In theory, there is no difference between theory and practice. In practice, there is.

Yogi Berra
Crystals in and out of equilibrium
Part 2: Growth modes
2D platelets
Kinetic Monte Carlo

\[ p_i = \nu_0 e^{-\frac{iE}{k_B T}} \]

\[ E = 0.1 \text{ eV} \]

\[ E_{\text{act}} = 0.2 \text{ eV} \]

\[ E_{\text{act}} = 0.3 \text{ eV} \]
Kinetic Monte Carlo

\[ N = 6250, \ T = 500\text{K} \]
Kinetic Monte Carlo

$N = 6250, \ T = 500\text{K}$

$N = 6250, \ T = 83\text{K}$
Equilibrium shapes
High temperatures

\[ t_{eq} \approx \frac{1}{\Gamma \nu_0} N^2 \exp \left[ \frac{3E}{k_B T} \right] \]

Low temperatures

\[ t_{eq} \approx \frac{D_0}{\nu_0^2} N \exp \left[ \frac{4E}{k_B T} \right] \]
When crystals grow unstable

Spontaneous structural pattern formation at the nanometre scale in kinetically restricted homoepitaxy on vicinal surfaces

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Cu (0,2,24)  Cu (1,1,17)
$J = -D \nabla c$

$J_{\text{down}} < J_{\text{up}}$

Net current “up”: leads to curved steps and/or 3D islands (mounds)
2D to 3D: interlayer transport barriers ("Schwoebel")
Fig. 3. Surface morphologies after growth of 1000 ML at two deposition rates, on substrates with different slopes, for an ES barrier $E/p_{49}$ 1 eV. One can see mounding on a # at substrate ($m_J^0$, $a_{fi9818}^{32}$) (a), initial step bunching followed by mounding for $m_J^0.2$ and $a_{fi9818}^{32}$ $1$ ML/s (b), fully developed step bunching with the beginning of a meandering (BZ) instability for $m_J^0.4$ and $a_{fi9818}^{32}$ $1$ ML/s (c), and BZ instability without bunching for $m_J^0.8$ and $a_{fi9818}^{32}$ $10$ ML/s (d).

The analytical results estimations are assembled in Fig. 2 together with the results of our kMC simulations. Indeed, triangles mark parameter values where simulations show mound formation, circles denote the formation of step bunches, and diamonds indicate the step meandering (BZ) instability.

Figs. 3a–d show four examples of surface morphologies after deposition of 1000 layers when the ES barrier for precursors is $E/p_{49}$ 1 eV, at the points shown as closed symbols in Fig. 2. When the surface slope ranges from $m_J^0$ (Fig. 3a) to $m_J^0.8$ (Fig. 3d) (i.e. from # at to $l$ $5$), the surface morphology changes from a mound pattern on the # at surface (Fig. 3a, $a_{fi9818}^{32}$ $10$ ML/s) to the step # M. Vladimiro v a et al. / Journal of Crystal Growth 220 (2000) 631–635 # Mounds

Bunches

Curved steps “Meanders”
Meandering of steps on Cu vicinals extensively studied by Ernst et al. Compact [110] and open [100] steps both unstable. Variation of wavelength with deposition rate disagrees with B&Z.

Cu(100): for both compact ([110]) and open ([100]) steps meandering occurs! \( \lambda_{\text{Cu}} \approx \text{Flux}^{-0.16\div0.2} \) (T. Maroutian et al., PRB 64 (2001) 165401)

\( E_{\text{Cu}(111)} = 92\text{meV} \)
\( E_{\text{Cu}(022)} = 132\text{meV} \)

Real out of equilibrium surfaces

Cu vicinals — unstable growth: curved step + 3D pyramids
ing energy is \( E_{ai} = 0.2 \) eV. With these values, the simulations produce morphologies indistinguishable from the experimental picture. On looking carefully, one notes that in the experiments the pyramids tend to align along the step direction, a feature missing in the simulations. Elastic interactions, or a slightly varying average step density, both obviously absent in the simulations, may explain the discrepancy.

Figure 4 exhibits the different computed morphologies for various impurity concentrations, ranging between 0 and 0.05, for both close-packed steps (top panel) and open steps (bottom panel).

In order to quantify the simulated morphologies, we computed the surface roughness, root-mean-square width of the surface profile as a function of the concentration of deposited impurities. This is presented on Fig. 5. The roughness increases linearly for small concentrations, twice as fast for close-packed steps as for open ones, then it saturates exponentially for larger impurity densities.

As we have seen, impurities seem to hold the answer to the riddle of the pyramids. Figure 6 shows that they may also provide the solution to the riddle of the wavelength. Indeed, in the top panel the morphology of the unstable surface at different deposition rates, without impurities, may be seen. In the leftmost bottom panel, the wavelength of the mean-dering structure is plotted as a function of the concentration of impurities.
ing energy is $E_{ai} = 0.2 \text{ eV}$. With these values, the simulations produce morphologies indistinguishable from the experimental picture. On looking carefully, one notes that in the experiments the pyramids tend to align along the step direction, a feature missing in the simulations. Elastic interactions, or a slightly varying average step density, both obviously absent in the simulations, may explain the discrepancy.

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The rightmost panel shows the $m$ vs $F$ plot for varying concentrations of impurities. For strongly interacting impurities, $E_{ai} = 0.2 \text{ eV}$, the power decreases steadily with the concentration.
ing energy is $E_{ai} = 0.2$ eV. With these values, the simulations produce morphologies indistinguishable from the experimental picture. On looking carefully, one notes that in the experiments the pyramids tend to align along the step direction, a feature missing in the simulations. Elastic interactions, or a slightly varying average step density, both obviously absent in the simulations, may explain the discrepancy.

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As we have seen, impurities seem to hold the answer to the riddle of the pyramids. Figure 6 shows that they may also provide the solution to the riddle of the wavelength. Indeed, in the top panel the morphology of the unstable surface at different deposition rates, without impurities, may be seen. In the leftmost bottom panel, the wavelength of the mean-diffusing structure is plotted as a function of $F$. A power law of the form $m \sim F^{-0.5}$ is apparent, with $m$ consistent with the BZ value $1/2$.
Inverse Schwoebel effect

\[ J_{\text{down}} > J_{\text{up}} \]

Net current “down”

Leads to step bunching

Common wisdom is:

• Surface current “up”: step meandering;

• Surface current “down”: step bunching
Common wisdom is:

- Surface current “up”: step meandering;
- Surface current “down”: step bunching

Common wisdom is wrong

\[
\nu_{\parallel} = \ell J(\ell) \quad \nu_{\perp} = -\ell^2 \frac{dJ(\ell)}{d\ell}
\]

(\(\nu_{\parallel}\) step meandering if < 0) (\(\nu_{\perp}\) step bunching if < 0)
Complex growth: multiple components

A new model of morphological instabilities during epitaxial growth: from step bunching to mounds formation
Masha Vladimirova, Alberto Pimpinelli, Arnaud Videcoq

Available online at www.sciencedirect.com

Direct condensation modelling for a two-particle growth system: application to GaAs grown by hydride vapour phase epitaxy
E. Gil-Lafon, J. Napierala, A. Pimpinelli, R. Cadoret, A. Trassoudaine, D. Castelluci

Available online at www.sciencedirect.com
ES barrier at step edges implies coexistence of mounding, bunching *and* meandering...

\[ D_B \nabla^2 c^B - v_B c^B + \Phi_B = 0, \]
\[ D_A \nabla^2 c^A + v_B c^B = 0, \]
Epitaxy on a crystal

Figure 1. Top panel: The initial shape of the core nanoparticle that spans 125 FCC lattice spacings along the shown coordinate axes (see text for details). The white segments were added...
Low T, low and high growth rates

Figure 1. Top panel: The initial shape of the core nanoparticle that spans 125 FCC lattice spacings along the shown coordinate axes (see text for details). The white segments were added.

Figure 2. Top panel: Particle shape obtained for growth with parameter values $\alpha = 2$, $\rho = 4 \pm 1.0$, $\sigma = 5 \pm 1.0$. The core was initially the same as in Fig. 1. Bottom panel: Shape obtained for the same value of $\alpha = 2$, but with $\rho = 2 \pm 1.0$, $\sigma = 1.0 \pm 0.0$. In both cases approximately $4.4 \pm 10^4$ atoms were deposited.
Low T, high T and intermixing

Figure 2. Top panel: Particle shape obtained for growth with parameter values $\alpha = 2$, $\rho = 4 \times 10^4$, $\sigma = 5 \times 10^4$. The core was initially the same as in Fig. 1. Bottom panel: Shape obtained for the same value of $\alpha = 2$, but with $\rho = 2 \times 10^4$, $\sigma = 10$. In both cases approximately $4.4 \times 10^4$ atoms were deposited.

Figure 3. Top panel: Onset of clustering in growth at low temperatures, for $\alpha = 2.5$, $\rho = 2 \times 10^4$, $\sigma = 10$. Here the core remains practically intact. The atoms originally in the core are color coded in green, whereas the added atoms are color coded in burgundy. The shell is primarily formed by the added atoms and its growth morphology is initially governed by the emergence of ziggurat-type clusters. For the selected process time the shell contains approximately 6% of atoms when compared to the number of atoms in the core. Bottom panel: Absence of any significant clustering at high temperatures. Here $\alpha = 1$, with the same $\rho = 2 \times 10^4$, but the simulation time was taken as $\sigma = 5 \times 10^4$. The growing surface remains rather smooth even for the large time selected, and it includes a significant admixture of atoms from the original core. For this process time the shell here contains about 25% atoms when compared to the initial count of atoms in the core.
Very low T, high and low growth rate: Instability nucleated by pyramid growth

Figure 4. Top panel: Development of clustering for the same particle as shown in the top panel of Fig. 3, but for large time. Here $\alpha = 2.5$, $\alpha_0 = 2.10$, $\alpha = 8.10$.

Bottom panel: Smaller-scale clustering for the case of $\alpha = 2.5$, $\alpha_0 = 6.10$, $\alpha = 3.10$.

Figure 5. Illustration of the morphology of pyramid-shaped instabilities initiating the irregular cluster-mode growth in situations such as those presented in Fig. 4, and also in the top panel in Fig. 3 (for larger times than shown there).

Top panel: Pyramidal clusters developing on growing (100) type FCC faces, with all the side faces of the type (111).

Bottom panel: Pyramidal clusters developing on growing (111) type FCC faces, compared to a schematic depicting a pyramidal shape made of fragments of various (111) and (100) FCC faces.

Figure 3. Top panel: Onset of clustering in growth at low temperatures, for $\alpha = 2.5$, $\alpha_0 = 2.10$, $\alpha = 1.10$. Here the core remains practically intact. The atoms originally in the core are color coded in green, whereas the added atoms are color coded in burgundy. The shell is primarily formed by the added atoms and its growth morphology is initially governed by the emergence of ziggurat-type clusters. For the selected process time the shell contains approximately 6% of atoms when compared to the number of atoms in the core.

Bottom panel: Absence of any significant clustering at high temperatures. Here $\alpha = 1$, with the same $\alpha_0 = 2.10$, but the simulation time was taken as $\alpha = 5.10$. The growing surface remains rather smooth even for the large time selected, and it includes a significant admixture of atoms from the original core. For this process time the shell here contains about 25% atoms when compared to the initial count of atoms in the core.
Modeling of Growth Morphology of Core-Shell Nanoparticles

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Abstract

We model shell formation of core-shell noble metal nanoparticles. A recently developed kinetic Monte Carlo approach is utilized to reproduce growth morphologies realized in recent experiments on core-shell nanoparticle synthesis, which reported smooth epitaxially grown shells. Specifically, we identify growth regimes that yield such smooth shells, but also those that lead to the formation of shells made of small clusters. The developed modeling approach allows us to qualitatively study the effects of temperature and supply of shell-metal atoms on the resulting shell morphology, when grown on a pre-synthesized nanocrystal core.

Keywords: core-shell; crystal; diffusion; epitaxy; growth; morphology; nanoparticle

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Chemistry: the role of precursors
Synthesis of Al nanocrystals

Figure 7. (A) TEM images of reactions after three hours with different ratios of AlH$_3$ to Tebbe’s reagent. 10:1 Inset: possibly an Al nanocube seed. (B) SEM of Al nanorods from an Al nanocube reaction with a 200:1 ratio of AlH$_3$ to Tebbe’s reagent. Inset: 45° tilted SEM image of an individual Al nanorod with a pentagonal cross-section. (C) 45° tilted SEM of trigonal right bipyramidal Al nanocrystals produced alongside Al nanocubes. (D) Statistics of Al nanocrystal shapes from three separate Al nanocube reactions (472 particles measured).

The ratio of AlH$_3$ to Tebbe’s reagent is critical to controlling the Al nanocube morphology as depicted in Figure 7. When there is too much Tebbe’s reagent in the reaction, irregular cubic Al nanocrystals with lumpy surfaces are produced (Figure 7A, 10:1 ratio of AlH$_3$:Tebbe). As the ratio of AlH$_3$ to Tebbe’s reagent increases, Al nanocubes with concave high index facets are produced alongside the cubic Al nanoclusters with bumpy surfaces (Figure 7A, 50:1 ratio). Between a 100:1 and 200:1 ratio of AlH$_3$ to Tebbe’s reagent, regular Al nanocubes terminated by {100} facets are the major product of the reaction (Figure 7 and Figure 7A). Further increasing the ratio of AlH$_3$ to Tebbe’s reagent results in the truncation of the Al nanocubes, exposing {111} facets at the corners of the cubes (Figure 7A, 500:1 ratio). The formation of truncated Al nanocubes with low amounts of Tebbe’s reagent is attributed to the reduced concentration of the molecular species responsible for producing {100} faceted Al nanocubes.
Chemistry: the role of precursors

Synthesis of Al nanocrystals

- Product in the synthesis of branched Al nanowires, particularly if the reaction time was only five minutes. Many of the Al nanowires had multiple branches extending in an orthogonal manner from a central limb.

- The branched Al nanowires are single crystalline and surrounded by a native oxide shell as evident from bright field TEM and the associated <100> selected area electron diffraction pattern (Figure 4D-E).

- High-resolution TEM of the junction of a branched Al nanowire and its Fourier transform indicated the nanowires are elongated along the <100> direction (Figure 4E). This is the first report of anisotropic Al nanocrystal growth in the <100> direction, in our previous examples only <110> directed anisotropic growth was observed.

- Figure 5. Influence of the ratio of TIBA to Tebbe's reagent on the final Al nanocrystal morphology. Top row: Representative TEM images of reactions with 100:1, 140:1, 200:1, and 300:1 ratios of TIBA to Tebbe produce isotropic Al nanocrystals, branched Al nanowires, and Al nanowire bundles respectively. Bottom row: High magnification TEM images display the diversity of the morphology of these Al nanocrystals.

- Using fresh Tebbe's reagent, the molar ratio of TIBA to Tebbe's reagent was found to dramatically influence the morphology of the Al nanocrystals produced by this reaction (Figure 5). With a 100:1 molar ratio of TIBA to Tebbe isotropic Al nanocrystals with an average size of 20-30 nm were produced (Figure 5). As the molar ratio of TIBA to Tebbe increased to 140:1, long multiply branched Al nanowires with a typical diameter of 35 ± 3 nm were produced. A 200:1 molar ratio of TIBA to Tebbe produced Al nanowire bundles with a typical diameter of 70 ± 5 nm. With a 300:1 molar ratio of TIBA to Tebbe, Al nanocrystals with a diameter of 150-200 nm were produced.
Chemistry: the role of precursors
Synthesis of Al nanocrystals

Figure 1. Synthesis of Al octopods by high-temperature decomposition of AlH$_3$ with Tebbe's reagent in diglyme.

A. Reaction scheme for the synthesis of Al octopods. B. Tilted SEM image of an individual Al octopod. C. High-resolution TEM image of an Al octopod. D. Zoo med in image of the top corner of this octopod. E. <100> selected area electron diffraction pattern of the Al octopod in C and D.

Since the supply of Al atoms is effectively controlled by the amount of Tebbe's reagent and the reaction temperature, these parameters can be optimized for the growth of highly anisotropic Al nanocrystals. It is worth noting that precursor concentration would also influence this rate but was not explored owing to the sensitivity of reactions more dilute than ~25 mM of AlH$_3$ on the Schlenk line.

Recent kinetic Monte Carlo simulations of the diffusive growth of nanoparticles based on the relative flux of incoming atoms (which was controlled by concentration and temperature) and surface migration of adatoms have shown that increasing the incoming flux leads to the growth of highly anisotropic nanoparticles such as concave cubes.

By increasing the incoming atom flux beyond a certain threshold, the growth of nanoparticles with bumpy surfaces was observed using kinetic Monte Carlo simulations of the diffusive nanoparticles growth. This family of nanoparticle morphologies are considered kinetic products because during crystal growth, an atom is deposited at the reactive sites (undercoordinated atoms at corners, edges and steps) before the previous adatom has time to diffuse on the surface to a thermodynamically favored position in the crystal lattice.

As the nanocrystal grows, these atoms become kinetically trapped in thermodynamically unfavorable positions that manifest in Al nanocrystals with high-index surfaces and anisotropic shapes such as concave cubes.
Based on these observations, thermal decomposition of TIBA in an suitable solvent may be a reliable method to produce Al nanocrystals. To investigate this hypothesis, TIBA was pyrolyzed in hexadecane, dioctylether, trioctylamine, and trioctylphosphine. Scanning electron microscopy (SEM) images of the resulting particles are shown in Figure 2.

Without a coordinating atom in the solvent as in the case with hexadecane, coral-like Al microstructures were produced. Introducing Lewis bases with O, N, or P coordinating atoms resulted in the production of large Al nanocrystals. In the cases with trioctylamine and dioctylether, a small fraction of the nanocrystal geometries included single crystalline Al nanorods. To the best of our knowledge, this work demonstrates the first heat-up synthesis of colloidal Al nanocrystals and Al nanorods.

Figure 4: Colorized SEM images of the diversity of Al nanocrystals synthesized by high-temperature pyrolysis of TIBA or DIBAH in trioctylamine. For scale, the edge of each image is ~3 microns. Interestingly, {111} facets appear smoother than {100} facets.
Stacking 1 over 2: wetting & elasticity
Wetting

Contact angles on flat and patterned surfaces in an ESEM

Increasing condensation

Flat

Static contact angle (98°)
Advancing contact angle (101°)
Receding contact angle (95°)

5-μm diameter, 10-μm height, and 12.5-μm pitch pillars

Static contact angle (129°)
Advancing contact angle (132°)
Receding contact angle (127°)
Solid wetting
\[ \Delta \mathcal{F} = A \left( 2\sigma_{\text{film}} - \sigma_{\text{substrate}} - \sigma_{\text{film}} + \sigma_{\text{interface}} \right) \]
Solid wetting

\[ \Delta \mathcal{F} = \mathcal{A} (2\sigma_{\text{film}} - \sigma_{\text{substrate}} - \sigma_{\text{film}} + \sigma_{\text{interface}}) = \mathcal{A} (\sigma_{\text{film}} + \sigma_{\text{interface}} - \sigma_{\text{substrate}}) \]
\[ \sigma_{\text{film}} + \sigma_{\text{interface}} - \sigma_{\text{substrate}} \leq 0 \]  

2D growth

\[ \sigma_{\text{substrate}} \geq \sigma_{\text{film}} + \sigma_{\text{interface}} \]
\[ \sigma_{\text{film}} + \sigma_{\text{interface}} - \sigma_{\text{substrate}} \leq 0 \]

2D growth

\[ \sigma_{\text{substrate}} \geq \sigma_{\text{film}} + \sigma_{\text{interface}} \]

3D growth

\[ \sigma_{\text{film}} + \sigma_{\text{interface}} - \sigma_{\text{substrate}} > 0 \]

\[ \sigma_{\text{substrate}} < \sigma_{\text{film}} + \sigma_{\text{interface}} \]
\( \sigma_{\text{film}} + \sigma_{\text{interface}} - \sigma'_{\text{first layer}} = ? \)

Reconsider 2D growth

\( \sigma'_{\text{first layer}} \geq \sigma_{\text{film}} + \sigma_{\text{interface}} \)

\( \sigma_{\text{film}} + \sigma_{\text{interface}} - \sigma'_{\text{first layer}} > 0 \)

2D+3D growth

\( \sigma'_{\text{first layer}} < \sigma_{\text{film}} + \sigma_{\text{interface}} \)
Crystal-crystal interface misfit create strain: larger in the (thin) film than in the substrate
Epitaxial growth modes

Frank-van der Merwe mode
(2 dimensional growth mode)

Volmer-Weber mode
(Island growth mode)

Stranski-Krastanov mode
Epitaxial growth and elasticity
Growing deformable layers over a deformable substrate
The harmonic crystal

\[
E(\{x_i\}) = \frac{k}{2} \sum_i (x_{i+1} - x_i - a)^2 \sim \frac{1}{2} \int \left( \frac{\partial u}{\partial x} \right)^2
\]

\[
\epsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)
\]

\[x_{i+1} - x_i \rightarrow u \quad ai \rightarrow x_i\]
The elastic crystal

\[ \varphi (\{\epsilon\}) = \frac{\lambda}{2} \left( \sum_\alpha \epsilon_{\alpha\alpha} \right)^2 + \mu \sum_{\alpha\gamma} \epsilon_{\alpha\gamma}^2 \]

\[ \mathcal{F}_V = \int_V \varphi (\{\epsilon(r)\}) \, d^3r \]

\begin{align*}
\text{Stress} & & \sigma_{ij} = \sum_{kl} C_{ijkl} \epsilon_{kl}, & & \epsilon_{ij} = \sum_{kl} S_{ijkl} \sigma_{kl} & & \text{Strain} \\
\quad & & P = - \frac{1}{3} \sum_i \sigma_{ii} & & \epsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)
\end{align*}
The elastic crystal

\[
\epsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)
\]

\[
P = -\frac{1}{3} \sum_i \sigma_{ii}
\]
The Shuttleworth Equation
The Shuttleworth Equation

• Solids are not Liquids
The Shuttleworth Equation

- Solids are not Liquids
- What is surface tension?
The Shuttleworth Equation

- Solids are not Liquids
- What is surface tension?
- Why we should never speak of surface tension for solids
Applying a tensile stress on a liquid

\[ F_s = \gamma_0 A \]

\[ \delta F_s = \delta(\gamma_0 A) = \gamma_0 \delta A \]
Applying a tensile stress on a solid

\[ \mathcal{F}_s = \gamma A \]

\[ \delta \mathcal{F}_s = \delta(\gamma A) \]

\[ = \frac{\partial \gamma}{\partial \epsilon_{xx}} \delta \epsilon_{xx} A_0 + \gamma \delta A \]

\[ = \left[ \frac{\partial \gamma}{\partial \epsilon_{xx}} + \gamma \right] A_0 \delta \epsilon_{xx} \]

where \( \delta A = A_0 \delta \epsilon_{xx} \)
The Shuttleworth Equation: surface stress

\[ \delta \mathcal{F}_s = s_{xx} \delta A \]

Work of the surface stress

\[ \rightarrow s_{xx} = \gamma + \frac{\partial \gamma}{\partial \epsilon_{xx}} \]

Atomistic picture of the surface stress

\[ \frac{3}{2} f_1 - \frac{\sqrt{3}}{2} f_2 = f_1 \]
In a liquid, the surface energy does not depend on the strain

\[ s_{xx} = \gamma_0 \]

\[ \delta \mathcal{F}_s = s_{xx} \delta A = \gamma_0 \delta A \]

In a liquid, the surface free energy can be called “surface tension”
Elastic instabilities: Grinfeld
Misfit-induced strain: \( \epsilon_{xx} = \epsilon_{yy} = \epsilon_0 = \delta a / a \)

\[
p_0 = - \frac{E}{1 - \zeta} \epsilon_0 = \frac{E}{1 - \zeta} \frac{\delta a}{a}
\]
Contributions to the free energy of the undulating film  \( \delta Z(x,y) = Z(x,y) - \bar{Z} \)

\( \delta Z(x) = h \cos(qx) \)

1) \( \frac{dF_{\text{cap}}}{dA} = \sigma h^2 q^2 / 2 \)  
   Capillarity (surface free energy)  
   \( \text{curvature} \sim \frac{\partial^2 z}{\partial x^2} \rightarrow z_q q^2 \sim h q^2 \)  
   \( dV = hdA \)

2) \( \frac{dF_{\text{relax}}}{dA} \approx -hp_0 \varepsilon \)  
   Relaxation, proportional to elastic energy and to volume change  
   \( dV = hdA \)

3) \( \frac{dF_{\text{el}}}{dA} \approx C \varepsilon^2 / (2q) \)  
   Elastic energy cost proportional to penetration length of the strain  
   \( \lambda \approx 1/q \)
Minimizing 2 and 3 with respect to $\epsilon$ yields:

$$\epsilon \approx hqp_0/C$$

The total free energy in the undulating film is the sum of 1), 2) and 3):

$$\frac{d\mathcal{F}}{dA} = \sigma h^2 q^2/2 - h^2 p_0^2 q/(2C)$$

Instability

$$q_{\text{most unstable}} \sim \left(\frac{\delta a}{a}\right)^2$$
Kinetics 2D to 3D: misfit-induced, layer-dependent interlayer transport barriers ("effective Schwoebel")

\[ E_n > 0, \ n \geq 3 \]

\[ E_n = 0, \ n < 3 \]
\[ E_n = 0, \quad n < 3 \]
\[ E_n > 0, \quad n \geq 3 \]

Temperature dependence of the 2D-3D transition in the growth of PTCDA on Ag(111): A real-time X-ray and kinetic Monte Carlo study

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Thank you for your attention!