Existence of pearled patterns in the planar functionalized Cahn-Hilliard equation

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Outline

1. Introduction: pearled patterns and FCH model
2. Main result: existence of pearled bilayers in FCH
3. Proof: spatial dynamics & degenerate 1:1 resonance
4. Outlook: multicomponent FCH systems

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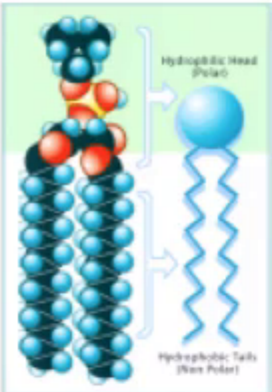
Amphiphilic morphology

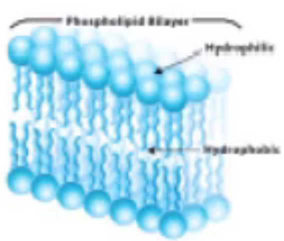
Amphiphiles

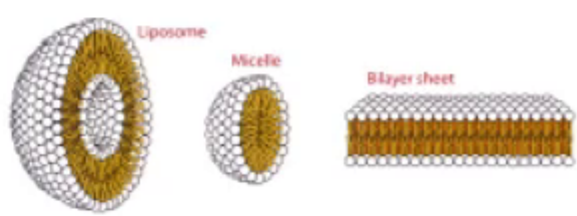


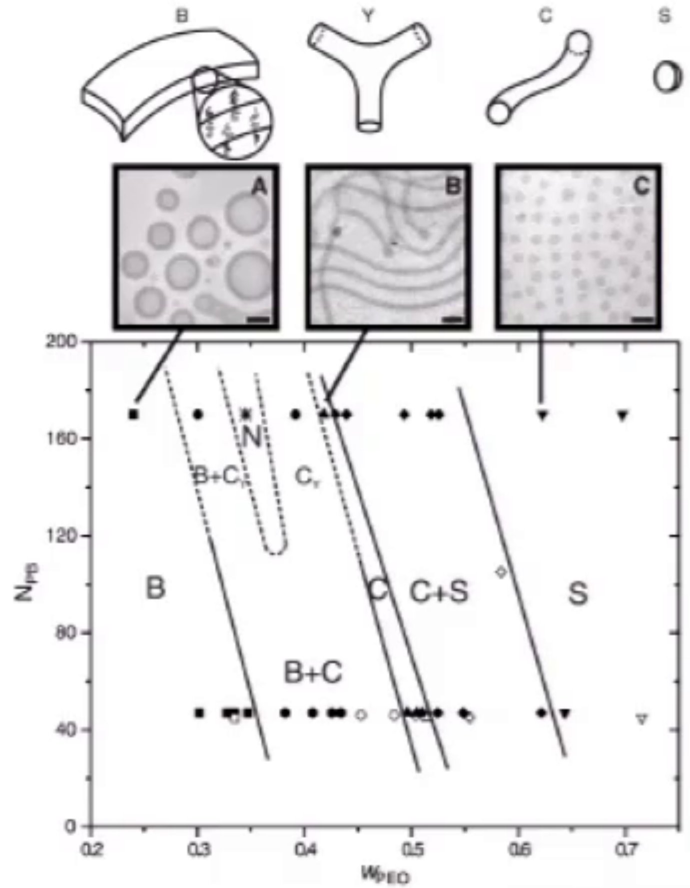
- Molecules having both hydrophobic and hydrophilic components.
- Abundant in biological structures; Wide applications.

Morphology

Rich self-assembly structures: bilayers (co-dim 1), pores (co-dim 2), micelles (co-dim 3), pearled structures, Y-junctions, etc.







Morphological diagram for PB-PEO in water[Bates *et al*, '03]

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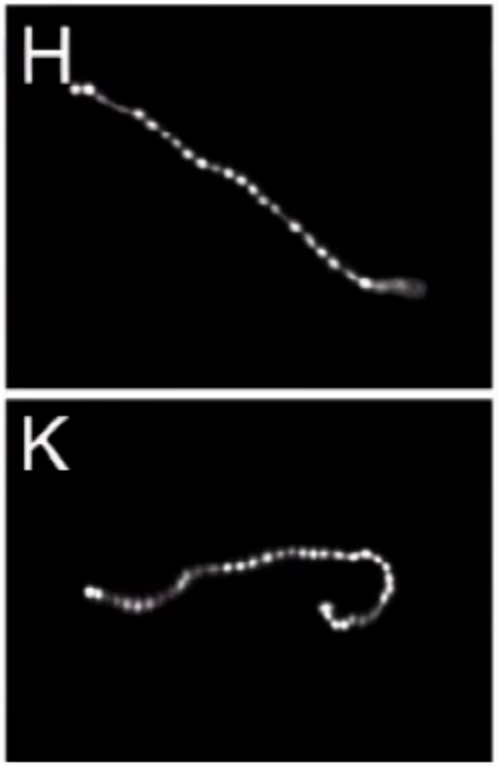
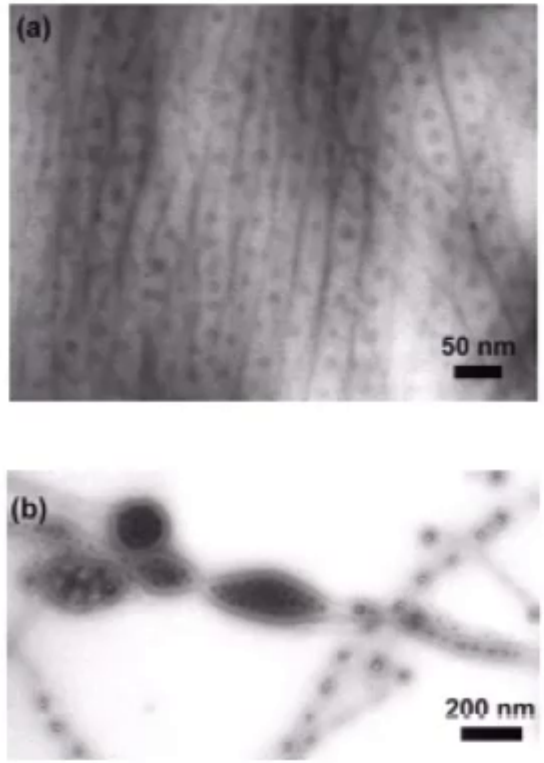
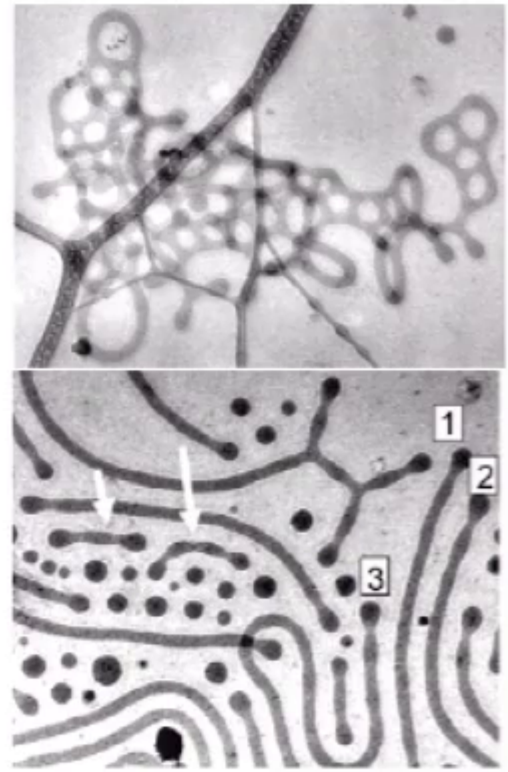
Pearling: Transition from low codim to high codim



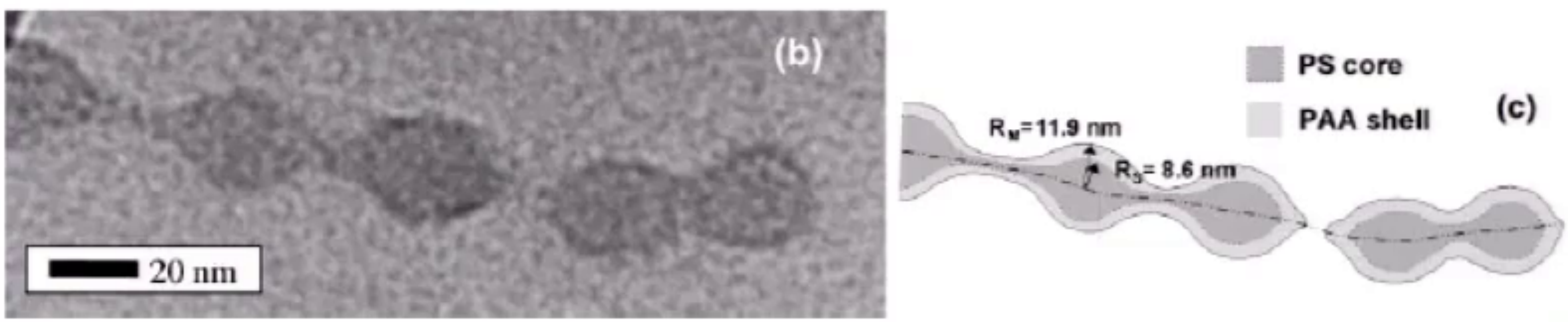
Primitive membranes[Szostak *et al*, '11]



Diblock copolymer[Hayward *et al*, '08]



Diblock copolymer[Bates *et al*, '04]



Copolymers[Bendejacq *et al*, '05]

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FCH: Cahn-Hilliard expansion

For amphiphilic mixtures: added higher derivatives to the classical Cahn-Hilliard energy [Teubner, Strey, '87; Gompper, Schick, '90]

$$\mathcal{F}(u) := \int_\Omega \overbrace{f(u) + \varepsilon^2 A(u)|\nabla u|^2 + \varepsilon^2 B(u)\Delta u}^{\text{Cahn-Hilliard}} + \overbrace{C(u)}^{\geqslant 0} (\varepsilon^2 \Delta u)^2 \, dx.$$

For the primitive $\overline{A}$ of A, replace $A(u)\nabla u$ with $\nabla \overline{A}(u)$ and integrate by parts

$$\mathcal{F}(u) := \int_\Omega f(u) + (B(u) - \overline{A}(u))\varepsilon^2 \Delta u + C(u)(\varepsilon^2 \Delta u)^2 \, dx,$$

Complete the square

$$\mathcal{F}(u) := \int_\Omega \overbrace{C(u)}^{\frac{1}{2}} \Big(\varepsilon^2 \Delta u - \overbrace{\boxed{\frac{\overline{A} - B}{2C}}}^{W'(u)} \Big)^2 + \overbrace{\boxed{f(u) - \frac{(\overline{A} - B)^2}{C(u)}}}^{\varepsilon^p P(u)} \, dx.$$

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FCH: stabilization of equilibria of Cahn-Hilliard energy

Consider the functionalized Cahn-Hilliard energy in a domain $\Omega \in \mathbb{R}^2$

$$\mathcal{F}_{CH} = \int_\Omega \frac{1}{2}\boxed{\left(\varepsilon^2 \Delta u - W'(u)\right)^2} - \varepsilon^p\left(\frac{1}{2}\eta_1 \varepsilon^2 |\nabla u|^2 + \eta_2 W(u)\right)\mathrm{d}x,$$

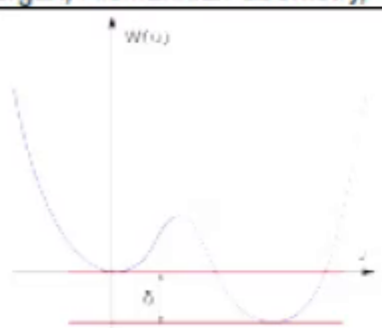
[Morgan, Riemannian Geometry, '98]

- The square term stabilizes all the equilibria of CH energy, including the saddle points.

Unstable equilibrium in CH

$\Downarrow$

Potential stable equilibrium in FCH



A tilted double well

- W–a tilted double-well potential.

Equal depth($\delta = 0$): Single layers (heteroclinics)

$\Downarrow$

Tilted($\delta > 0$): Bilayers (homoclinics)

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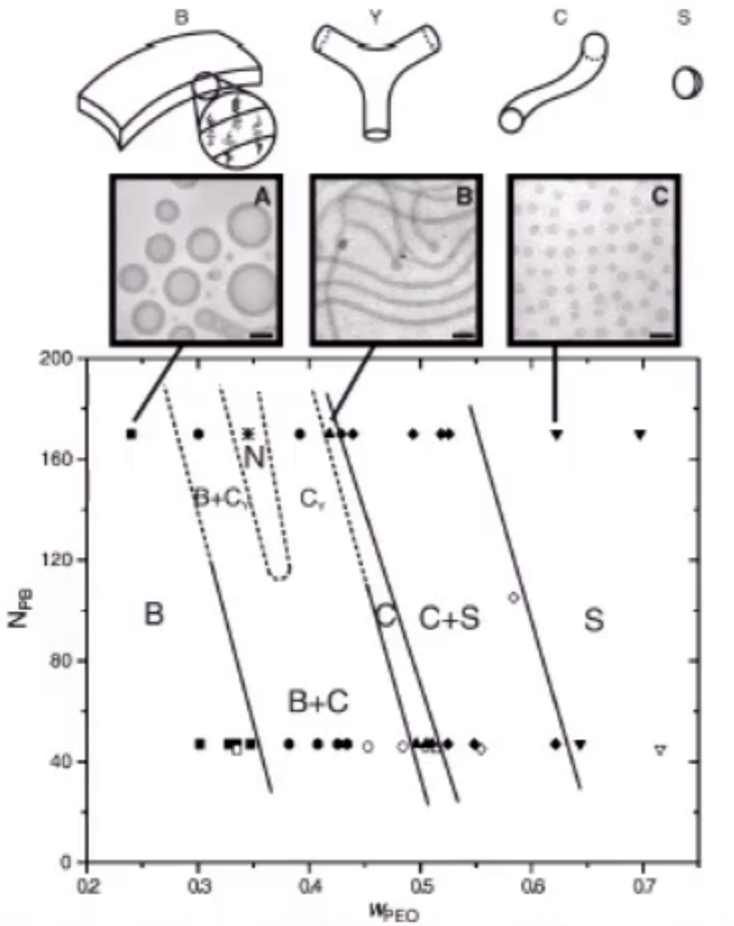
FCH: slection of equilibria of Cahn-Hilliard energy

Consider the functionalized Cahn-Hilliard energy in a domain $\Omega \in \mathbb{R}^2$

$$\mathcal{F}_{CH} = \int_\Omega \frac{1}{2}(\varepsilon^2 \Delta u - W'(u))^2 - \varepsilon^p \boxed{(\frac{1}{2}\eta_1 \varepsilon^2 |\nabla u|^2 + \eta_2 W(u))} \mathrm{d}x, \quad (1)$$



Morphological diagram for PB-PEO in water[Bates *et al*, '03]

The small functionalized term selects stable equilibria out of the admissible set of "CH equilibria" who maximize the εP term.

- The interface term $\frac{1}{2}\eta_1 \varepsilon^2 |\nabla u|^2$:

  $\eta_1 \leftrightarrow$ Amphiphilicity $\leftrightarrow W_{PEO}$

- The volume term $\eta_2 W(u)$:

  $-\eta_2 \leftrightarrow$ Length of tail $\leftrightarrow N_{PB}$

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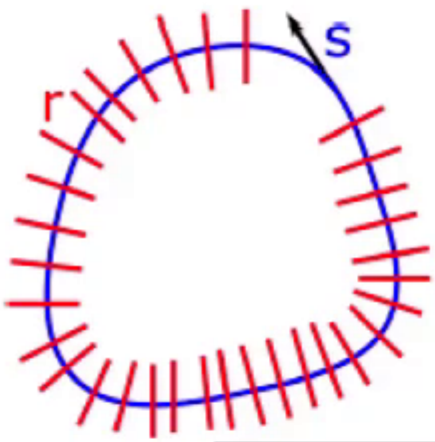
FCH: distinguished limits of the functionalized terms

Consider the functionalized Cahn-Hilliard energy in a domain $\Omega \in \mathbb{R}^2$

$$\mathcal{F}_{CH} = \int_\Omega \overbrace{\frac{1}{2}\left(\varepsilon^2 \Delta u - W'(u)\right)^2}^{\text{Willmore:}\mathcal{O}(\varepsilon^2)} - \overbrace{\boxed{\varepsilon^p}\left(\frac{1}{2}\eta_1 \varepsilon^2 |\nabla u|^2 + \eta_2 W(u)\right)}^{\text{functionalization:}\mathcal{O}(\varepsilon^p)} \mathrm{d}x,$$

$p = 1$: strong functionalization; $p = 2$: weak functionalization.



Local whisker coordinates at interface Γ:

- r–ε-scaled signed distance
- s–the tangential variable
- $H_0(s)$–mean curvature of the interface Γ at s

$$\varepsilon^2 \Delta = \partial_r^2 + \varepsilon H_0(s)\partial_r + \varepsilon^2 \Delta_s + \mathcal{O}(\varepsilon^2).$$

$$\varepsilon^2 \Delta u - W'(u) = \overbrace{\partial_r^2 u - W'(u)}^{\text{homoclinic: 0}} + \overbrace{\varepsilon H_0(s)\partial_r u}^{\text{Willmore term}} + \mathcal{O}(\varepsilon^2).$$

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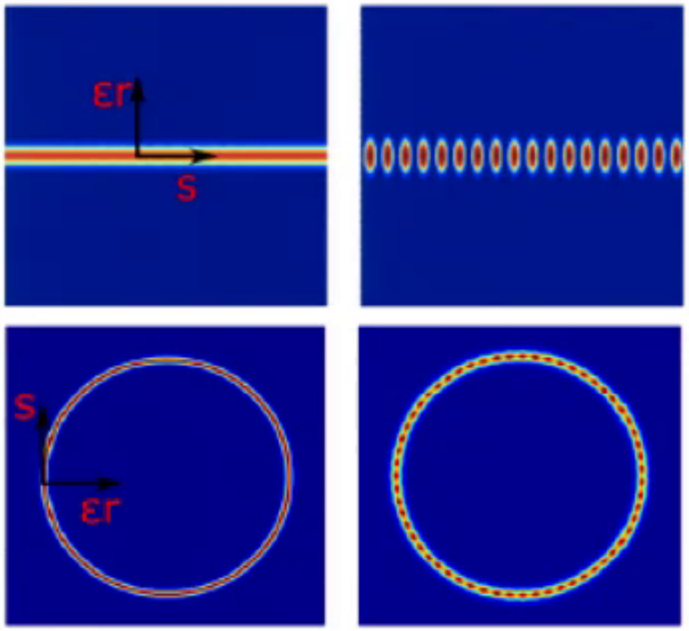
Pearling: bifurcation of bilayers along interfaces

We look for pearled solutions to the stationary strong ($p = 1$) FCH

$$\frac{\delta \mathcal{F}_{CH}}{\delta u} = (\Delta - W''(u) + \varepsilon\eta_1)(\Delta u - W'(u)) + \varepsilon\eta_d W'(u) = \varepsilon\gamma. \qquad (2)$$



- Variation: Minimizers of FCH with mass conservation.
- $\varepsilon\gamma$–the Lagrange multiplier of the mass conservation.
- γ–the background state in the sense that

$$\lim_{r\to\pm\infty} u_b(r;\varepsilon) = \frac{\gamma}{W''(0)}\varepsilon + \mathcal{O}(\varepsilon^2).$$

- Bilayers $u_b(r;\varepsilon)$–symmetric pulses in r. [Doelman, Hayrapetyan, Promislow, Wetton, '14]
- Pearled patterns $u_p(r, s; \varepsilon)$–small periodic modulations of bilayer width in s. [W., Promislow, '14]

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FCH: spectral analysis

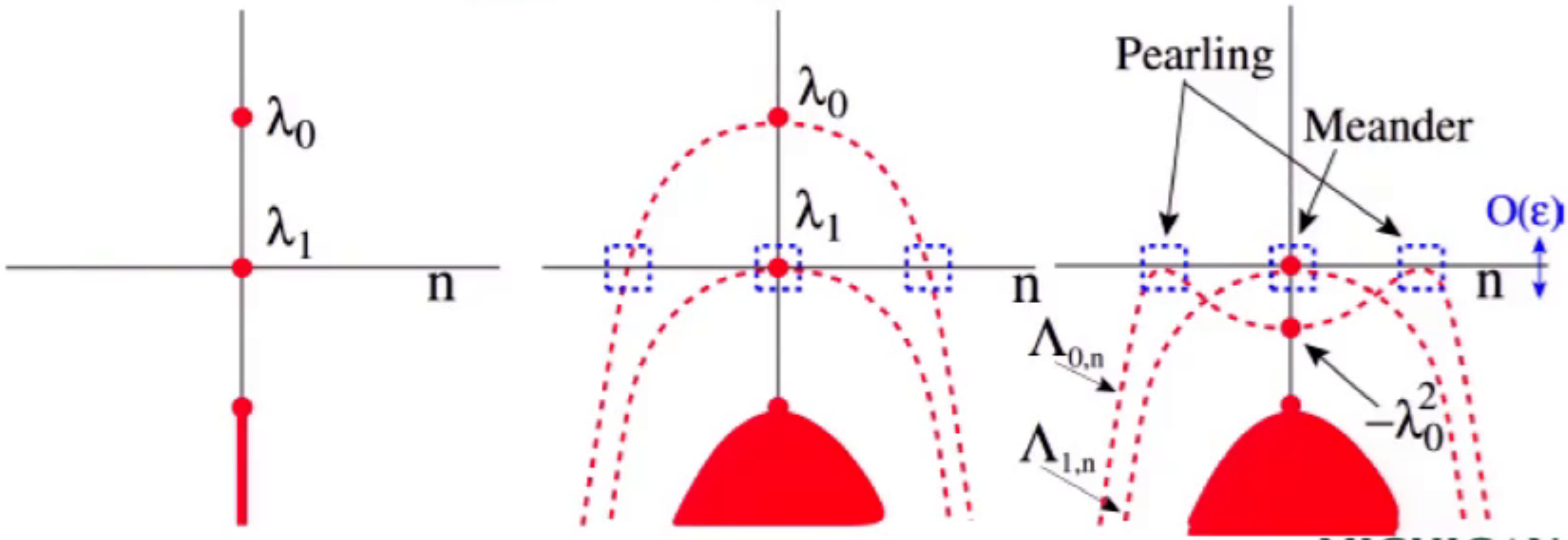
In the local coordinates, the stationary strong FCH becomes

$$(\partial_r^2 - W''(u) + \varepsilon^2\partial_s^2 + \varepsilon\eta_1)\left(\boxed{\partial_r^2 u - W'(u)} + \varepsilon^2\partial_s^2 u\right) + \varepsilon\eta_d W'(u) = \varepsilon\gamma, \tag{3}$$

- u_0 the homoclinic orbit to $u_{rr} - W'(u) = 0$.
- $\mathcal{L}_0 := \partial_r^2 - W''(u_0)$ admits a positive eigenvalue λ_0. (S-L)

Linearizing (3) at the bilayer $u_b = u_0(r) + \mathcal{O}(\varepsilon)$:

$$\mathbb{L} := \frac{\delta^2\mathcal{F}}{\delta u^2}(u_b) = \boxed{(\mathcal{L}_0 + \varepsilon^2\partial_s^2)^2} + \mathcal{O}(\varepsilon).$$



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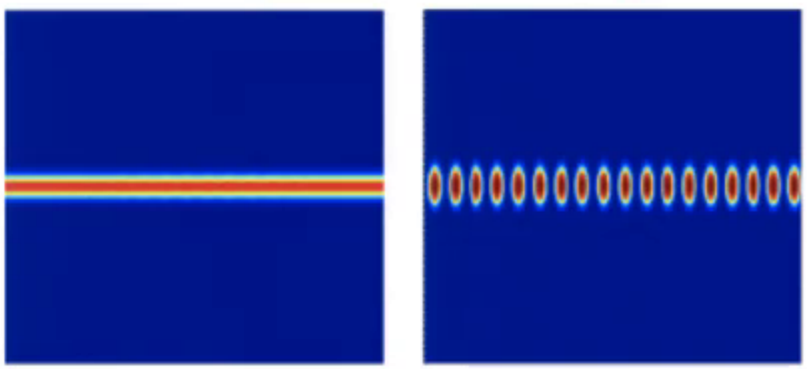
Main result I–existence of flat pearled solutions

Theorem (W., Promislow, '14; Two free parameters)

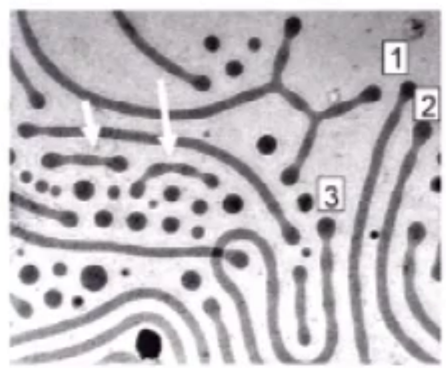
Given η_1, η_d, for sufficiently small $\varepsilon > 0$, the stationary strong FCH admits a family of bilayer solutions u_b, parameterized by the background state γ. For any $\gamma \in \mathbb{R}$ so that

$$\alpha_0 := c_1\gamma + c_2(\eta_1 - \eta_2) > 0,$$

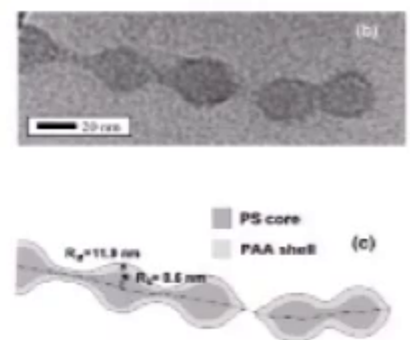
up to translation, the stationary FCH admits a family of flat pearled solutions u_p with period T_p, parameterized by the amplitude $|\kappa|$.



Flat bilayer and pearled flat bilayer



Diblock copolymer[Bates *et al*, '04]



Copolymers[Bendejacq *et al*, '05]

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The family of flat pearled solutions admits the following expansions:

$$\begin{aligned} u_{\mathrm{p}} &= u_{\mathrm{b}}(r;\gamma) + \boxed{2\frac{\sqrt{\varepsilon|\kappa|}}{\sqrt[4]{\alpha_0}}} \cos\left(\frac{2\pi}{T_{\mathrm{p}}}s\right)\psi_0(r) + h.o.t., \\ T_{\mathrm{p}} &= \frac{2\pi\varepsilon}{\sqrt{\lambda_0}}(1-\sqrt{\alpha_0\varepsilon}) + \mathcal{O}\left(\varepsilon^2 + \boxed{\varepsilon^2\sqrt{|\kappa|}}\right), \\ u_\infty &= \lim_{r\to\infty} u_{\mathrm{b}}(r;\gamma). \end{aligned} \tag{4}$$

where the error is in the $L^\infty(\mathbb{R}^2)$-norm and $\mathcal{L}_0\psi_0 = \lambda_0\psi_0$.

- Tuning of the period T_p: Fixed in $\mathcal{O}(\varepsilon)$; γ in $\mathcal{O}(\varepsilon^{3/2})$; $|\kappa|$ in $\mathcal{O}(\varepsilon^2)$.
- Supercritical characteristics:

$$\sqrt{\varepsilon_0}\kappa_0 < C\alpha_0 \Rightarrow \lim_{\alpha_0\to 0}\frac{\sqrt{\varepsilon|\kappa|}}{\sqrt[4]{\alpha_0}} = 0.$$

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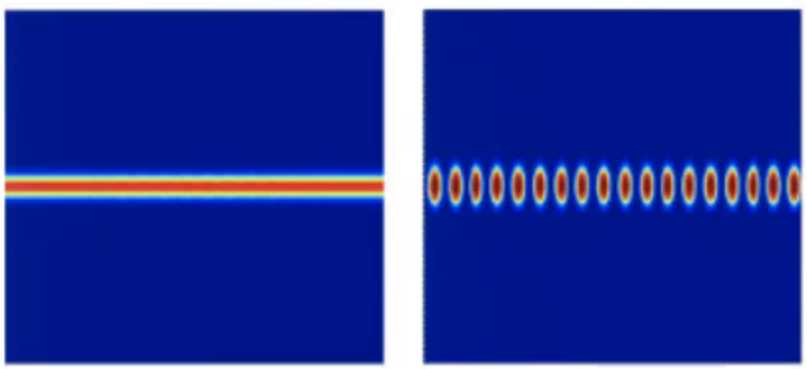

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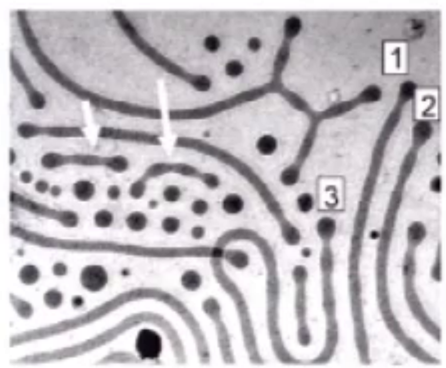

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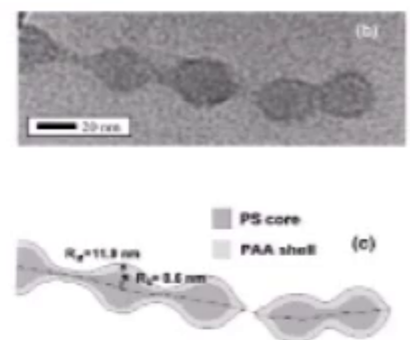

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Main result II–existence of circular pearled solutions

Theorem (Q., Promislow, '14)

Given $\eta_1, \eta_d \in \mathbb{R}$, $R_0 \in \mathbb{R}^+$, *for sufficiently small* $\varepsilon > 0$, *there exists a unique* $\gamma(\varepsilon) \in \mathbb{R}$ *such that the stationary strong FCH admits a bilayer solution. Meanwhile, if*

$$\boxed{\alpha_0 := c_1\gamma + c_2(\eta_1 - \eta_2) > 0,}$$

the stationary strong FCH, up to translation, admits a discrete family of circular pearled solutions u_{p} *parameterized by the amplitude* $\{\kappa_j\}_{j\in I}$ *with the period*

$$T_{\mathrm{p}} = \frac{2\pi\varepsilon}{R_0\sqrt{\lambda_0}}(1 - \sqrt{\alpha_0\varepsilon}) + \mathcal{O}\left(\varepsilon^2 + \varepsilon^2\sqrt{\kappa}\right) \in \{\frac{2\pi}{n} \mid n \in \mathbb{Z}^+\}. \qquad (5)$$

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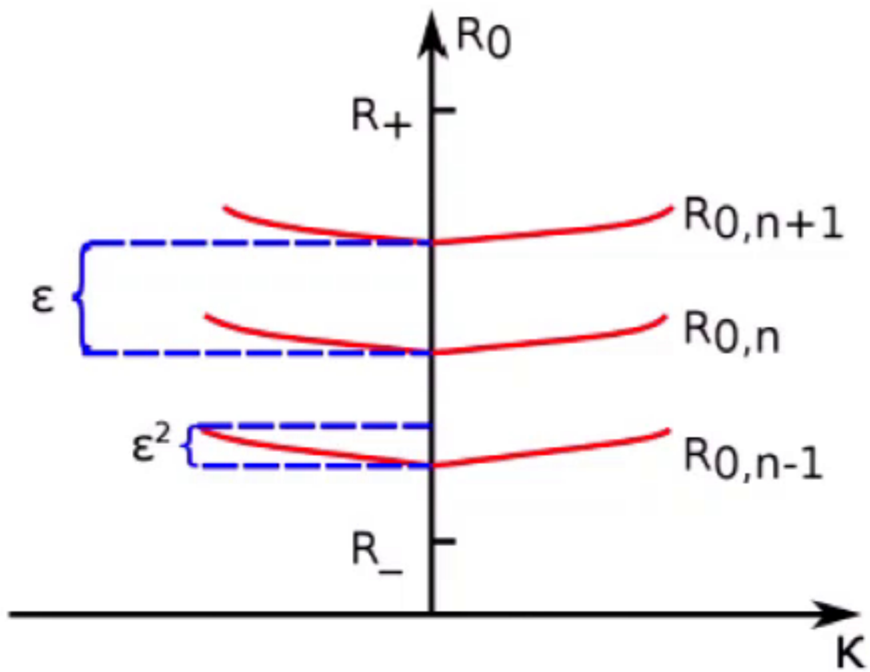
Main result II–existence of circular pearled solutions

Every admissible radius,

$$R_{0,\mathrm{n}}(\kappa) = \frac{\mathrm{n}\varepsilon}{\sqrt{\lambda_0}}(1 - \sqrt{\alpha_0\varepsilon}) + \mathcal{O}(\varepsilon^2 + \varepsilon^2\sqrt{|\kappa|}),$$

depends only weakly upon the internal parameter κ, with variation of the order $\mathcal{O}(\varepsilon^2)$ while the gap between consecutive radii is of order $\mathcal{O}(\varepsilon)$.



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Idea of the proof

The proof can be summarized into the following steps:

- Rewrite the PDE (3),

$$\left(\partial_r^2 - W''(u) + \varepsilon^2\partial_s^2 + \varepsilon\eta_1\right)\left(\partial_r^2 u - W'(u) + \varepsilon^2\partial_s^2 u\right) + \eta_d W'(u) = \varepsilon\gamma,$$

  as an infinite-dimension dynamical system via spatial dynamics,
- Reduce the PDE (3) to an ODE system via center manifold reduction,
- Obtain the normal form of the reduced ODE system,
- Find transformed pearling solutions in the degenerate 1:1 resonance normal form,
- Show persistence of pearling solutions in the full ODE via an implicit-function-theorem argument on a Poincaré map.

Spatial dynamics & center manifold reduction

Spatial dynamics: PDE (3) $\Rightarrow$ infinite-dim dynamical system (IDDS)

- View s as the "time" variable; rescaling $t = \frac{\sqrt{\lambda_0}}{\varepsilon} s$
- With $U := (u, u_t, \mathcal{L}_b u + \lambda_0 u_{tt}, (\mathcal{L}_b u + \lambda_0 u_{tt})_t)$, the rescaled PDE (3)$\Rightarrow$

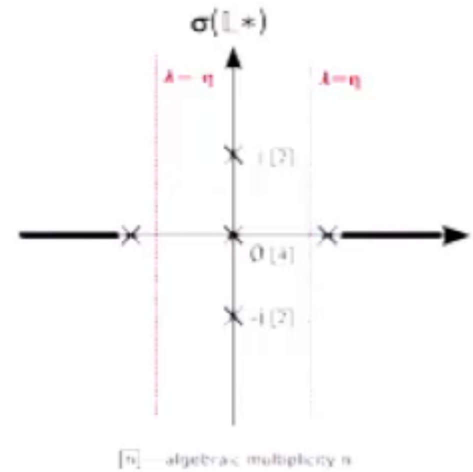
$$\dot{U} = \mathbb{L}(\varepsilon)U + \mathbb{F}(U, \varepsilon), \tag{6}$$

where $\mathbb{L}(\varepsilon)$ is the linearized operator the system at u_b.

Center Manifold Reduction: IDDS (6)$\Rightarrow$ Reduced ODE

- Spectral analysis on $\mathbb{L}_\star := \mathbb{L}(0) \sim (\mathcal{L}_0 + \lambda_0 \partial_{tt})^2$.
- IDDS (6) $\Rightarrow$ 8th-order reversible ODE

$$\frac{\mathrm{d}U_c}{\mathrm{d}t} = \mathbb{P}_c \mathbb{L}(\varepsilon)(U_c + \Psi(U_c, \varepsilon)) + \mathbb{P}_c \mathbb{F}(U_c + \Psi(U_c, \varepsilon)), \tag{7}$$



U_c–the center projection $\mathbb{P}_c$ of U,
Ψ–the center manifold map.

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Normal form: degenerate 1:1 resonance

Up to cubic terms, the 8th-order ODE (7) admits a 4-dim invariant space, yielding a degenerate1:1 resonance[Iooss, Pérouème, '93],

$$\begin{cases} \dot{C}_1 = & \mathrm{i}(1+\omega_1\varepsilon)C_1 + C_2 + \mathrm{i}C_1\left[\alpha_7 C_1\bar{C}_1 + \alpha_8\mathrm{i}(C_1\bar{C}_2 - \bar{C}_1 C_2)\right], \\ \dot{C}_2 = & \mathrm{i}(1+\omega_1\varepsilon)C_2 + \mathrm{i}C_2\left[\alpha_7 C_1\bar{C}_1 + \alpha_8\mathrm{i}(C_1\bar{C}_2 - \bar{C}_1 C_2)\right] + \\ & C_1\left[-\alpha_0\varepsilon + \cancel{\alpha_1 C_1\bar{C}_1} + \mathrm{i}\alpha_2(C_1\bar{C}_2 - \bar{C}_1 C_2)\right], \end{cases} \quad (8)$$

which, when $\alpha_0 > 0$, admits a family of periodic sols parameterized by $\kappa := \varepsilon^{-3/2}K$.

- Two symmetries $\Rightarrow$ two first integrals(Noether's theorem)

$$K = \frac{\mathrm{i}}{2}(C_1\overline{C_2} - \overline{C_1}C_2), \quad H = |C_2|^2 + (-\alpha_0\varepsilon + 2\alpha_2 K)|C_1|^2.$$

- For fixed K and H, ODE (8) $\Rightarrow$ a 2nd order ODE.

$$\left(\frac{\mathrm{d}u_1}{\mathrm{d}t}\right)^2 = 4f_{H,K}(u_1) := 4\left[(-\alpha_0\varepsilon + 2\alpha_2 K)u_1^2 + Hu_1 - K^2\right], \quad (9)$$

where $u_1 = |C_1|^2$.

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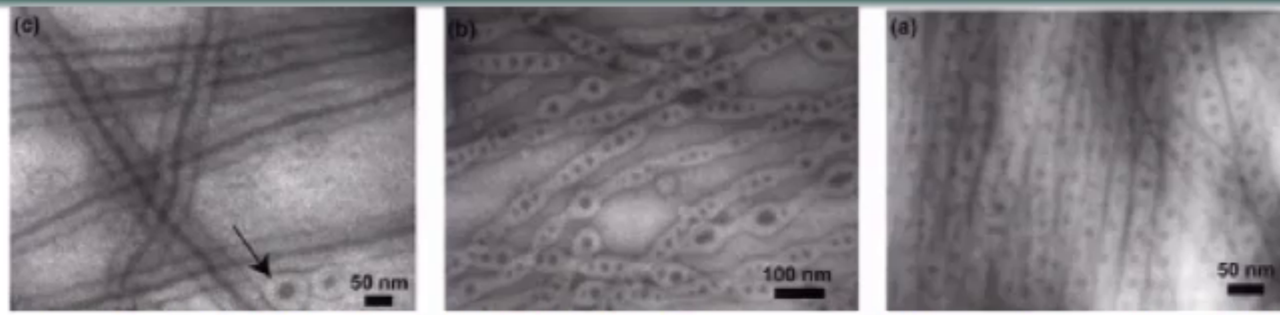
Outlook: bilayers in multicomponent FCH systems



From blends of PS9.5K-PEO5K with PS56K-P2VP21K into pearled P2VP cores[Tlusty, Safran, '00]

Motivation

- Cell membrane: favorable properties with $\sim$ 10 types of lipids.
- Block co-polymers: expensive and unnecessary purification.

Multicomponent FCH free energy

$$\mathcal{F}(\mathbf{u}) = \int_\Omega |\overbrace{\varepsilon^2 \boxed{\mathbf{D}} \Delta \mathbf{u} - \nabla_{\mathbf{u}} W(\mathbf{u}) + \boxed{\varepsilon \mathbf{P}(\mathbf{u})}}^{\text{Willmore term:}\mathcal{O}(\varepsilon)}|^2 - \boxed{\varepsilon^2}\left(\frac{1}{2}\eta_1 \varepsilon^2 |\nabla \mathbf{u}|^2 + \eta_2 W(\mathbf{u})\right) \mathrm{d}x \tag{10}$$

- $\mathbf{u} \in \mathbb{R}^2$: 2 species of amphiphiles; $\mathbf{D}$: the diffusive matrix.
- $\varepsilon \mathbf{P}$: the vector filed is not conservative but ε-close.
- ε^2: the Willmore term from the Laplacian is balanced by the functionalized term.

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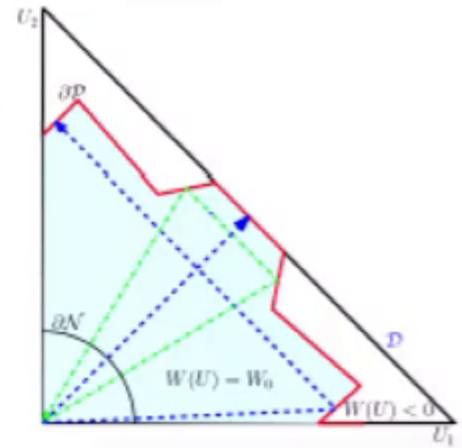
Melnikov parameter: persistence of homoclinics



Existence of a limiting homoclinic ϕ_∞:
the leading order ODE $\mathbf{Du}_{rr} - \nabla_{\mathbf{u}} W(u) = 0$ admits a continuous homoclinic orbit to origin, provided

- $\mathbf{D} = \mathbf{I}$; W is a billiard limit potential.
- $W(0) = 0$ and 0 a strict local miminum.
- A well-chosen billiard boundary.

Existence of a smooth homoclinic ϕ_h:
There is a family of smooth potential close to the billiard potential, each of which admits a smooth homoclinic ϕ_h close to ϕ_∞.

Persistence of the homoclinic ϕ_h:
the perturbed ODE

$$\mathbf{u}_{rr} + \boxed{\varepsilon b(\varepsilon)\mathbf{u}_r} - \nabla_{\mathbf{u}} W(\mathbf{u}) + \varepsilon \mathbf{P}(\mathbf{u}) = \mathcal{O}(\varepsilon^2). \tag{11}$$

admits a smooth homoclinic orbit ϕ_ε for small ε provided that the Melnikov parameter $b(\varepsilon)$ is chosen as

$$b(\varepsilon) = \overbrace{\|\mathbf{u}_r\|_{L^2}^{-2} \|\mathbf{P} \cdot \mathbf{u}_r\|_{L^1}}^{b_0} + \mathcal{O}(\varepsilon).$$

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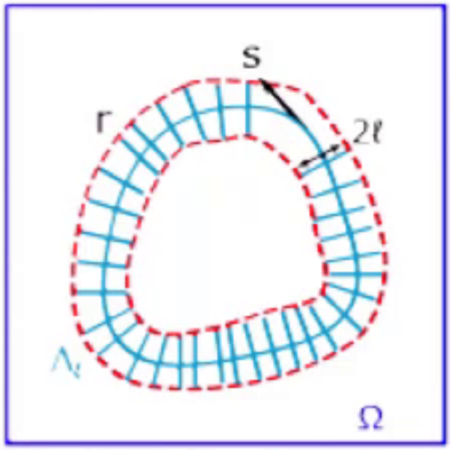
Intrinsic curvature: Canham-Helfrich energy



Given the base interface Γ, a bilayer solution $\mathbf{u}_b$ can be approximated by

$$\mathbf{u}_q(x) = \begin{cases} \phi_\varepsilon(r(x)), & x \in \Gamma_\ell, \\ \phi_\varepsilon(\infty), & x \in \Omega \backslash \Gamma_\ell. \end{cases}$$

Under the Laplacian under the whisker coordinates,

$$\varepsilon^2 \Delta \phi_\varepsilon - W(\phi_\varepsilon) + \varepsilon \mathbf{P}(\phi_\varepsilon) = \varepsilon(H_0(s) - b_0)\partial_r \phi_\varepsilon + \mathcal{O}(\varepsilon^2).$$

More precisely, the mFCH free energy $\mathcal{F}(\mathbf{u}_q)$ admits the expansion

$$\mathcal{F}_M(\mathbf{u}_q) = \varepsilon^3 C \overbrace{\boxed{\int_S (H_0(s) - b_0)^2 - (\eta_1 + \eta_2)\mathrm{d}s}}^{\text{Canham-Helfrich energy}} + \mathcal{O}(\varepsilon^4).$$

Melnikov parameter↔traveling speed↔intrinsic curvature

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