Bifurcation & Competitive Evolution of Network Morphologies in the Functionalized Cahn-Hilliard

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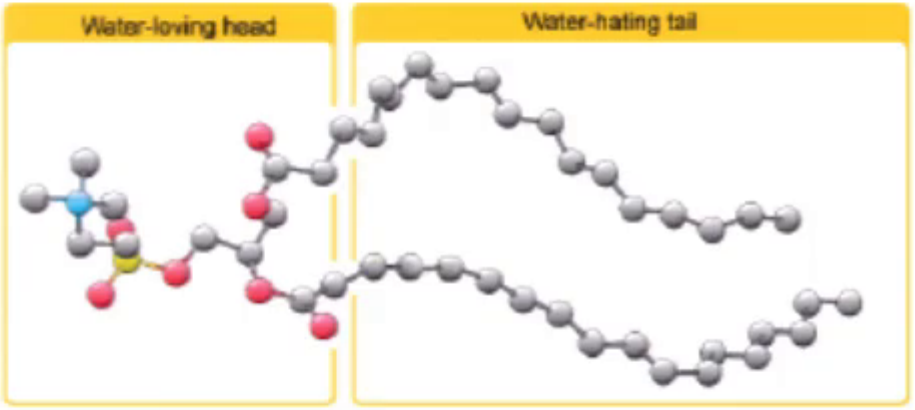
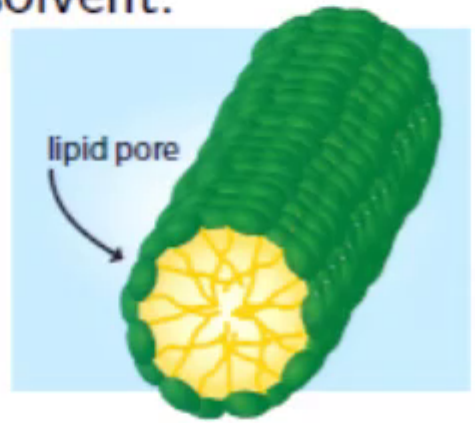
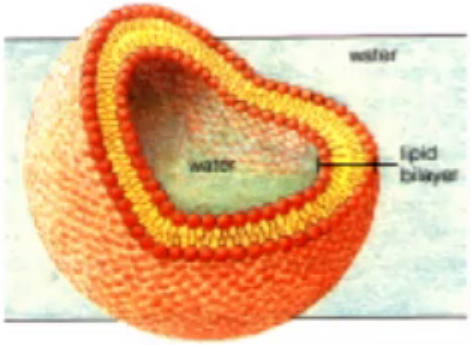
May 17, 2015

Very Brief Overview

We are interested in a model which describes phase separation of a binary mixtures of an amphiphilic molecules and solvent.





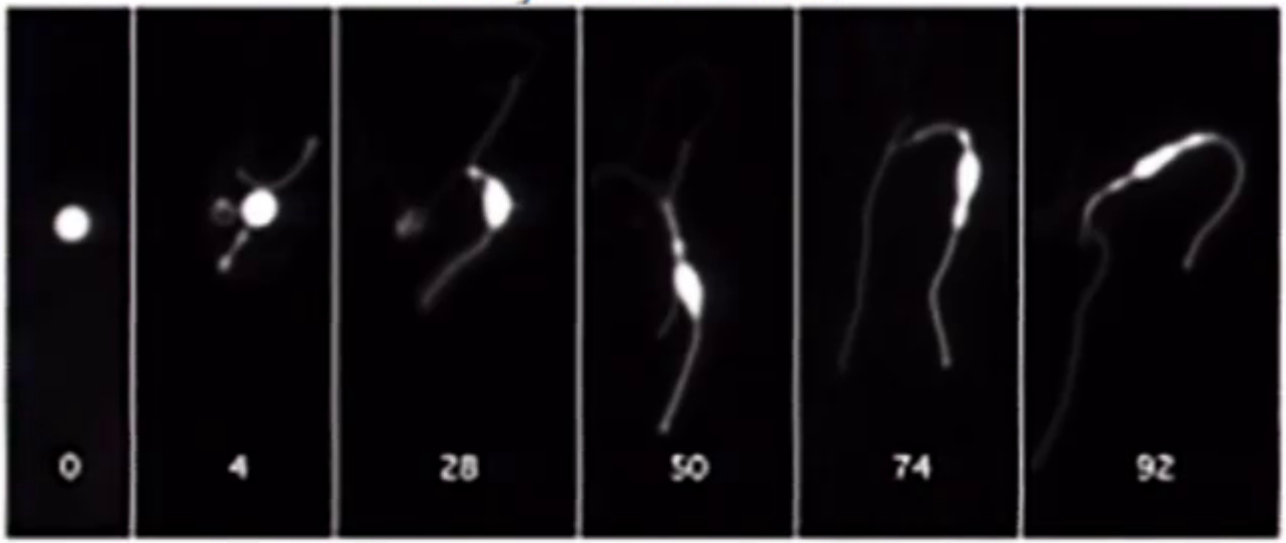


We consider the flow of interfaces under a generalized free energy.

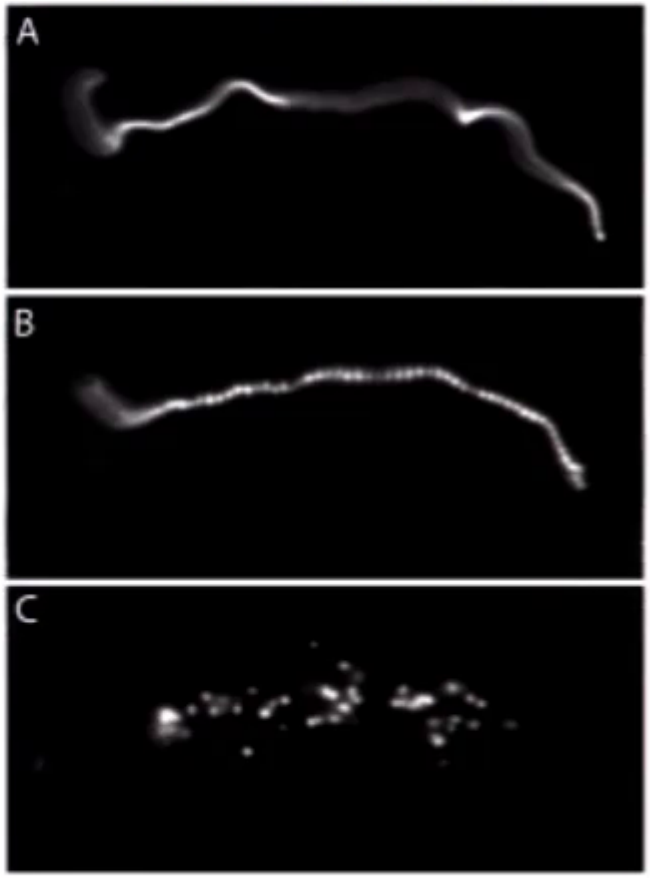
- The Functionalized Cahn-Hilliard free energy,
- The coexistence of bilayer & pore structures,
- Bifurcation of bilayer & pore morphologies.

Motivation - Szostak: Primitive cell division

Bilayers to Pores



Pores to Micelles



PNAS 2011&2012 : Increasing background lipid concentration derives the bilayer into fingering (top), oxidation via illumination induces surface charge which drives the pore into micelles (right).

The Cahn-Hilliard Energy

Cahn & Hilliard (1958) expended the free energy

$$\tilde{\mathcal{E}}(u) = \int_\Omega f(u, \varepsilon^2|\nabla u|^2, \varepsilon^2 \Delta u)\, dx$$

$$= \int_\Omega f(u,0,0) + \varepsilon^2 A(u)|\nabla u|^2 + \varepsilon^2 B(u)\Delta u\, dx$$

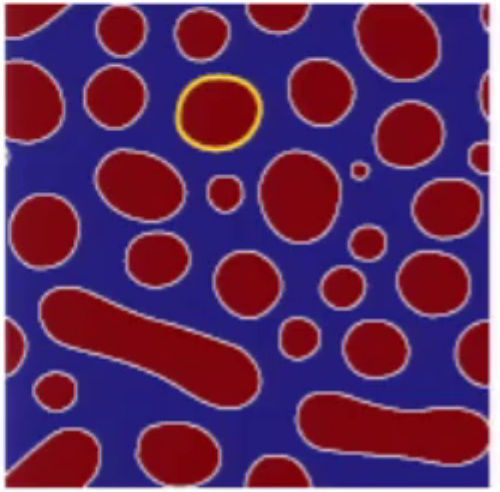
Integrating by parts the B term yields the classical

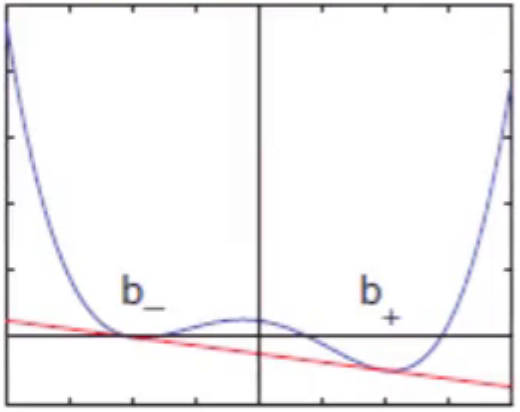
Cahn-Hilliard free energy

$$\mathcal{E}(u) = \int_\Omega \frac{\varepsilon}{2}|\nabla u|^2 + \frac{1}{\varepsilon} W(u)\, dx$$

where, considering a binary mixture,

- $\Omega \in \mathbb{R}^d$ bounded domain, $d \geq 2$,
- $u : \Omega \to \mathbb{R}$ is the volume fraction of one species,
- ε controls the width of the boundary layer,
- $W(u) : \mathbb{R} \to \mathbb{R}$ is a tilted double-well potential with minima at $u = b_\pm$ and $W''(b_\pm) > 0$.





From Cahn-Hilliard to Functionalized Cahn-Hilliard

For amphiphilic mixtures: Tuebner & Strey (1987), Gompper & Schick (1990) added higher order terms

$$\tilde{\mathcal{F}}(u) := \int_\Omega f(u,0,0) + \varepsilon^2 A(u)|\nabla u|^2 + \varepsilon^2 B(u)\Delta u + \overbrace{c(u)}^{\geq 0}(\varepsilon^2\Delta u)^2\, dx$$

For the primitive $\bar{A}$ of A, so that $\nabla \bar{A} = A\nabla u$, integrating by parts and completing the square yields

$$\tilde{\mathcal{F}}(u) := \int_\Omega C(u)\left(\varepsilon^2\Delta u - \frac{\bar{A}-B}{2C}\right)^2 + f(u,0,0) - \frac{(\bar{A}-B)^2}{4C}\, dx.$$

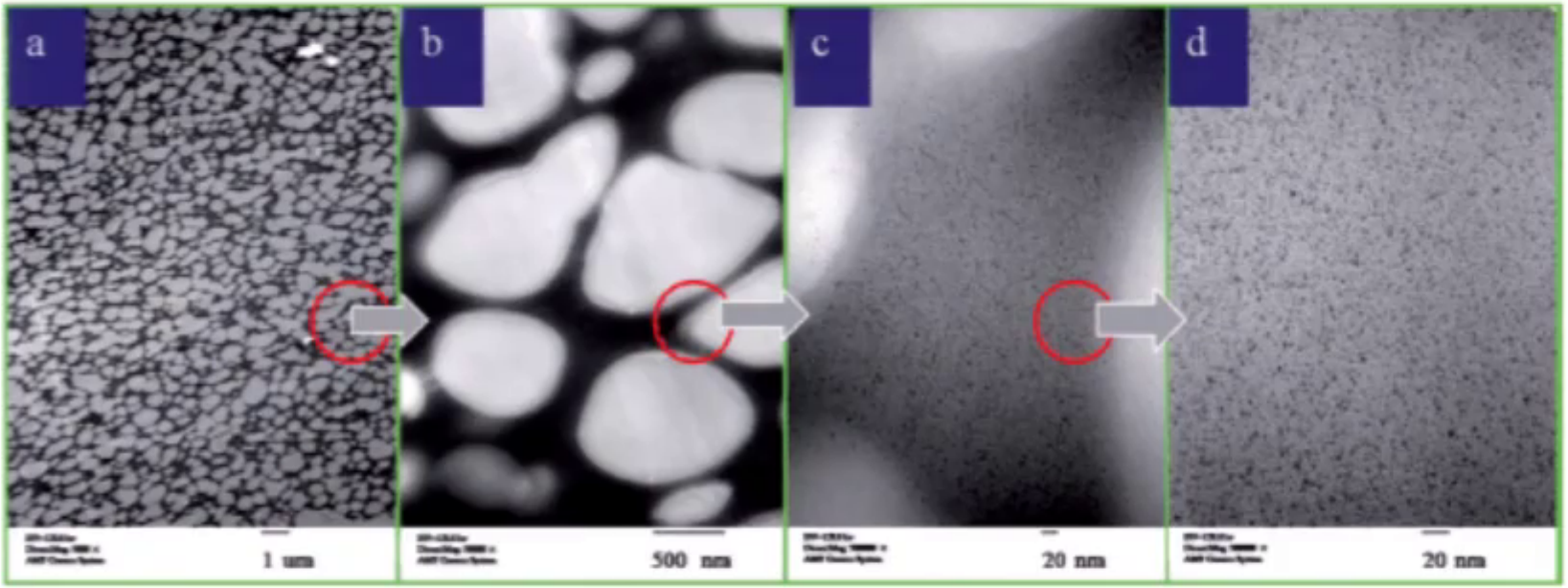
Fixing the constants we have

$$\tilde{\mathcal{F}}(u) := \int_\Omega \frac{1}{2}\left(\varepsilon^2\Delta u - W'(u)\right)^2 + \tilde{P}(u)\, dx.$$

The Functionalized Cahn-Hilliard free energy

$$\mathcal{F} = \int_\Omega \frac{1}{2}(\varepsilon^2\Delta u - W'(u))^2 - \varepsilon(\eta_1\frac{\varepsilon^2}{2}|\nabla u|^2 + \eta_2 W(u))\, dx$$

Functionalized Cahn-Hilliard Vs. Cahn-Hilliard



Cahn-Hilliard to Functionalized Cahn-Hilliard: Zooming $\times 500$.

A porous membrane assembled from cholormethylated polysufone (CPSF) with pyridine graphed via nucleophilic substitution (ammonium agent). *Energy Environ. Sci.* **6** 776 (2013).

The Cahn-Hilliard Euler-Lagrange Equation

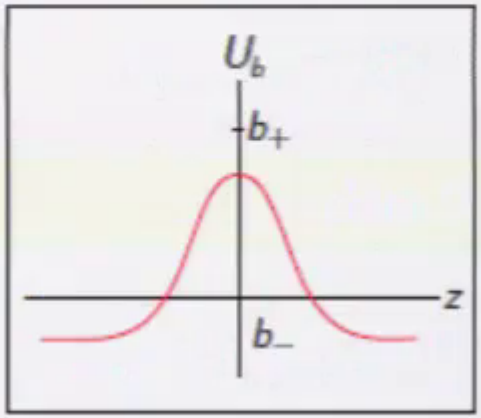
Fix an admissible interface Γ_*, solve the Euler-Lagrange equation

$$-\varepsilon^2 \Delta_x U + W'(U) = 0 \text{ in } \Gamma_{*,\ell}.$$

Co-dim 1, *=b

Bilayer profile, $U_b(z)$, solves

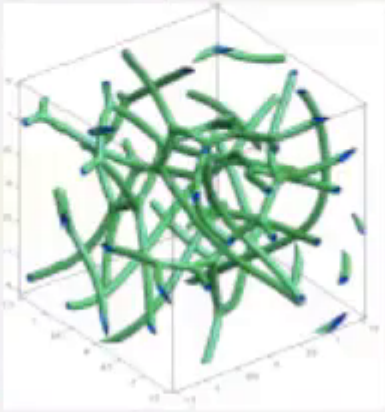
$$\begin{cases} \partial_z^2 U_b = W'(U_b) \\ U_b(-\infty) = b_-, \ U_b(\infty) = b_- \end{cases}$$



Co-dim 2, *=p

Pore profile, $U_p(z)$, solves

$$\begin{cases} \partial_R^2 U_p + \frac{1}{R} \partial_R U_p = W'(U_p), \\ \partial_R U_p(0) = 0, \ U_p(\infty) = b_-. \end{cases}$$



Formal Multi-Scale Analysis of Curvature Driven Flow

Geometric evolution of bilayer and pore structures under the strong FCH equation.

To generate a mass-preserving gradient flow, consider

$$u_t = \Delta\mu,$$

where μ is defined to be the chemical potential,

$$\mu := \frac{\delta \mathcal{F}}{\delta u} = \left(\varepsilon^2\Delta - W''(u) + \varepsilon\eta_1\right)\left(\varepsilon^2\Delta u - W'(u)\right) + \varepsilon(\eta_1 - \eta_2)W'(u).$$

Assumption : The interface is pearling stable.

Bilayers Evolution vs. Pores Evolution

Bilayers

The formal expansion

$$u_b(x,t) = U_b + \varepsilon \frac{\mu_1(t_1)}{W''(b_-)^2}.$$

The normal velocity is coupled to the chemical potential

$$V = (\mu_1 - B)\, H_0,$$

$$\frac{d\mu_1}{dt_1} = -(\mu_1 - B) \int_{\Gamma_b} H_0^2 \, dS$$

Interface area evolution

$$\frac{d|\Gamma_b|}{dt_1} = \int_{\Gamma_b} V(s) H_0(s) \, dS$$

Pores

The formal expansion

$$u_p(x,t) = U_p(x) + \varepsilon \frac{\mu_1(t_1)}{W''(b_-)^2}.$$

The normal velocity is coupled to the chemical potential

$$\vec{V} = (\mu_1 - P)\vec{\kappa}$$

$$\frac{d\mu_1}{dt_1} = -\varepsilon (\mu_1 - P) \int_{\Gamma_p} |\kappa|^2 \, ds$$

Interface area evolution

$$\frac{d|\Gamma_p|}{dt_1} = \int_{\Gamma_p} \vec{V}(s) \cdot \vec{\kappa}(s) \, ds$$

Competitive geometric evolution of bilayers and pores

Bilayers and Pores

- Γ_b is an admissible co-dim 1 interface, $|\Gamma_b| \sim O(1)$,
- Γ_p is an admissible co-dim 2 interface, $|\Gamma_p| \sim O(\varepsilon^{-1})$.

Introduce the composite solution

$$u_{b,p}(x,t) = U_p + U_b - b_- - \varepsilon \frac{\mu_1}{W'''(b_-)^2} + O(\varepsilon^2)$$

- The two morphologies compete with each other for surfactant phase through the common, temporally varying, value $\mu_1(t_1)$.

Assumption : The interfaces are pearling stable.

Competitive geometric evolution of bilayers and pores

Bilayers interface area evolution

$$\frac{d|\Gamma_b|}{dt_1} = (\mu_1 - B)\int_{\Gamma_b} H_0^2\, ds$$

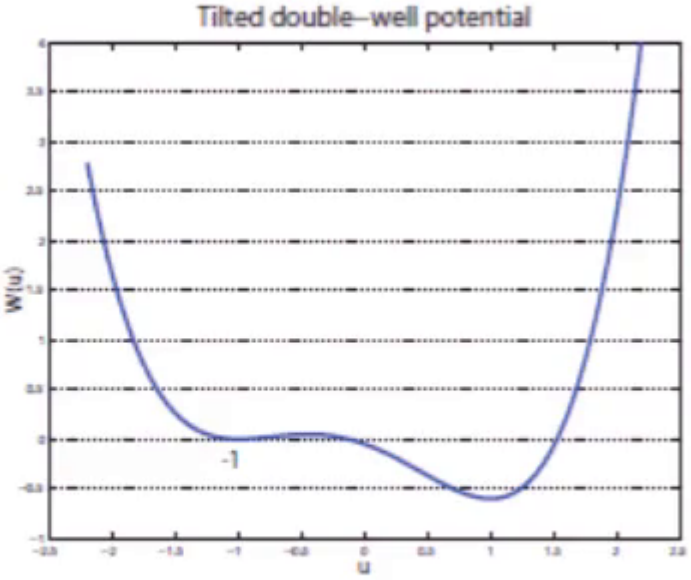
Pores interface area evolution

$$\frac{d|\Gamma_p|}{dt_1} = (\mu_1 - P)\int_{\Gamma_p} |\vec{\kappa}|^2\, ds$$

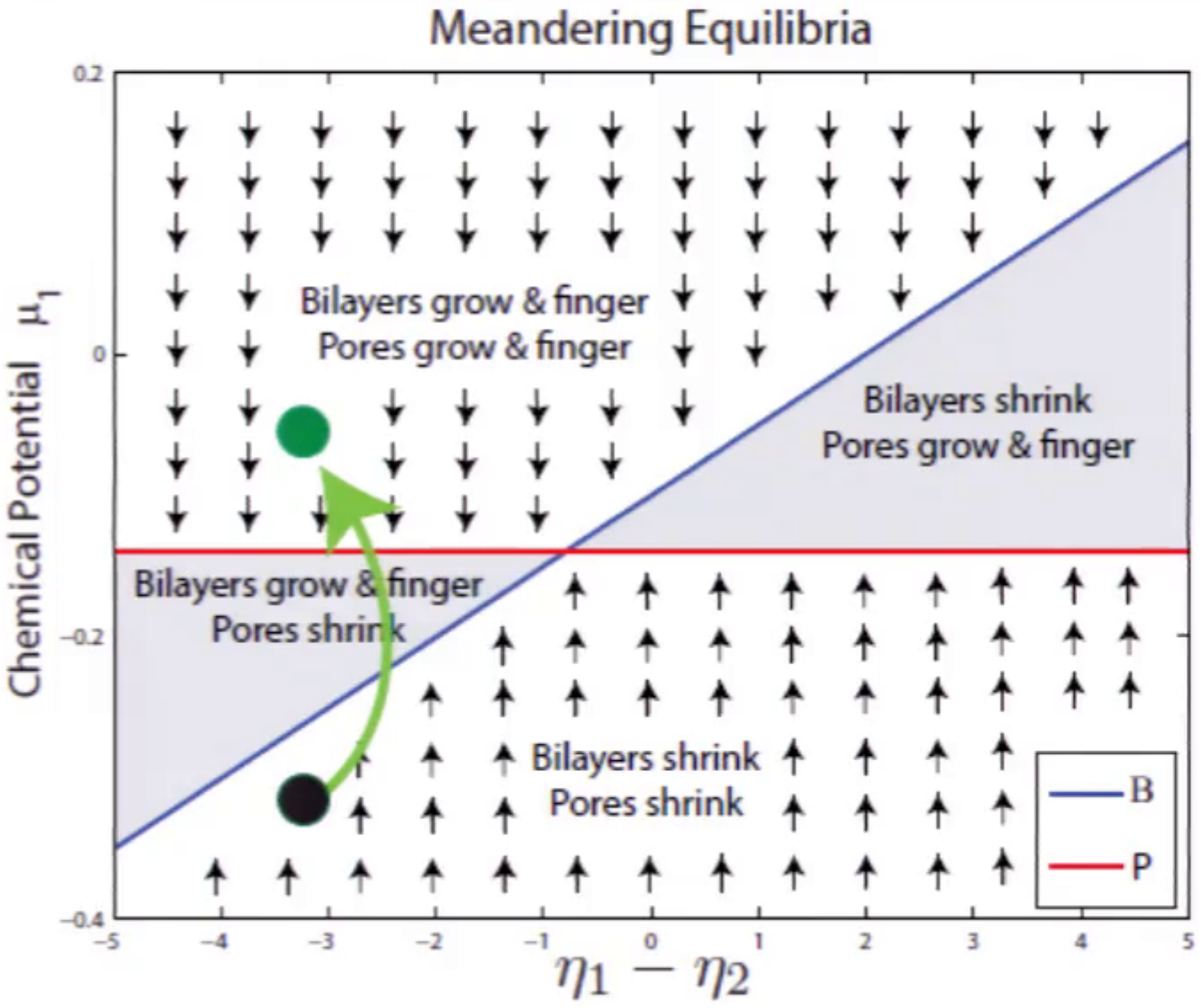
- The value of μ_1 is determined by the mass constraint for the combined bilayer-pore structures

$$M = \frac{\mu_1}{W''(b_-)^2}|\Omega| + m_b|\Gamma_b| + \varepsilon m_p|\Gamma_p$$

- The critical values depend only upon the functionalization parameters, η_1, η_2 and the potential well W.

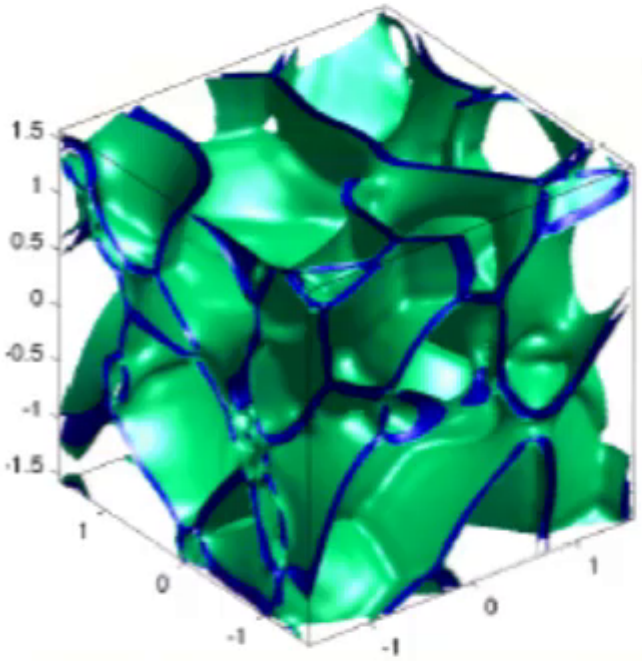


Fingering Instability

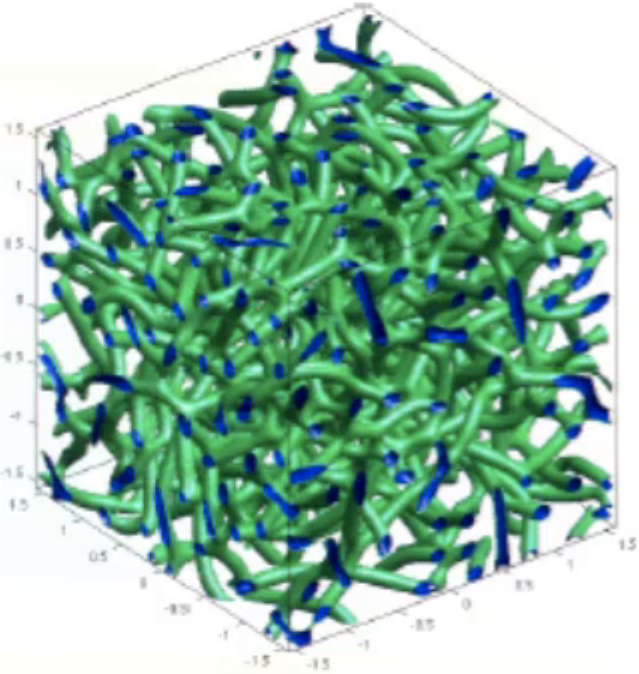


Generic Interfaces : Reduction to Finite (Big) Problem

Decomposing $\mathbb{L}$ into a 2×2 block form

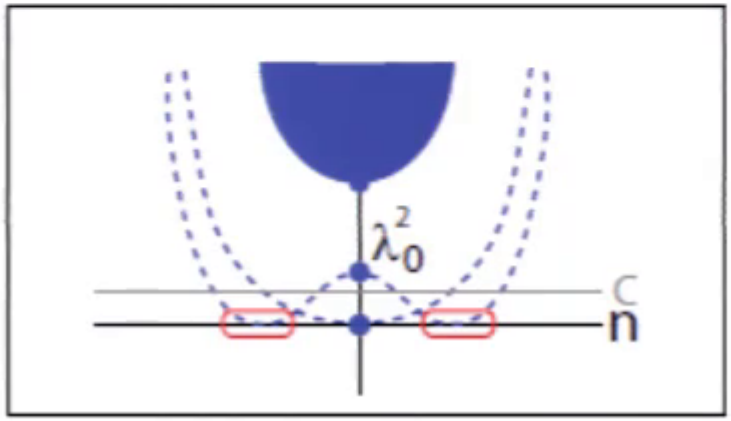


$$\mathbb{L} = \begin{bmatrix} \Pi\mathbb{L}\Pi & \tilde{\Pi}\mathbb{L}\Pi \\ \Pi\mathbb{L}\tilde{\Pi} & \tilde{\Pi}\mathbb{L}\tilde{\Pi} \end{bmatrix}$$



- The spectrum of the operator $\tilde{\Pi}\mathbb{L}\tilde{\Pi}$ is bounded below by $\delta > 0$ independent of ε (Promislow & Hayrapetyan, 2014)
- The off-diagonal operators are $O(\varepsilon)$, in norm.
- The spectrum of $\mathbb{L}$ is controlled by the spectrum of $\Pi\mathbb{L}\Pi$.

Generic Interfaces : The Eigenvalue Problem



- $N := dimR(\Pi) = O(\varepsilon^{3/2-d})$.
- Eigenvalues are coupled through the non-constant curvatures, $\nabla_s \kappa$.

Constant curvature part

$$\Pi \mathbb{L} \Pi = \overbrace{\begin{bmatrix} * & 0 & \cdots & 0 \\ 0 & * & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & \cdots & 0 & * \end{bmatrix}} + \varepsilon A(\kappa)$$

- $A \in \mathbb{R}^{(N \times N)}$ is uniformly bounded as an operator on $l^2(\mathbb{R}^N)$, if $||\kappa||_{W^{2,\infty}(\Gamma)}$ is bounded.

Generic Interfaces : The Eigenvalue Problem

The Functionalized Cahn-Hilliard

$$\mathcal{F} = \int_\Omega \frac{1}{2}(\varepsilon^2 \Delta u - W'(u))^2 - \delta(\eta_1 \frac{\varepsilon^2}{2}|\nabla u|^2 + \eta_2 W(u))\, dx$$

Bilayers Pearling stability

$$\mu_1 > P_b^* := C_b(\eta_1 - \eta_2),$$

Pores Pearling stability

$$\mu_1 > P_p^* := C_p(\eta_1 - \eta_2),$$

where C_b, C_p are constants, depend upon the well $W(u)$.

- At leading order, the pearling conditions are independent of the interface.
- As observed by Szostak, an increase in charge density impacts pearling.

Pearling Vs. Meandering

The geometric evaluation of the combined bilayer-pore system

$$\mathbf{V}_p = \nu_p(\mu_1 - P)\vec{\kappa},$$
$$V_b = \nu_b(\mu_1 - B)H_0,$$
$$\frac{d\mu_1}{d\tau} = -(\mu_1 - B)\int_{\Gamma_b} H_0^2\, ds - \varepsilon m_p(\mu_1 - P)\int_{\Gamma_p} |\vec{\kappa}|^2\, ds.$$

The bilayers and pores pearling stability condition
$\mu_1 > \mu_b^*, \mu_1 > \mu_p^*$.

- The chemical potential, μ_1, is dynamic on the $\tau = O(\varepsilon^{-1})$ time scale.
- The time-scale of the of the pearling instability is $\tau = O(\varepsilon)$.

The pearling instability manifests itself on a time scale that is instantaneous with respect to the underlying geometric evolution.