Solid-State Dewetting: Equilibrium & Dynamics

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Outline

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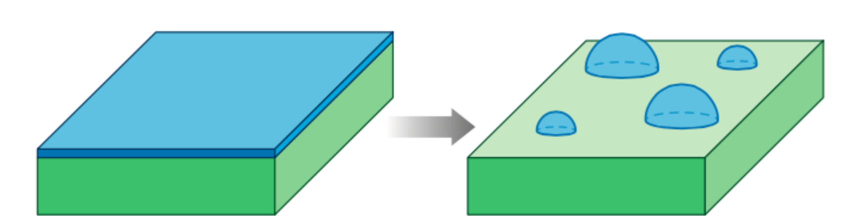
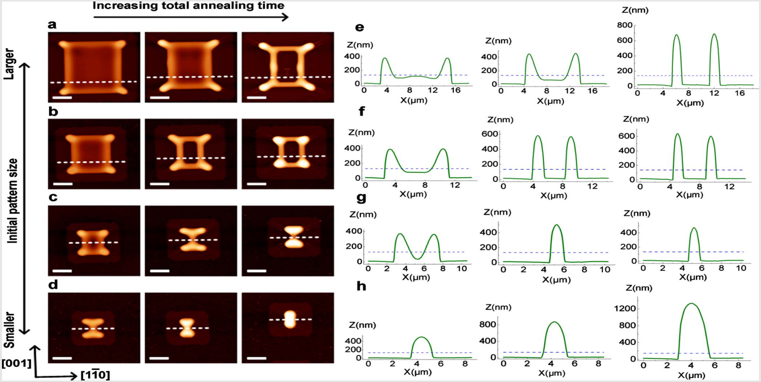
Solid-State Dewetting

- Most thin films are *metastable* in as-deposited state and *dewet* to form particles (C.V. Thompson, Annu. Rev. Mater. Res., 2012).



- *The dewetting* can occur well *below* the melting temperature of the material, i.e., which is still in the *solid-state*.

Dewetting Patterned Films: Ni(110) Square Patches[1]



[1] J. Ye & C.V. Thompson. PRB, 2010.

Dewetting on SOI system:

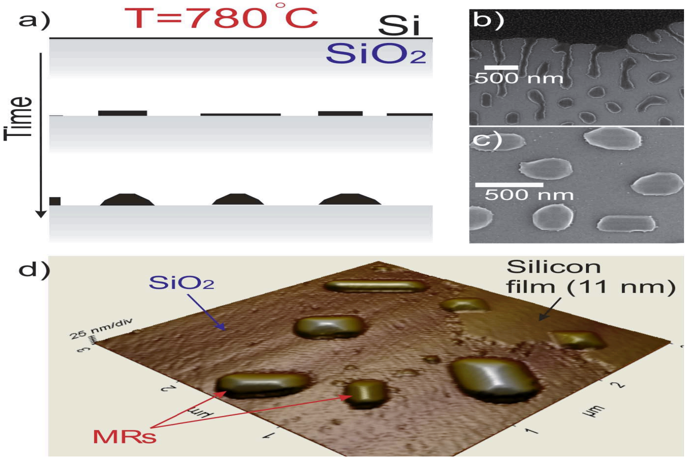


Figure: Abbarchi *et al.*, ACS Nano, 2014.

Solid-State Dewetting of Thin Films

Intrinsic Physics:

- Is driven by capillarity effects.
- Occurs through surface self-diffusion controlled mass transport.
- There exist moving contact lines in the thin film - substrate - vapor interface.
- Surface diffusion+Moving Contact Line.

Applications:

- Play an important role in microelectronics processing.
- A common method to produce nano-particles.
- Catalyst for the growth of carbon nanotubes & semiconductor nanowires.

Phenomena Observed from Experiments[2]:

- Pinch-off, Mass-shedding Instability, Geometric Complexity, Corner-induced Instability, Rayleigh Instability...
- Crystalline Anisotropy, Edge Faceting...

[2] C.V. Thompson. Annu. Rev. Mater. Res., 2012.

Outline

Solid-State Dewetting: Theoretical Models

- The Discrete Models. (Carter *et al.*, Acta Metall. Mater, 1995; Zucker *et al.*, JAP, 2013; Comp. Rend. Phys., 2013; Dornel *et al.*, PRB, 2006.)

- Kinetic Monte Carlo Method. (Pierre-Louis *et al.*, EPL,2009; PRL, 2009 & 2011.)

- Continuum Models based on PDEs. (Srolovitz *et al.*, JAP, 1986; Jiang *et al.* Acta Mater., 2012; PRB, 2015; Scripta Mater., 2016.)

- Others...

Outline

Sharp Interface Model – Equilibrium Problem

- Total Interfacial Free Energy:

$$W(\Gamma) = \int_\Gamma \gamma(\mathcal{N})\, d\Gamma + \underbrace{(\gamma_{FS} - \gamma_{VS})\Sigma_{FS}}_{\textbf{Wall Energy}}.$$

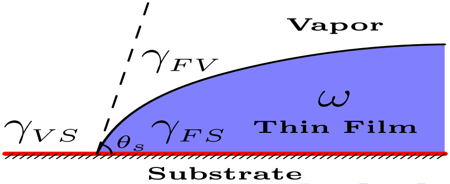
$\gamma(\mathcal{N})$ – The energy (density) of the film-vapor interface.

Σ_{FS} – interface length (2D) or surface area (3D) of the film-substrate interface.

- Equilibrium configuration:

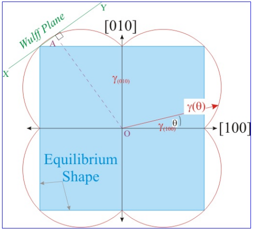
Min $W(\Gamma)$

Subject to $\int_\omega \mathrm{d}\omega =$ **Const.**



Equilibrium Problems

- Wulff Construction: not considering the wall energy. (C. Herring, W. Mullins, J. Taylor, I. Fonseca...)



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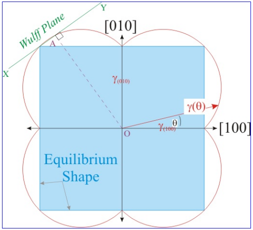

- Winterbottom Construction: considering the wall energy. (Kaishew, Commun. Bulg. Acad. Sci., 1950; Winterbottom, Acta Metall., 1967.)

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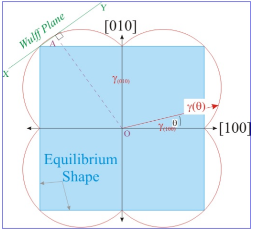


- Winterbottom Construction: considering the wall energy. (Kaishew, Commun. Bulg. Acad. Sci., 1950; Winterbottom, Acta Metall., 1967.)
- Problem: The classical Winterbottom **does not** address the problem about multiple equilibrium shapes, which have been *observed in the experiments* (e.g., Malyi *et. al.*, Acta Mater., 2011; Kovalenko, Scripta Mater., 2015).

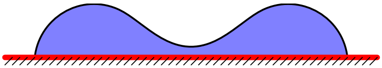
Outline

Sharp Interface Model: Dynamical Problem

Assumption: The surface energy is isotropic. [3] [4]

♠ *Sharp Interface Model*:

$$\frac{\mathrm{d}\mathbf{X}(t)}{\mathrm{d}t} = V_{\mathrm{n}}\mathcal{N} \quad \text{with} \quad V_{\mathrm{n}} = B\Delta_s\kappa$$



- $\mathbf{X}(t) = (x(t), y(t), z(t))$: moving front surface in 3D (curve in 2D).
- $\mathcal{N}$: unit outward normal direction.
- V_{n}: normal velocity of the moving interface.
- B: material constant.
- Δ_s: surface Laplacian or Laplace-Beltrami operator.
- κ: mean curvature of the surface.

$$V_{\mathrm{n}} = B\frac{\partial^2\kappa}{\partial s^2} \quad \textit{(in 2D)}$$

$$\kappa = -\frac{\partial^2 y}{\partial s^2}\frac{\partial x}{\partial s} + \frac{\partial^2 x}{\partial s^2}\frac{\partial y}{\partial s}$$

[3] D.J. Srolovitz & S.A. Safran, JAP, 1986.

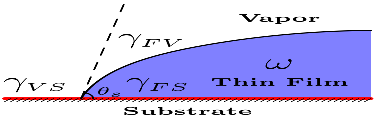
[4] H. Wong et al., Acta Mater., 2000.

In 2D, $\mathbf{X}(t) = (x(s,t), y(s,t))$ s – Arc length

Boundary Conditions: (2D)

- *Contact Point* Condition (BC1)

$$y(x_c, t) = 0$$



- *Contact Angle* Condition (BC2)

θ_i – isotropic Young contact angle.

$$\frac{\partial y/\partial s}{\partial x/\partial s}(x_c, t) = \tan\theta_i,$$

$$\sigma := \cos(\theta_i) = \frac{\gamma_{VS} - \gamma_{FS}}{\gamma_{FV}}$$

- *Zero-Mass Flux* Condition (BC3)

$$\frac{\partial \kappa}{\partial s}(x_c, t) = 0.$$

Total mass conservation of the film. No mass flux at the contact point– no mass diffuses under the thin film at the film/substrate interface.

Questions arising from Equilibrium and Dynamical Problems

We try to address the following questions by our research:

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- (**Q2**): How to derive a mathematical theory to connect with the equilibrium and dynamical problems?
- (**Q3**): What conditions should the stable equilibrium shapes satisfy?

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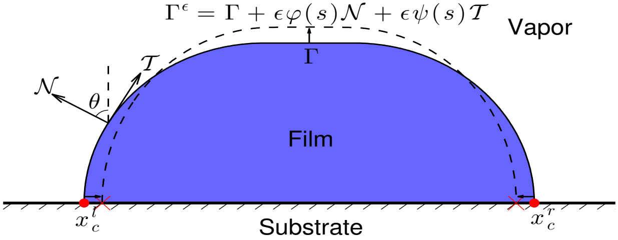
- (**Q1**): How to derive sharp-interface dynamical models, which include the surface energy anisotropy, to describe the dewetting evolution of solid thin films?
- (**Q2**): How to derive a mathematical theory to connect with the equilibrium and dynamical problems?
- (**Q3**): What conditions should the stable equilibrium shapes satisfy?
- (**Q4**): How to construct stable equilibrium shapes of the solid-state dewetting problem?

Outline

Thermodynamic Variation: The First Variation

Consider a two-dimensional thin solid film rested on a smooth and flat rigid substrate. The total interfacial free energy of the system can be written as:

$$W = \int_{\Gamma} \gamma(\theta)\, d\Gamma + (\gamma_{FS} - \gamma_{VS})(x_c^r - x_c^l),$$



- Perturb the interface Γ in both the normal and tangent directions;
- $\psi(s)$ is an arbitrary function, and $\varphi(s)$ satisfies: $\int_0^L \varphi(s) ds = 0$.

Thermodynamic Variation: The First Variation

The two components of the new curve $\Gamma^\epsilon(t)$ can be expressed as follows:

$$\begin{aligned} \Gamma^\epsilon(t) &= (x^\epsilon(s,t), y^\epsilon(s,t)) \\ &= (x(s,t) + \epsilon u(s,t), y(s,t) + \epsilon v(s,t)), \end{aligned} \tag{1}$$

where the two component increments along the $x-$aixs and $y-$axis are defined as

$$\begin{cases} u(s,t) = x_s(s,t)\psi(s) - y_s(s,t)\varphi(s), \\ v(s,t) = x_s(s,t)\varphi(s) + y_s(s,t)\psi(s), \end{cases} \tag{2}$$

and the increments along the $y-$axis at the two contact points must be zero, i.e.,

$$v(0,t) = v(L,t) = 0. \tag{3}$$

Thermodynamic Variation: The First Variation

The total interfacial energy W of the curve $\Gamma(t)$ before perturbation is:

$$
\begin{aligned}
W &= \int_{\Gamma} \gamma(\theta)\, d\Gamma + (\gamma_{FS} - \gamma_{VS})(x_c^r - x_c^l) \\
&= \int_0^L \gamma(\theta)\, ds + (\gamma_{FS} - \gamma_{VS})(x_c^r - x_c^l).
\end{aligned}
$$

The total interfacial energy W^ϵ of the new curve $\Gamma^\epsilon(t)$ after perturbation is:

$$
\begin{aligned}
W^\epsilon &= \int_{\Gamma^\epsilon} \gamma(\theta^\epsilon)\, d\Gamma^\epsilon + (\gamma_{FS} - \gamma_{VS})\Big[\big(x_c^r + \epsilon u(L,t)\big) - \big(x_c^l + \epsilon u(0,t)\big)\Big] \\
&= \int_0^L \gamma\Big(\arctan\big(\frac{y_s + \epsilon v_s}{x_s + \epsilon u_s}\big)\Big) \sqrt{(x_s + \epsilon u_s)^2 + (y_s + \epsilon v_s)^2}\, ds \\
&\quad + (\gamma_{FS} - \gamma_{VS})\Big[\big(x_c^r + \epsilon u(L,t)\big) - \big(x_c^l + \epsilon u(0,t)\big)\Big]. \qquad (4)
\end{aligned}
$$

Thermodynamic Variation: The First Variation

$$\begin{aligned}\frac{dW^\epsilon}{d\epsilon}\Big|_{\epsilon=0} &= \lim_{\epsilon\to 0}\frac{W^\epsilon - W}{\epsilon}\\ &= \int_0^L \Big(\gamma''(\theta)+\gamma(\theta)\Big)\kappa\,\varphi\,ds\\ &\quad - \Big[\gamma(\theta_d^l)\cos\theta_d^l - \gamma'(\theta_d^l)\sin\theta_d^l + \big(\gamma_{FS}-\gamma_{VS}\big)\Big]u(0,t)\\ &\quad + \Big[\gamma(\theta_d^r)\cos\theta_d^r - \gamma'(\theta_d^r)\sin\theta_d^r + \big(\gamma_{FS}-\gamma_{VS}\big)\Big]u(L,t).\end{aligned}$$

Thermodynamic Variation: The First Variation

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&\quad + \Big[\gamma(\theta_d^r)\cos\theta_d^r - \gamma'(\theta_d^r)\sin\theta_d^r + \big(\gamma_{FS}-\gamma_{VS}\big)\Big]u(L,t).
\end{aligned}$$

- **Chemical potential**:

$$\mu = \Omega_0\frac{\delta W}{\delta\Gamma} = \Omega_0\Big(\gamma(\theta)+\gamma''(\theta)\Big)\kappa,$$

- **Normal velocity** of the interface:

$$V_n = \frac{D_s\nu\Omega_0}{k_B T_e}\frac{\partial^2\mu}{\partial s^2}.$$

Thermodynamic Variation: The First Variation

$$
\begin{aligned}
\left.\frac{dW^\epsilon}{d\epsilon}\right|_{\epsilon=0} &= \lim_{\epsilon\to 0}\frac{W^\epsilon - W}{\epsilon} \\
&= \int_0^L \Big(\gamma''(\theta)+\gamma(\theta)\Big)\kappa\,\varphi\,ds \\
&\quad - \Big[\gamma(\theta_d^l)\cos\theta_d^l - \gamma'(\theta_d^l)\sin\theta_d^l + \big(\gamma_{FS}-\gamma_{VS}\big)\Big]u(0,t) \\
&\quad + \Big[\gamma(\theta_d^r)\cos\theta_d^r - \gamma'(\theta_d^r)\sin\theta_d^r + \big(\gamma_{FS}-\gamma_{VS}\big)\Big]u(L,t).
\end{aligned}
$$

- **Boundary conditions** for moving contact points:

$$
\begin{aligned}
\frac{dx_c^l(t)}{dt} = -\eta\frac{\delta W}{\delta x_c^l} &= \eta\Big[\gamma(\theta_d^l)\cos\theta_d^l - \gamma'(\theta_d^l)\sin\theta_d^l + \big(\gamma_{FS}-\gamma_{VS}\big)\Big], \\
\frac{dx_c^r(t)}{dt} = -\eta\frac{\delta W}{\delta x_c^r} &= -\eta\Big[\gamma(\theta_d^r)\cos\theta_d^r - \gamma'(\theta_d^r)\sin\theta_d^r + \big(\gamma_{FS}-\gamma_{VS}\big)\Big].
\end{aligned}
$$

Outline

According to the thermodynamic variation, we can obtain the following dimensionless sharp-interface model for simulating dewetting evolution of thin solid films with weakly anisotropic surface energies[5]:

$$\frac{\partial \mathbf{X}}{\partial t} = V_n \mathcal{N} = \frac{\partial^2 \mu}{\partial s^2} \mathcal{N} = \frac{\partial^2}{\partial s^2} \left[\Big(\gamma(\theta) + \gamma''(\theta) \Big) \kappa \right] \mathcal{N}, \qquad (5)$$

Remark: $\widetilde{\gamma}(\theta) := \gamma(\theta) + \gamma''(\theta)$ represents the surface stiffness, and if

$$\begin{cases} \widetilde{\gamma}(\theta) > 0, \quad \forall \theta \in [-\pi, \pi], & \text{Weakly anisotropic cases;} \\ \textbf{Otherwise}, & \text{Strongly anisotropic cases.} \end{cases}$$

[5] Wang-Jiang-Srolovitz-Bao, PRB, 2015.

Sharp-Interface Model: Weakly Anisotropic

1. *Contact Point Condition* (**BC1**)

$$y(x_c^l, t) = 0, \quad y(x_c^r, t) = 0. \tag{6}$$

2. *Relaxed Contact Angle Condition* (**BC2**)

$$\frac{dx_c^l}{dt} = \eta f(\theta_d^l), \qquad \frac{dx_c^r}{dt} = -\eta f(\theta_d^r), \tag{7}$$

where

$$f(\theta) := \gamma(\theta)\cos\theta - \gamma'(\theta)\sin\theta - \sigma, \quad \text{with} \quad \sigma := \frac{\gamma_{VS} - \gamma_{FS}}{\gamma_0}.$$

$f(\theta) = 0$ is the anisotropic Young equation, which determines equilibrium contact angles.

3. *Zero-Mass Flux Condition* (**BC3**)

$$\frac{\partial \mu}{\partial s}(x_c^l, t) = 0, \quad \frac{\partial \mu}{\partial s}(x_c^r, t) = 0. \tag{8}$$

Theorem (Mass conservation and energy dissipation)

Under the above proposed governing equation (5) *and boundary conditions (6-8), the total mass of the thin film conserves and the total interfacial energy always decreases during the evolution in the weakly anisotropic case.*

Remark: The above properties ensure that the evolution process converges to one of the minimizers of the total interfacial energy functional.

Outline

Sharp-Interface Model: Strongly Anisotropic

1. In the strongly anisotropic case, $\widetilde{\gamma}(\theta) := \gamma(\theta) + \gamma''(\theta)$ may **become negative** for some θ, which causes sharp corners in the equilibrium shape.
2. The proposed governing equation (5) becomes ill-posed in the strongly anisotropic case:

$$\frac{\partial \mathbf{X}}{\partial t} = \frac{\partial^2}{\partial s^2}\left[\Big(\gamma(\theta) + \gamma''(\theta)\Big)\kappa\right]\mathcal{N},$$

3. In order to regularize the equation, a high order regularization term can be added to the free energy:[6]

$$W_{\mathrm{r}} = \frac{\varepsilon^2}{2}\int_\Gamma \kappa^2 \, d\Gamma$$

4. The effect of the regularization is **highly localized at near corners** in the interface and tends to smooth the corners.

[6] A. Carlo *et al.*, SIAM J. Appl. Math., 52:1111, 1992.

Sharp-Interface Model: Strongly Anisotropic

Following with the above similar derivation, we can obtain the following dimensionless sharp-interface continuum model for simulating dewetting evolution of thin solid films with strongly anisotropic surface energies [7]:

$$\frac{\partial \mathbf{X}}{\partial t} = V_n \mathcal{N} = \frac{\partial^2 \mu}{\partial s^2}\mathcal{N} = \frac{\partial^2}{\partial s^2}\left[\Big(\gamma(\theta)+\gamma''(\theta)\Big)\kappa - \varepsilon^2\left(\frac{\partial^2 \kappa}{\partial s^2} + \frac{\kappa^3}{2}\right)\right]\mathcal{N}, \quad (9)$$

[7] Jiang *et al.*, Scripta Mater., 2016.

Sharp-Interface Model: Strongly Anisotropic

1. *Contact Point Condition* (**BC1**)

$$y(x_c^l, t) = 0, \quad y(x_c^r, t) = 0. \tag{10}$$

2. *Relaxed Contact Angle Condition* (**BC2**)

$$\frac{dx_c^l}{dt} = \eta f_\varepsilon(\theta_d^l), \qquad \frac{dx_c^r}{dt} = -\eta f_\varepsilon(\theta_d^r), \tag{11}$$

where $\quad f_\varepsilon(\theta) := \gamma(\theta)\cos\theta - \gamma'(\theta)\sin\theta - \sigma - \varepsilon^2 \frac{\partial \kappa}{\partial s}(\theta)\sin\theta.$

3. *Zero-Mass Flux Condition* (**BC3**)

$$\frac{\partial \mu}{\partial s}(x_c^l, t) = 0, \quad \frac{\partial \mu}{\partial s}(x_c^r, t) = 0. \tag{12}$$

4. *Zero-curvature Condition* (**BC4**)

$$\kappa(x_c^l, t) = 0, \qquad \kappa(x_c^r, t) = 0. \tag{13}$$

Sharp-Interface Model: Strongly Anisotropic

Theorem (Mass conservation and energy dissipation)

Under the proposed governing equation (9) *and boundary conditions (10-13), the total mass of the thin film conserves and the total interfacial energy always decreases during evolution in the strongly anisotropic case.*

Outline

Anisotropic Young Equation & Multiple Roots

Recall that the Anisotropic Young equation is

$$f(\theta) = \gamma(\theta)\cos\theta - \gamma'(\theta)\sin\theta - \sigma = 0, \quad \theta \in [0, \pi].$$

It may have multiple roots in the strongly anisotropic case since $f'(\theta)$ changes sign when there exist some $\theta \in [0, \pi]$ for which $\widetilde{\gamma}(\theta) < 0$:

$$f'(\theta) = -\widetilde{\gamma}(\theta)\sin\theta = -\Big(\gamma(\theta) + \gamma''(\theta)\Big)\sin\theta.$$

This implies that there may exist multiple roots (or multiple equilibrium shapes) in the strongly anisotropic case.

Necessary Conditions

Theorem

If a piecewise C^2 curve $\Gamma_e := \big(x(s),\ y(s)\big),\ s \in [0, L]$ *be a stable equilibrium shape (without scaling) of the solid-state dewetting problem with surface energy density* $\gamma(\theta) \in C^2[-\pi, \pi]$, *then the following three conditions are simultaneously satisfied* [a]*:*

$$\mu(s) = \widetilde{\gamma}(\theta(s))\kappa(s) \equiv C, \qquad a.e.\ s \in [0, L], \qquad \textbf{(C1)}$$

$$\widetilde{\gamma}(\theta(s)) \geq 0, \qquad a.e.\ s \in [0, L], \qquad \textbf{(C2)}$$

$$f(\theta) = 0, \qquad \theta = \theta_a^l, \theta_a^r, \qquad \textbf{(C3)}$$

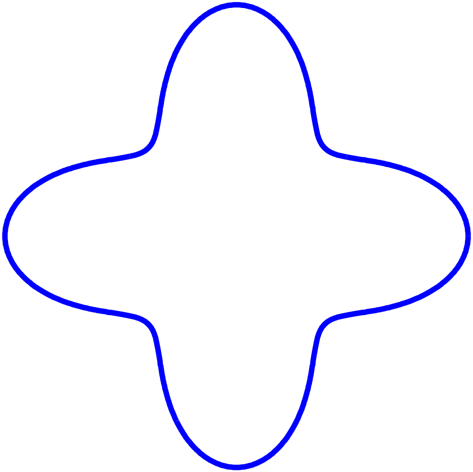
where C *is a constant, and* θ_a^l, θ_a^r *are respectively the left and right equilibrium contact angles of the equilibrium shape* Γ_e*.*

[a] Jiang *et al.*, submitted, 2016

Remark: The conditions (**C1**) and (**C3**) come from the first variation, while the condition (**C2**) comes from the second variation.

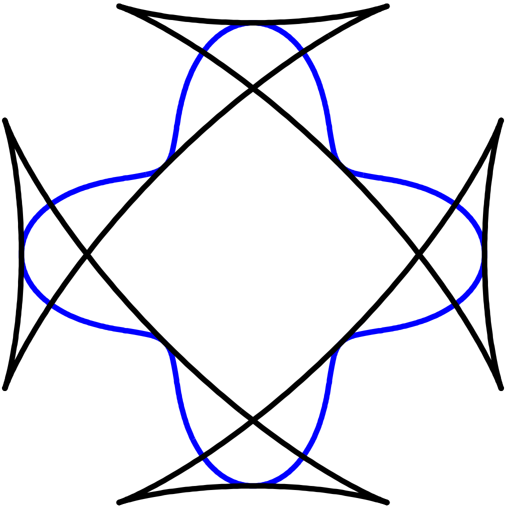
Generalized Winterbottom Construction

Example: $\gamma(\theta) = 1 + 0.3\cos(4\theta)$, and material constant $\sigma = -0.5$.



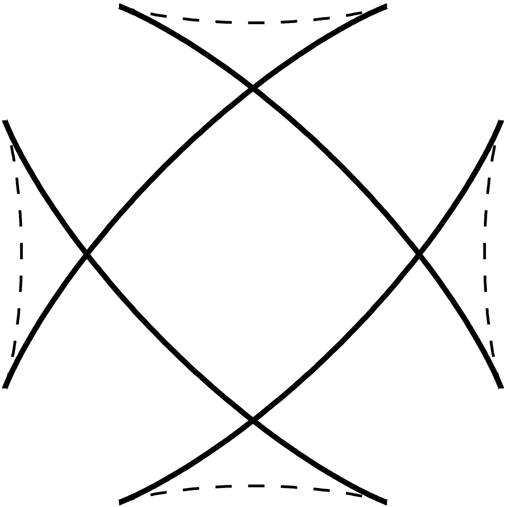
Generalized Winterbottom Construction

By condition (**C1**), $\mu(s) = \widetilde{\gamma}(\theta(s))\kappa(s) \equiv C, \qquad \text{a.e. } s \in [0, L]$.



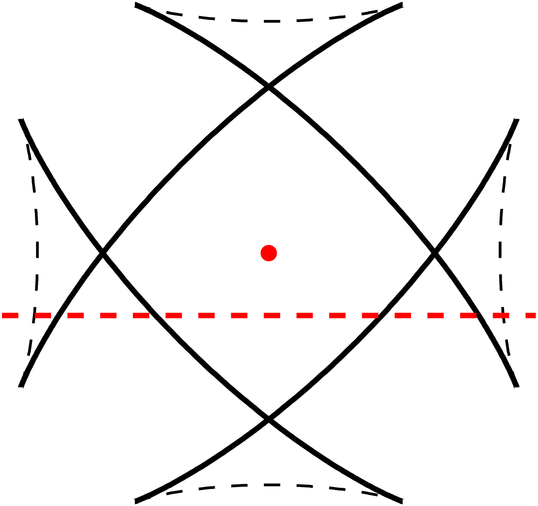
Generalized Winterbottom Construction

By condition (**C2**), $\widetilde{\gamma}(\theta(s)) \geq 0, \qquad \text{a.e. } s \in [0, L]$.



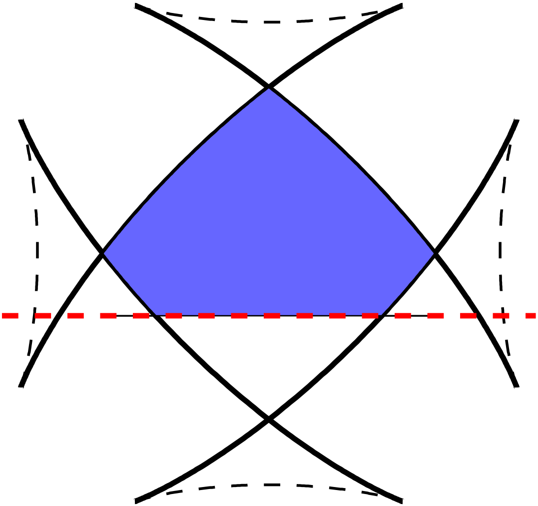
Generalized Winterbottom Construction

By condition (**C3**), $f(\theta) = \gamma(\theta)\cos\theta - \gamma'(\theta)\sin\theta - \sigma = 0, \quad \theta = \theta_a^l, \theta_a^r$.



Generalized Winterbottom Construction

We obtain four possible **stable equilibrium shapes**.



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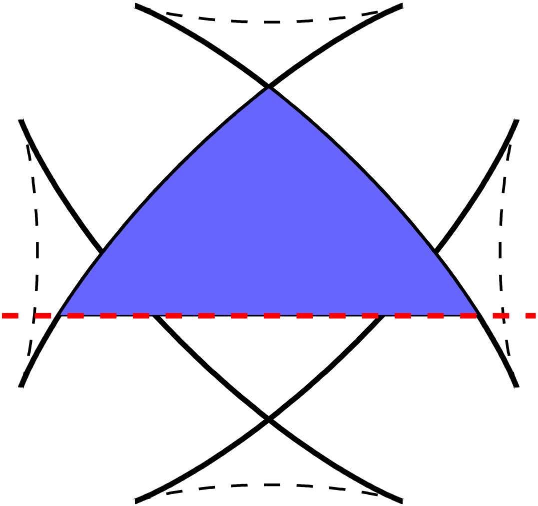

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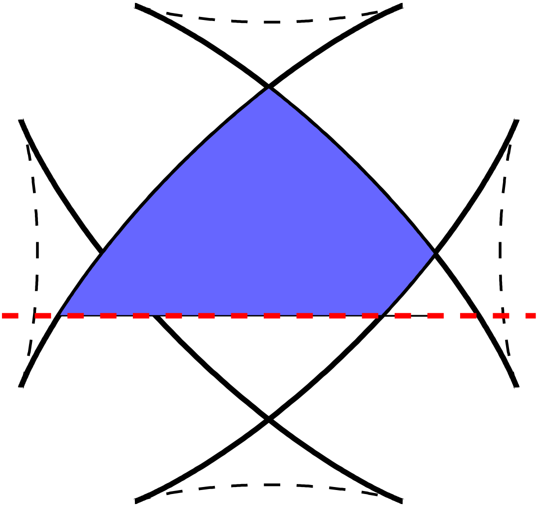

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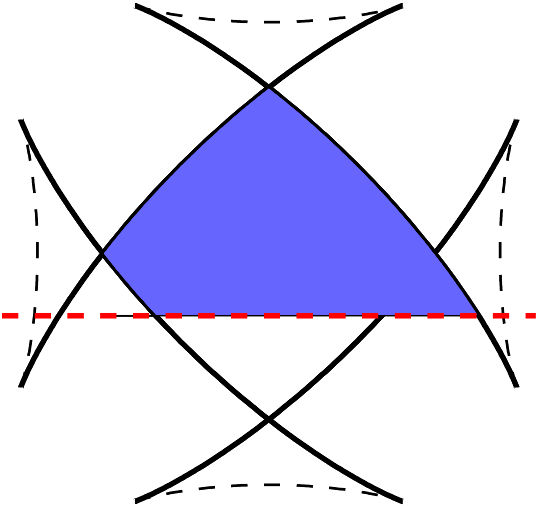

Numerical Verification

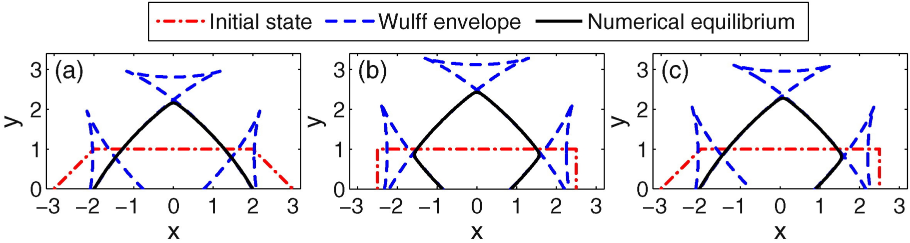

Figure: The equilibrium shapes of thin film with different initial states under the same parameters: $\gamma(\theta) = 1 + 0.3\cos(4\theta), \sigma = -0.5$, where the solid black lines show the different numerical equilibrium shapes, and the dashed blue lines represent the Wulff shape truncated by the flat substrate.

Outline

Summary and Future Works

Summary:

- Introduce a mathematical analysis to understand the thermodynamic variation of solid-state dewetting problems.
- Propose the sharp-interface model including surface energy anisotropy effects.
- Give necessary conditions for stable equilibrium shapes.
- Propose a generalized Winterbottom construction to predict multiple stable equilibrium shapes.

Summary and Future Works

Summary:

- Introduce a mathematical analysis to understand the thermodynamic variation of solid-state dewetting problems.
- Propose the sharp-interface model including surface energy anisotropy effects.
- Give necessary conditions for stable equilibrium shapes.
- Propose a generalized Winterbottom construction to predict multiple stable equilibrium shapes.

Future Works:

- ◇ Investigate the important roles of surface energy anisotropy.
- ◇ Mathematical analysis of the models.
- ◇ Develop accurate and efficient numerical methods for solving 3D solid-state dewetting problems.
- ◇ Compare with experiments & guide new experiments.

Thank You for Your Attention!