Minimizers of the Landau-de Gennes energy around a spherical colloid particle

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Results obtained with: S. Alama, X. Lamy

Nematic Liquid Crystals

- Fluid of rod-like particles, partially ordered: translation but rotational symmetry is broken.
- Nematic phase: $\nu\eta\mu\alpha$, thread/fil, particles prefer to order parallel to their neighbors
- Director $n(x)$, $|n(x)| = 1$ indicates local axis of preference: gives on average the direction of alignment.

Oseen–Frank energy

- A variational model for equilibrium configurations of liquid crystals.
- Equilibria $n : \Omega \subset \mathbb{R}^3 \to \mathbb{S}^2$ minimize elastic energy,

$$E(n) = \int_\Omega e(n, \nabla n)\, dx$$

$$e(n, \nabla n) = K_1(\nabla \cdot n)^2 + K_2[n \cdot (\nabla \times n)]^2 + K_3[n \times (\nabla \times n)]^2$$

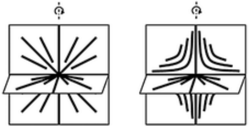
- Simple case: one-constant approximation $K_1 = K_2 = K_3 = 1$,

$$E(n) = \frac{1}{2}\int_\Omega |\nabla n|^2\, dx, \quad \text{the } \mathbb{S}^2 \text{ harmonic map energy.}$$

- n is not oriented, $-n \sim n$ gives same physical state.
  $\implies \quad n : \Omega \to \mathbb{R}P^2$.

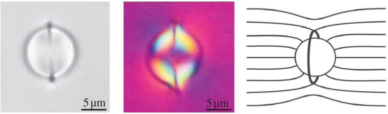
Harmonic Maps to $\mathbb{S}^2$ (or $\mathbb{R}P^2$)

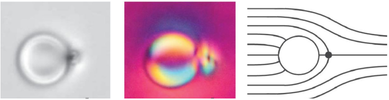
- Real-valued minimizers $f: \Omega \to \mathbb{R}$ of the Dirichlet energy $E(f) = \frac{1}{2}\int_\Omega |\nabla f|^2\,dx$ are harmonic functions, $\Delta f = 0$.
  - Linear elliptic PDE; solutions are smooth, bounded singularities removable.
- When $u: \Omega \to M$, M a smooth manifold, minimizers solve a nonlinear elliptic system of PDE.
- For $M = \mathbb{S}^k$ or $\mathbb{R}P^k$, $-\Delta n = |\nabla n|^2 n$
- Regularity theory for $\mathbb{S}^2$ or $\mathbb{R}P^2$-valued harmonic maps:
  - Schoen-Uhlenbeck (1982): $\mathbb{S}^2$-valued minimizers are Hölder continuous except for a discrete set of points.
  - Brezis-Coron-Lieb (1986): singularities have degree ± 1, $n \simeq \frac{Rx}{|x|}$, R orthogonal. ("hedgehog", "antihedgehog")

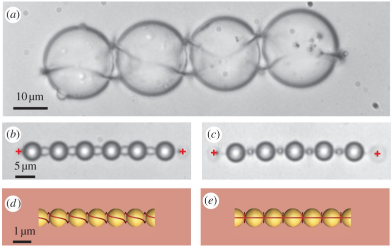


  - Hardt-Kinderlehrer-Lin (1986): for Oseen-Frank, min are real analytic except for a closed set Z, $\mathcal{H}^1(Z) = 0$.

Applications of colloidal suspensions in nematic liquid crystals: photonics, biomedical sensors, ...

- 

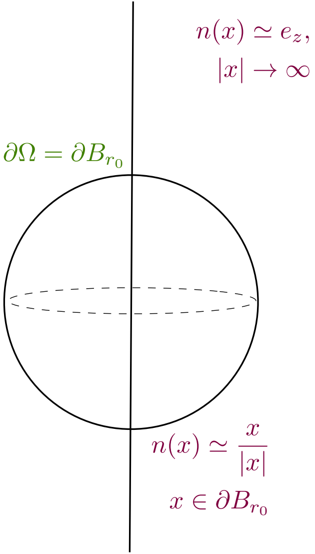
- 

- 

I. Musevic, M. Skarabot and M. Ravnik, Phil Trans Roy Soc A, 2013

The spherical colloid

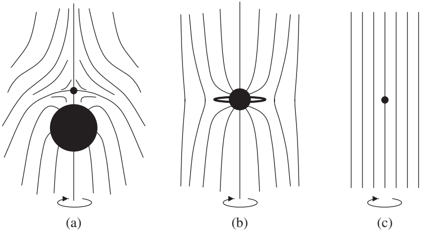
Consider a nematic in $\mathbb{R}^3$ surrounding a spherical particle $B_{r_0}(0)$.



- $\Omega = \mathbb{R}^3 \setminus B_{r_0}(0)$, exterior domain.
- As $|x| \to \infty$, tend to vertical director, $n(x) \to \pm e_z$
- On ∂B_{r_0}, homeotropic (normal) anchoring:
  - Strong (Dirichlet) with $n = e_r = \frac{x}{|x|}$,
  - Weak anchoring, via surface energy, $\frac{W}{2} \int_{\partial B_{r_0}} |n - e_r|^2 \, dS$

Size matters

Physicists observe that the character of the minimizers should depend on particle radius r_0 and anchoring strength $\mathcal{W}$.



Kleman & Lavrentovich, *Phil. Mag. 2006*.

(a) For large r_0, a "dipolar" configuration, with a detached (antihedghog) defect;

(b) For small r_0 with large $\mathcal{W}$, a "quadripolar" minimizer, with no point singularity but a "Saturn ring" disclination;

(c) For small r_0 and low $\mathcal{W}$, no singular structure at all.

Problems with Oseen-Frank

- "Saturn ring":
  - Solution should have a 1-D singular set.
  - Harmonic map or Oseen-Frank minimizers have only isolated point defects.
- Dipolar, with detached point defect:
  - This may be observed in a harmonic map model.
  - But harmonic map/Oseen-Frank has no fixed length scale; cannot distinguish different radii.
- New approach: embed the harmonic map problem in a larger family of variational problems with a natural length scale. The harmonic maps may be recovered in an appropriate limit.

Landau–de Gennes Model

A relaxation of the harmonic map energy.

- Introduce space of Q-tensors: $Q(x) \in \mathcal{Q}_3$, symmetric, traceless 3×3 matrix-valued maps. Q(x) models second moment of the orientational distribution of the rod-like molecules near x.
- Eigenvectors of $Q(x)$ = principal axes of the nematic alignment.
- Uniaxial Q-tensor: two equal eigenvalues; principal eigenvector defines a director $n \in \mathbb{S}^2$,

$$Q_n = s(n \otimes n - \tfrac{1}{3}\mathrm{Id}).$$

- $Q_n = Q_{-n}$; these represent $\mathbb{R}P^2$-valued maps.
- Biaxial Q-tensor: all eigenvalues are distinct. Strictly speaking, no director; but the principal eigenvector is an approximate director.
- Isotropic Q-tensor: all eigenvalues are equal, so $Q = 0$. No preferred direction, the liquid crystal has no alignment or ordering.

The LdG Energy

$$\mathcal{F}_{\hat{L}}(Q) = \int_\Omega \left[\frac{\hat{L}}{2} |\nabla Q|^2 + f(Q) \right] dx,$$

,

- Potential $f(Q) = -\frac{a}{2}\mathrm{tr}\,(Q^2) + \frac{b}{3}\mathrm{tr}\,(Q^3) + \frac{c}{4}(\mathrm{tr}\,(Q^2))^2 - d,$
- $a = a(T_{NI} - T)$, $b, c > 0$ constant, d chosen so $\min_Q f(Q) = 0$.
- $f(Q)$ depends only on the eigenvalues of Q.
- $f(Q) = 0 \iff Q = s_*(n \otimes n - \frac{1}{3} Id)$ with $n \in \mathbb{S}^2$ (uniaxial) and $s_* := (b + \sqrt{b^2 + 24ac})/4c > 0$
- Euler–Lagrange equations are semilinear,
$$\hat{L}\Delta Q = \nabla f(Q) = -aQ - b\left(Q^2 - \tfrac{1}{3}|Q|^2 I\right) + c|Q|^2 Q$$
- Uniaxial solutions are the exception; in most geometries expect biaxiality rules [Lamy, Contreras–Lamy]
- Analogy: Ginzburg–Landau model, a relaxation of the $\mathcal{S}^1$-harmonic map problem:
$$\int_\Omega [\tfrac{\varepsilon^2}{2}|\nabla u|^2 + (|u|^2 - 1)^2],\ u:\ \Omega \to \mathbb{C}$$

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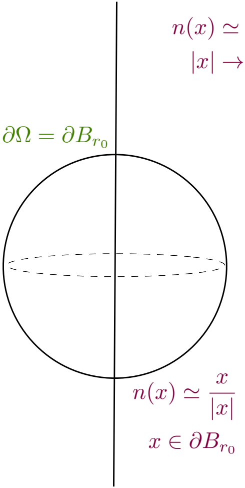


- $\Omega = \mathbb{R}^3 \setminus B_{r_0}(0)$, exterior domain.
- Minimize LdG over $Q(x) \in H^1(\Omega; \mathcal{Q}_3)$.
- As $|x| \to \infty$, Q is uniaxial, with vertical director, $Q(x) \to s_* \left(e_z \otimes e_z - \frac{1}{3} I\right)$.
- On ∂B_{r_0}, homeotropic (normal) anchoring:
  - Strong (Dirichlet) with $n = e_r = \frac{x}{|x|}$,
    $Q(x)|_{\partial B_{r_0}} = Q_s := s_* \left(e_r \otimes e_r - \frac{1}{3} I\right)$.
  - Weak anchoring, via surface energy,
    $\frac{\hat{W}}{2} \int_{\partial B_{r_0}} |Q(x) - Q_s|^2 \, dS$
  - $\Longrightarrow \ \frac{\hat{L}}{\hat{W}} \frac{\partial Q}{\partial \nu} = Q_s - Q$ on ∂B_{r_0}.

Two scaling limits

First rescale by the particle radius r_0; $\Omega = \mathbb{R}^3 \setminus B_1(0)$,

$$\mathcal{F}(Q) = \int_\Omega \left[\frac{\hat{L}}{2r_0^2} |\nabla Q|^2 + f(Q) \right] dx + \frac{\hat{W}}{2r_0} \int_{\partial B_1} |Q_s - Q|^2 dA.$$

and non-dimensionalize by dividing by the reference energy $a(T_{NI})$:

$$\tilde{\mathcal{F}}(Q) = \int_\Omega \left[\frac{L}{2} |\nabla Q|^2 + f(Q) \right] dx + \frac{W}{2} \int_{\partial B_1} |Q_s - Q|^2 dA.$$

with $L = \frac{\hat{L}}{r_0^2 a(T_{NI})}$, $W = \frac{\hat{W} r_0^2 a(T_{NI})}{\hat{L}}$.

- Set $Q_\infty = s_*(e_z \otimes e_z - \frac{1}{3} I)$, and $\mathcal{H}_\infty = Q_\infty + \mathcal{H}$, with
$$\mathcal{H} = \{ Q \in H^1_{loc} : \int_\Omega \left[|\nabla Q|^2 + |x|^{-2} |Q|^2 \right] dx < \infty \}.$$
- For fixed parameters L, W, there exists a minimizer in $\mathcal{H}_\infty$, $Q(x) \to Q_\infty$ uniformly as $|x| \to \infty$.
  Open question: at what rate?
- We consider two limits:
  - Small particle limit. $L \to \infty$, with $W \to w \in (0, \infty]$.
  - Large particle limit. $L \to 0$, with Strong (Dirichlet) anchoring.

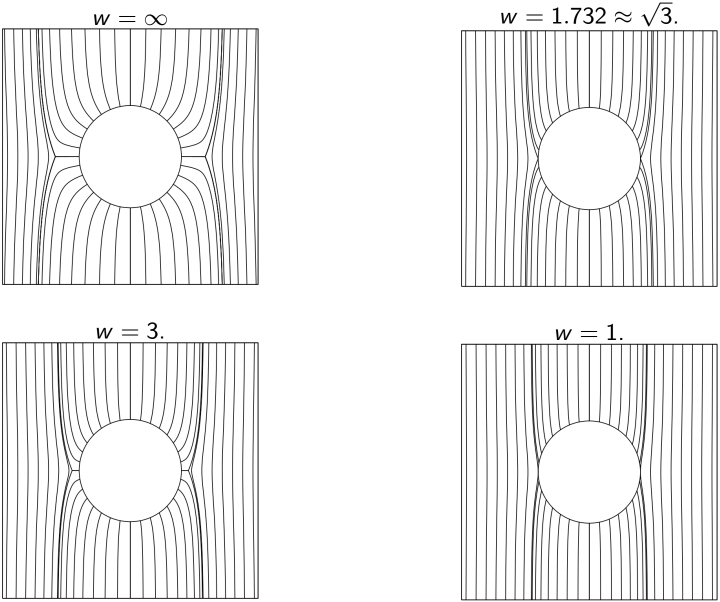
Small particle limit

$$\tilde{\mathcal{F}}(Q)=\int_\Omega\left[\frac{L}{2}|\nabla Q|^2+f(Q)\right]dx+\frac{W}{2}\int_{\partial B_1}|Q_s-Q|^2dA.$$

When $L\to\infty$, $W\to w\in(0,\infty]$:

- converge to a harmonic (linear) function, $\Delta Q_w=0$ in $\Omega=\mathbb{R}^3\setminus B_1(0)$.
- Explicit solution, $Q_w(x)$!! In spherical coordinates (r,θ,φ),
  $$Q_w=\alpha(r)(e_r\otimes e_r-I/3)+\beta(r)(e_z\otimes e_z-I/3),\qquad (r>1),$$
  with $\alpha(r)=s_*\frac{w}{3+w}\frac{1}{r^3}$, $\quad\beta(r)=s_*(1-\frac{w}{1+w}\frac{1}{r})$.
- The eigenvalues of Q_w may also be calculated explicitly,
  $$\lambda_{1,2}(x)=\frac{[\alpha+\beta]}{6}\pm\sqrt{\frac{[\alpha+\beta]^2}{4}-\alpha\beta\sin^2\varphi},\quad \lambda_3(x)=-\frac{\alpha+\beta}{3}<0.$$
- At eigenvalue crossing $\lambda_1=\lambda_2$, eigenvectors exchange $\Longrightarrow$ discontinuous director!
- This occurs along a circle, $(r_w,\theta,0)$, with r_w root of:
  $$r^3-\frac{w}{1+w}r^2-\frac{w}{3+w}=0.$$

The Saturn Ring

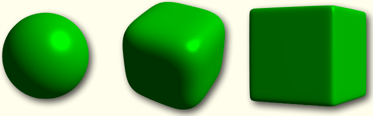


Colloidal cuboids (homeotropic)

"Superellipsoid"

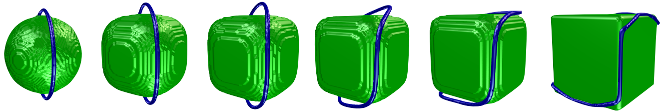
$$\left(\frac{x}{b}\right)^{2p} + \left(\frac{y}{b}\right)^{2p} + \left(\frac{z}{a}\right)^{2p} = 1$$

Aspect ratio: a/b.
"Sharpness": p.



$p = 1$ $\quad$ $p = 2$ $\quad$ $p = 10$

$a/b = 1$



$p = 1$ $\quad$ 1.5 $\quad$ 2 $\quad$ 2.5 $\quad$ 3 $\quad$ 10

Beller, Gharbi & Liu, Soft Matter, 2015, 11, 1078

Large particle limit

Now we consider $L \to 0$, with Dirichlet $Q|_{\partial B_1} = s_*(e_r \otimes e_r - \frac{1}{3}I)$.

- Coincides with singular limit as elastic constant $L \to 0$. (Majumdar-Zarnescu; Nguyen-Zarnescu)
- Minimizer converges to uniaxial Q-tensor, $Q_* = s_*(n \otimes n - \frac{1}{3}I)$, locally uniformly, away from a discrete set of singularities.
- Director $n(x) \in \mathbb{S}^2$ is a minimizing harmonic map.
- No "Saturn ring", or any other line defects are possible. (Schoen-Uhlenbeck; Hardt-Kinderlehrer-Lin)
- Solution must have at least one singularity; but generally, neither boundary topology nor energy determine the number of defects.
  - Hardt-Lin-Poon (1992) There exist axisymmetric harmonic maps in $\Omega = B_1(0)$, with degree-zero Dirichlet BC and arbitrarily many pairs of degree ± 1 defects on the axis.
  - Hardt-Lin (1986) For any N, $\exists\ g : \partial B_1(0) \to \mathbb{S}^2$ with degree zero such that the *minimizing* harmonic map has N defects in $B_1(0)$.

Our result: large particle limit

- We assume axial symmetry; this improves regularity (D. Zhang) and constrains the possible singularities.
- Axial symmetry is consistent with physical intuition and numerical studies.

Theorem

For any sequence of axisymmetric minimizers with $L \to 0$, a subsequence converges to a map $Q_*(x) = s_*(n(x) \otimes n(x) - I/3)$, locally uniformly in $\overline{\Omega} \setminus \{p_0\}$. Here n minimizes the Dirichlet energy in Ω, among axially symmetric $\mathbb{S}^2$-valued maps satisfying the boundary conditions

$$n = e_r \text{ on } \partial B_1, \qquad \text{and } \int_\Omega \frac{(n_1)^2 + (n_2)^2}{|x|^2} \, dx < \infty,$$

and n is analytic away from **exactly one point defect** *p_0, located on the axis of symmetry.*

Why only one singularity?

- Use cylindrical coords (ρ, θ, z) in $\Omega = \mathbb{R}^3 \setminus B_1$; by axial symmetry,
  - it suffices to consider the cross-section Ω_{cyl} with $\theta = 0$;
  - Ω_{cyl} is simply connected, so the director n is oriented;
  - $n \in \mathbb{S}^2$ is determined by the spherical angle $\phi = \psi(\rho, z)$,

$$n = \sin\psi(\rho, z)\, e_\rho + \cos\psi(\rho, z)\, e_z$$

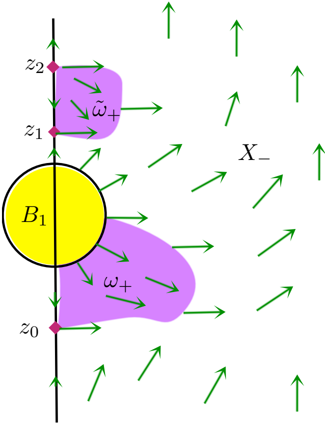
- Harmonic map energy, integrated in a cross-section Ω_{cyl}:

$$E(\psi) = \int_{\Omega_{cyl}} \left[|\partial_\rho \psi|^2 + |\partial_z \psi|^2 + \frac{1}{\rho^2} \sin^2 \psi \right] \rho d\rho dz$$

- Single nonlinear PDE,

$$\partial_z^2 \psi + \partial_\rho^2 \psi + \frac{1}{\rho} \partial_\rho \psi = \frac{1}{2\rho^2} \sin(2\psi) \quad \text{in } \Omega_{cyl}$$

Key observation: $X_- = \{\psi(\rho, z) < \frac{\pi}{2}\}$ and $X_+ = \{\psi(\rho, z) > \frac{\pi}{2}\}$ are both connected.



- Assume several defects; each lies on the z-axis, degree ± 1, n is vertical away from z_j on axis.
- ψ turns between $\psi = 0$ and $\psi = \pi$ around defect, creates components of $X_\pm$ in Ω_{cyl}
- If X_+ has a component $\tilde{\omega}_+$ whose boundary is disjoint from ∂B_1, replace ψ in $\tilde{\omega}_+$ by $\tilde{\psi}(\rho, z) = \pi - \psi(\rho, z)$;
- The new function has the same energy as ψ, so it also solves the PDE;
- Solutions are analytic away from the z-axis (Zhang), so this is not possible.
- $X_\pm$ connected + topological argument $\Longrightarrow$ exactly one defect!