Energy-driven pattern formation via competing long- and short-range interactions

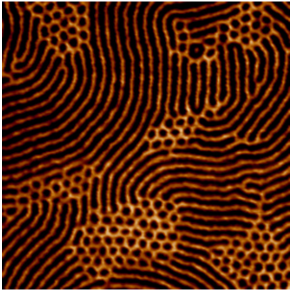
Florian Theil

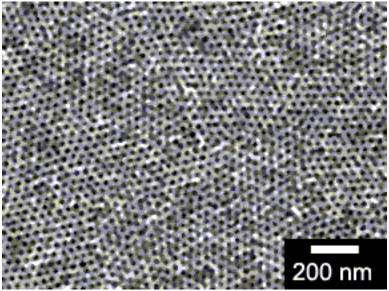
joint work with Mark Peletier (Eindhoven), David Bourne (Glasgow)

Heraklion, 16 April 2013

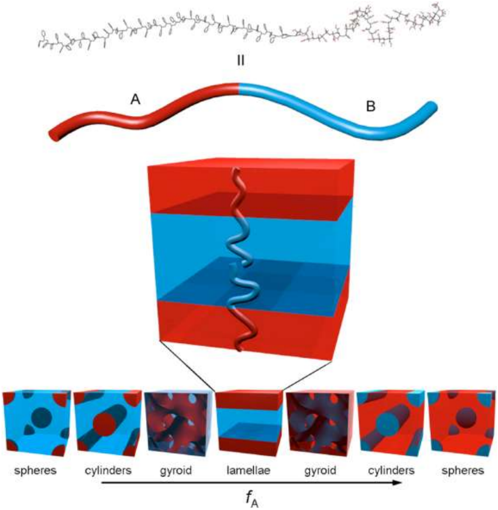
Block copolymers

Diblock copolymer melts are well-known pattern formation systems.





Schematic picture



Otha-Kawasaki model

$u : \Omega \to \mathbb{R}$ local concentration of A

$f = \frac{1}{|\Omega|} \int_\Omega u$ volume fraction

Total energy:

$$\mathcal{E}_\varepsilon^{\mathrm{OK}}(u) = \varepsilon \int_\Omega |\nabla u|^2 \, \mathrm{d}x + \frac{1}{\varepsilon} \int_\Omega (1-u)^2 \, u^2 \, \mathrm{d}x + \gamma \, \|u - f\|^2_{H^{-1}(\Omega)} \, .$$

ε: interface width γ: strength of nonlocal interactions	functions of physical parameters

$$\|v\|^2_{H^{-1}} = \int \int v(x) \, v(y) \, G(x,y) \, \mathrm{d}x \, \mathrm{d}y$$

$=$ the electrostatic energy of charge distribution v

$\to$ arises here from inter-chain interactions.

Limiting behavior

2000 onwards: Fonseca, Cicalese, Dal Maso, Chermisi et al send ε to 0 and show that $\mathcal{E}_\varepsilon^{\mathrm{OK}}(u)$ converges to a sharp interface model

$$\mathcal{E}_0^{\mathrm{OK}}(u) = \alpha \int |\nabla u| + \gamma \|u - f\|_{H^{-1}}^2$$

where $u \in \{0, 1\}$ almost everywhere, $\frac{1}{\Omega} \int_\Omega u = f$.

Dilute limit: $f \to 0$

Choksi-Peletier (2011): As f tends to 0 the functional $\mathcal{E}_0^{\mathrm{OK}}(u)$ converges in the sense of Γ-limits to

$$\Gamma_\Omega^2(\mu) = \lambda \sum_i e_0(m_i) + f^p \sum_{i \neq j} m_i m_j G(x_i, x_j),$$

if $\mu = \sum m_i \delta(\cdot - x_i)$, where $\lambda > 0$ and $e_0(m) = m^{\frac{d-1}{d}}$ is the surface energy. An explicit expression for the constant λ and the exponent p exists.

Variational generalization of the Coulombic interaction energy

Let $\Omega \subset \mathbb{R}^2$ have unit area ($|\Omega| = 1$) and $\mu \in \mathcal{P}(\Omega)$ be an atomic probability measure.

$$\Lambda_\Omega^p(\mu) = \begin{cases} \sup\left\{\int_\Omega (1-\mu)\,\phi\,\mathrm{d}x - \frac{1}{p}\int_\Omega |\nabla\phi|^p\,\mathrm{d}x \;:\; \phi \in W^{1,p}(\Omega)\right\} & 2 < p < \infty, \\ \sup\{\int_\Omega (1-\mu)\,\phi\,\mathrm{d}x \;:\; \|\nabla\phi\|_\infty \le 1\} & p = \infty, \end{cases}$$

It can be shown that Λ_Ω^p converges to $\sum_{i<j} m_i\, m_j\, G(x_i, x_j)$ as $p \to 2$, $p > 2$ after renormalization (Serfaty-Sandier 2012).
In the case $p = \infty$ we obtain the 1-Wasserstein distance between the Lebesgue measure $\mathcal{L}_\Omega$ and μ.

Wasserstein distance

Let $\Omega \subset \mathbb{R}^2$ bounded, $\mu, \nu \in \mathcal{P}(\Omega)$ probability measures. The associated Wasserstein-energy is defined as

$$W^r(\nu, \mu) = \inf\Big\{ \int_\Omega |x-y|^r \,\mathrm{d}\Psi(x,y) \;:\; \Psi \in \mathcal{P}(\Omega \times \Omega) \\ \int_\Omega \Psi(x,y)\,\mathrm{d}x = \mu,\; \int_\Omega \Psi(x,y)\,\mathrm{d}y = \nu \Big\}.$$

Theorem (Rubinstein-Kantorovich (1958))

$$W^1(1, \mu) = \sup\left\{ \int_\Omega (1-\mu)\,\phi\,\mathrm{d}x \;:\; \|\nabla\phi\|_\infty \leq 1 \right\}.$$

Well known consequences: $d_r(\mu, \nu) = W^r(\mu, \nu)^{\frac{1}{r}}$ metrizes weak-* convergence in $P(\Omega)$, $(\mathcal{P}(\Omega), d_r)$ is compact.

Final model: Long-range interaction is approximated with the 2-Wasserstein energy

$$\hat{E}_\lambda(\mu) = \lambda \sum_{z \in \operatorname{supp}(\mu)} \mu(\{z\})^{\frac{1}{2}} + W^2(\mathcal{L}_\Omega, \mu),$$

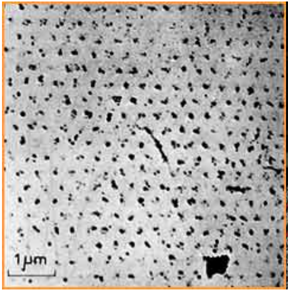
where $\Omega \subset \mathbb{R}^2$, $|\Omega| = 1$, $\mathcal{L}_\Omega$ is the Lebesgue measure and $\mu \in \mathcal{P}(\Omega)$ is an atomic probability measure ($\operatorname{supp}(\mu)$ is countable).

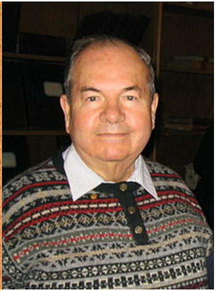
- Copolymers consist of A parts and B parts.
- A parts and B parts repel each other $\rightarrow$ phase separation.
- B parts have much higher volume than A parts, $v_z = \mu(\{z\})$ is the relative amount of A at z.
- The term $\lambda \sum_{z \in \operatorname{supp}(\mu)} \mu(\{z\})^{\frac{1}{2}}$ measures the energy of the interfacial area separating the two phases.

Nonlocal model of a pattern-forming system.
Question: What is the asymptotic behavior of the minimizers of $\hat{E}_\lambda$ as $\lambda \rightarrow 0$?

Related system: Abrikosov lattice in type-II superconductor

[U. Essmann & H. Trauble, Phys. Lett. 24A, 526 (1967)]





1952/57: Abrikosov (* 1928) predicts flux tube lattice

2003: several thousand citations and a nobel prize

Mathematical model: renormalized Coulomb interaction

[E. Sandier & S. Serfaty, 2012, CMP]

The renormalized interaction energy of an (infinite) flux vortex configuration $Z \subset \mathbb{R}^2$ is defined as

$$F(Z) = \limsup_{R\to\infty} \lim_{\eta\to 0} \left(\frac{1}{2} \int_{\mathbb{R}^2 \setminus \cup_{p\in Z} B(p,\eta)} \chi_R \, |\nabla h|^2 + \pi \log \eta \sum_{p\in Z} \chi(p) \right).$$

where $\chi_R(x) = 1$ if $|x| < R$ and

$$\frac{1}{2\pi} \Delta h = 1 - \sum_{p\in Z} \delta_p.$$

F is a Gamma-limit of the more accurate Ginzburg-Landau model.
Conjecture (Abrikosov 1957) F is minimized if Z is a triangular lattice with density 1. (Actually Abrikosov originally conjectured that the square lattice minimizes F.)

Results

Let $\Omega_\lambda = V_\lambda^{1/2}\Omega$, $V_\lambda = \left(\frac{2c_6}{\lambda}\right)^{\frac{3}{2}}$, $c_6 = \frac{5\sqrt{3}}{54} = 0.16\ldots$

$$E_\lambda(\mu) = 2c_6 \sum_{z\in Z} \mu(\{z\})^{\frac{1}{2}} + W^2(\mathcal{L}_{\Omega_\lambda}, \mu),$$

if $\mu(\Omega_\lambda) = |\Omega_\lambda| = V_\lambda$ and ∞ otherwise.

Theorem (Minimum energy)

A *If Ω is a polygon with at most 6 sides, then*

$$E_\lambda \geq 3c_6 V_\lambda.$$

B *If $\partial\Omega$ is Lipschitz, then*

$$\lim_{\lambda\to 0} V_\lambda^{-1} \inf E_\lambda = 3c_6.$$

The limit is achieved by a triangular lattice.

Results (cont'd)

Theorem (Minimizers)

Assume that Ω is a polygon with at most 6 sides.

- *If $E_\lambda(\mu) = 3c_6 V_\lambda$, then μ is an atomic measure with all masses equal to 1, and $\mathrm{supp}(\mu)$ is a translated and rotated copy of the triangular lattice.*
- *There exists $C > 0$ such that after eliminating*

$$d = \left(V_\lambda^{-1} E_\lambda(\mu) - 3c_6\right)^{\frac{1}{6}}$$

points in $\mathrm{supp}(\mu)$ the remaining points have six neighbors whose distance lies between $(1 - C\,d)$ and $(1 + C\,d)$ of the optimal distance $2^{1/2}3^{-3/4}$.

Cells and an alternative formulation

Theorem (Kantorovich (1942), Optimal mass transportation)

If ν is absolutely continuous with respect to the Lebesgue measure, then for each μ there exists an optimal transport plan $T : \Omega \to \Omega$ such that μ is the push-forward of ν under T and

$$W^p(\nu, \mu) = \int_\Omega |x - T(x)|^p \, \mathrm{d}\nu(x).$$

Associate to each $z \in Z$ the characteristic function

$$\chi_z(x) = \begin{cases} 1 & \text{if } T(x) = z, \\ 0 & \text{else.} \end{cases} \quad \text{and } F_\lambda(\chi) = \sum_z \left[2c_6 \left(\int \chi_z \right)^{\frac{1}{2}} + I_\lambda(\chi_z) \right]$$

with

$$I_\lambda(\chi) = \inf_z \int |x - z|^2 \, \chi(x) \, \mathrm{d}x.$$

Easy to see:

$$E_\lambda(\mu) \geq F_\lambda(\chi).$$

Cells can assumed to by polygonal

Lemma

The support of χ_z is convex with a polygonal boundary.

Proof.

Brenier's theorem (1991, CMP) states that there exists a convex Lipschitz solution $u : \Omega \to \mathbb{R}$ of the Monge-Ampére equation

$$\det(D^2 u) = 1$$

such that $T = Du$.
Since u is piecewise affine the Hadamard jump condition implies

$$(\nabla u(z) - \nabla u(z')) \cdot (x - x') = 0,$$

if $x, x' \in \mathrm{supp}\chi_z \cap \mathrm{supp}\chi_{z'}$. □

Geometric results

Lemma (Fejes Tóth (1972))

If $\mathrm{supp}(\chi)$ *is a polygon with n sides, then*

$$I(\chi) \geq c_n\Big(\int \chi\Big)^{\frac{1}{2}},$$

where $c_n = \frac{1}{2n}\left(\frac{1}{3}\tan\frac{\pi}{n} + \cot\frac{\pi}{n}\right)$.
Equality is attained if and only if $\mathrm{supp}(\chi)$ *is a regular n-gon.*

Lemma (Euler's polytope formula)

The average number of edges per face in a planar graph where the degree of each vertex has degree ≥ 3 *is less than 6.*

Weak localization

$$E_\lambda(\mu) \geq \sum_{z \in Z} f(v_z, n_z),$$

where $v_z = \int \chi_z$ and n_z is the number of sides of $\operatorname{supp} \chi_z$, $\sum_z v_z = V_\lambda$, $\sum_z (n_z - 6) \leq 0$ and

$$f(v, n) = 2c_6\, v^{1/2} + c_n v^2.$$

Define $\kappa = \frac{\partial f}{\partial n}(1, 6) = \frac{2\pi}{243} - \frac{5\sqrt{3}}{324} \sim -8.7 * 10^{-4} < 0$.
We are done if

$$f(v, n) - 3c_6 v + \kappa(6 - n) \geq 0 \text{ for all } n \geq 3,\ v \leq 0. \tag{1}$$

because (1) implies that

$$E_\lambda(\mu) \geq 3\, c_6\, \sum_z v_z + \kappa \underbrace{\sum_z (n_z - 6)}_{\leq 0 \text{ by Euler}} \geq 3\, c_6\, V_\lambda.$$

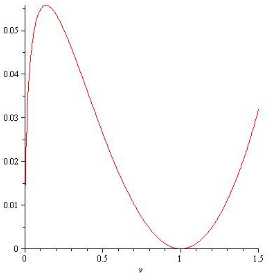
Bounds on holes and masses

Unfortunately

$f(v,n) \geq 3\,c_6\,v + \kappa\,(n-6)$

is only guaranteed for

$v \geq 1.5 \times 10^{-4}$.



Lemma (Lower bound on the masses)

If μ is a minimizer of E_λ, then $\mu(\{z\}) > 0$ implies $\mu(\{z\}) > 2.4 \cdot 10^{-4}$.

The result is certainly not optimal and relies on the following upper bound bound on the size of holes:

$$\mu(B(z,R) \setminus \{z\}) > 0$$

if $\mu(z) > 0$ and $R > 3.3$.

Summary

- Existence of periodic minimizers has been established for an interesting class of nonlocal two-dimensional models.
- The result relies strongly on methods from optimal mass transportation theory.

Outlook

- It would be desirable to apply the method to the p-Laplacian model.
- Establish links to other models where crystallization can be shown, e.g.

$$G_{\mathrm{pair}}(Z) = \sum_{\substack{z,z' \in Z \\ z \neq z'}} V(|z - z'|),$$

  for suitable potentials V. Here even three-dimensional results are available (joint work with Lisa Flatley).
- Consider the finite temperature case

$$P_\beta(\mu) = \frac{1}{N(\beta)} \exp(\beta E(\mu))$$