Modeling and computational studies of surface shape dynamics of ultrathin single-crystal films with anisotropic surface energy, part I

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Lecture Outline

- Motivations
  - Nanoscale Physics & Technology of Thin Film Crystal Growth
  - Mathematics
- Modeling Approaches
- Physical factors
  - Epitaxial Stress
  - Surface Diffusion
  - Surface Energy Anisotropy
  - Wetting Energy
- Historical background on modeling
- Problem: Dewetting (Pitting) of Silicon-On-Insulator
  - Stability analysis
  - Computational results
- References

Substrate growth of high-quality thin solid films and crystals is extremely challenging due to very tough environments: temperatures higher than 1000 C, local stresses in the MPa range

30 years of crystal growth research:

- Growth mechanisms still are not well understood $\rightarrow$
- Long delay in the transition of imagined applications from the growth experiment stage to a nanoscale semiconductor device-building stage

Example: Formation of single-crystal, nanometer-sized "islands" from the initially continuous single-crystal film grown on a single-crystal substrate made from different material than the film (*Stranski-Krastanow heteroepitaxial thin film growth*)

Figure : Flat, single-crystal semiconductor film ($Si_{1-x}Ge_x$ on Si) grown by MBE or CVD to height h_0.

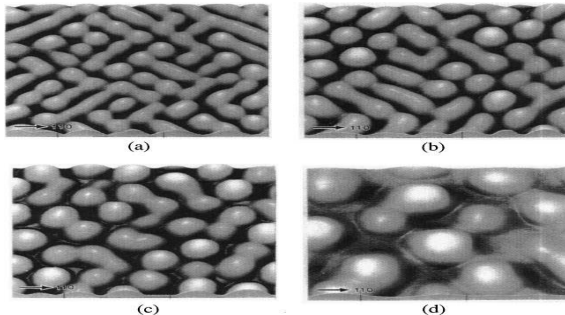and then, suddenly, ... **Instability and pattern formation**

Figure : AFM images of 10nm-thick $Si_{0.82}Ge_{0.18}$/Si alloy films annealed at 850 C for (a) 1 min, (b) 5 min, (c) 20 min, and (d) 2 h (from [1]).

The ultimate goal: production of uniform, defect-free superlattices of nicely-shaped crystal islands (pyramids, domes, cubes, etc.)

- Methods of shape and order control must be perfected
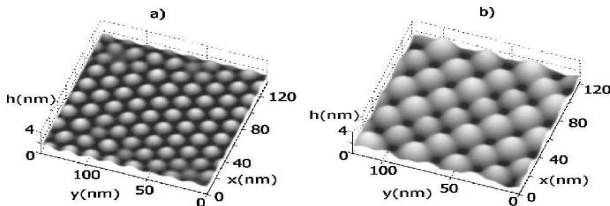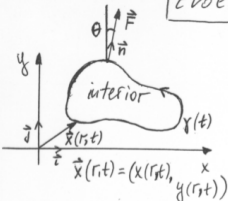- Factors influencing **pattern formation and pattern coarsening** must be fully understood

Figure : Computer simulation results of a mathematical model (from [2]). (a) Stationary hexagonal lattice; (b) Stationary square lattice. **This is MUCH better than the best experiments to-date !**

High-order, very nonlinear "geometric" evolution PDEs comprise the models of thin solid films → complicated mathematics

What is a geometric PDE?

Modeling approaches

- Continuum: this talk. Provides qualitative information on the process
- Atomistic (Molecular Dynamics, Kinetic Monte-Carlo): computationally expensive, thus limited to a few thousand atoms and short time scales (microseconds)
- Atomistic/continuum multiscale methods: state-of-the art, combine best of both worlds

The simplest continuum approach: PDE IBVP for the **film height function** $h = h(x, y, t)$, $0 \leq x \leq X$, $0 \leq y \leq Y$:

$$h_t = F(h, h_x, h_y, h_{xx}, h_{yy}, ...)$$

+ the initial condition: $h(x, y, 0) = h_0(x, y)$
+ the boundary conditions:
$h(0, y, t)$, $h(X, y, t)$, $h(x, 0, t)$, $h(x, Y, t)$ are prescribed

This approach works iff the films surface does not overhang onto itself (is a graph); otherwise, a parametric formulation (the previous slide)

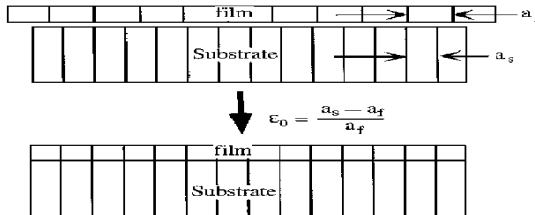1. Compressive or tensile stress generated by lattice mismatch of the film and the substrate

Figure : A heteroepitaxial thin-film structure. The mismatch between the lattice parameters of the film and substrate is accommodated by a (compressive) elastic stress in the film (from [1]).

2. Diffusive mass transport of **adatoms** along the film surface.

   - Is very fast due to the high-T environment
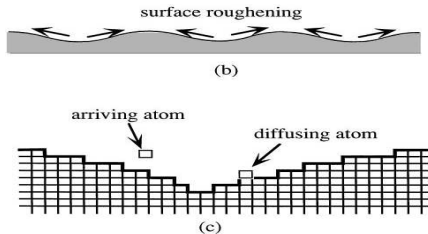   - Causes the *morphology* (= shape) of the film surface to evolve continuously

Figure : Continuum and atomistic view of surface diffusion (from [1]).

Introduce the **surface chemical potential**
$\mathcal{M}(h, h_x, h_y, ...) = \mathcal{M}_\gamma + \mathcal{M}_e + \mathcal{M}_w + ...$, where

$$\gamma : \quad \text{surface energy density;}$$

$$e : \quad \text{elastic energy density;} \quad w : \quad \text{wetting energy density}$$

Gradients of $\mathcal{M}$ drive the diffusion flux of adatoms along the surface: $j = -\nabla \mathcal{M}(h, h_x, h_y, ...)$ (thermodynamic Fick's law)

Thus surface height $h(x, y)$ changes

When either $\mathcal{M}_e \neq 0$, or $\mathcal{M}_w \neq 0$, or $\mathcal{M}_e = \mathcal{M}_w = 0$, but the surface energy γ is anisotropic, the planar film is the **unstable equilibrium**, because:

In equilibrium the surface diffusion flux vanishes,

$$j = -\nabla \mathcal{M}(h, h_x, h_y, ...) = 0 \rightarrow \mathcal{M}(h, h_x, h_y, ...) = const.,$$

where value of *const.* depends on film volume and boundary conditions.

Solution of this elliptic PDE gives equilibrium surface shape $h(x, y)$, termed the **Wulff shape**
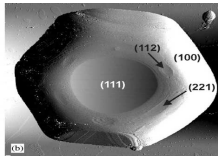

Figure : Wulff shape of a free-standing, micrometer-sized Pb crystal (from [3]).

Planar film surface is the stable equilibrium only when $\mathcal{M}_e = \mathcal{M}_w = 0$, and the surface energy γ is isotropic $\rightarrow$ the PDE $\mathcal{M}(h, h_x, h_y, ...) = const.$ has the single linearly stable solution $h = h_0 = const.$ (will be shown later)

$\mathcal{M}_\gamma$ and $\mathcal{M}_w$ are easy to model since they are **local** quantities (defined on the film surface)

$\mathcal{M}_e$ is very difficult to model since it is **non-local**:

- Solve the elasticity problem for deformations and stresses in the bulk of the film
- Take the solution on the film surface $h(x, y, t)$ (which is itself the problem unknown)
- $\rightarrow$ a free-boundary problem

The film surface is the geometrical boundary of the crystalline solid $\rightarrow$

- Inherits the short- and long-range order of the arrangement of atoms in the crystal lattice $\rightarrow$

- A surface is a collection of finite-size atomic planes, called **facets**. Each facet has distinct surface energy γ, which is different from the surface energy of another facet with different *orientation* $\rightarrow$

- 3. $\gamma = \gamma(\theta(x, y), \phi(x, y))$, where θ and ϕ are two angles of the *unit normal* to the surface at point (x, y)

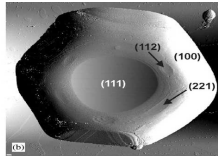# Physical factors, continued: Anisotropy of surface energy density II

Figure : Wulff shape of a free-standing, micrometer-sized Pb crystal grown from a seed (from [3]).
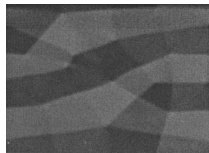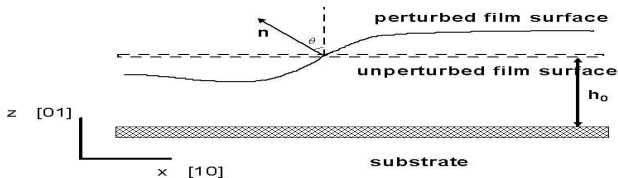

Figure : Facetted surface of a film. Facets appear as regions of uniform color (from [4]).

Dimensionless anisotropic surface energy for typical 1D surfaces:

$$\gamma^{(f)}(\theta) = 1 + A\cos 4\theta, \quad A \text{ is the anisotropy strength}$$

For $A > 1/15$ (strong anisotropy) there exist solutions of $\gamma^{(f)} + \gamma^{(f)}_{\theta\theta} < 0$:

- At such θ there is a corner (formed by two facets) on the equilibrium Wulff shape (Wulff'1901, Herring'1950s)

It is said that these orientations are *missing* from the equilibrium shape

$\tilde{\beta} = \gamma^{(f)} + \gamma^{(f)}_{\theta\theta}$: the **surface stiffness**

Evolution PDEs are *ill-posed* when the Wulff shape of a crystal has corners (when $\tilde{\beta} < 0$)

Ill-posedness means (some) solutions are exponentially growing.
Example: the backward heat equation $h_t = -h_{xx} \rightarrow$
$h(x, t) = \exp(k^2 t) \cos kx$

Question: how to compute surface dynamics with corners ?

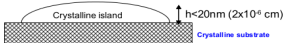Answer: need to *regularize* (penalize corners) ... will discuss later

4. Energy of a long-range molecular repulsion or attraction between the atoms of the film surface and the atoms of the substrate surface

Long-range $\equiv$ larger than atomic length: 0.1 - 10 nm

For some film-substrate materials an interaction is repulsive $\rightarrow$ film always covers the substrate everywhere: substrate can't get exposed. *The film* **wets** *the substrate.* Example: SiGe alloy on Si

For other film-substrate materials an interaction is attractive $\rightarrow$ film tries to expose substrate. *The film* **does not wet** *the substrate.* Example: Si on *amorphous* SiO_2 (silicon-on-insulator)

"Wetting" island (solid 1 on substrate 1):
likes the substrate, tries to spread and maximize the contact area

"Non-wetting" island (solid 1 on substrate 2):
hates the substrate, tries to contract and minimize the contact area

Dewetting = dynamical transition from "wetting" to "non-wetting"

To account for W, let the surface energy be a function of film thickness: $\gamma = \gamma(\theta(x,y), \phi(x,y), h(x,y))$.

1D crystal surface: the **two-layer interpolation model** (1990s):

$$\gamma(h,\theta) = \gamma^{(f)}(\theta) + \left(G - \gamma^{(f)}(\theta) \right) e^{-h}, \quad G \text{ is the energy of the substrate}$$

$$\gamma^{(f)}(\theta) = 1 + A\cos 4\theta, \ \lim_{h\to\infty} \gamma(h,\theta) = \gamma^{(f)}(\theta), \ \lim_{h\to 0} \gamma(h,\theta) = G$$

Now:

$$\mathcal{M}_w = \frac{\partial \gamma(h,\theta)}{\partial h} \cos\theta = \left(\gamma^{(f)}(\theta) - G \right) e^{-h} \cos\theta$$
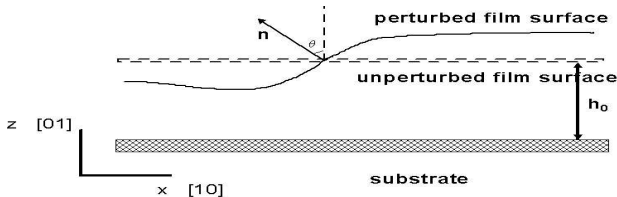
Stages of concept/modeling framework development

- Surface energy (including anisotropy), surface diffusion: 1950's and 1960's (William Mullins, Conyers Herring, others)
- Stress: 1970's and 1980's (Asaro, Tiller, Grinfeld, Srolovitz, others), 1990's (Spencer, Voorhees, Tersoff, Freund, others)
- Wetting energy: 2000's (Ortiz, Golovin, others)

Also, alloy composition/segregation effects have been studied since 1990s

PDE for shape evolution by high-T surface diffusion (note: surface energy $\gamma = const.$!)[*]

[*] Derivation on request

$$z = h(x,t), \quad h_t \cos\theta = h_t \left(1 + h_x^2\right)^{-1/2} = V = -\Omega j_s, \quad \frac{\partial}{\partial s} = \cos\theta \frac{\partial}{\partial x}$$

$$j = -\frac{D\nu}{kT}\mathcal{M}_s, \quad \mathcal{M} \equiv \mathcal{M}_\gamma = \Omega\gamma\kappa, \quad \kappa = \frac{-h_{xx}}{(1+h_x^2)^{3/2}}$$

Thus $h_t = B\dfrac{\partial}{\partial x}\left((1+h_x^2)^{-1/2}\left[\dfrac{-h_{xx}}{(1+h_x^2)^{3/2}}\right]_x\right), \quad B = \dfrac{\Omega^2\nu D\gamma}{kT}$

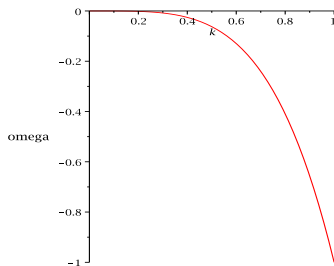Next, make the PDE dimensionless $\rightarrow h_0 = 1$

Linear Stability Analysis:

$$h = 1 + \xi(x,t) \quad \rightarrow \quad \xi_t = -B\xi_{xxxx}$$

Let

$$\xi(x,t) = e^{\omega t}\cos kx \equiv e^{\omega t} Re\left(e^{ikx}\right)$$

Solution is shape-preserving:

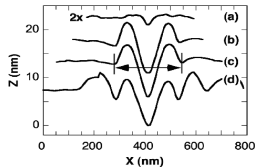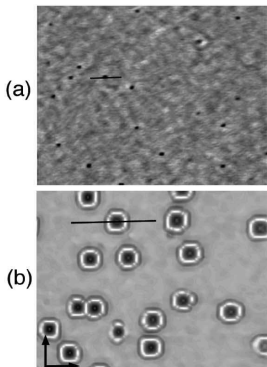$$h(x,t) = 1 + \exp\left(-Bk^4 t\right)\cos kx, \quad \omega(k) = -Bk^4$$

The dispersion curve $\omega(k)$

Problem: Dewetting of silicon-on-insulator (Si on *amorphous* SiO$_2$); strong surface energy anisotropy

AFM images at $t = 1$ h after the start of annealing at $T = 550C$.
(a) $h_0 = 5$ nm; (b) $h_0 = 20$ nm. (from [5]). Pits form in the film !

- Lattice mismatch of Si and SiO_2 is zero $\rightarrow$ there is no epitaxial stress in the film $\rightarrow$ $\mathcal{M}_e = 0$ $\rightarrow$ no need to solve the free-boundary elasticity problem

- Alloy composition/segregation effects are not present $\rightarrow$
- Only two components of the chemical potential are relevant: $\mathcal{M}_\gamma$ and $\mathcal{M}_w$

How is pitting initiated and how it proceeds ? What are the factors influencing pit width and depth ? More generally, what are the factors influencing instability of Si surface ?

Nonlinear evolution PDE (dimensionless):

$$h_t = B(1 + h_x^2)^{1/2}\frac{\partial^2}{\partial s^2}\left(\mathcal{M}_w + \mathcal{M}_\gamma\right), \quad \frac{\partial}{\partial s} = (\cos\theta)\frac{\partial}{\partial x}$$

With the two-layer interpolation model for the surface energy:

$$\mathcal{M}_w = \frac{\partial\gamma(h,\theta)}{\partial h}\cos\theta = \left(\gamma^{(f)}(\theta) - G\right)e^{-h}\cos\theta,$$

$$\mathcal{M}_\gamma = (\gamma(h,\theta) + \gamma_{\theta\theta}(h,\theta))\,\kappa = \tilde{\beta}\left(1 - e^{-h}\right)\kappa + Ge^{-h}\kappa,$$

$$\kappa = -h_{xx}/(1 + h_x^2)^{3/2}, \quad \cos\theta = (1 + h_x^2)^{-1/2}$$

However, the PDE is ill-posed when $\tilde{\beta} \equiv \gamma^{(f)} + \gamma_{\theta\theta}^{(f)} < 0$: next slide, the cure
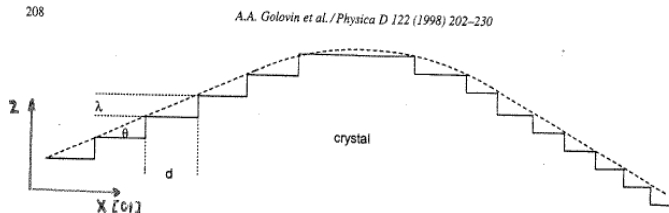
Problem: Dewetting of silicon-on-insulator, continued

To regularize the PDE we add the squared curvature dependence to $\gamma^{(f)}(\theta)$:

$$\gamma^{(f)}(\theta) = 1 + A\cos 4\theta + \frac{\Delta}{2}\kappa^2, \quad \Delta > 0 \text{ if } A > 1/15; \quad \cos 4\theta = f(\cos\theta)$$

The last term in $\gamma^{(f)}(\theta)$ is the energy penalty to form a corner, arising from repulsive interaction of micro-steps inside the corner (Golovin *et al.*'98)
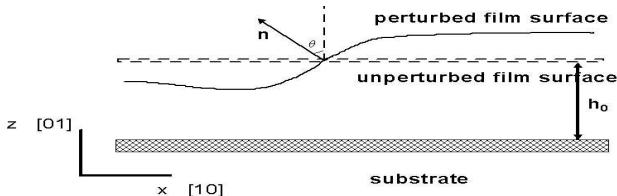
With regularization, *corners are smooth* on a small length scale and ill-posedness is removed ... but 6th-order derivative terms appear

208   A.A. Golovin et al. / Physica D 122 (1998) 202–230

Plan for Linear Stability Analysis (LSA):

(ii) Perturb the surface about the equilibrium constant height h_0 by the perturbation $\xi(x, t)$, obtain PDE for ξ

(iii) Linearize PDE for ξ and obtain linear PDE
$\xi_t = F(\xi, \xi_x, \xi_{xx}, ...)$

(iv) Take $\xi = e^{\omega t} \cos kx$ and substitute in PDE $\rightarrow \omega(h_0, k, A)$

(v) Examine for what values of h_0, k, A the growth rate is positive or negative. $\omega < 0$: surface is stable; $\omega > 0$: surface is unstable
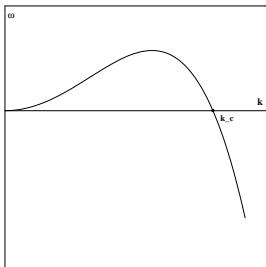
The perturbation growth rate from LSA:

$$\omega(h_0, k, A) = B\left[\left(\Lambda - (G + \Lambda)e^{-h_0}\right)k^4 - (G - 1 - A)e^{-h_0}k^2 - \Delta k^6\right]$$

$\Lambda = 15A - 1, \Delta > 0$ when $A > 1/15$ (strong anisotropy)

Attractive surface-substr. interaction (non-wetting film): $0 < G < 1$

The dispersion curve $\omega(k)$; $k_c = \sqrt{\Lambda/\Delta}$: the cut-off wavenumber

- If perturbation wavenumber $k > max\left(k_c, k_c^{(u)}\right)$, where

$$k_c = \sqrt{\Lambda/\Delta}, \quad k_c^{(u)} = \sqrt{-(G-1-A)/(G+\Lambda)},$$

  then film of any thickness is stable

- If $k_c < k_c^{(u)}$ and $k_c < k < k_c^{(u)}$, then film is stable if $h_0 > h_0^{(c_1)}$ and unstable otherwise, where

$$h_0^{(c_1)} = -ln\frac{\Lambda k^2 - \Delta k^4}{G - 1 - A + (G+\Lambda)k^2}, \quad \text{typically} \quad 2-4nm$$

- If $k_c > k_c^{(u)}$ and $k_c^{(u)} < k < k_c$, then the film is stable if $h_0 < h_0^{(c_1)}$ and unstable otherwise $\rightarrow$ **typically seen in experiments**

- If $k < min\left(k_c, k_c^{(u)}\right)$, then the film of any thickness is unstable

Computer simulations of a pit using the nonlinear evolution PDE
$h_t = F(h, h_x, h_{xx}, ...)$

The initial condition:

$$h(x, 0) = 1 - d \exp\left[-\left(\frac{x-5}{w}\right)^2\right], \quad 0 \le x \le 10$$

$d = 0.5$ (shallow pit) AND one of the following:

$w = 0.15$ (narrow pit), or

$w = 1$ (intermediate pit), or

$w = 2$ (wide pit)

Periodic b.c.'s at $x = 0$ and $x = 10$

$G = 0.5, \quad A = 1/12, \quad B = 3.57 \times 10^{-3}$

Numerical method: Non-graph (overhanging) surface shapes are possible at large deviations from (planar) equilibrium $\rightarrow$ PDE in parametric form

Let (x, z) be the components of the position vector of a point (a marker particle) on the evolving surface:

$$x_t = V \frac{z_u}{g} \tag{1}$$

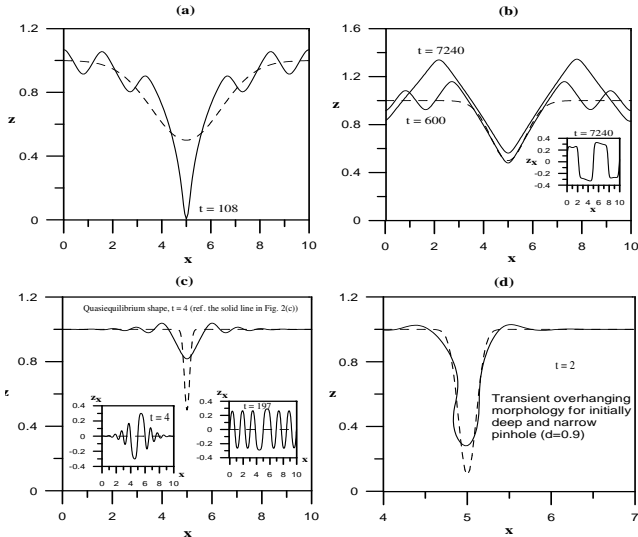$$z_t = -V \frac{x_u}{g}, \ \ 0 \leq u \leq U : \text{ the parameter} \tag{2}$$

$$V = B \frac{\partial^2}{\partial s^2} \left(\mathcal{M}_w + \mathcal{M}_\gamma \right), \ \ g = \sqrt{x_u^2 + z_u^2}, \ \ \frac{\partial}{\partial s} = \frac{1}{g} \frac{\partial}{\partial u}$$

Use Method of Lines:

- Discretize PDE in u using FDs, leave time continuous $\rightarrow$ system of coupled ODEs in time

- Integrate using the stiff ODE solver (IRK-RADAU by Hairer & Wanner)

- To maintain accuracy, must remesh the surface grid to keep marker particles optimally spaced (ideally, equidistant in the arclength)

Computer simulation results: Pit shapes

(a): $w = 2$, (b): $w = 1$, (c): $w = 0.15$

Computer simulation results: Pit shapes

Rotate sample, expose different crystallographic orientation:
$\gamma^{(f)}(\theta) = 1 + A\cos 4(\theta + \beta)$
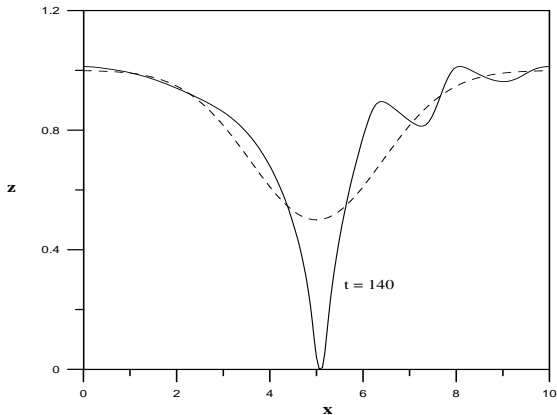
$w = 2,\ \beta = 10°$

Other models of wetting interactions have been proposed, for instance:

Two-layer algebraic model

$$\gamma(h,\theta) = \frac{1}{2}\left(\gamma^{(f)}(\theta) + \gamma_S\right) + \frac{1}{2}\left(\gamma^{(f)}(\theta) - \gamma_S\right) f(h/\ell)$$

$$\lim_{h \to \infty} f(h/\ell) = 1, \quad \lim_{h \to -\infty} f(h/\ell) = -1$$

Let

$$f(h/\ell) = \frac{2}{\pi}\arctan\left[\left(\frac{h}{\ell}\right)^m\right], \quad m = 1, 3, 5, \ldots$$

Note that

$$f(h/\ell) = 1 - \frac{2}{\pi}(h/\ell)^{-m} + \ldots \quad \text{as } h \to \infty.$$

i.e., this tends to the limiting value $+1$ as an algebraic power. Then,

$$\mathcal{M}_w \sim 1/h^{m+1}, \quad \text{for} h \gg 1$$

- Increased stability of the equilibrium $h = 1$
- only wide and deep pinholes dewet for the same set of parameters, and only for $m = 1$

References

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3. M. Khenner, "Comparative study of a solid film dewetting in an attractive substrate potentials with the exponential and the algebraic decay", Mathematical Modeling of Natural Phenomena 3(5), (2008) 16-29.