline{h}(x)\}.$$

For $u\in X(\Omega)$, we set

$$E(\Omega,u)\quad=\quad K\int_{\Omega\cap Q^+}\mathbf{A}e(u)(x,y){:}e(u)(x,y)\,dxdy\,+\,L(\Omega), \tag{3}$$

where

$$L(\Omega)\quad=\quad \sigma_c\mathcal{H}^1(\partial\overline{\Omega}\cap Q^+)\,+\,(\sigma_c\wedge\sigma_s)\mathcal{H}^1(\partial\overline{\Omega}\setminus Q^+)\,+\,2\sigma_c\sum_{x\in\mathbf{S}^1}\Big(\overline{h}(x)-h(x)\Big)\,. \tag{4}$$

In these expressions, A denotes the positive–definite, symmetric, matrix of elastic coefficients, $e(u)=1/2(\nabla u+\nabla u^t)$ is the linear deformation tensor, σ_c and σ_s denote the respective surface tensions of the film and of the substrate and K is a parameter that relates to the physical dimensions of the cell of periodicity.

Notice that if Ω is the subgraph of a smooth function, then the surface energy $L(\Omega)$ reduces to the two first terms in (4). Indeed, the last term in (4) is the contribution of vertical cracks, twice their length. The middle term is the contribution of the parts of the substrate, which are not covered by the film. It can be shown that this term has to be proportional to the lowest surface tension $\sigma_c\wedge\sigma_s$, which reflects the possible presence of a wetting layer, i.e. an infinitesimally thin layer of film. Equilibrium shapes are defined as global minimizers of

$$\min\{E(\Omega,u)\quad/\,\Omega\in\mathcal{G},\ \ u\in X(\Omega),\quad \text{such that } |\Omega\cap Q^+|=1\}\,. \tag{5}$$

Theorem 1 *There exists an equilibrium state.*

The proof consists in showing that the functional L defined on $\mathcal{G}$ is a relaxation of the functional

$$L^0(\Omega)\quad=\quad\sigma_c\mathcal{H}^1(\partial\Omega\cap Q^+)\,+\,\sigma_s\mathcal{H}^1(\partial\Omega\setminus Q^+),$$

defined on the set of smooth subgraphs.

3 Approximate energies and numerical computation of equilibrium shapes

Since subgraphs of *l.s.c.* functionals are rather delicate to manipulate, we introduce phase field approximations of the energy functional (3). From a physical point of view, this amounts to replacing the sharp interface between the film (or the substrate) and the degenerate phase above the film, by a diffuse interfacial zone of size ε, where the density of film varies continuously from 1 to 0. A phase function v, with value 1 in the film and 0 above it, keeps track of the geometry of the interface. The approximate energies are defined as follows: for $\varepsilon > 0$ let

$$E_\varepsilon(v,u) \;=\; \int_{Q^+} (v(x,y)+\eta_\varepsilon)\mathbf{A}e(u)(x,y){:}e(u)(x,y)\,dxdy \,+\, L_\varepsilon(v), \tag{6}$$

where

$$L_\varepsilon(v) \;=\; 2\sigma_c\left(\frac{4\varepsilon}{\pi^2}\int_{Q^+}|\nabla v(x,y)|^2\,dxdy \,+\, \frac{1}{\varepsilon}\int_{Q^+} v(x,y)(1-v(x,y))\,dxdy\right). \tag{7}$$

The Cahn–Hilliard energy L_ε is defined for $v \in H^1(Q^+)$ such that $0 \le v(x,y) \le 1$, $\partial_y v(x,y) \le 0$ a.e. in Q^+, and $v \ge v_s$ on $S^1 \times \{0\}$; and for $u \in H^1_{loc}(\mathbf{R}\times\mathbf{R}_+;\mathbf{R}^2)$ such that $u(x,y)-(x,0)$ is 1–periodic in x and vanishes on $\mathbf{R}\times\{0\}$. The constant $v_s \in (0,1]$ is given by

$$\int_0^{v_s}\sqrt{t(1-t)}\,dt \;=\; \frac{\sigma_c\wedge\sigma_s}{\sigma_c}\int_0^1\sqrt{t(1-t)}\,dt \;=\; \frac{\sigma_c\wedge\sigma_s}{\sigma_c}\frac{\pi}{8}. \tag{8}$$

If v,u do not satisfy these properties we set $E_\varepsilon(v,u)=+\infty$.

The functional L_ε is known to be an approximation, in the sense of Γ–convergence of the perimeter [6]. The following result is proven in [1]

Theorem 2 *If $(v_\varepsilon,u_\varepsilon)$ is a sequence of minimizers for E_ε, subject to $\int_{Q^+} v_\varepsilon(x,y)dxdy = 1$, then to each limit point u of (u_ε) corresponds a set $\Omega \in \mathcal{G}$, such that $|\Omega \cap Q^+| = 1$ and*

$$E(\Omega,u) \;=\; \min_{\tilde\Omega\in\mathcal{G}}\min_{\tilde u\in X(\tilde\Omega)} E(\tilde\Omega,\tilde u).$$

From a computational point of view, the approximating energies (6) are easier to handle. For a fixed value of ε, one can write an Euler–Lagrange equation for both fields u_ε and v_ε. We solve these equations iteratively, starting from an initial configuration. At the nth step of the algorithm, the displacement is updated via the resolution of a problem of linear elasticity of the form

$$\mathrm{div}\,((v_n+\eta_\varepsilon)Ae(u_{n+1})) \;=\; 0.$$

The marker function v_ε is then upated by minimizing $E_\varepsilon(.,u_{n+1})$ using a gradient flow method. Note that the corresponding Euler equation for v is linear:

$$\left\{\begin{array}{l} \partial_t v \;=\; 2\sigma_c\left(\dfrac{8\varepsilon}{\pi^2}\Delta v - 1/\varepsilon(1-2v)\right) - Ae(u_{n+1}) : e(u_{n+1}) - \lambda \\ \qquad\qquad 0 \,\le\, v \,\le\, 1\,,\;\; \partial_y v \,\le\, 0\,, \end{array}\right.$$

The bounds on v_ε and the constraint that v_ε should be a graph are imposed by truncation, while the volume constraint is imposed via a Lagrange multiplier.

Although Theorem 2 has only been established in 2 dimensions, we think that the energies (6) could also be used in 3 dimensions to compute approximate equilibrium configurations. The figure 1 shows the results of such a 3–d computation, in a regime where the flat configuration is unstable.

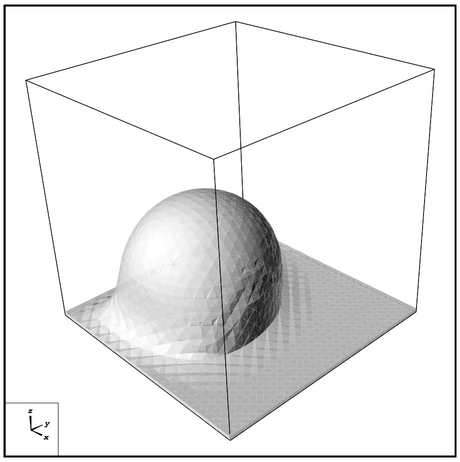

Figure 1: *Equilibrium shape in 3–d*

4 Qualitative properties of equilibria

The variational framework (5) allows us to show existence of equilibrium shapes, without making any *a–priori* smoothness assumption. Once existence has been established, one can ask whether minimizers satisfy local equilibrium conditions such as (2).

Let (Ω, u) be a minimizer for the variational problem (5). Let x_0 denote a point on the free surface and assume that for some $R > 0$, $\partial\Omega$ is smooth ($\mathcal{C}^{1,1}$) in the ball $B = B(x_0, R)$. Let ϕ be a $\mathcal{C}^\infty$ vector field with compact support in B and, for $\eta > 0$, consider the perturbed configuration $\Omega_\eta = \{x + \eta\phi(x),\ x \in \Omega\}$ and the displacement u_η associated to Ω_η. Assuming that ϕ has been chosen so that $|\Omega_\eta| = 1$ and so that Ω_η is also a graph, the comparison of $E(\Omega_\eta, u_\eta)$ with $E(\Omega, u)$ shows the following

Theorem 3 *If* Γ *is a smooth part of the free surface of* Ω*, then the local equilibrium condition (2) holds on* Γ*.*

5 Conclusions

In the variationnal method presented here, no *a priori* smoothness assumptions are made on admissible shapes. Optimal shapes with singularities, such as those observed experimentally (cracks, cusps) can thus be captured. Moreover, the approximating energies we introduced, provide an efficient way to track the free surface, even when it becomes singular.

These investigatons could proceed in several directions : For instance, we only considered steady state solutions. The numerical method, however, could be thought as an evolution equation governed by a particular mass transport mechanism, although not that corresponding to the one in (1). It would be interesting to modify our algorithm to model the same dynamics. On more theoretical grounds, it would also be interesting to obtain well–posedness results in 3d, where the situation is more complex.

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