Asymptotic analysis of phase-field and sharp-interface models for surface diffusion

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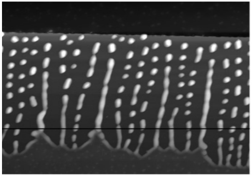
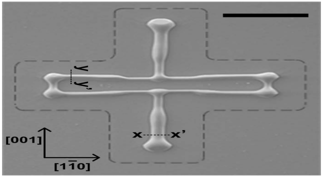
Review: Pattern formation by surface diffusion



Leroy et al 2012 (Si/SiO_2)



Ye et al 2010 (Ni/MgO)

Mullins (1957): $v_n = B\Delta_s \kappa$ $\kappa \propto \mu$ chemical potential per atom

Nernst-Einstein relation: $\mathbf{J} \propto -\nabla_s \mu$ for surface current

Mass conservation: $v_n = -\nabla_s \cdot \mathbf{J}$ speed of interface

Outline

I. Phase field models for surface diffusion.

II. Extension: Anisotropy

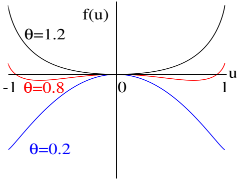
III. Solid dewetting: Finger instability

IV. Extension: Two-phase layers

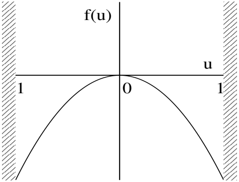
Phase field models for surface diffusion

- **How do we address topological changes?**
  Phase-field models:
  - Smooth phase field variable $u \approx \pm 1$ far away from the interface.
  - u transitions between $+1$ and -1 or vice-versa in the **interface region** of width proportional to ε.
- **What is the appropriate equation for u?**
- **Do we recover Mullins' model in the sharp-interface limit as $\varepsilon \to 0$?**

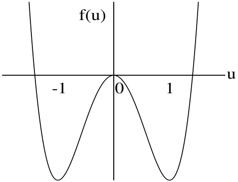
Cahn-Hilliard models



logarithmic



double obstacle



double well

Cahn-Hilliard models with degenerate mobility

$$u_t = \nabla \cdot \left[(1 - u^2) \nabla \mu \right], \qquad \mu = -\varepsilon^2 \nabla^2 u + f'(u)$$

Logarithmic free energy

$$f(u) = \theta \left[(1 - u) \ln(1 - u) + (1 + u) \ln(1 + u) \right] + (1 - u^2), \quad \theta = O(\varepsilon^\alpha)$$

Double obstacle free energy

$$f(u) = \begin{cases} 1 - u^2 & \text{for } |u| \le 1 \\ \infty & \text{for } |u| > 1 \end{cases}$$

Double well free energy

$$f(u) = (1 - u^2)^2$$

Double Well Cahn-Hilliard models

Torabi et al 2007, 2009, Jiang et al 2012; Abels et al. 2012, ...

$$u_t = \nabla \cdot \left[(1-u^2)\nabla\mu\right], \quad \mu = -\varepsilon^2\nabla^2 u + f'(u), \quad f(u) = (1-u^2)^2$$

Yeon et al. 2006, Torabi et al. 2012, ...

$$u_t = \nabla \cdot \left[(1-u^2)^{\mathbf{2}}\nabla\mu\right], \quad \mu = -\varepsilon^2\nabla^2 u + f'(u), \quad f(u) = (1-u^2)^2$$

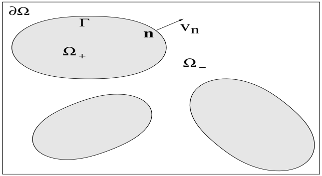
Rätz et al. 2006

$$u_t = \nabla \cdot \left[(1-u^2)\nabla\mu\right], \quad (1-u^2)\mu = -\varepsilon^2\nabla^2 u + f'(u), \quad f(u) = (1-u^2)^2$$

Smooth **double-well free energies** are commonly used.

Do these models capture surface diffusion?

Cahn-Hilliard with constant mobility



Cahn-Hilliard equation with constant mobility.

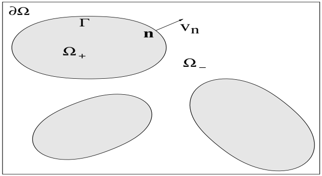
$$u_t = \Delta\mu, \qquad \mu = -\varepsilon^2\nabla^2 u + f'(u),$$
$$f(u) = (u^2 - 1)^2$$

Sharp-interface limit $t = \tau/\varepsilon$, $\varepsilon \to 0$ (Pego 1989):
Mullins-Sekerka problem

$$\Delta\mu = 0 \qquad \text{in } \Omega_\pm,$$
$$\mu = -\sigma\kappa,$$
$$v_n = [\nabla\mu \cdot \mathbf{n}]_-^+ .$$

Rigorous proof: Alikakos et al. (1994)

Cahn-Hilliard with degenerate mobility & double obstacle



Cahn-Hilliard equation with degenerate mobility.

$$u_t = \nabla \cdot \left[(1-u^2)\nabla\mu\right], \qquad \mu = -\varepsilon^2\nabla^2 u + f'(u)$$

$$f(u) = \begin{cases} 1-u^2 & \text{for } |u| \le 1 \\ \infty & \text{for } |u| > 1 \end{cases}$$

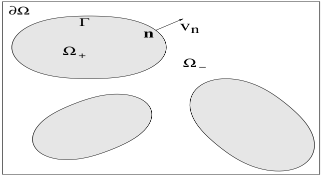
double obstacle

Sharp-interface limit $t = \tau/\varepsilon^2$, $\varepsilon \to 0$:
Mullins surface diffusion model

$$\mu = \sigma\kappa, \qquad v_n = \frac{\partial^2\mu}{\partial s^2}$$

Cahn,Elliott,Novick-Cohen (1996), also for log free energy with $\theta = O(\varepsilon^\alpha)$
No rigorous proof!

Cahn-Hilliard with degenerate mobility & double well



CHE with **degenerate mobility** and **double well free energy**

$$u_t = \nabla \cdot \left[(1-u^2)\nabla\mu\right], \qquad \mu = -\varepsilon^2\nabla^2 u + f'(u)$$
$$f(u) = (1-u^2)^2$$

Sharp interface limit $t = \tau/\varepsilon^2$, $\varepsilon \to 0$:
Torabi et al. (2007+8), Abels et al. (2012) ... : Mullins surface diffusion model.

BUT: Gugenberger et al. 2008: Inconsistencies in asymptotic derivations

Instructive: Stationary radially symmetric solutions

Spatially constant μ.

$$\frac{\varepsilon^2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}u}{\mathrm{d}r}\right) + 2u(u^2-1) = \mu$$
$$u'(1) = 0, \quad u'(0) = 0, \quad u(r_0) = 0$$

Solve for $\varepsilon \to 0$ using **matched asymptotics** (Niethammer 1995).

Outer solution is trivial: $u = 1$ inside and $u = -1$ outside

Inner variables: $\rho = \dfrac{r - r_0}{\varepsilon}$

$$U'' + \varepsilon\frac{U'}{\kappa^{-1} + \varepsilon\rho} + \mu - 2(U^3 - U) = 0, \qquad \kappa = 1/r_0,$$
$$U = U_0 + \varepsilon U_1 + \cdots, \quad \mu = \varepsilon\eta_1 + \varepsilon^2\eta_2 \cdots$$

Solution

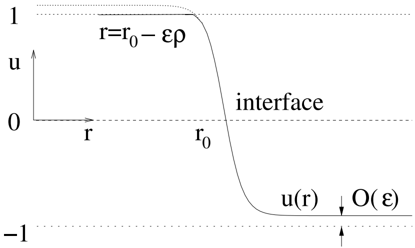
$$U_0 = -\tanh\rho$$

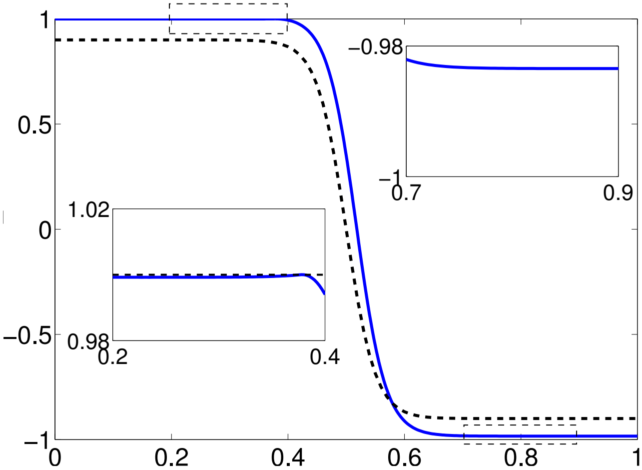
$$U_1 = C_1 \mathsf{sech}^2\rho + C_2 \mathsf{sech}^2\rho\left(\frac{3\rho}{8} + \frac{1}{4}\sinh 2\rho + \frac{1}{32}\sinh 4\rho\right)$$

$$+\frac{1}{8}(2\kappa - \eta_1) + \frac{1}{48}(2\kappa - 3\eta_1)(2\cosh 2\rho - 5\,\mathsf{sech}^2\rho)$$

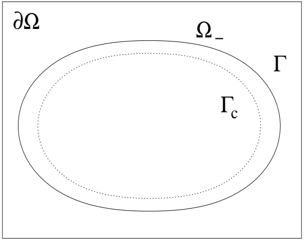
$$C_1 = -\frac{1}{16}(\eta_1 + 2\kappa), \quad C_2 = \frac{1}{3}(3\eta_1 - 2\kappa), \quad \eta_1 = \frac{2}{3}\kappa$$

Outer limits $r \to \pm\infty:$ $\qquad U_0 + \varepsilon U_1 + \ldots = \mp 1 + \varepsilon\frac{\kappa}{6} + \ldots$




1
0.5
0
−0.5
−1
0
0.2
0.4
0.6
0.8
1
1.02
0.98
0.2
0.4
−0.98
−1
0.7
0.9

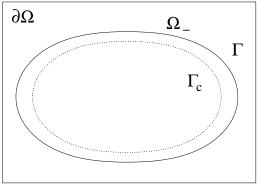
Final problem formulation



$$\varepsilon^2 \partial_\tau u = \nabla \cdot \mathbf{j} \qquad \mathbf{j} = (1 - u^2)\nabla \mu,$$
$$\mu = -\varepsilon^2 \nabla^2 u + f'(u), \qquad f = (1 - u^2)^2$$

$$\mathbf{n} \cdot \nabla u = 0, \qquad \mathbf{n} \cdot \mathbf{j} = 0 \qquad \text{on } \partial\Omega$$
$$u = 1, \qquad \mathbf{n} \cdot \nabla u = 0, \qquad \mathbf{n} \cdot \mathbf{j} = 0 \qquad \text{at } \Gamma_c$$

Scaling regimes



Outer expansion in Ω_-:

$$u = u_0 + \varepsilon u_1 + \cdots\,, \quad \mu = \mu_0 + \varepsilon \mu_1 + \cdots\,, \quad \mathbf{j} = \mathbf{j}_0 + \varepsilon \mathbf{j}_1 + \cdots$$

Inner layer at interface Γ: $\quad \mathbf{r}(s, r, \tau) = \mathbf{R}(s, \tau) + r\mathbf{n}(s, \tau), \quad r = \varepsilon\rho$

Expansions: $\quad U = U_0 + \varepsilon U_1 + \cdots\,, \quad \eta = \eta_0 + \varepsilon \eta_1 + \cdots\,,$

$$\mathbf{J} = \varepsilon^{-1}\mathbf{J}_{-1} + \mathbf{J}_0 + \cdots$$

Inner layer at Γ_c: $\quad \rho = z + \sigma$

Expansions: $\quad \bar{U} = \bar{U}_0 + \varepsilon \bar{U}_1 + \cdots\,, \quad \bar{\eta} = \bar{\eta}_0 + \varepsilon \bar{\eta}_1 + \cdots$

$$\bar{\mathbf{J}} = \varepsilon^{-1}\bar{\mathbf{J}}_{-1} + \bar{\mathbf{J}}_0 + \cdots\,,$$

Matching

Leading order

Outer	$\mathbf{j}_0 = 0,$	$\mu_0 = 0,$	$u_0 = -1$
Inner @ Γ	$J_{n,-1} = 0,$	$\eta_0 = 0,$	$U_0 = -\tanh\rho$
Inner @ Γ_c	$\bar{J}_{n,-1} = 0,$	$\bar{\eta}_0 = 0,$	$\bar{U}_0 = 1$

Next order

Outer	$\mathbf{j}_1 = 0,$	$\mu_1 = 4u_1$	?
Inner @ Γ	$J_{n,0} = 0,$	$\eta_1 = \frac{2}{3}\kappa,$	$U_1(s,\rho,\tau) =$ as before
Inner @ Γ_c	$\bar{J}_{n,0} = 0,$	$\eta_1 = \frac{2}{3}\kappa,$	$\bar{U}_1 = \frac{\kappa}{6}(1 - \cosh(2z))$

Matching μ_1 and red terms $\Rightarrow$ $\boxed{\mu_1 = \frac{2}{3}\kappa}$ **condition at Γ**

Matching continued

Next Order

Outer $\qquad \nabla \cdot \mathbf{j}_2 = 0, \qquad \mathbf{j}_2 = \frac{1}{2}\mu_1 \nabla \mu_1$

$$\Longrightarrow \quad \boxed{\nabla \cdot (\mu_1 \nabla \mu_1) = 0} \qquad \textbf{PDE in } \Omega_-$$

Inner @ Γ $\qquad v_n = \frac{1}{2}[J_{n,2}]_{-\infty}^{+\infty} + \frac{2}{3}\partial_{ss}\kappa$

Inner @ Γ_c $\qquad \bar{J}_{n,2} = 0$

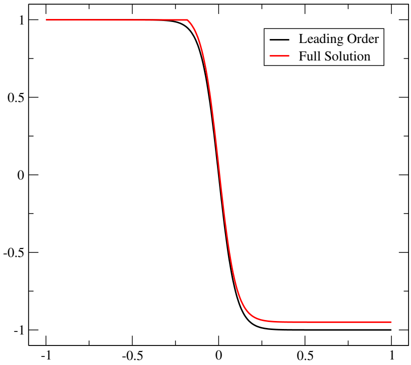
Matching $\Rightarrow$ $J_{n,2}|_{-\infty} = 0, \quad J_{n,2}|_{+\infty} = \frac{1}{2}\mu_1 \nabla_n \mu_1 \neq 0$

Problem: $\quad J_{n,2} = \left(1 - \tanh^2(\rho)\right)\partial_\rho \eta_3$ $\qquad$ in inner layer at Γ

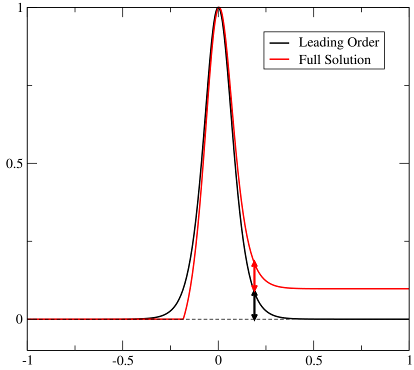
$J_{n,2}|_{+\infty} \neq 0 \quad \Longrightarrow \quad \eta_3 = O\left(e^{2\rho}\right)$ $\quad$ as $\rho \to +\infty$

Exponentially growing term!

Density profile $u(x)$



Mobility $|1 - u(x)|^2$



Additional inner layer with exponential matching

$$\eta_3 = \frac{\mu_1 \nabla_n \mu_1|_\Gamma}{16} e^{2\rho} + \dots \quad \text{as } \rho \to \infty$$

Additional layer $\quad \rho = \frac{1}{2}\log\left(\frac{1}{\varepsilon}\right) + y$

$$\hat{U} = -1 + \varepsilon \hat{U}_1 + \varepsilon^2 \hat{U}_2 + \cdots, \quad \hat{\eta} = \varepsilon \hat{\eta}_1 + \hat{\varepsilon}^2 \hat{\eta}_2 + \cdots,$$
$$\hat{\mathbf{J}} = \varepsilon \hat{\mathbf{J}}_1 + \varepsilon^2 \hat{\mathbf{J}}_2 + \cdots,$$

Solution for $\hat{\eta}_2$:

$$\hat{\eta}_2 = \frac{3\mu_1 \nabla_n \mu_1|_\Gamma}{4\kappa} \ln\left(\frac{\kappa}{12} \mathrm{e}^{2\mathrm{y}} + 1\right) + \frac{\kappa^2}{36}.$$

Re-expand $y \to -\infty$ and substitute in $y = \rho + \log(\varepsilon)/2$.

$$\hat{\eta}_2 = \frac{3\mu_1 \nabla_n \mu_1|_\Gamma}{4\kappa} \frac{\kappa}{12} e^{(2\rho + \log(\varepsilon))} + \cdots = \frac{\mu_1 \nabla_n \mu_1|_\Gamma}{16} \varepsilon \, e^{2\rho} + \cdots$$

(Exponential matching: Lange (1983), Korzec, Münch, Wagner (2008))

Additional inner layer with exponential matching

$$\eta_3 = \frac{\mu_1 \nabla_n \mu_1|_\Gamma}{16} e^{2\rho} + \dots \quad \text{as } \rho \to \infty$$

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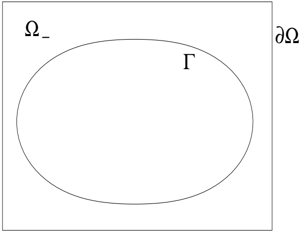
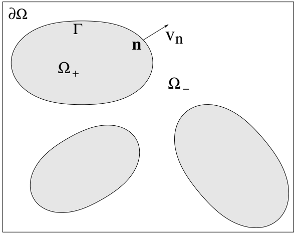
Summary of sharp-interface model





PDE in Ω_- (no Ω_+!): $\nabla \cdot (\mu_1 \nabla \mu_1) = 0$

Conditions at Γ: $\mu_1 = \frac{2}{3}\kappa,$ $\boxed{v_n = \frac{2}{3}\partial_{ss}\kappa + \frac{1}{4}\mu_1 \nabla_n \mu_1}$

Condition at $\partial\Omega$: $\nabla \mu_1 \cdot \mathbf{n} = 0$

Linear stability analysis for an inclusion with unit diameter.

Perturb interface position $r = (1/2) + \delta \exp(\lambda t) \cos(2\theta)$, $\quad 0 < \delta \ll 1$, then solve $O(\delta)$ to determine decay rate λ (analytically or numerically).

Sharp-interface models:

$$\lambda_{\text{pure}} = \boxed{-128} \qquad \text{for pure surface diffusion}$$

$$\lambda_{\text{new}} = \boxed{-137.4} \qquad \text{new sharp interface model}$$

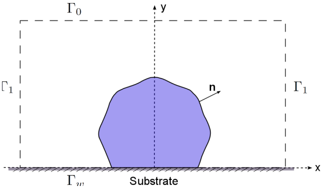
Linearised phase-field model:

ε	0.005	0.003	0.002	0.001
λ_*	−133.8	−136.0	−136.3	−137.0

Lee, Münch and Süli, APL 2015 & SIAP 2016
Dai and Du, MMS 2014

II. Extension: Anisotropy

Cahn-Hilliard model with weak anisotropy



Cahn-Hilliard equation:

$$u_t = \nabla \cdot \mathbf{j}, \qquad \mathbf{j} = (1 - u^2)^2 \nabla \mu,$$

$$\mu = F'(u) - \varepsilon^2 \nabla \left(\gamma(\theta)\gamma(\theta)' \begin{pmatrix} -u_y \\ u_x \end{pmatrix} + \gamma^2 \nabla u \right), \qquad \theta \equiv \text{atan2}(u_y, u_x)$$

γ assumed to be 2π-periodic and $\gamma + \gamma'' > 0$

Boundary conditions at substrate Γ_w:

$$\varepsilon\ \mathbf{n} \cdot \left[\gamma(\theta)\gamma'(\theta) \begin{pmatrix} -u_y \\ u_x \end{pmatrix} + \gamma(\theta)^2 \nabla u \right] + \frac{3 - 2u}{4\lambda_m}(\sigma_{VS} - \sigma_{FS}), \qquad \mathbf{n} \cdot \mathbf{j} = 0.$$

Boundary conditions on $\Gamma_0 \cup \Gamma_1$: $\quad \mathbf{n} \cdot \nabla u = 0, \qquad \mathbf{n} \cdot \mathbf{j} = 0.$

Sharp-interface model

Condition at interface (no bulk contribution!):

$$v_n = \left(\frac{2}{3}\right)^2 \partial_s \left[\gamma \partial_s((\gamma + \gamma'')\kappa)\right],$$

Laplace-Young condition at triple contact line:

$$0 = \frac{4}{3}\left(-\gamma'(\alpha)\sin\alpha + \gamma(\alpha)\cos\alpha\right) - \frac{1}{\lambda_m}(\sigma_{VS} - \sigma_{FS})$$

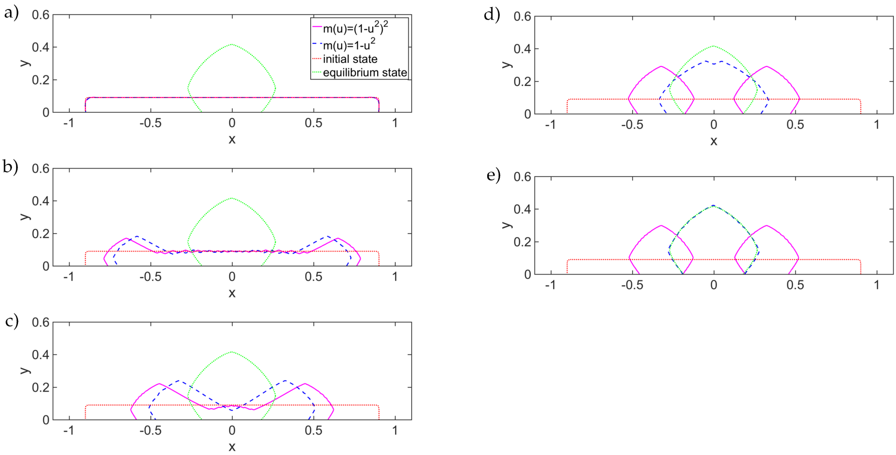
No-flux at triple contact line:

$$\partial_s \left[(\gamma + \gamma'')\kappa\right] = 0$$

McFadden et al. 1993, Raetz et al 2006
Owen et al. 1990, Novick-Cohen 2000, Garcke and Novick-Cohen 2000

Dziwnik, Münch and Wagner (submitted)

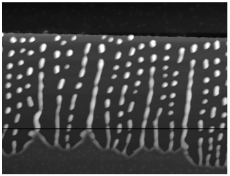
Numerical comparisons

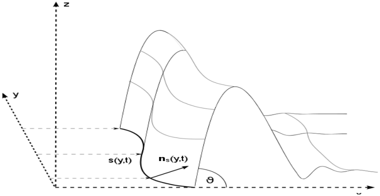


Correct mobility $M(u) = (1-u^2)^2$ (pink solid line)
Incorrect mobility $M(u) = 1-u^2$ (blue dashed line)
$\varepsilon = 0.02$, contact angle $\theta_c = 135^o$, $\gamma(\theta) = 1 + 0.05\cos(4\theta)$.
Results shown for $t = 0,\ 1,\ 5,\ 10,\ 20$.

III. Solid dewetting: Finger instability

Surface diffusion - “solid dewetting”





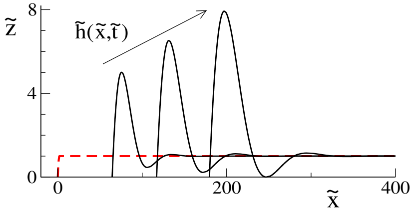
Sharp-interface model: $v_n = \Delta_s \kappa$

Thin-film approximation: $h_t + \Delta^2 h = 0$

$$h \to 1 \quad \text{for} \quad x \to \infty$$

$$h = 0, \quad \nabla h \cdot \mathbf{n}_s = 1, \quad \nabla \Delta h \cdot \mathbf{n}_s = 0 \quad \text{at } x = s(y,t)$$

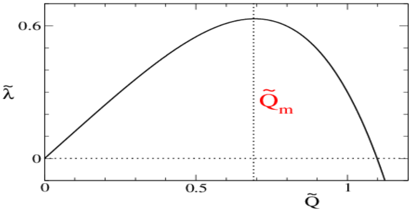
"Frozen Mode" stability analysis



Growth of rim

Spanwise (frozen mode) perturbation:

$$h(x, y, t) = h_b(x, t_0) + \delta h_1(x) \exp(iqy + \lambda t), \quad 0 < \delta \ll 1$$



Dispersion relation

McCallum, et al., J. Appl. Phys., 1996; Kan, Wong, J. Appl. Phys., 2005

Is $2\pi/\tilde{Q}_m$ the wavelength you see?

Similarity solution for $t \to \infty$

Shift origin $X = x - s(t)$ and assume $\max h \gg 1$ for $t \to \infty$.

Dominant balance and matching $h \to 0$ as $X \to \infty$ gives ridge solution

$$h(X,t) = \frac{2}{\sqrt{3}\dot{s}^{1/3}} \exp\left(-\frac{\dot{s}^{1/3}X}{2}\right) \sin\left(\frac{\sqrt{3}\dot{s}^{1/3}X}{\sqrt{2}}\right)$$

Mass conservation

$$\int_0^\infty h(X,t)\,dX = s \qquad \Longrightarrow \qquad s \propto t^{2/5}$$

Notice scaling of height of ridge: $\max_X h \propto t^{1/5}$

Stability analysis using WKB

Linearise

$$h(x,y,t) = h_b(x,t) + \varepsilon\, h_1(x,y,t), \quad s(y,t) = \varepsilon\, s_1(y,t), \quad 0 < \varepsilon \ll 1,$$

Fourier transform

$$h_1 = \int_{-\infty}^{\infty} \hat{h}_1(x,t;q)\, \exp(iqy)\, dq, \quad s_1 = \int_{-\infty}^{\infty} \hat{s}_1(t;q)\, \exp(iqy)\, dq.$$

Use slow time $t = \tau/\delta$, $\delta \ll 1$, and

$$h_1 = \Psi(x,\tau;q) \exp\left(\delta^{-1/5}\sigma(\tau;q)\right)$$

Leading order solution:

$\sigma(\tau;q) = \int^{\tau}$ top eigenvalue $\neq$ $\tau *$ top eigenvalue (frozen mode result)

Amplification and dominant wavenumber

$$h_1(x,y,t) \sim \int_{-\infty}^{\infty} \Psi_0(x;q) \exp\left(\int^t \lambda(\rho;q)\ d\rho\right) \exp(iqy)\ dq.$$

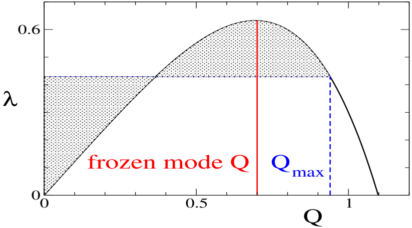
Obtain maximally amplified wavenumber $q_{\max}$ from

$$\frac{d}{dq}\left(\int^t \lambda(\rho;q)\ d\rho\right) = 0$$

Result: $q_{\max} = t^{-1/5}\, Q_{\max}$, where $Q_{\max}$ satisfies

$$\int_0^{Q_{\max}} \lambda(Q) - \lambda(Q_{\max})\ dQ \ = 0$$

Equal Area Rule

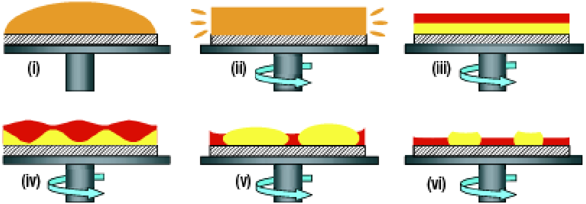


(Dziwnik, Korzec, Münch, Wagner 2014)

IV. Extension: Two-phase layers

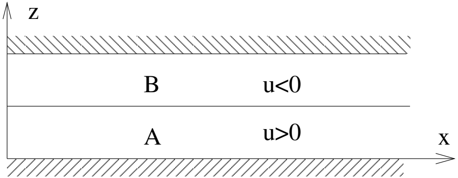
Review: Pattern formation in bilayer films

Fabrication of organic photovoltaic devices



Heriot & Jones 2005

Evolution of confined bilayers



Cahn-Hilliard equation with constant mobility (bulk diffusion)

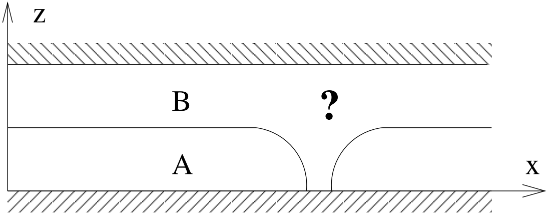
$$u_t = \Delta\left(-\varepsilon^2 \Delta u + F'(u)\right)$$
$$F(u) = -u^2 + u^4$$

Antisymmetric walls at $z = 0,\ 2$:

$$\partial_z\left[-\varepsilon^2 \Delta u + F'(u)\right] = 0 \qquad \text{(no-flux)}$$
$$\varepsilon u_z = \beta_1(1 - u^2) \qquad \text{(surface energy)}$$

Cahn 1977, Binder 1995, Puri & Binder (2002, 2007,...), Gheoghegan & Krausch (2003)

Evolution of confined bilayers



Sharp-interface limit $\varepsilon \to 0$
Mullins-Sekerka problem (Pego 1989).

$$\Delta\mu = 0 \qquad \text{in A and B}$$

$$\mu \propto \kappa_{AB} \qquad \text{Curvature at AB interface}$$

$$v_{AB} = [\nabla\mu \cdot \mathbf{n}_{AB}]_-^+ \qquad \text{AB interface velocity}$$

Thin-film approximation
Evolution of AB interface $z = h(x,t)$

$$\boxed{h_t + h_{xxxx} = 0}$$

Conditions at 3-phase contact line $x = s(t)$:

$$h = 0, \quad h_x = \tan\theta, \quad h_{xxx} = 0$$

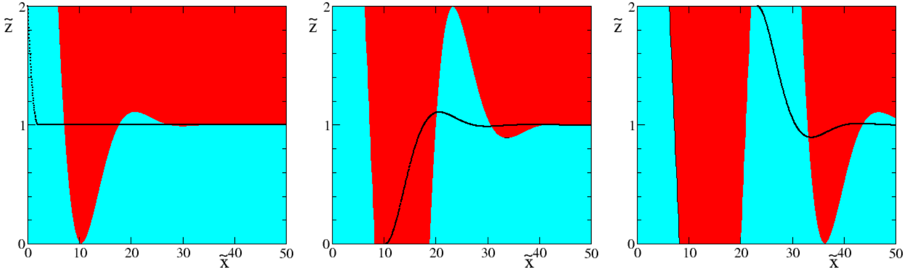
Conditions at $x \to \infty$:

$$h \to 1$$

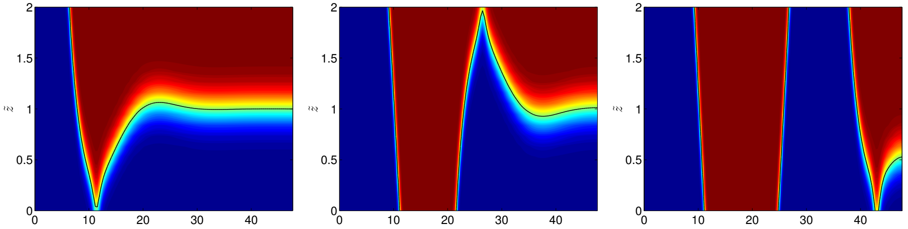
Hennessy et al., 2014, 2015; $\theta = \theta(\beta_1)$ contact angle (Cahn 77 - Modica 87)

Simulations

Lubrication model (contact angle $\theta = 50°$)



Phase field model ($\varepsilon = 0.03$, $\beta_1 = 0.11$)



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