Modeling Colloidal Particles in a Liquid Crystal Matrix

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Motivation:

- Liquid crystal colloids have applications in new display technologies as well as nanofluidic devices. For this reason, they are an advancing area of research in material science and biological systems.

- In order for further advancement, we must improve our understanding of simple fluid colloids and the defect structures seen in the liquid crystal matrix.

Outline

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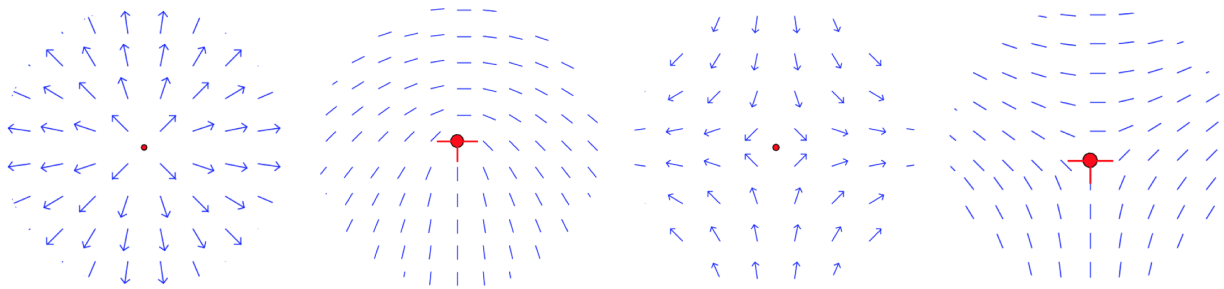
Order of Defects

- A defect is a localized loss of nematic order.
- If the director field at the boundary has topological degree zero, the order of the defects in the bulk must sum to zero.
- The topological order is found by taking a 2π rotation around the defect and measuring the corresponding change in angle of the director. In other words, k defines the $2\pi k$ change of the angle in the director
- Consider the following graphic[1]



(a) (b) (c) (d)

[1] Stan Alama, Lia Bronsard, and Bernardo Galvao-Sousa. "Weak Anchoring for a Two-Dimensional Liquid Crystal". In: *arXiv preprint arXiv:1405.3024* (2014).

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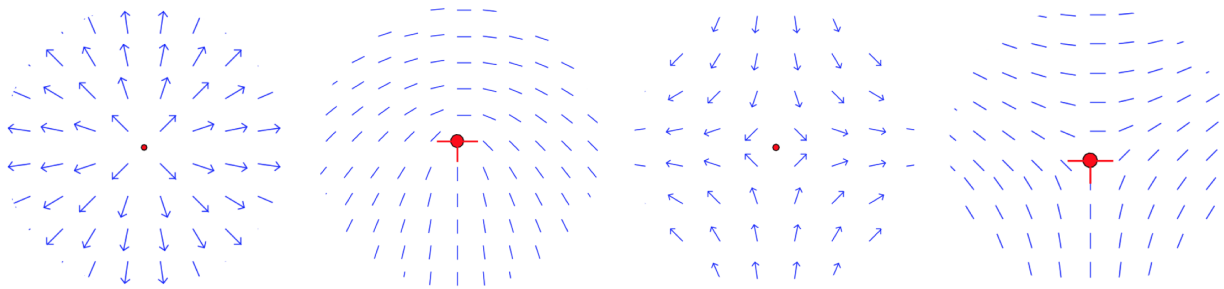

$$\textit{Order}: \quad (a)1, \quad (b)\frac{1}{2}, \quad (c)-1, \quad (d)\frac{-1}{2}$$

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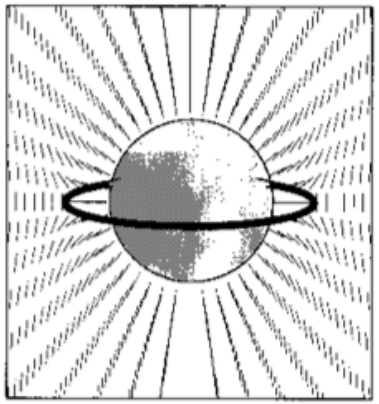
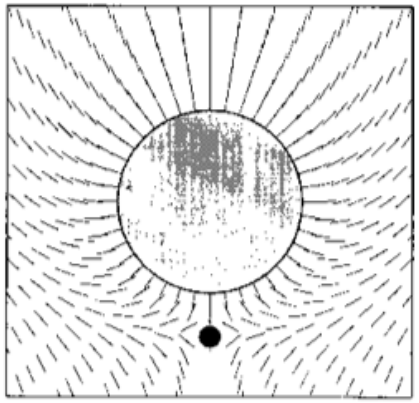
Types of Defects when One Particle is Present

- When a particle is introduced, two defects commonly develop: hedgehog and Saturn ring. Which develops depends on a variety of factors including the size of the particle and the boundary conditions imposed[2].



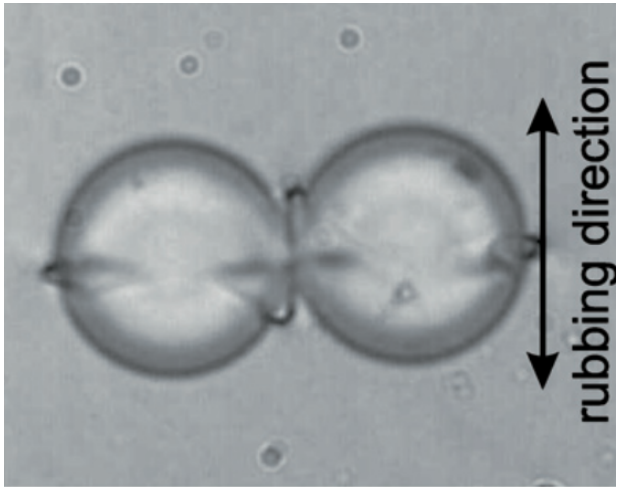


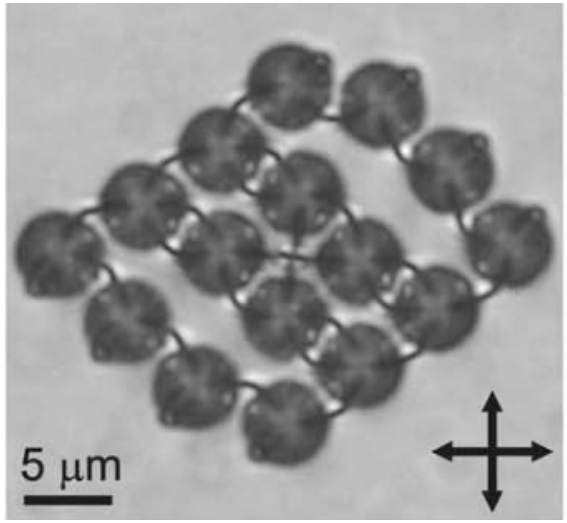
- Larger particles tend to be accompanied by a point defect, while smaller particles favor Saturn rings.
- Boundary conditions on the particle and the container also affect the type of defects seen experimentally.

[2] RW Ruhwandl and EM Terentjev. "Monte Carlo simulation of topological defects in the nematic liquid crystal matrix around a spherical colloid particle". In: *Physical Review E* 56.5 (1997), p. 5561.

Defects Around Multiple Particles

- When more than one particle is present defects can cause the particles to link together in an ordered fashion as shown below[3,4].





[3] Miha Ravnik and Slobodan Žumer. "Nematic colloids entangled by topological defects". In: *Soft Matter* 5.2 (2009), pp. 269–274.

[4] Uroš Tkalec et al. "Reconfigurable knots and links in chiral nematic colloids". In: *Science* 333.6038 (2011), pp. 62–65.

Outline

Surface Alignment

- We can treat the surfaces with a surfactant or by rubbing it in a set direction in order to align particles.
- There are two possible types of molecular alignments of liquid crystal particles that can we enforced of the surface of the particles and the wall of the domain:
  - Strong anchoring: Corresponds to Dirichlet boundary conditions and will be reflected in the definition of the admissible set.
  - Weak anchoring: Reflected by a term which penalizes the energy
- For weak anchoring, the Rapini-Papoular surface energy is often used[5]

$$E_s = \tau \int_\Gamma 1 - \alpha(\mathbf{n} \cdot \mathbf{v})^2 \, dS$$

where $\tau > 0$, $\mathbf{v}$ is the unit normal to the boundary, Γ is the surface of the particle, and $-1 < \alpha < 1$.

[5] Epifanio G Virga. *Variational theories for liquid crystals*. Vol. 8. CRC Press, 1995.

Outline

Oseen-Frank Model

- Let $\mathbf{n}$ be a unit vector which describes average molecular alignment of the molecules in the liquid crystal
- Equilibrium states of liquid crystal are minimizers of[a]

$$E_{OF}(\mathbf{n}) = \int_{\Omega} W(\nabla \mathbf{n}, \mathbf{n}) d\mathbf{n}, \ |\mathbf{n}| = 1$$

where

$$W(\nabla \mathbf{n}, \mathbf{n}) = k_1(\nabla \cdot \mathbf{n})^2 + k_2(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + k_3|\mathbf{n} \times \nabla \times \mathbf{n}|^2 + (k_2 + k_4)(tr(\nabla \mathbf{n})^2 - (\nabla \cdot \mathbf{n})^2),$$

and the Frank's constants k_i are experimentally measured.

- We assume $k_1, k_2, k_3 > 0$, $k_2 \geq |k_4|$, $2k_1 \geq k_2 + k_4$[b].
- For our energy to be finite we assume $\mathbf{n} \in W^{1,2}(\Omega)$. 1

[a] Epifanio G Virga. *Variational theories for liquid crystals*. Vol. 8. CRC Press, 1995.

[b] Robert Hardt, David Kinderlehrer, and Fang-Hua Lin. "Existence and partial regularity of static liquid crystal

Outline

Point defects according to the Oseen-Frank model

- Consider the one-constant approximation of the Oseen-Frank model

$$E_{OF}(\mathbf{n}) = K \int_{\Omega} |\nabla \mathbf{n}|^2 \, d\mathbf{x}, \quad |\mathbf{n}| = 1$$

- Let Ω be a ball of radius 1 in $\mathbb{R}^n$, $n = 2, 3$, composed of a liquid crystal with radial alignment. The director will necessarily have the form $\frac{\mathbf{x}}{|\mathbf{x}|}$.
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$$\text{In 3D: } E_{OF} = K \int_{\Omega} \frac{3}{|\mathbf{x}|^2} d\mathbf{x} = K \int_0^1 \int_0^{2\pi} \int_0^{\pi} 3 \sin(\theta) d\theta d\phi dr = 12\pi K$$

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$$\text{In 2D: } E_{OF} = K \int_{\Omega} \frac{2}{|\mathbf{x}|^2} d\mathbf{x} = K \int_0^{2\pi} \int_0^1 \frac{2}{r} dr d\theta = \infty$$

Outline

Landau-de Gennes

- Q is a symmetric, traceless, second order tensor which describes the liquid crystal alignment.
- The energy expression is given by[6]

$$E_{LDG}(Q) = \int_\Omega (f_E(\partial Q) + f_B(Q))d\Omega + \int_\Gamma f_S(Q)dS.$$

where

$$f_E(\partial Q) = \frac{1}{2}L_1 Q_{\alpha\beta,\gamma} Q_{\alpha\beta,\gamma} + \frac{1}{2}L_2 Q_{\alpha\beta,\beta} Q_{\alpha\gamma,\gamma} + \frac{1}{2}L_3 Q_{\alpha\beta,\gamma} Q_{\alpha\gamma,\beta},$$

$$f_B(Q) = \frac{A}{2}tr(Q^2) + \frac{B}{3}tr(Q^3) + \frac{C}{4}tr(Q^2)^2,$$

$$f_S(Q) = \frac{W}{2}\left|Q|_\Gamma - Q_0\right|^2.$$

[6] Apala Majumdar and Arghir Zarnescu. "Landau-de Gennes theory of nematic liquid crystals: the Oseen-Frank limit and beyond". In: *Archive for rational mechanics and analysis* 196.1 (2010), pp. 227–280.

The Tensor Q

- Most general form of Q is given by:

$$Q = s(\mathbf{n} \otimes \mathbf{n} - \frac{1}{3}I) + r(\mathbf{m} \otimes \mathbf{m} - \frac{1}{3}I)$$

  and describes biaxial alignment.
- Phase transitions are now described by eigenvalue behavior. If $\lambda_1 = \lambda_2 = \lambda_3 = 0$, the liquid crystal is isotropic, if two eigenvalues are equal the tensor corresponds to the uniaxial phase, and if all are different, we have the biaxial phase.
- Since Q is invariant under $n \to -n$, Q will describe line fields as opposed to vector fields.

When is Landau-de Gennes equal to Oseen-Frank

First we must assume that the liquid crystal is uniaxial which implies $Q = s(\mathbf{n} \otimes \mathbf{n} - \frac{1}{3}I)$. Consider the one-constant approximation of the Landau-de Gennes model

$$E^*_{LDG}(Q) = \int_\Omega |\nabla Q|^2 = \int_\Omega \frac{\partial Q_{ij}}{\partial x_k} \frac{\partial Q_{ij}}{\partial x_k}$$

- Plugging in the Q and expanding, we find

$$= \int_\Omega \frac{2}{3}|\nabla s|^2 + 2s^2|\nabla n|^2$$

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- While we have algebraic equivalence there is the subtle matter that the Oseen-Frank model does not respect the head to tail symmetry of the nematic molecules.

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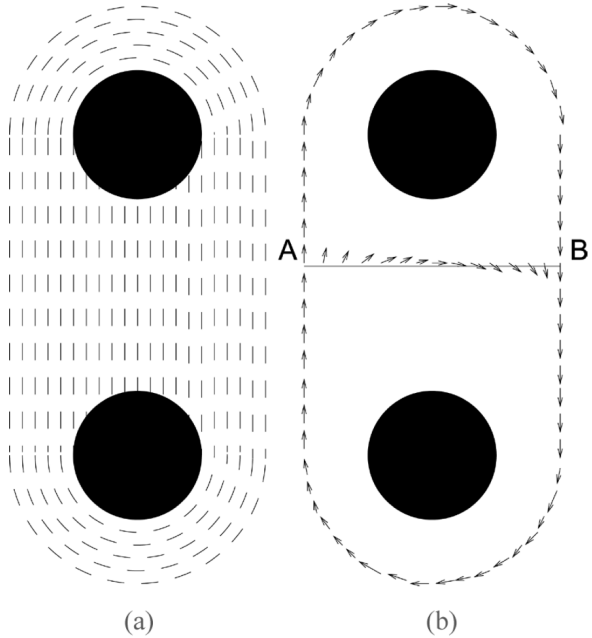
Orientability

Theorem: A line field $Q \in W^{1,p}(\Omega)$ is orientable if and only if there exists a vector field in the same functional space[a].

Lemma: For simply connected domains, line fields belonging to $W^{1,p}$ for some $p \geq 2$ are orientable[b].



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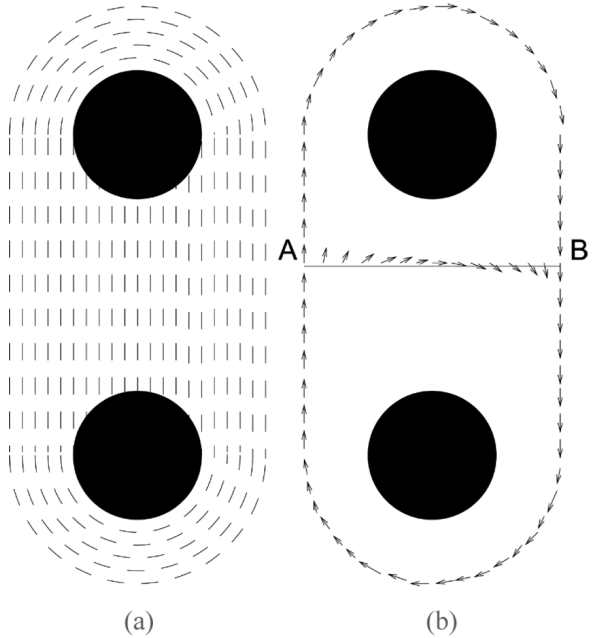
Let us consider the following example[c]:

The configuration in (a) is not claimed to be the minimizer, but it will always have lower energy than the oriented configuration (b).



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Complications with the Landau-de Gennes Model

Landau-de Gennes accomodates the biaxial state, issues with orientability and gives finite energy for line defects, but contains complications.

- The constants for the elastic and bulk energies differ by 10^{16}.
  - As an example, 5CB has the following constants: $L = 4.0 \times 10^{-11} N, A = -0.172 \times 10^6 N/m^2, B = -2.12 \times 10^6 N/m^2, C = 1.73 \times 10^6 N/m^2$
  - Notice that the very small size of the constant L implies that the elastic contribution is nearly non-existent.
- The length scales over which the defects are occurring are on the order of 10-100nm. Since we want to capture this behavior, we need a very fine mesh.

Using Fenics to Find an Energy Minimizer

- We consider the one-constant approximation of Landau-de Gennes:

$$E^*_{LDG}(Q) = \int_\Omega 2L|\nabla Q|^2 + f_B(Q)\ d\Omega$$

- It is straightforward to find the first variation of this expression:

$$\delta E^*_{LDG}(Q) = \int_\Omega 4L\nabla \mathbf{q} \cdot \nabla \mathbf{v} + (2A + 4C(q_0^2 + q_1^2))\mathbf{q} \cdot \mathbf{v}\ d\Omega$$

where $\mathbf{v} \in H_0^1$ and

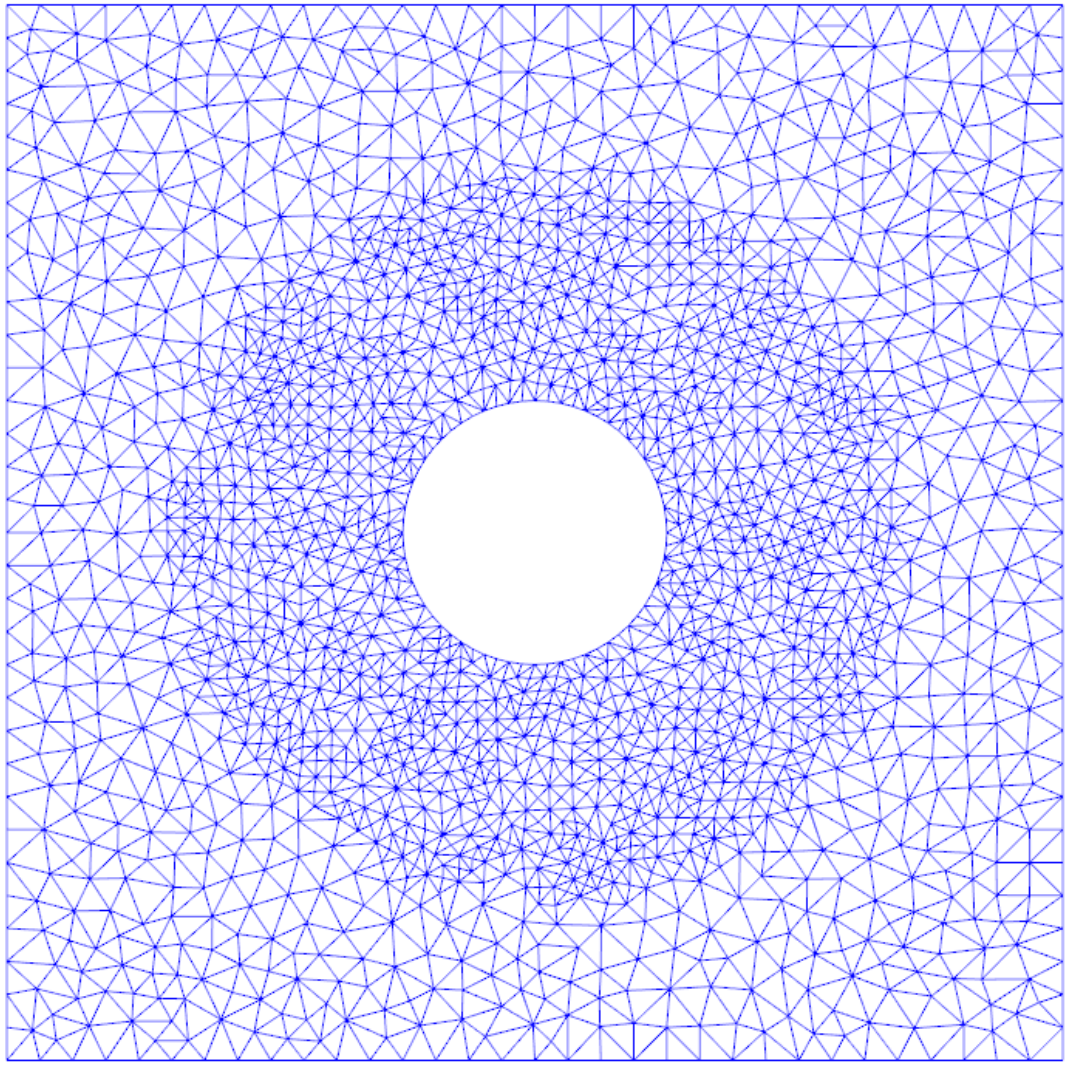
$$Q = \begin{bmatrix} q_0 & q_1 \\ q_1 & -q_0 \end{bmatrix}.$$

- For 2D, using C to nondimensionalize the bulk and letting L_0 be the characteristic length scale, the above expression becomes:

$$\delta \bar{E}^*_{LDG}(Q) = \int_{\Omega/L_0^2} \frac{4L}{L_0^2 C}\bar{\nabla}\mathbf{q} \cdot \bar{\nabla}\mathbf{v} + \frac{1}{C}(2A + 4C(q_0^2 + q_1^2))\mathbf{q} \cdot \mathbf{v}\ d\Omega$$

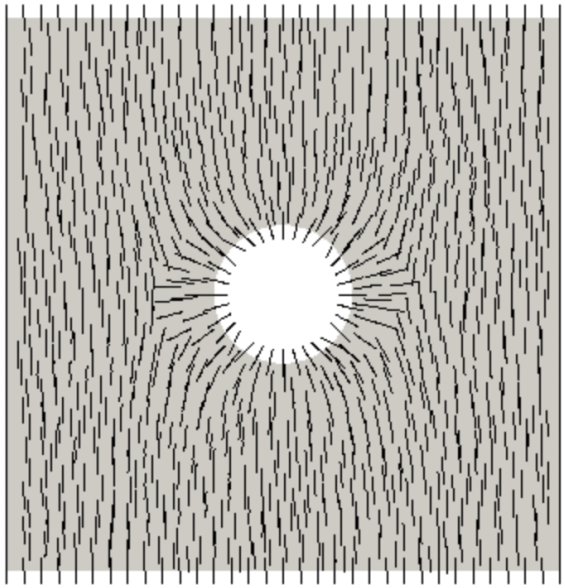
Mesh:

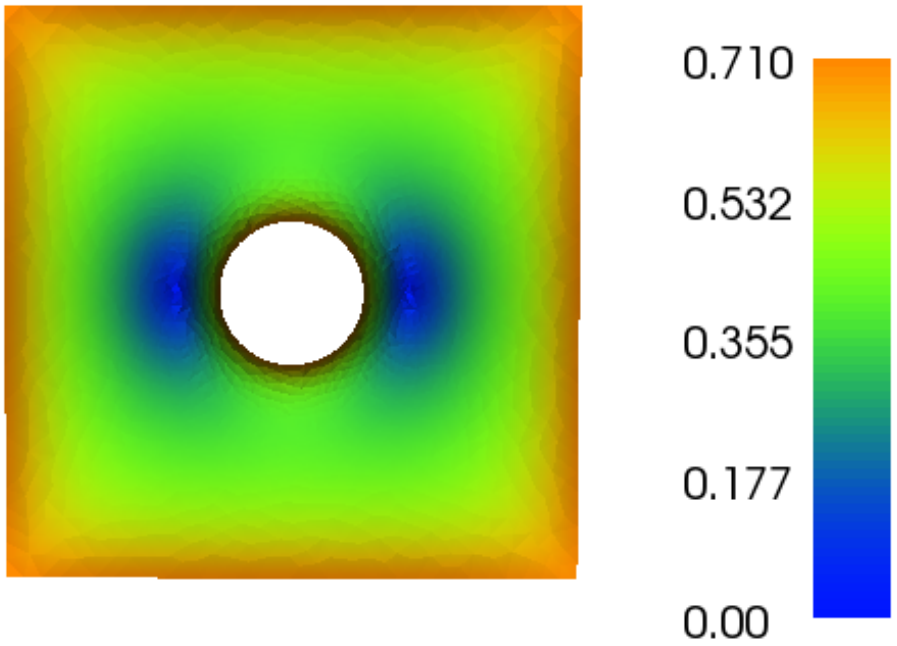
The original particle radius is 5 nanometers and the box has sidelengths of 40 nanometers. We scale with $L_0 =$ particle radius.



Using the Measured Bulk and Elastic Constants for 5CB:

On the left we have the line field from minimizing the Landau-de Gennes energy and on the right we plot s.





Future Direction

- Re-evaluate the relationship between the elastic and bulk constants.
- Run simulations with large particle radii.
- Include different L_i's in the energy expression.
- Extend to 3 dimensions.

Thank you!