Droplet phase in a nonlocal isoperimetric problem under confinement

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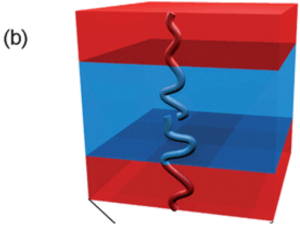
Diblock Copolymers

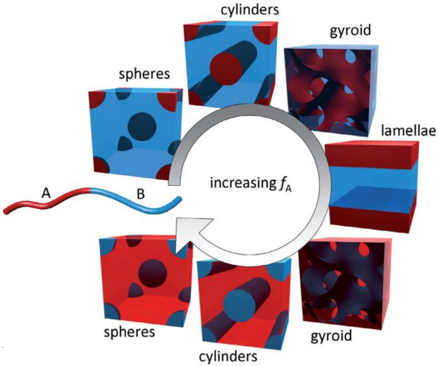
- Polymer strands composed of two monomers *A*, *B* glued together.

- Monomers of the same type attract; of opposite type repel.
- Diffuse-interface energy (Ohta-Kawasaki) model, $u : \ \Omega = \mathbb{T}^3 \to \mathbb{R}$ phase function.
- $u = 1$ in pure *A*-phase, $u = 0$ in pure *B*-phase.



Images from S. Darling, Energy Environ Sci. (2009)

- Γ-convergence $\rightsquigarrow$ sharp interface model, a nonlocal isoperimetric problem (NLIP).



f_A denotes the volume fraction of A-type monomers.

Images from S. Darling, Energy Environ Sci. (2009)

The Nonlocal Isoperimetric Problem (NLIP)

Seek periodic patterns, $u \in BV(\mathbb{T}^3; \{0, 1\})$ on unit torus $\mathbb{T}^3$, with given mass $m = \int_{\mathbb{T}^3} u \, dx$,

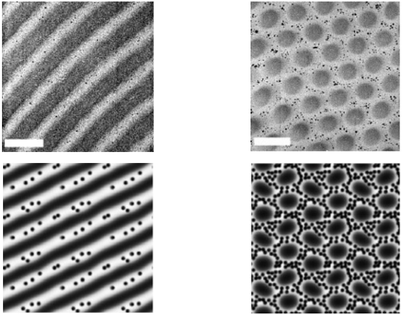
$$\mathcal{E}_\gamma(u) = \int_{\mathbb{T}^3} |\nabla u| + \gamma \big\| u - m \big\|^2_{H^{-1}}$$
$$= \int_{\mathbb{T}^n} |\nabla u| + \gamma \int_{\mathbb{T}^n} \int_{\mathbb{T}^n} G(x, y) u(x) u(y) \, dx \, dy$$

- The first term is perimeter of the interfaces.
  - $u \in BV(\mathbb{T}^n; \{0, 1\})$ is a characteristic function, $u = \chi_E$
  - The total variation $|\nabla u|(\mathbb{T}^3) = \int_{\mathbb{T}^3} |\nabla u| = \mathrm{Per}_{\mathbb{T}^3}(E)$.
- The second term introduces nonlocal interactions; G is the (periodic, mean-zero) Laplace Green's function.
- $\mathcal{E}_\gamma$ is obtained as a Γ-limit of Ohta-Kawasaki mean-field model.
- **Extensive literature:** Acerbi-Fusco-Morini, Alberti-Choksi-Otto, Bonacini-Cristoferi, Choksi-Glasner, Choksi-Peletier, Choksi-Ren, Choksi-Sternberg, Frank-Lieb-Nam, Goldman-Muratov-Serfaty, Knüpfer-Muratov, Lu-Otto, Muratov, Ren-Wei, Sternberg-Topalaglu,...

How to Influence Phase Separation?

- Goal (applications): alter the morphology of the phase domains.
- Idea: add filler nanoparticles, which are coated so as to prefer one of the polymer phases.
- By adjusting the density of the nanoparticles we hope to confine the domains to specified regions and select a different minimizing morphology.

Study by the research group of Fredrickson: first column shows **low-density**, second column shows **high-density** of nanoparticles.



Sharp Interface Model with Confinement

Confinement: seek to alter minimizing configurations via nanoparticles, coated to prefer one of the phases.

Set-up: Minimize over periodic configurations $u \in BV(\mathbb{T}^n; \{0, 1\})$ with given mass $m = \frac{1}{|\mathbb{T}^n|} \int_{\mathbb{T}^n} u$,

$$\mathrm{E}_{\gamma,\sigma}(u) := \int_{\mathbb{T}^n} |\nabla u| + \gamma \int_{\mathbb{T}^n} \int_{\mathbb{T}^n} G(x, y) u(x) u(y) \, dx \, dy \\ - \sigma \int_{\mathbb{T}^n} u(x) \, \rho(x) \, dx$$

Here, G is the (periodic, mean-zero) Laplace Green's function, and $\mu \in \mathscr{P}_{\mathrm{ac}}(\mathbb{T}^n)$ represents the limiting nanoparticle density as a measure.

- The first term and second are exactly as in the NLIP, perimeter and nonlocal interactions.
- The third term models nanoparticle interactions. $\rho \in L^\infty(\mathbb{T}^n)$ gives the density of nanoparticles, which attract the phase $u = 1$.
- $E_{\gamma,\sigma}$ is obtained as a Γ-limit of Ohta-Kawasaki with the inclusion of a large number of nanoparticles of negligible volume. Ginzburg-Qiu-Balacz; A-B-T

Droplet Regime

$$\mathsf{E}_{\gamma,\sigma}(u) := \int_{\mathbb{T}^3} |\nabla u| + \gamma \int_{\mathbb{T}^3} \int_{\mathbb{T}^3} u(x)u(y)G(x,y)\,dxdy - \sigma \int_{\mathbb{T}^3} u\,\rho(x)\,dx$$

We seek a regime in which all three terms (perimeter, nonlocal, confinement) are felt. We choose the "droplet scaling" (Choksi-Peletier):

- Assume the volume ratio (of phase A to phase B) is very small.
- Expect small balls of phase A in a sea of phase B.
- Advantage: treat droplets as particles in an appropriate limit.
- Introduce small length scale parameter (droplet radius) $0 < \eta \ll 1$, assume total mass $m = M\eta^3$, for fixed M.
- We rescale the order parameter, to have mass M but concentrate on its support,
$$v(x) = \frac{u(x)}{\eta^3}, \qquad \int_{\mathbb{T}^3} v = M.$$
- Choose the "critical scaling" $\gamma = \eta^{-3}$, $\sigma = \eta^{-1}$, so that all terms in the energy contribute at the same scale.

The energy transforms to...

$$E_\eta(v) := \eta \int_{\mathbb{T}^3} |\nabla v| + \eta \int_{\mathbb{T}^3} \int_{\mathbb{T}^3} v(x)v(y)G(x,y)\, dxdy - \int_{\mathbb{T}^3} v(x)\rho(x)\, dx$$

with $\int_{\mathbb{T}^3} v = M$.

Heuristics:

- $v \sim \sum_{i=1}^n m^i \delta_{x_i}$, with $M = \sum_i m^i$.
- First term wants to minimize droplet perimeter (spheres?)
- Droplet centers x_i sample nanoparticle density $\rho(x_i)$, seek *maxima* of $\rho(x)$.
- For simplicity, assume ρ attains its max at the origin, with

$$\boxed{\rho(x) = \rho_{max} - \rho_1 |x|^2 + o(|x|^2)}$$

- Will all the mass simply form a single droplet at the origin? And if not, how does it split?

Choksi-Peletier: Same scaling limit, but no confinement, $\rho = 0$. Droplets form uniform lattice on $\mathbb{T}^3$ [Coulomb repulsion].

Ansatz (upper bound construction)

Recall:

$$E_\eta(v) = \eta \int_{\mathbb{T}^3} |\nabla v| + \eta \int_{\mathbb{T}^3}\int_{\mathbb{T}^3} v(x)v(y)G(x,y)\,dxdy - \int_{\mathbb{T}^3} v(x)\rho(x)\,dx, \quad \int_{\mathbb{T}^3} v = M$$

Assume v forms n droplets near the origin (max point of ρ),

$$v(x) = v_\eta(x) = \sum_{i=1}^{n} \eta^{-3} z_i \left(\frac{x - x_i}{\eta} \right),$$

with $z_i(x)$ compactly supported, $z_i(x) \in \{0,1\}$, and $\int_{\mathbb{R}^3} z_i = m_i$, and each $x_i = x_i^\eta \to 0$ (to maximize $\rho(x)$.)

- At what rate do $x_i \to 0$? Scale $x_i = \delta y_i$, with $\delta = \delta(\eta) \to 0$.
- For $|x_i - x_j|$ small, $\eta G(x_i, x_j) \sim \eta |x_i - x_j|^{-1} = O(\eta\delta^{-1})$
- Also, $\rho(x_i) = \rho_{max} - \delta^2 |y_i|^2 + o(\delta^2)$

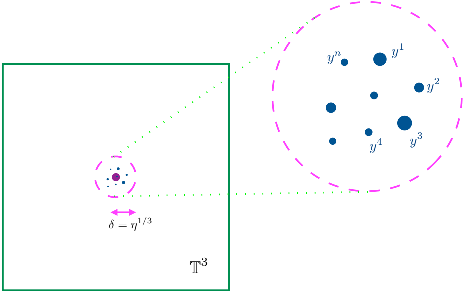
$$E_\eta(v) \simeq \sum_{i=1}^{n} \underbrace{\left[\int_{\mathbb{R}^3} |\nabla z_i| + \|z_i\|^2_{H^{-1}(\mathbb{R}^3)} \right]}_{\text{self-energy}} + \frac{\eta}{\delta} \sum_{i \neq j} \frac{m_i m_j}{4\pi |y_i - y_j|} + \delta^2 \rho_1 \sum_{i=1}^{n} m^i y_i^2 - M\rho_{max}$$

Thus, the optimal separation scale is $\delta = O(\eta^{1/3})$...

Droplets accumulate at max of ρ

Droplets have "radii" $O(\eta)$, and are separated by $\delta = O(\eta^{1/3})$,

$$v(x) = v_\eta(x) = \sum_{i=1}^{n} \eta^{-3} z_i \left(\frac{x - x_i}{\eta} \right) ,$$



- To construct a complementing lower bound we use a Concentration Compactness type lemma by Frank–Lieb.
- But why should there be more than one droplet?

The blowup problem

To understand the splitting of the droplets, we look at the "self-energy" terms. The droplet "profiles" z_i minimize (for $m = m^i$)

$$e_0(m) = \inf \left\{ \int_{\mathbb{R}^3} |\nabla z| + \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{z(x)z(y)}{4\pi|x-y|} \ : \ z \in BV(\mathbb{R}^3; \{0,1\}), \int_{\mathbb{R}^3} z = m \right\}.$$

Theorem (Lu-Otto, Knupfer-Muratov)

There exist constants $0 < m_{c_1} \leq m_{c_2} \leq m_{c_3}$ such that

- *For $m \leq m_{c_2}$, there exists a minimizer of $e_0(m)$;*
- *For $m \leq m_{c_1}$ the minimizer is a ball;*
- *For $m > m_{c_3}$ the minimum is not attained.*

- The nonexistence of a minimizer is due to splitting of the mass into pieces. So when our M is large, the minimizers v_η must split into several pieces, each of which is small enough that the minimizer $e_0(m^i)$ exists!
- This is also related to Gamow's Liquid Drop model for nuclei (1930). (Frank-Killip-Nam, Bonacini-Cristoferi)

Our result (A-Bronsard-Choksi-Topaloglu)

Recall:

$$\mathrm{E}_\eta(v) = \eta \int_{\mathbb{T}^3} |\nabla v| + \eta \int_{\mathbb{T}^3}\int_{\mathbb{T}^3} v(x)v(y)G(x,y)\,dxdy - \int_{\mathbb{T}^3} v(x)\rho(x)\,dx, \quad \int_{\mathbb{T}^3} v = M$$

$$\rho(x) = \rho_{max} - \rho_1|x|^2 + o(|x|^2)$$

Define: $\mathcal{M}_0 := \Big\{ M > 0 \colon e_0(M)$ admits a minimizer$\Big\}$.

Let v_η minimize E_η. Then along a subsequence of $\eta \to 0$, there exists $n \in \mathbb{N}$, points $\{y_i\}_{i=1,\dots,n}$ in $\mathbb{R}^3$, and masses $m^i \in \mathcal{M}_0$, $\sum_{i=1}^n m^i = M$, with:

- $v_\eta - \sum_{i=1}^n m^i \delta_{\eta^{1/3} y_i} \rightharpoonup 0$ in the sense of measures;
- The energy admits an asymptotic expansion,

$$E_\eta(v_\eta) = \sum_{i=1}^n \left[e_0(m^i) - m^i \rho_{max} \right] + \eta^{2/3} F_0(y_1,\dots,y_n; m^1,\dots,m^n) + o\left(\eta^{2/3}\right),$$

  where

$$F_0(y_1,\dots,y_n; m^1,\dots,m^n) = \rho_1 \sum_{i=1}^n m^i |y_i|^2 + \frac{1}{4\pi} \sum_{\substack{i,j=1 \\ i\neq j}}^n \frac{m^i\, m^j}{|y_i - y_j|}.$$

- The renormalized droplet centers $y^1,\dots,y^n$ minimize the energy F_0 for given $\{m^i\}$, n.

Lower Bound

Take a minimizing sequence $v_\eta = \eta^{-3}\chi_{\Omega_\eta}$, and blow up at order η, $E_\eta = \eta^{-1}\Omega_\eta \subset \mathbb{R}^3$

- Frank-Lieb: after translation by $y_\eta \in \mathbb{R}^3$, there is concentration:

$$F_\eta := E_\eta \cap B_R \to E, \quad G_\eta := E_\eta \cap B_R^c \to 0 \text{ locally},$$

$$|E| \in (0, M], \quad \lim_{\eta\to 0}(\operatorname{Per}(E_\eta) - \operatorname{Per}(F_\eta) - \operatorname{Per}(G_\eta)) = 0.$$

- If $|E| = M$, the seqence converges, and there is no splitting.
- If $|E| < M$, we repeat with G_η replacing E_η, to get a sequence of droplet sets, each of which will be minimizers for the NLIP in $\mathbb{R}^3$.
- Problem: How to control errors $o(\eta^{2/3})$ to get 2nd Gamma limit?
- u_η and rescaled limits do solve an NLIP, so they are ω-minimizers of the perimeter functional.
- By regularity theory, $F_\eta \to E$ in $C^{1,\alpha}$ (de Giorgi-Miranda, Tamanini, Acerbi-Fusco-Morini)
- So in fact $\operatorname{Per}(E_\eta) = \operatorname{Per}(F_\eta) + \operatorname{Per}(G_\eta)$, and *a forteriori* no error is introduced by the splitting of mass.

Remarks

- If $M \in \mathcal{M}_0$, then there is no splitting of the droplets, and a single droplet center concentrates at the origin (where ρ is maximized.)
- Although stated for minimizers, the energy decomposition may be proved in the more general framework of Γ-convergence.
- The case without the nanoparticle confinement was studied by Choksi-Peletier. In that case, the droplets remain $O(1)$ apart, there is no $\eta^{1/3}$ length scale involved, and the second order term in the energy is governed by the purely Coulombic repulsion term given by $G(x, y)$.
- Ditto for piecewise constant ρ: the droplets will distribute themselves in the region of strongest nanoparticle density, according to the Coulomb repulsion (as in Choksi-Peletier).
- The two-scale concentration recalls many features of the 2D Ginzburg-Landau energy with magnetic field: vortices accumulating at minima of the Meissner field [Sandier–Serfaty]
- A slightly different scaling done by Goldman-Muratov-Serfaty on the 2D NLIP allows for a divergent number of droplets, "Abrikosov lattice".
- The droplet interaction energy F_0 is of an attractive+repulsive form which recalls studies of flocking and other models of self-assembly. (Burchard-Choksi-Topolaglu)

Remarks, II

- We may treat more general $\rho(x)$: either with nondegenerate global max at the origin, or of the form
$$\rho(x) := \left(\rho(0) - \rho_1 |x|^q + o(|x|^q)\right), \quad q > 2.$$
In the latter case, we obtain a droplet interaction energy of the form:
$$\mathsf{F}_0(v) := \rho_1 \sum_{i=1}^{n} m^i |x_i|^q + \frac{1}{4\pi} \sum_{\substack{i,j=1 \\ i \neq j}}^{n} \frac{m^i\, m^j}{|x_i - x_j|}$$
Droplets will converge to the max of ρ at the rate $\eta^{1/q+1}$.
- What do minimizers of F_0 look like? Here are $q = 2$ and $q = 10$: