Solid-State Dewetting: Equilibrium & Dynamics

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   - Equilibrium Problems
   - Dynamical Problems

3 Dynamical Models with Anisotropic Surface Energies
   - Weakly Anisotropic Cases
   - Strongly Anisotropic Cases

4 Stable Equilibrium Shapes

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

**Dewetting Patterned Films:** Ni(110) Square Patches

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Physical Experiments

Dewetting on SOI system:

![Diagram of dewetting process 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...

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Solid-State Dewetting: Theoretical Models


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

- **Others...**
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Total Interfacial Free Energy:

\[ W(\Gamma) = \int_{\Gamma} \gamma(N) \, d\Gamma + (\gamma_{FS} - \gamma_{VS})\Sigma_{FS}. \]

\( \gamma(N) \) – The energy (density) of the film-vapor interface.
\( \Sigma_{FS} \) – interface length (2D) or surface area (3D) of the film-substrate interface.

Equilibrium configuration:

Minimize \( W(\Gamma) \)
Subject to \( \int_{\omega} d\omega = \text{Const.} \)
Equilibrium Problems

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

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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).
Equilibrium Problems

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![Equilibrium Shape Diagram](image)
Equilibrium Problems

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Assumption: The surface energy is isotropic.  

♦ Sharp Interface Model:

\[
\frac{d\mathbf{X}(t)}{dt} = V_n \mathbf{N} \quad \text{with} \quad V_n = B \Delta_s \kappa
\]

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

\[V_n = B \frac{\partial^2 \kappa}{\partial s^2} \quad \text{(in 2D)}\]

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

\(^3\)D.J. Srolovitz & S.A. Safran, JAP, 1986.  
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)
  
  $$ \frac{\partial y}{\partial s}(x_c, t) = \tan \theta_i, \quad \sigma := \cos(\theta_i) = \frac{\gamma_{VS} - \gamma_{FS}}{\gamma_{FV}} $$

- **Zero-Mass Flux** Condition (BC3)
  
  $$ \frac{\partial \kappa}{\partial s}(x_c, t) = 0. $$
Questions arising from Equilibrium and Dynamical Problems

We try to address the following questions by our research:

▶ \((Q1)\): 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?
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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:

\[ W = \int_{\Gamma} \gamma(\theta) \, d\Gamma + (\gamma_{FS} - \gamma_{VS})(x'_c - x'^l_c), \]

- Perturb the interface \( \Gamma \) in both the normal and tangent directions;
- \( \psi(s) \) is an arbitrary function, and \( \varphi(s) \) satisfies: \( \int_0^L \varphi(s)ds = 0 \).
The two components of the new curve $\Gamma^\epsilon(t)$ can be expressed as follows:

$$
\Gamma^\epsilon(t) = (x^\epsilon(s, t), y^\epsilon(s, t))
= (x(s, t) + \epsilon u(s, t), y(s, t) + \epsilon v(s, t)),
$$

(1)

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

$$
\begin{align*}
    u(s, t) &= x_s(s, t)\psi(s) - y_s(s, t)\varphi(s), \\
    v(s, t) &= x_s(s, t)\varphi(s) + y_s(s, t)\psi(s),
\end{align*}
$$

(2)

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

$$
v(0, t) = v(L, t) = 0.
$$

(3)
Thermodynamic Variation: The First Variation

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

$$ W = \int_{\Gamma} \gamma(\theta) \, d\Gamma + (\gamma_{FS} - \gamma_{VS})(x^r_c - x^l_c) $$

$$ = \int_0^L \gamma(\theta) \, ds + (\gamma_{FS} - \gamma_{VS})(x^r_c - x^l_c). $$

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

$$ W^\epsilon = \int_{\Gamma^\epsilon} \gamma(\theta^\epsilon) \, d\Gamma^\epsilon + (\gamma_{FS} - \gamma_{VS}) \left[ (x^r_c + \epsilon u(L, t)) - (x^l_c + \epsilon u(0, t)) \right] $$

$$ = \int_0^L \gamma\left( \arctan\left( \frac{y_s + \epsilon v_s}{x_s + \epsilon u_s} \right) \right) \sqrt{(x_s + \epsilon u_s)^2 + (y_s + \epsilon v_s)^2} \, ds $$

$$ + (\gamma_{FS} - \gamma_{VS}) \left[ (x^r_c + \epsilon u(L, t)) - (x^l_c + \epsilon u(0, t)) \right]. \quad (4) $$
\[
\frac{dW^\varepsilon}{d\varepsilon} \bigg|_{\varepsilon=0} = \lim_{\varepsilon \to 0} \frac{W^\varepsilon - W}{\varepsilon} \\
= \int_0^L \left( \gamma''(\theta) + \gamma(\theta) \right) \kappa \varphi \, ds \\
- \left[ \gamma(\theta_d^I) \cos \theta_d^I - \gamma'(\theta_d^I) \sin \theta_d^I + (\gamma_{FS} - \gamma_{VS}) \right] u(0, t) \\
+ \left[ \gamma(\theta_d^r) \cos \theta_d^r - \gamma'(\theta_d^r) \sin \theta_d^r + (\gamma_{FS} - \gamma_{VS}) \right] u(L, t).
\]
Thermodynamic Variation: The First Variation

\[
\left. \frac{dW^\epsilon}{d\epsilon} \right|_{\epsilon=0} = \lim_{\epsilon \to 0} \frac{W^\epsilon - W}{\epsilon} = \int_0^L \left( \gamma''(\theta) + \gamma'(\theta) \right) \kappa \varphi \, ds
\]

\[
- \left[ \gamma(\theta_d^l) \cos \theta_d^l - \gamma'(\theta_d^l) \sin \theta_d^l + (\gamma_{FS} - \gamma_{VS}) \right] u(0, t)
+ \left[ \gamma(\theta_r^r) \cos \theta_r^r - \gamma'(\theta_r^r) \sin \theta_r^r + (\gamma_{FS} - \gamma_{VS}) \right] u(L, t).
\]

- **Chemical potential:**

\[
\mu = \Omega_0 \frac{\delta W}{\delta \Gamma} = \Omega_0 \left( \gamma(\theta) + \gamma''(\theta) \right) \kappa,
\]

- **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

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

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

\[
\frac{dx_c^l(t)}{dt} = -\eta \frac{\delta W}{\delta x_c^l} = \eta \left[ \gamma(\theta_d^l) \cos \theta_d^l - \gamma'(\theta_d^l) \sin \theta_d^l + (\gamma_{FS} - \gamma_{VS}) \right], \\
\frac{dx_c^r(t)}{dt} = -\eta \frac{\delta W}{\delta x_c^r} = -\eta \left[ \gamma(\theta_d^r) \cos \theta_d^r - \gamma'(\theta_d^r) \sin \theta_d^r + (\gamma_{FS} - \gamma_{VS}) \right].
\]
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Sharp-Interface Model: Weakly Anisotropic

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\(^5\):

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

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

\[
\begin{cases}
\tilde{\gamma}(\theta) > 0, & \forall \theta \in [-\pi, \pi], \\
\text{Otherwise}, & \text{Strongly anisotropic cases.}
\end{cases}
\]

\(^5\text{Wang-Jiang-Srolovitz-Bao, PRB, 2015.}\)
Sharp-Interface Model: Weakly Anisotropic

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

\[ y(x_l^c, t) = 0, \quad y(x_r^c, t) = 0. \]  \hspace{1cm} (6)

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

\[ \frac{dx_l^c}{dt} = \eta f(\theta_d^l), \quad \frac{dx_r^c}{dt} = -\eta f(\theta_d^r), \]  \hspace{1cm} (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)**

\[ \frac{\partial \mu}{\partial s}(x_l^c, t) = 0, \quad \frac{\partial \mu}{\partial s}(x_r^c, t) = 0. \]  \hspace{1cm} (8)
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.
In the strongly anisotropic case, $\tilde{\gamma}(\theta) := \gamma(\theta) + \gamma''(\theta)$ may become negative for some $\theta$, which causes sharp corners in the equilibrium shape.

The proposed governing equation (5) becomes ill-posed in the strongly anisotropic case:

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

In order to regularize the equation, a high order regularization term can be added to the free energy:

$$W_r = \frac{\varepsilon^2}{2} \int_{\Gamma} \kappa^2 \, d\Gamma$$

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

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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\(^7\): 

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

\(^7\)Jiang et al., Scripta Mater., 2016.
1. **Contact Point Condition (BC1)**

\[ y(x^l_c, t) = 0, \quad y(x^r_c, t) = 0. \]  

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

\[
\frac{dx^l_c}{dt} = \eta f_\varepsilon(\theta^l_d), \quad \frac{dx^r_c}{dt} = -\eta f_\varepsilon(\theta^r_d),
\]  

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

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

\[
\frac{\partial \mu}{\partial s}(x^l_c, t) = 0, \quad \frac{\partial \mu}{\partial s}(x^r_c, t) = 0.
\]

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

\[
\kappa(x^l_c, t) = 0, \quad \kappa(x^r_c, t) = 0.
\]
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.
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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 \( \tilde{\gamma}(\theta) < 0 \):

\[ f'(\theta) = -\tilde{\gamma}(\theta) \sin \theta = -\left( \gamma(\theta) + \gamma''(\theta) \right) \sin \theta. \]

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 $\Gamma_e := (x(s), y(s)), \ s \in [0, L]$ 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:

\[
\mu(s) = \tilde{\gamma}(\theta(s)) \kappa(s) \equiv C, \quad a.e. \ s \in [0, L], \quad (C1)
\]
\[
\tilde{\gamma}(\theta(s)) \geq 0, \quad a.e. \ s \in [0, L], \quad (C2)
\]
\[
f(\theta) = 0, \quad \theta = \theta^l, \theta^r, \quad (C3)
\]

where $C$ is a constant, and $\theta^l, \theta^r$ are respectively the left and right equilibrium contact angles of the equilibrium shape $\Gamma_e$.\(^a\)

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\(^a\)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.
Example: $\gamma(\theta) = 1 + 0.3 \cos(4\theta)$, and material constant $\sigma = -0.5$. 
By condition (C1), $\mu(s) = \tilde{\gamma}(\theta(s))\kappa(s) \equiv C$, a.e. $s \in [0, L]$. 
By condition (C2), $\tilde{\gamma}(\theta(s)) \geq 0$, a.e. $s \in [0, L]$. 
Generalized Winterbottom Construction

By condition (C3), \( f(\theta) = \gamma(\theta) \cos \theta - \gamma'(\theta) \sin \theta - \sigma = 0 \), \( \theta = \theta_a^l, \theta_a^r \).
Generalized Winterbottom Construction

We obtain four possible **stable equilibrium shapes**.
Generalized Winterbottom Construction

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Generalized Winterbottom Construction

We obtain four possible stable equilibrium shapes.
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.
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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.
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◊ Compare with experiments & guide new experiments.
Thank You for Your Attention!