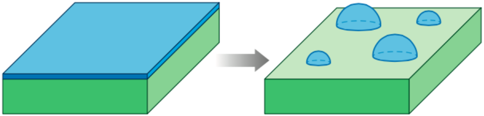

Solid-State Dewetting: From Flat to Curved Substrates

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IMS, 2 May, 2018

Outline

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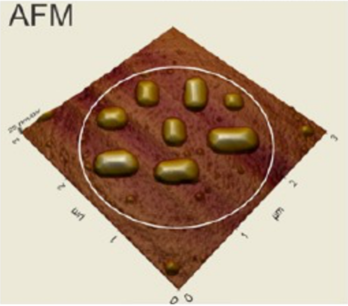
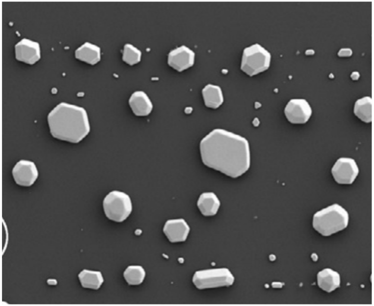
1. Introduction
2. Mathematical models
   - Flat substrate
   - Curved substrate
3. Numerical results
4. Summary and future works

Background





Background

Solid-state dewetting

- Thin films are generally metastable in the as-deposited state and will dewet or agglomerate to form arrays of islands when heated.
- This process occurs well below the melting temperature of the solid material.

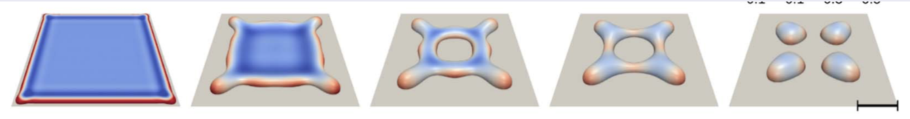


Figure: A schematic view of solid-state dewetting. Thin films dewet to form isolated islands when it remains in the solid state (M. Naffouti et al., 2017).

Application

Suppress dewetting

Thin films are basic components in many microelectronic and optoelectronic devices, and for these devices to function properly, the structural integrity of the thin films must be maintained. Dewetting destabilizes a thin film structure and limits the device reliability.

Induce dewetting

Ordered arrays of metal nanoparticles has a wide range of potential applications in plasmonics, magnetic memories, DNA detection and catalysis for nanowire and nanotube growth. Dewetting (template-assisted dewetting, dewetting of single crystal thin film) provides a easy way to produce ordered arrays of nanoparticles of controlled size and geometry.

Experimental results

Dewetting on a flat substrate generally leads to disordered arrays of islands, the irregularities of dewetting morphologies have limited the application for fabrication of ordered structures.

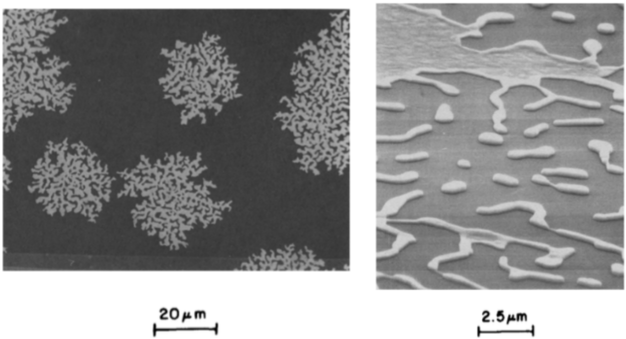


Figure: Dewetting of 30-nm-thick gold films on a flat substrate. (E. Jiran and C.V. Thompson, 1990).

Experimental results

Dewetting on a flat substrate generally leads to disordered arrays of islands, the irregularities of dewetting morphologies have limited the application for fabrication of ordered structures.

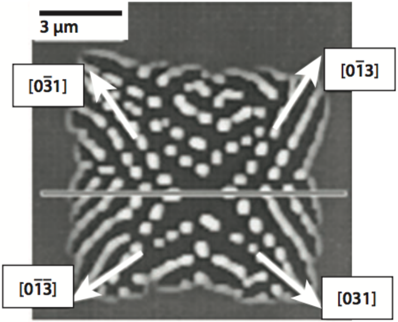


Figure: Dewetting of a single-crystal Si film on oxidized Si on a flat substrate. (R. Nuryadi et. al., 1990).

Experimental results

Template-assisted dewetting, i.e., dewetting on a pre-patterned (curved) substrate can lead to formation of ordered structures.

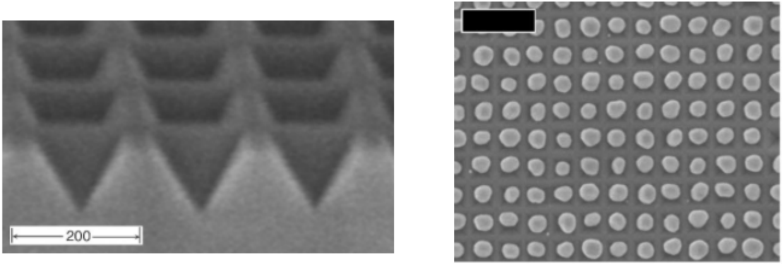


Figure: Template-assisted solid-state dewetting of gold films on oxidized silicon surfaces patterned with arrays of inverted pyramid shaped pits. (A.L. Giermann and C.V. Thompson, 2005).

Experimental results

Template-assisted dewetting, i.e., dewetting on a pre-patterned (curved) substrate can lead to formation of ordered structures.

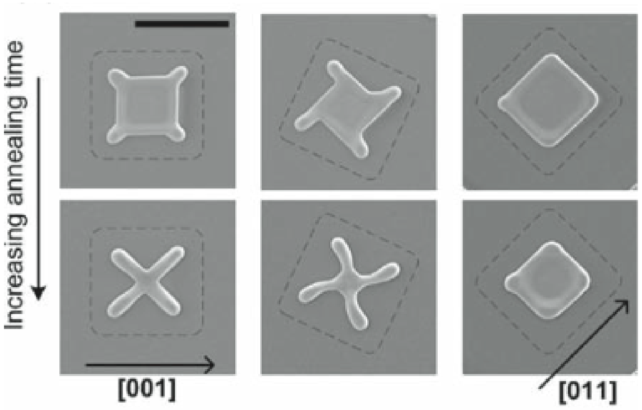
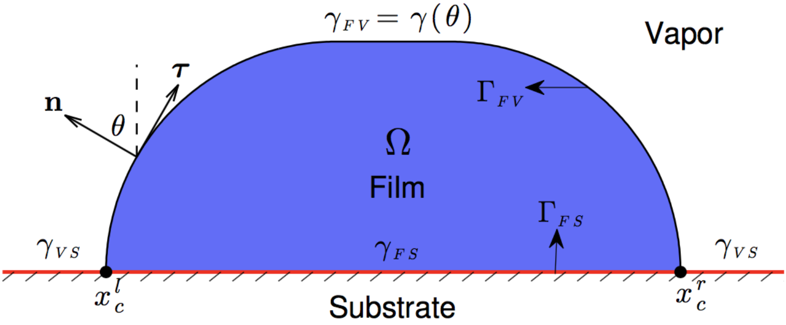


Figure: Dewetting of Ni(100) (J. Ye and C.V. Thompson, 2011).

Schematic illustration



- x_c^l, x_c^r are the contact points
- γ_{VS}, γ_{FS} are vapor/substrate and film/substrate interfacial energy densities (usually treated as constants)
- $\gamma_{FV} = \gamma(\theta)$ is the film/vapor interfacial energy density, where θ is the normal angle of the film/vapor interface

Film/vapor interfacial energy densities

The smooth case: $\gamma(\theta) \in C^2([-\pi, \pi])$

- Isotropic case: $\gamma(\theta)$ is a constant.
- Weakly anisotropic case: $\widetilde{\gamma}(\theta) := \gamma(\theta) + \gamma''(\theta) > 0, \quad \forall \theta \in [-\pi, \pi]$.
- Strongly anisotropic case: $\widetilde{\gamma}(\theta) < 0$ for some $\theta \in [-\pi, \pi]$.

The cusped case:

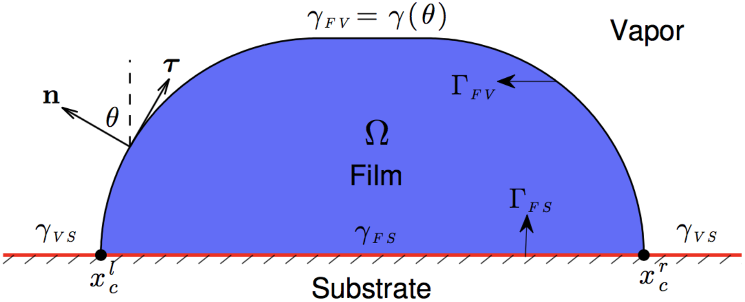
- $\gamma(\theta)$ is piecewise smooth (C^2) and not differentiable at finite points.

Figure: Different energy densities.

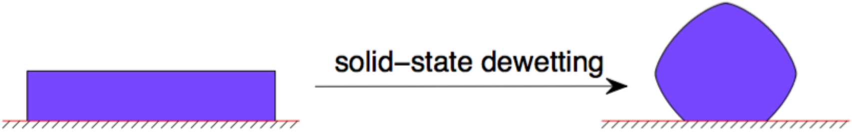
Equilibrium problem

- Energy minimization problem (J. Gibbs, 1878; G. Wulff, 1901; J. Taylor, 1974; I. Fonseca and S. Müller, 1991; R. Kaischew, 1950; W. Winterbottom, 1967; W. Bao et al., 2017)

$$\min_{\Omega} \; W = \int_{\Gamma_{FV}} \gamma_{FV} d\Gamma_{FV} + \underbrace{\int_{\Gamma_{FS}} (\gamma_{FS} - \gamma_{VS}) d\Gamma_{FS}}_{\text{Substrate Energy}} \quad \text{s.t.} \quad |\Omega| = \text{const.}$$



Dynamic problem



- Surface diffusion (mass transport) (W. Mullins, 1957; J. Cahn and D. Hoffman, 1974)

Chemical potential: $$\mu = \Omega_0 \frac{\delta W}{\delta \Gamma},$$

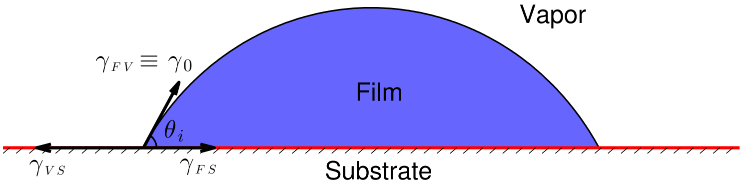
Mass flux: $$J = -\frac{D_s \nu}{k_B T_e} \nabla_s \mu,$$

Normal velocity: $$V_n = -\Omega_0 \nabla_s \cdot J = \frac{D_s \nu \Omega_0}{k_B T_e} \nabla_s^2 \mu.$$

Dynamic problem

- Surface diffusion (mass transport)
- Moving contact line
  At the equilibrium state, the following (isotropic) Young equation should be satisfied (T. Young, 1805):

$$\gamma_{VS} = \gamma_{FS} + \gamma_0 \cos\theta_i.$$



Existing models/methods

1. **Sharp interface model/methods**:
   - D. Srolovitz and S. Safran (1986): Isotropic, cylindrically symmetric case;
   - H. Wong *et al.* (2000): Isotropic, semi-infinite step in 2D, and a "marker-particle" method
   - P. Du *et al.* (2010): Isotropic, cylindrical wire
   - Wang et al. (2015); Jiang et al., (2016); Bao et al., (2017): Anisotropic case in 2D, and a parametric finite element method
2. **Phase field model**:
   - Isotropic case (W. Jiang *et al.*, 2012; M. Naffouti et al., 2017);
   - Weakly anisotropic case (M. Dziwnik *et al.*, 2017)
3. Others (e.g. E. Dornel *et al.*, 2006; L. Klinger and E. Rabkin, 2011; R.V. Zucker *et al.*, 2013; O. Pierre-Louis *et al.*, 2009; T. Lee et al., 2015)

Objective

Mathematical modeling

- ▷ Rigorously derive the sharp interface model;
- ▷ Include the interfacial anisotropy;
- ▷ Consider both flat and curved substrates.

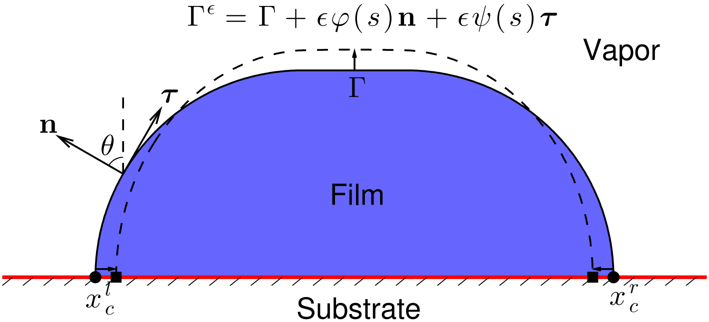
Numerical simulation

- ▷ Equilibrium;
- ▷ Morphological evolution;
- ▷ Template-assisted dewetting;
- ▷ ......

Outline

Outline

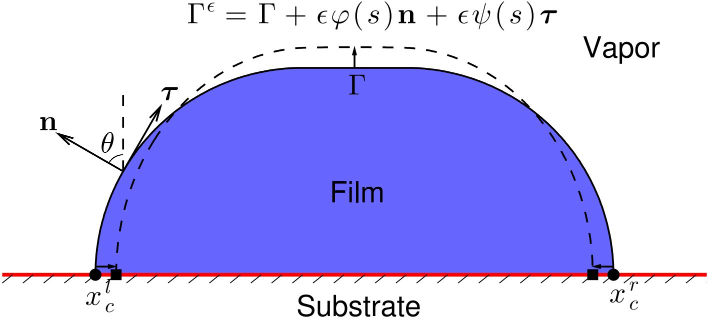
Thermodynamic variation: Perturbation



- Derive the model via thermodynamic variation;
- Perturb Γ in both normal and tangent directions;
- $\psi(s)$ is an arbitrary function, and $\varphi(s)$ satisfies

$$\int_0^L \varphi(s)ds = 0.$$

Thermodynamic variation: Perturbation



We express
$$\Gamma = (x(s),\ y(s)),$$
$$\Gamma^{\epsilon} = (x^{\epsilon}(s),\ y^{\epsilon}(s)) = (x(s) + \epsilon u(s),\ y(s) + \epsilon v(s)).$$
Then the increments along the $y-$axis at the two contact points must be zero, i.e.,
$$v(0) = v(L) = 0.$$

Thermodynamic variation 1

The total interfacial energy 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 free energy W^ϵ of the new curve Γ^ϵ as follows:

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

Thermodynamic variation 2

$$
\begin{aligned}
\frac{dW^\epsilon}{d\epsilon}\Big|_{\epsilon=0} = & \int_0^L \Big(\gamma''(\theta)+\gamma(\theta)\Big)\kappa\,\varphi\,ds \\
& + \Big[\gamma(\theta_d^l)\cos\theta_d^l - \gamma'(\theta_d^l)\sin\theta_d^l + \big(\gamma_{FS}-\gamma_{VS}\big)\Big]u(0) \\
& - \Big[\gamma(\theta_d^r)\cos\theta_d^r - \gamma'(\theta_d^r)\sin\theta_d^r + \big(\gamma_{FS}-\gamma_{VS}\big)\Big]u(L).
\end{aligned}
$$

- Chemical potential:

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

- Surface normal velocity:

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

Thermodynamic variation 2

$$\frac{dW^\epsilon}{d\epsilon}\Big|_{\epsilon=0} = \int_0^L \Big(\gamma''(\theta)+\gamma(\theta)\Big)\kappa\,\varphi\,ds$$
$$+\Big[\gamma(\theta_d^l)\cos\theta_d^l - \gamma'(\theta_d^l)\sin\theta_d^l + \big(\gamma_{FS}-\gamma_{VS}\big)\Big]u(0)$$
$$-\Big[\gamma(\theta_d^r)\cos\theta_d^r - \gamma'(\theta_d^r)\sin\theta_d^r + \big(\gamma_{FS}-\gamma_{VS}\big)\Big]u(L).$$

- Assuming that the moving process of the contact point can be taken as an energy gradient flow:

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

Governing equation

According to the thermodynamic principle, we have the following dimensionless sharp-interface model for weakly anisotropic solid-state dewetting problems:

$$\frac{\partial \mathbf{X}}{\partial t} = V_n \mathbf{n} = \frac{\partial^2 \mu}{\partial s^2} \mathbf{n}$$

$$\mu = \Big(\gamma(\theta) + \gamma''(\theta)\Big)\kappa,$$

where $\kappa = \partial_{ss} x \partial_s y - \partial_s x \partial_{ss} y$ is the curvature.

Boundary conditions

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

$$y(x_c^l, t) = 0, \quad y(x_c^r, t) = 0.$$

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

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

where

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

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

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

Regularization

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

- Well-posed in the isotropic and weakly anisotropic cases, i.e., $\widetilde{\gamma}(\theta) := \gamma(\theta) + \gamma''(\theta) > 0$ for all $\theta \in [0, 2\pi]$;
- Ill-posed in the strongly anisotropic case where $\widetilde{\gamma}(\theta)$ may become negative for some θ.
- In order to regularize the equation, a high order regularization term can be added to the free energy (M.E. Gurtin and M.E. Jabbour, 2002; S. Torabi *et al.*, 2009):

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

Governing equation (strong anisotropy)

By calculating the variation of the regularized interfacial energy $W + W_{\mathrm{w}}$, we can form the dimensionless model for the strongly anisotropic case as:

$$\frac{\partial \mathbf{X}}{\partial t} = V_n \mathbf{n} = \frac{\partial^2 \mu}{\partial s^2} \mathbf{n},$$

$$\mu = \Big(\gamma(\theta) + \gamma''(\theta)\Big)\kappa - \varepsilon^2 \left(\kappa_{ss} + \frac{\kappa^3}{2}\right),$$

where $\kappa = \partial_{ss} x \partial_s y - \partial_s x \partial_{ss} y$ is the curvature.

Boundary conditions (strong anisotropy)

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

$$y(x_c^l, t) = 0, \quad y(x_c^r, t) = 0.$$

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

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

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**)

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

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

$$\kappa(x_c^l, t) = 0, \qquad \kappa(x_c^r, t) = 0.$$

Outline

Schematic illustration on a curved substrate

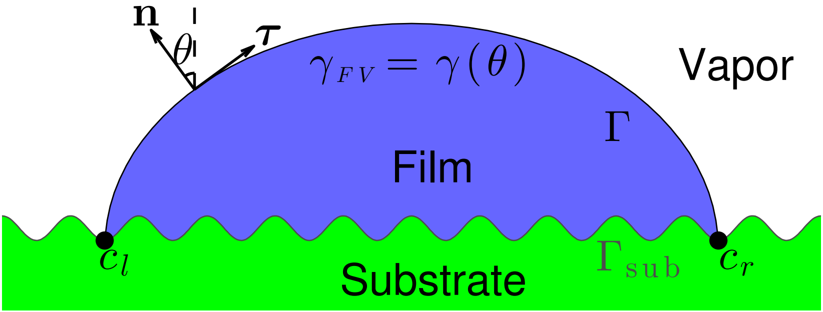


Figure: A schematic illustration of a film island in two dimension. Interfacial energy densities: $\gamma_{FV} = \gamma(\theta)$, γ_{FS} and γ_{VS} are contants.

- The interfacial energy:

$$W = \int_\Gamma \gamma(\theta)\, d\Gamma + \underbrace{(\gamma_{FS} - \gamma_{VS})(c_r - c_l)}_{\textbf{Substrate Energy}},$$

Thermodynamic variation

Similarly, we can perturb the film/vapor interface and calculate the thermodynamic variation of the total interfacial energy as

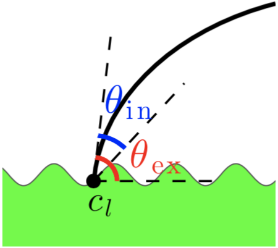
$$\frac{\delta W}{\delta \Gamma} = \Big(\gamma(\theta) + \gamma''(\theta)\Big)\kappa,$$

$$\frac{\delta W}{\delta c_r} = \gamma(\theta_{\text{ex}}^r)\cos\theta_{\text{in}}^r - \gamma'(\theta_{\text{ex}}^r)\sin\theta_{\text{in}}^r + (\gamma_{FS} - \gamma_{VS}),$$

$$\frac{\delta W}{\delta c_l} = -\Big[\gamma(\theta_{\text{ex}}^l)\cos\theta_{\text{in}}^l - \gamma'(\theta_{\text{ex}}^l)\sin\theta_{\text{in}}^l + (\gamma_{FS} - \gamma_{VS})\Big].$$

Thermodynamic variation

Similarly, we can perturb the film/vapor interface and calculate the thermodynamic variation of the total interfacial energy as



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

$$\frac{\delta W}{\delta c_r} = \gamma(\theta_{\rm ex}^r)\cos\theta_{\rm in}^r - \gamma'(\theta_{\rm ex}^r)\sin\theta_{\rm in}^r + (\gamma_{FS} - \gamma_{VS}),$$

$$\frac{\delta W}{\delta c_l} = -\Big[\gamma(\theta_{\rm ex}^l)\cos\theta_{\rm in}^l - \gamma'(\theta_{\rm ex}^l)\sin\theta_{\rm in}^l + (\gamma_{FS} - \gamma_{VS})\Big].$$

Model formulation

The two-dimensional solid-state dewetting of a thin film on a rigid curved solid substrate can be described in the following dimensionless form by the sharp interface model (isotropic/weakly anisotropic case):

$$\frac{\partial \mathbf{X}}{\partial t} = V_n \mathbf{n} = \frac{\partial^2 \mu}{\partial s^2} \mathbf{n}$$

$$\mu = \Big(\gamma(\theta) + \gamma''(\theta)\Big)\kappa,$$

where $\kappa = \partial_{ss} x \partial_s y - \partial_s x \partial_{ss} y$ is the curvature.

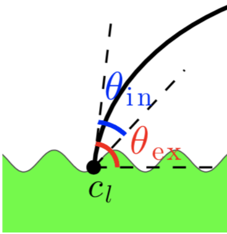
Boundary conditions for the weakly anisotropic case

1. *Contact point condition* (**BC1**)

$$\mathbf{X}(0,t) = \mathbf{X}_{\rm sub}(c_l), \qquad \mathbf{X}(L,t) = \mathbf{X}_{\rm sub}(c_r).$$

2. *Relaxed contact angle condition* (**BC2**)

$$\frac{dc_l}{dt} = \eta f(\theta_{\rm ex}^l, \theta_{\rm in}^l), \qquad \frac{dc_r}{dt} = -\eta f(\theta_{\rm ex}^r, \theta_{\rm in}^r),$$



where the binary function f is defined as

$$f(\theta_{\rm ex}, \theta_{\rm in}) := \gamma(\theta_{\rm ex})\cos\theta_{\rm in} - \gamma'(\theta_{\rm ex})\sin\theta_{\rm in} - \sigma,$$

with the dimensionless coefficient $\sigma := (\gamma_{VS} - \gamma_{FS})/\gamma_0 = \cos\theta_i$.

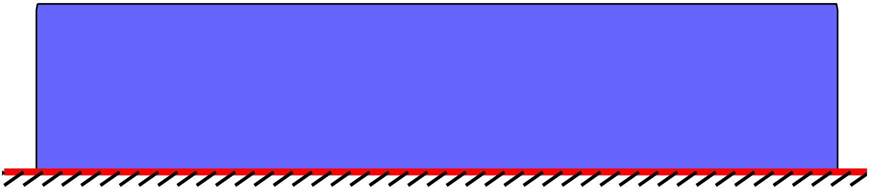
3. *Zero-mass flux condition* (**BC3**)

$$\frac{\partial\mu}{\partial s}(s=0,t) = 0, \qquad \frac{\partial\mu}{\partial s}(s=L,t) = 0,$$

Outline

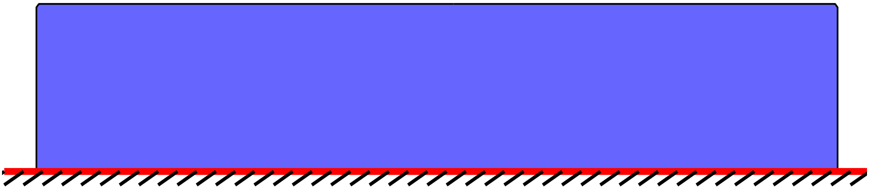
Isotropic, short island

$$L = 5, \beta = 0, \sigma = \cos(3\pi/4)$$



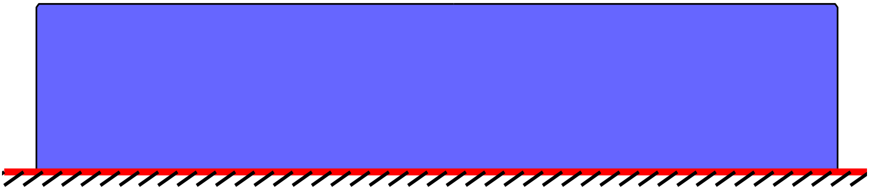
Weakly anisotropic, short island

$$L = 5, m = 4, \beta = 0.06, \sigma = \cos(3\pi/4)$$



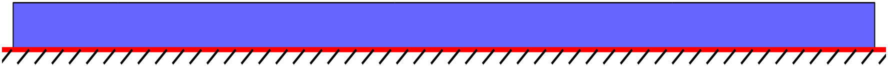
Strongly anisotropic, short island

$$L = 5, m = 4, \beta = 0.2, \sigma = \cos(3\pi/4)$$

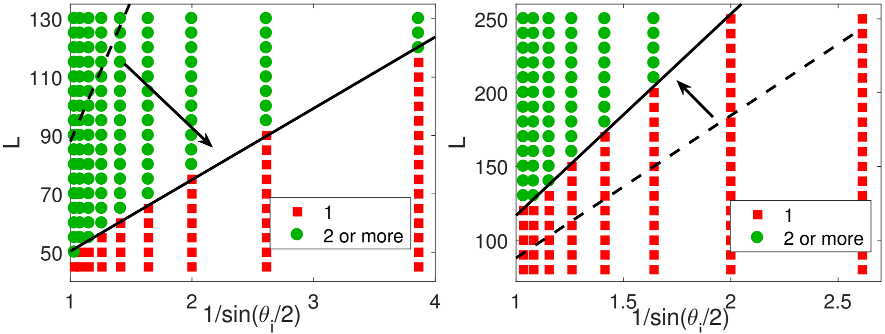


Weakly anisotropic, long island

$$L = 60, m = 4, \beta = 0.06, \sigma = \cos(5\pi/6)$$



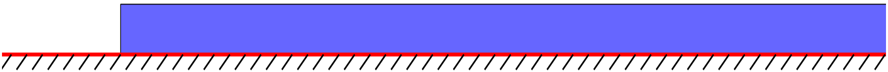
Critical length for pinch-off



$$\gamma(\theta) = 1 + 0.06\cos(4\theta), \qquad \gamma(\theta) = 1 - 0.06\cos(4\theta)$$

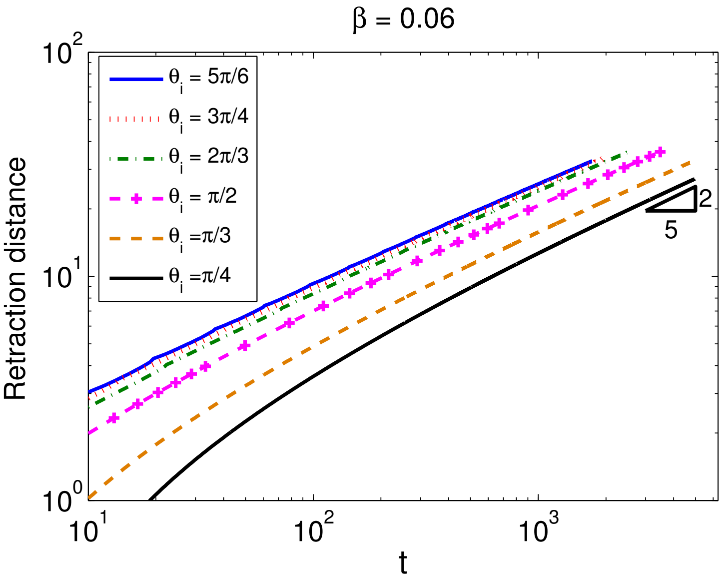
Weakly anisotropic, semi-infinite island

$$m = 4, \beta = 0.06, \sigma = \cos(5\pi/6)$$



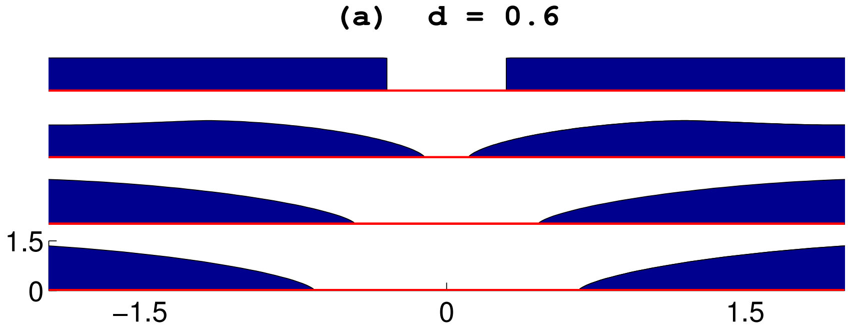
- Power-law for the retraction distance: $l \sim t^{0.4}$ (H. Wong et al., 2000)

Power law


β = 0.06
10^2
10^1
10^0
Retraction distance
10^1
10^2
10^3
t
$\theta_i = 5\pi/6$
$\theta_i = 3\pi/4$
$\theta_i = 2\pi/3$
$\theta_i = \pi/2$
$\theta_i = \pi/3$
$\theta_i = \pi/4$
2
5

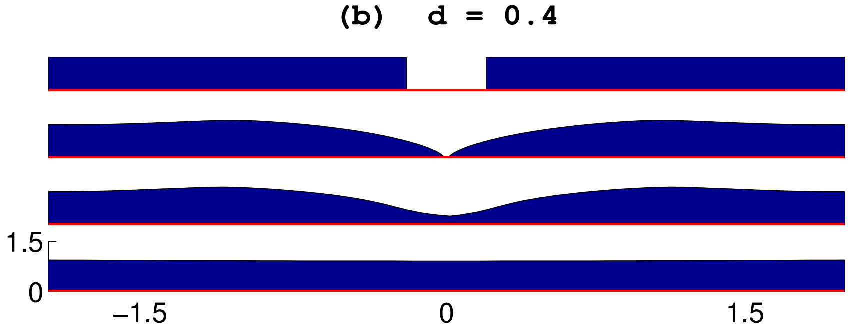
Hole: Dewetting – I

$\beta = 0.06, \ m = 4, \ \sigma = \cos(\pi/2).$



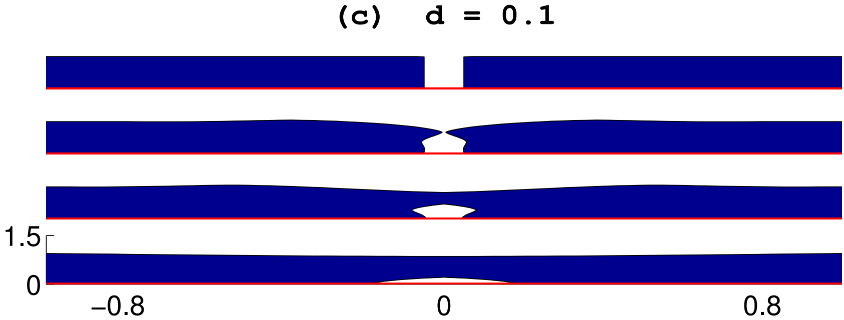
Hole: Wetting – II

$\beta = 0.06, \; m = 4, \; \sigma = \cos(\pi/2).$

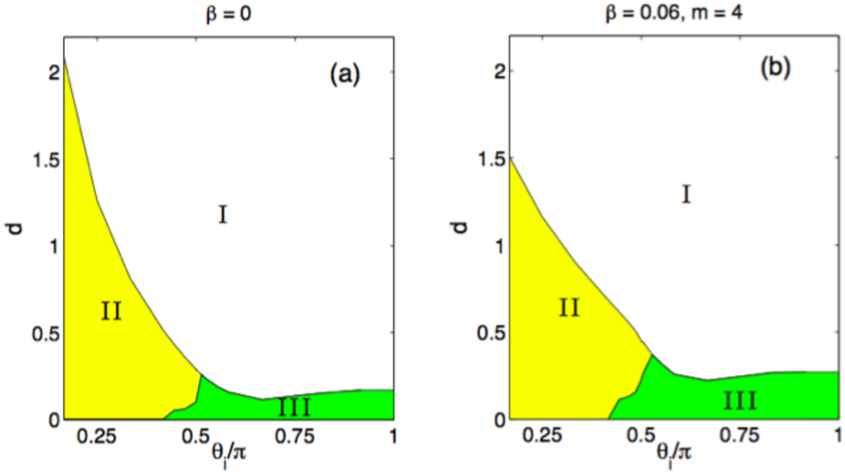


Hole: Void – III

$\beta = 0.06,\ m = 4,\ \sigma = \cos(\pi/2).$



Hole


β = 0
(a)
I
II
III
d
θ_i/π
0
0.5
1
1.5
2
0.25
0.5
0.75
1
β = 0.06, m = 4
(b)
I
II
III
d
θ_i/π
0
0.5
1
1.5
2
0.25
0.5
0.75
1

Equilibria on a sawtooth substrate

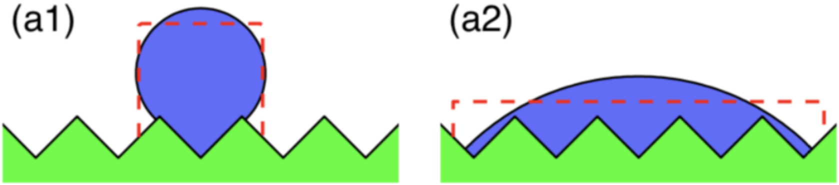


Figure: (a1-a2): Two equilibrium shapes of thin films on a sawtooth substate with initial area $A = 2$.

Asymmetric equlibrium

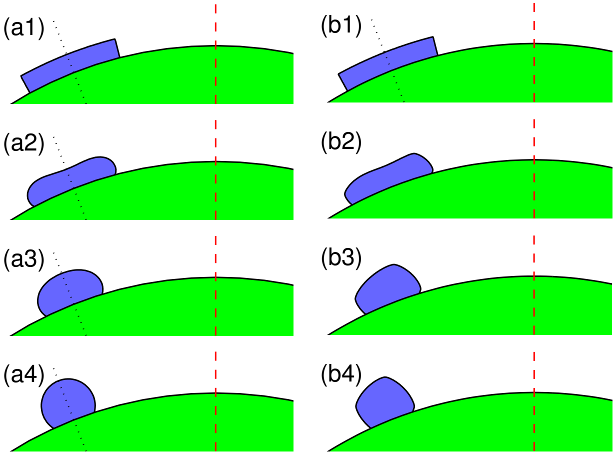


Figure: Evolution of thin films on a circular substrate ($R = 20$). (a) isotropic case, (b) weakly anisotropic case with $m = 4, \beta = 0.06$. $\sigma = -0.5$ in both cases. The intrinsic (contact) angles in (b4) are (left) 2.025 and (right) -2.319.

Pinch-off

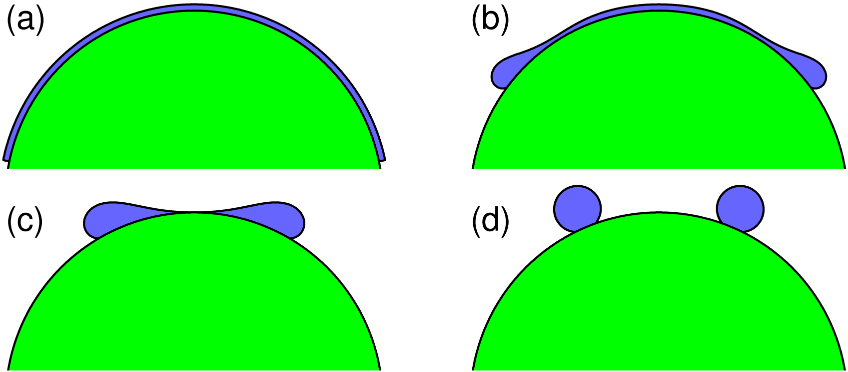
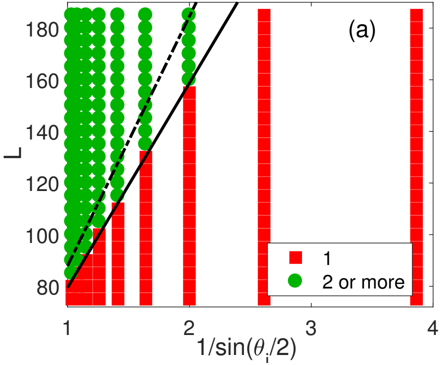
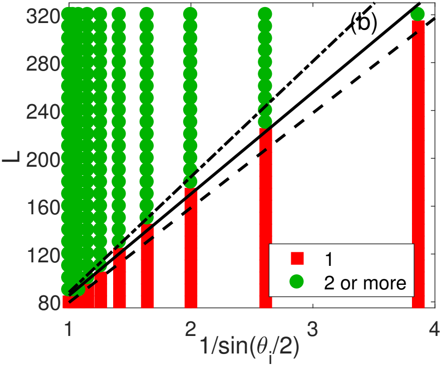


Figure: Evolution of a large island with isotropic surface energy on a spherical substrate of radius $R = 30$. Film length $L = 82$, $\sigma = -\sqrt{3}/2$.

Pinch-off



$R = 30$



$R = 60$

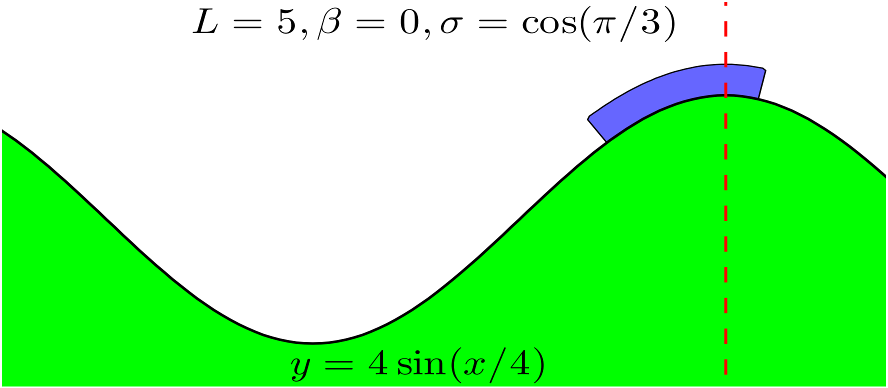
Pinch-off

Assuming isotropic surface energy, for given R and θ_i, we suggest that the critical pinch-off length can be predicted according to the following relation

$$L = \frac{-320.2/R + 89.9}{\sin(\theta_i/2)}, \quad R \geq 10. \tag{1}$$

Here, the radius is restricted to be larger than 10 since pinch-off won't occur for small R.

Movement on a sinusoidal substrate



Templated solid-state dewetting

- Consider sinusoidal substates $y = H\sin(wx)$.
- Consider enough long films.

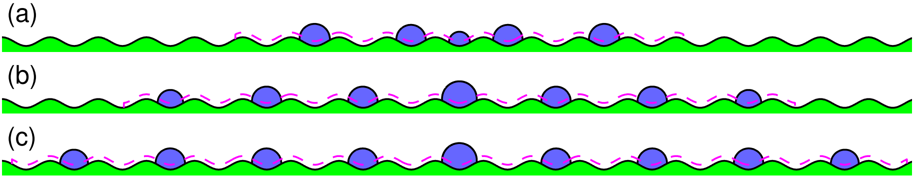


Figure: Dewetting of thin films with different length on a pre-patterned sinusoidal substrate. The lengths of the films are $L = 100, 150$ and 200.

Templated solid-state dewetting

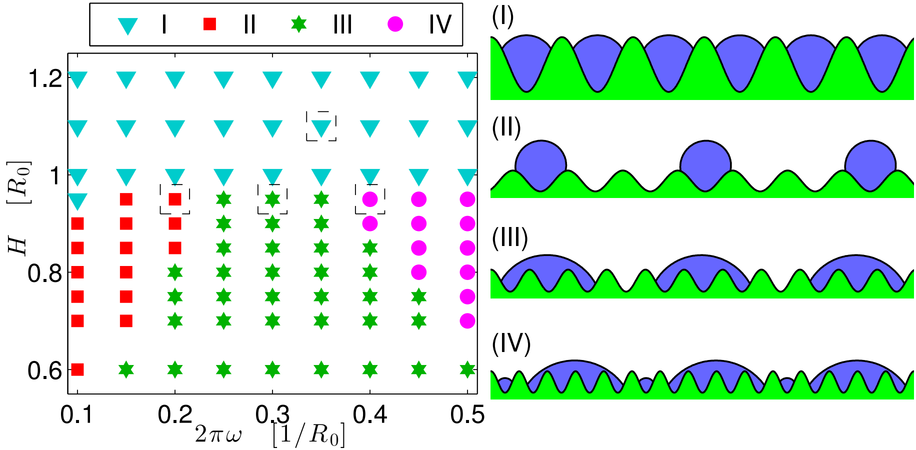
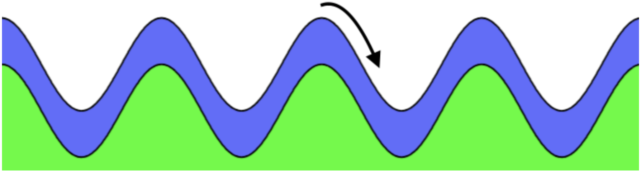
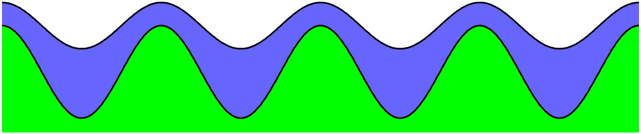


Figure: Phase diagram of the four observed categories of solid-state dewetting of thin films on pre-patterned sinusoidal substrates $y = H\sin(wx)$

Templated solid-state dewetting



⇓



Outline

Summary and future works

Summary

- Proposed sharp interface models for solid-state dewetting problems in 2D for both flat and curved substrates.
- Presented a series of numerical results to show the influence of anisotropy and curved substrates in solid-state dewetting.

Future works

- Analysis for the physical laws that we observed or summarized from numerical studies.
- 3D simulations.
- ......

Summary and future works

Thank You for Your Attention!