# Sharp-interface theory for transitions between the isotropic and uniaxial nematic phases of a liquid crystal

Eliot Fried

*Department of Mechanical and Aerospace Engineering*
*Washington University in St. Louis*

With: Paolo Cermelli (U. Torino) & Morton E. Gurtin (CMU)

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## Outline

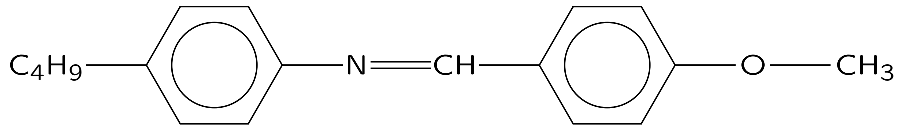
- History and characteristics of nematic liquid-crystals
- Simple model for flows of uniaxial nematic liquid-crystals: the Ericksen–Leslie theory.
- Extension of the Ericksen–Leslie theory to account for transformations between the isotropic and uniaxial nematic phases.
- Application: Evolution of a spherical isotropic droplet surrounded by a radially aligned nematic phase.
  - Problem without fluid flow.
  - Problem with fluid flow.
- Summary; Work in progress; Directions for further work.

## History and characteristics of nematic liquid-crystals

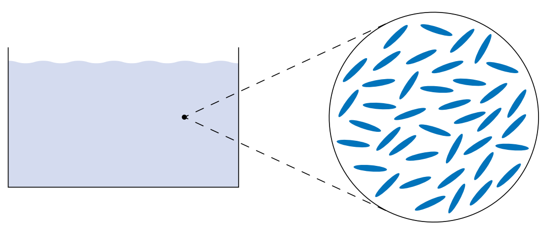
- In 1888, the botanist Reinitzer observed that cholesteryl benzoate melted to a cloudy liquid at 145.5°C and became a clear liquid at 178.5°C.
- Colloboration between Reinitzer and the physicist Lehmann, who developed the heated stage microscope, led to the identification of the nematic liquid-crystalline phase.

- The term *nematic* comes from the Greek word $\nu\hat{\eta}\mu\alpha$, meaning thread, and is used here because the molecules in the liquid align themselves into threadlike shapes.

- A nematic liquid-crystal can be thought of as a fluid constituted by highly rigid, rod- or disk-like molecules (called *mesogens*).
- A typical rod-like mesogen is Methoxybenzilidene Butylanaline (MBBA).

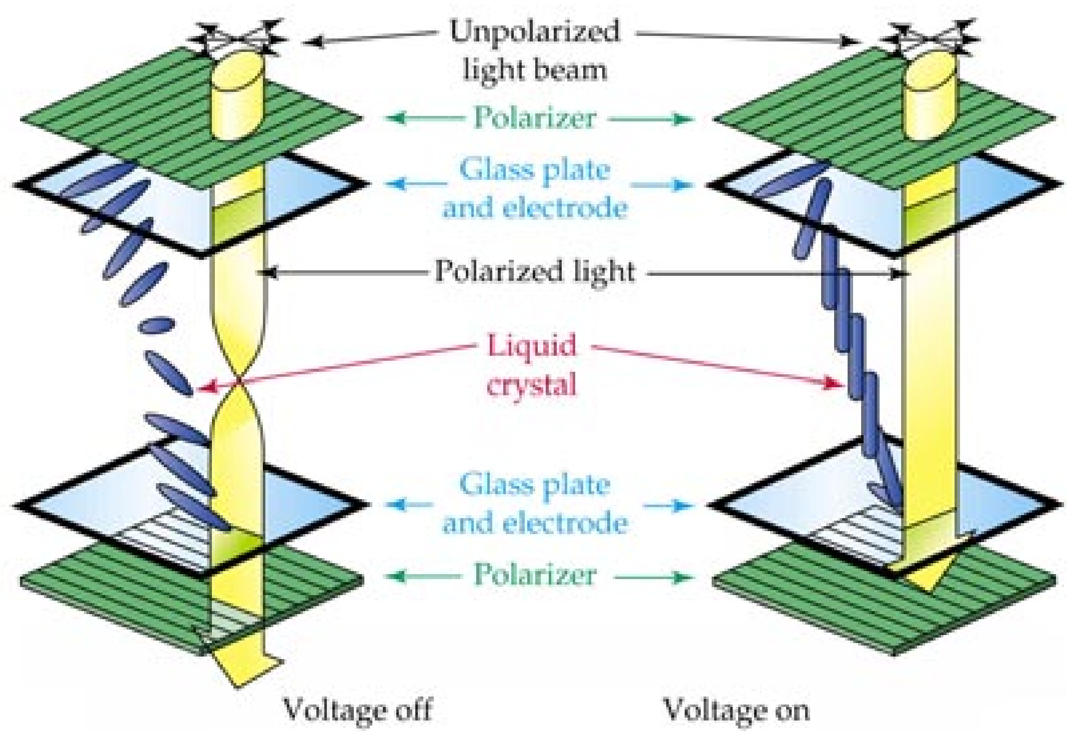



- Rod-like mesogens have diameters on the order of 0.25 nm and lengths on the order of 1 nm.
- Interactions between neighboring mesogens tend to make them parallel to one another, leading to orientational order.



- The molecular orientation, and hence the optical response, of a nematic liquid crystal can be tuned by applied electric or flow fields.

- In the presence of electric field, mesogens align with the electric field, altering the polarization of the light.
- The extent of the change of the polarization can be varied by controlling the intensity of an applied electric field.
- Nematic liquid-crystals are used in twisted nematic displays, the most common form of liquid crystal display.



## Simple model: Ericksen–Leslie (E–L) theory

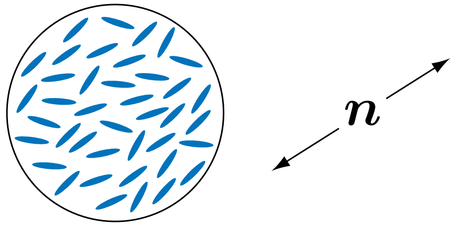
- Accurately describes the flow of uniaxial nematic liquid crystals.

- Macroscopic kinematical descriptor: velocity field

$$\boldsymbol{u} \qquad (\operatorname{div} \boldsymbol{u} = 0)$$

- Microscopic kinematical descriptor: director field

$$\boldsymbol{n} \qquad (|\boldsymbol{n}| = 1)$$



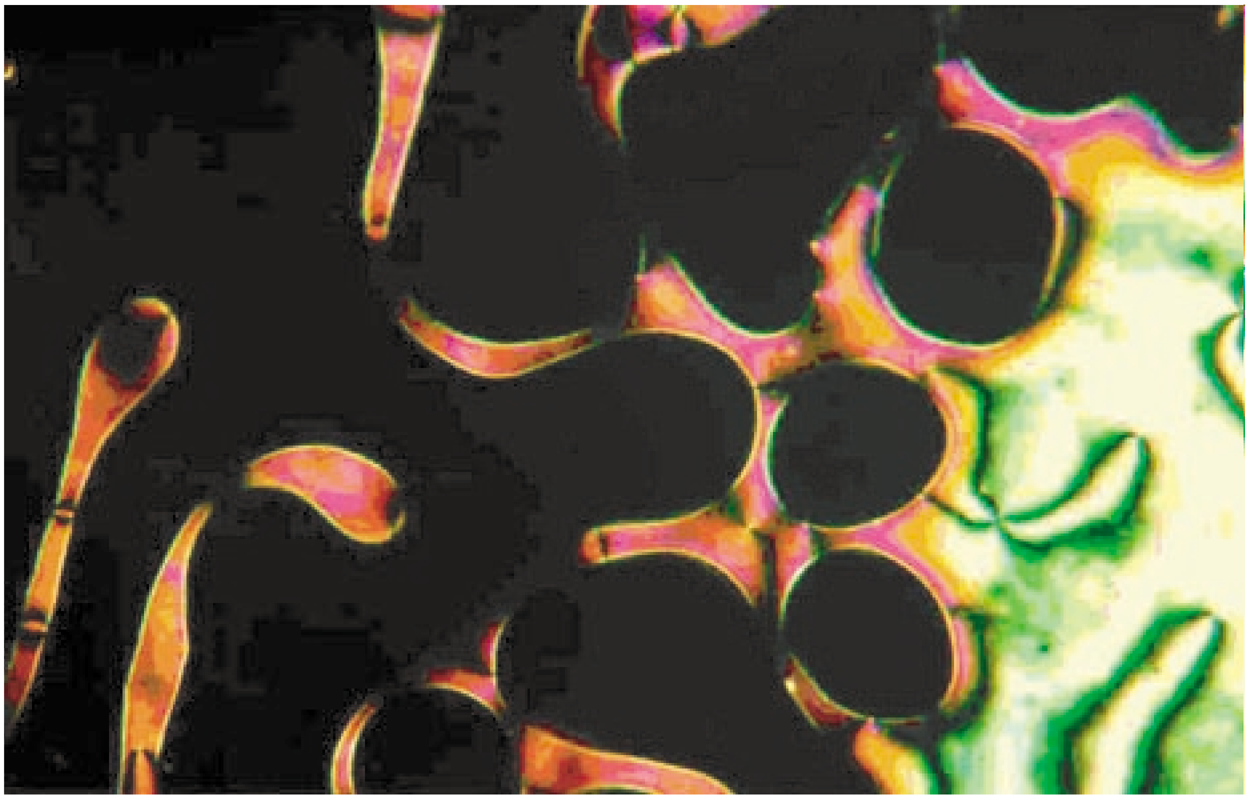

- Supplemental evolution equation for $\boldsymbol{n}$.

- Macroscopic and microscopic degrees of freedom are coupled via dissipative structure.

- Cannot describe transformations between the isotropic and uniaxial phases ...

## Goal of this work

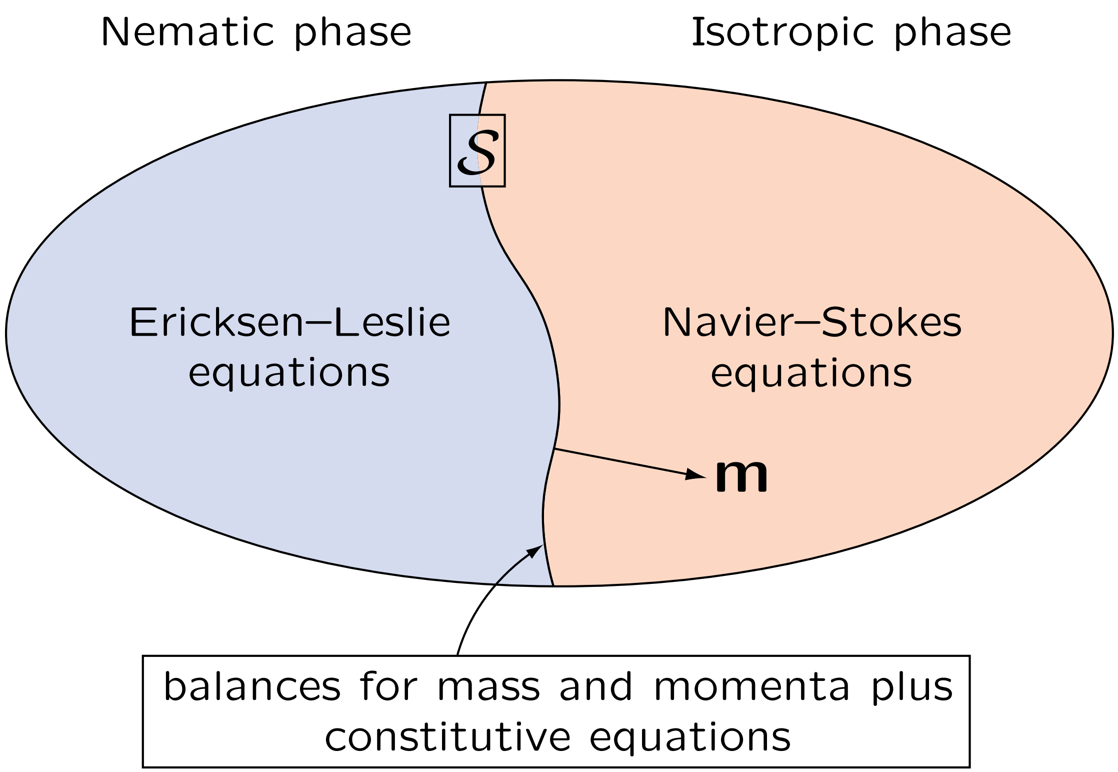
Extend the E–L theory to account for transformations between the isotropic and uniaxial nematic phases ...



T. J. Sluckin, *Contemporary Physics* **41** (2000), 37–56

## Alternative approaches to extending the E–L theory

- Phase field
  - V. Popa-Nita & T. J. Sluckin. Surface modes at the nematic-isotropic interface. *Physical Review E* **66** (2002), 041703.
- Sharp-interface



## Precedent for a sharp-interface approach

- Theory for material nematic-isotropic interfaces
  - A. D. Rey. Viscoelastic theory for nematic interfaces. *Physical Review E* **61** (2000), 1540–1549.
  - A. D. Rey. Young–Laplace equation for liquid crystal interfaces. *Journal of Chemical Physics* **113** (2000), 10820–10822.
  - A. D. Rey. Theory of interfacial dynamics of nematic polymers. *Rheologica Acta* **39** (2000), 13–19.
  - A. Poniewierski. Shape of the nematic-isotropic interface in conditions of partial wetting. *Liquid Crystals* **27** (2000), 1369–1380.

## Distinction between material and nonmaterial interfaces

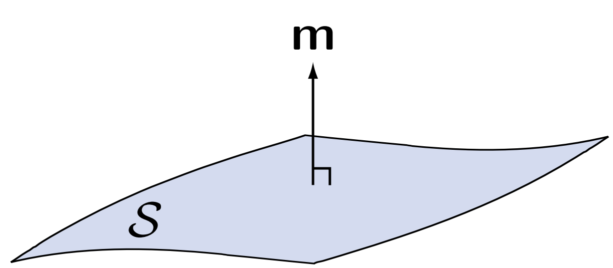
- Matter cannot be transported across a material interface.
  - The standard principles of balance together with appropriate constitutive relations provide a closed description of a material interface.

- Matter can be transported across a nonmaterial interface.
  - The standard ingredients do not provide a closed description of a material interface.
  - To obtain a closed description requires the introduction of additional ingredients that describe the physics underlying the exchange of matter across a nonmaterial interface.

## Variational paradigm: Gibbs–Thomson relation

$$\boxed{\mathcal{F} = \int_{\mathcal{R}} \Psi \, dv + \int_{\mathcal{S}} \psi \, da} \qquad \boxed{\frac{\delta \mathcal{F}}{\delta \mathcal{S}} = 0}$$

$$\boxed{\psi K - \mathrm{div}_{\mathcal{S}}\left(\frac{\partial \psi}{\partial \mathbf{m}}\right) + \mathbf{m}\cdot\left\{\Psi \mathbf{1} - (\mathrm{grad}\, \boldsymbol{n})^{\top} \frac{\partial \Psi}{\partial(\mathrm{grad}\, \boldsymbol{n})}\right\}\mathbf{m} = 0}$$




$$K = -\mathrm{div}_{\mathcal{S}}\mathbf{m}$$

## Limitations of the variational paradigm

- Predicated on the provision of constitutive equations ...

- Restricted to equilibrium ...

## Benefit of the variational paradigm

- Indicates the number and variety of balances needed for a closed dynamical theory that accounts for dissipation ...

## Configurational forces and their balance

- The idea of configurational forces surfaced during the 1950s in the works of Herring, Eshelby, and Peach & Koehler ...

- Configurational forces are related to the integrity of the material structure ...

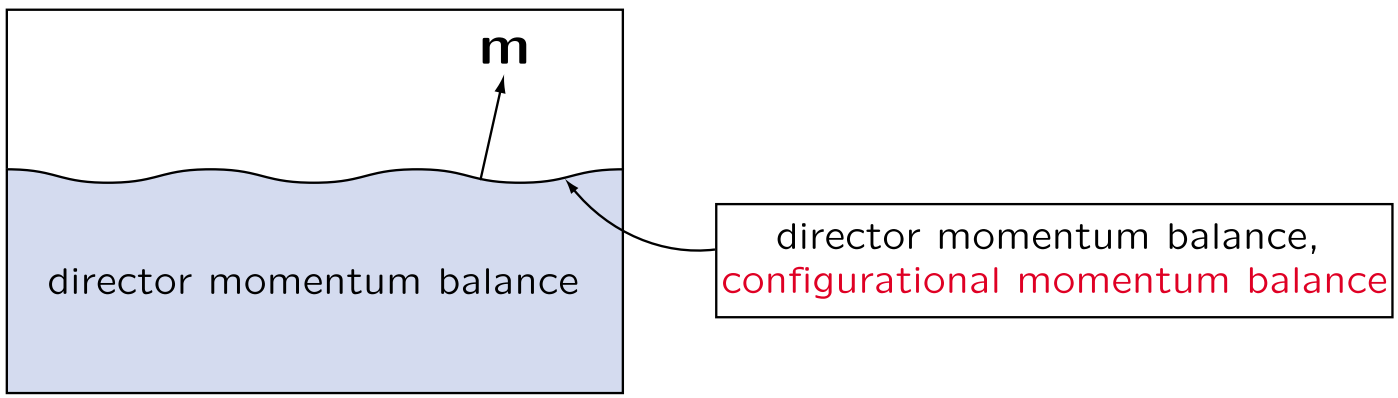
- Configurational forces expend power over the motion of non-material defects with respect to the underlying material ...

- The role of configurational forces in the evolution of defects, such as dislocations, cracks, and phase interfaces, in materials like crystalline solids that are most naturally described in the referential setting is relatively well-understood ...

- The role of configurational forces in the evolution of defects in materials that are most naturally described in the spatial setting is almost entirely unexplored ...

## Simple theory neglecting flow

- P. Cermelli, E. Fried & M. E. Gurtin, Sharp-interface nematic-isotropic phase transitions without flow. *Archive for Rational Mechanics and Analysis* **174** (2004), 151–178.
  - Treat the isotropic phase as a thermal reservoir
  - Measure the free-energy density of the nematic phase relative to that of the isotropic phase




  - Normal velocity of the interface: $V$
  - Total curvature of the interface: $K = -\mathrm{div}_{\mathcal{S}}\mathbf{m}$
  - Cosine of the angle between $\boldsymbol{n}$ and $\mathbf{m}$: $\xi = \boldsymbol{n}\cdot\mathbf{m}$

Director momentum balance in bulk:

$$\boxed{\iota\big(\ddot{\boldsymbol{n}} + |\dot{\boldsymbol{n}}|^2\boldsymbol{n}\big) + \gamma\dot{\boldsymbol{n}} = \mathrm{div}\left(\frac{\partial\widehat{\Psi}}{\partial(\mathrm{grad}\,\boldsymbol{n})}\right) + \left(\mathrm{grad}\,\boldsymbol{n}\cdot\frac{\partial\widehat{\Psi}}{\partial(\mathrm{grad}\,\boldsymbol{n})}\right)\boldsymbol{n} - \frac{\partial\widehat{\Psi}}{\partial\boldsymbol{n}}}$$

Director momentum balance on the interface:

$$\boxed{\beta_1\mathring{\boldsymbol{n}} + \iota V\dot{\boldsymbol{n}} = \frac{d\psi}{d\xi}(\xi\boldsymbol{n} - \mathbf{m}) - \frac{\partial\Psi}{\partial(\mathrm{grad}\,\boldsymbol{n})}\mathbf{m}}$$

Normal configurational momentum balance on the interface:

$$\boxed{\begin{aligned}&(\beta_3 + \beta_2|\mathrm{grad}_{\mathcal{S}}\mathbf{m}|^2)V - \beta_2\mathring{K} + \frac{d\beta_2}{d\xi}\mathrm{grad}_{\mathcal{S}}\xi\cdot\mathring{\mathbf{m}}\\ &\qquad = \psi K - \mathrm{div}_{\mathcal{S}}\left\{\frac{d\psi}{d\xi}(\boldsymbol{n} - \xi\mathbf{m})\right\} - \mathbf{m}\cdot(\mathrm{grad}\,\boldsymbol{n})\mathbf{m}\frac{d\psi}{d\xi} - \Psi + \tfrac{1}{2}\iota|\dot{\boldsymbol{n}}|^2\end{aligned}}$$

## Bulk free-energy density

- F. C. Frank. On the theory of liquid crystals, *Discussions of the Faraday Society* **25** (1958), 19–28.

$$\boxed{\begin{aligned}\Psi = \Psi_0 &+ \tfrac{1}{2}k_1(\mathrm{div}\,\boldsymbol{n})^2 + \tfrac{1}{2}k_2(\boldsymbol{n}\cdot\mathrm{curl}\,\boldsymbol{n})^2 \\ &+ \tfrac{1}{2}k_3|\boldsymbol{n}\times\mathrm{curl}\,\boldsymbol{n}|^2 + \tfrac{1}{2}k_4\Big(\mathrm{tr}\,((\mathrm{grad}\,\boldsymbol{n})^2) - (\mathrm{div}\,\boldsymbol{n})^2\Big)\end{aligned}}$$

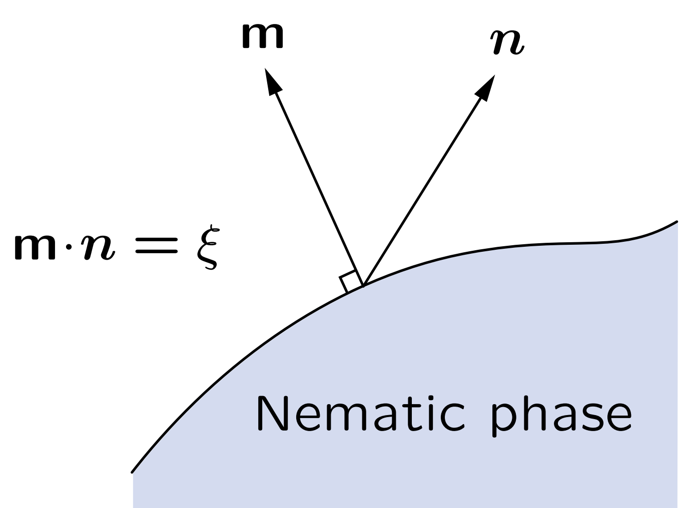
$$10^{-7}\ \mathrm{erg/cm} \lesssim k_i \lesssim 10^{-6}\ \mathrm{erg/cm}$$

## Interfacial free-energy density

- A. D. Rey & M. M. Denn. Dynamical phenomena in liquid-crystalline materials. *Annual Reviews of Fluid Mechanics* **34** (2002), 233–266.

$$\boxed{\psi = \sigma_0 + \sigma_2\xi^2 + \sigma_4\xi^4}$$

$$\sigma_0 \sim 10^{-2}\,\mathrm{erg/cm^2}, \qquad 10^{-4}\,\mathrm{erg/cm^2} \lesssim \sigma_2, \sigma_4 \lesssim 10^{-2}\mathrm{erg/cm^2}$$



## Extrapolation length(s)

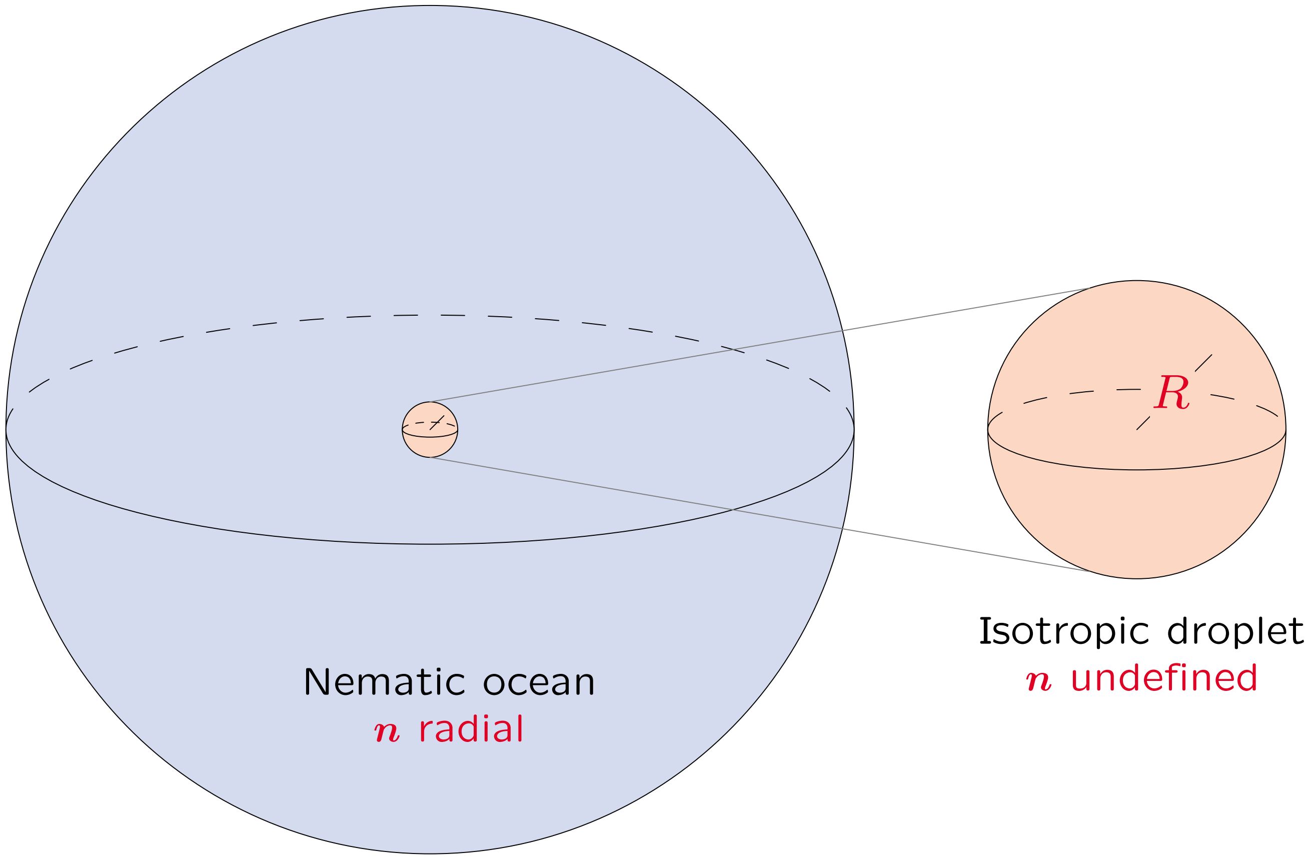
$$\boxed{\ell = \frac{k}{\sigma}}$$

$\ell \sim$ molecular length ... strong anchoring

$\ell \gg$ molecular length ... weak anchoring

- $10^{-7}$ erg/cm $\lesssim k_i \lesssim 10^{-6}$ erg/cm
- $\sigma_0 \sim 10^{-2}$ erg/cm$^2$
- $10^{-4}$ erg/cm$^2 \lesssim \sigma_2, \sigma_4 \lesssim 10^{-2}$erg/cm$^2$
- molecular length $\sim 1$ nm $= 10^{-7}$ cm

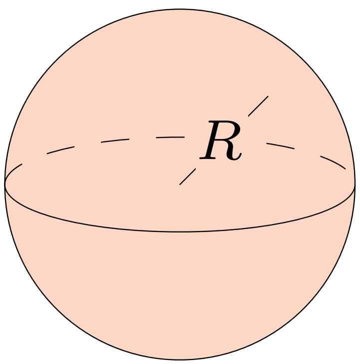
## Application: Sphericial isotropic droplet in a nematic ocean




Sole nontrivially satisfied equation (configurational balance!):

$$\boxed{\beta_3 \dot{R} = \Psi_0 - \frac{2\sigma}{R} + \frac{\kappa}{R^2}} \qquad \kappa = 2k_1 - k_2 - k_4 > 0, \quad \sigma = \psi(1) > 0$$

## Equilibria




Isotropic droplet

| | |
|---|---|
| $\Psi_0 < 0$ | $R_* = \left(\sqrt{1 + \frac{\kappa\lvert\Psi_0\rvert}{\sigma^2}} - 1\right)\frac{\sigma}{\lvert\Psi_0\rvert}$ |
| $\Psi_0 = 0$ | $R_* = \frac{\kappa}{2\sigma}$ |
| $0 < \Psi_0 < \frac{\sigma^2}{\kappa}$ | $R_*^{\pm} = \left(1 \pm \sqrt{1 - \frac{\kappa\Psi_0}{\sigma^2}}\right)\frac{\sigma}{\Psi_0}$ |
| $\Psi_0 = \frac{\sigma^2}{\kappa}$ | $R_* = \frac{\sigma}{\Psi_0} = \frac{\kappa}{\sigma}$ (unstable) |
| $\Psi_0 > \frac{\sigma^2}{\kappa}$ | $R_* \to \infty$ |

## Results

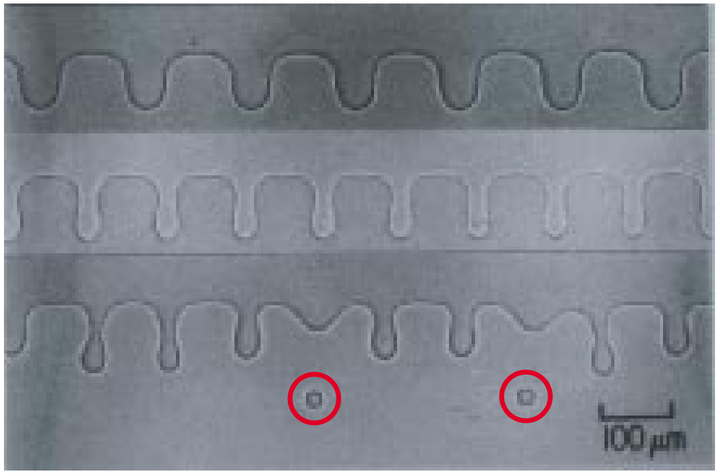
- Suppose that $\Psi_0 < \sigma^2/\kappa$, so that the isotropic to nematic transition is not favored. For

$$\kappa \sim 10^{-7}\ \mathrm{erg/cm}, \qquad \sigma \sim 10^{-2}\ \mathrm{erg/cm}^2,$$

the theory yields

$$R_* \sim 10^2\ \mathrm{nm} \approx 100\ \text{molecular lengths.}$$

The theory is effective down to submicron scales!




J. Bechhoefer & J. L. Hutter, *Physica A* **249** (1998), 82–87.

- Suppose that $\Psi_0 > \sigma^2/\kappa$, so that the isotropic to nematic transition is favored.
  - When $R$ is sufficiently small, the ode is well-approximated by
    $$\beta\dot{R} \sim \frac{\kappa}{R^2},$$
    which implies that, in the initial stage of growth immediately following nucleation to a radius $R_0$, the drop radius evolves according to
    $$R(t) \sim \sqrt[3]{R_0 + \frac{3\kappa t}{\beta}}.$$
  - Subsequently, there is an intermediate stage of growth where both terms $-2\sigma/R$ and $\kappa/R^2$ are important.
  - Thereafter,
    $$\beta\dot{R} \sim \Psi_0 - 2\sigma/R,$$

so that

$$R(t) \sim \sqrt{t}$$

and the growth rate is diffusive.

- Finally, for $R$ sufficiently large,

$$\beta \dot{R} \sim \Psi_0$$

and the growth rate is linear.

The theory predicts that a variety of time scales are active during the growth process.

In particular, the growth rate immediately following nucleation is much faster than that associated with the steady growth of sufficiently large inclusions.

- If we considered instead a radially-aligned nematic drop in an isotropic ocean, the foregoing results would be unchanged. (To achieve it all we would need to do is alter a few words and signs ($\mathbf{m}$ would be outward).) The analog of the foregoing result concerning an initial stage of rapid growth followed by steady growth at a slower rate is then consistent with the experiments of:
  - W. Ostner, S.-K. Chan & M. Kahlweit. On the transformation of a liquid crystal (p-Azoxydianisole) from its isotropic to its nematic state, *Berichte der Bunsen-Gesellschaft für physicalische Chemie* **77** (1973), 1122–1126.

- A small isotropic spherical drops in a nematic radially oriented phase may be used to model the core of a radial point defect.
  - The net (bulk plus surface) free-energy in a sphere of radius $\bar{R} > R_*$ containing an isotropic drop is given by

$$4\pi\Big(\tfrac{1}{3}\Psi_0\bar{R}^3 + \kappa\bar{R}\Big) + 4\pi\Big(\sigma R_*^2 - \tfrac{1}{3}\Psi_0 R_* - \kappa R_*\Big),$$

    the first term of which is the bulk energy of a radial point defect and the second term of which is the correction due to the isotropic core. If $\Psi_0 \leq 0$ and

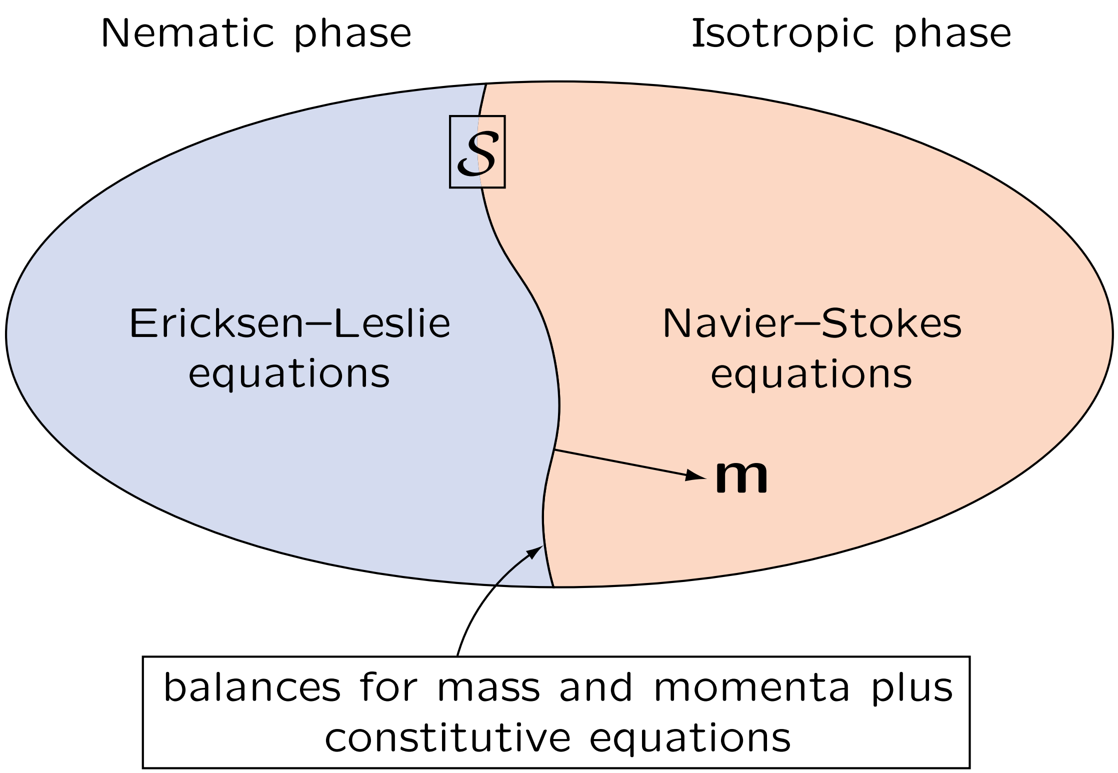
$$R_* = \left(\sqrt{1 + \frac{\kappa|\Psi_0|}{\sigma^2}} - 1\right)\frac{\sigma}{|\Psi_0|} \quad \text{or} \quad R_* = \frac{\kappa}{2\sigma}$$

    a direct calculation shows that

$$4\pi\Big(\sigma R_*^2 - \tfrac{1}{3}\Psi_0 R_* - \kappa R_*\Big) < 0.$$

The theory therefore predicts that the presence of an isotropic core region decreases the free energy stored in the defect.

## Flow-related effects




- Velocity and pressure fields: $\boldsymbol{u}$, $p$
- Specific volume in isotropic phase: $v^+$
- Specific volume in uniaxial nematic phase: $v^-$

$\boxed{[\![v]\!] > 0}$

## Velocity field

$$\boxed{\boldsymbol{u}(\boldsymbol{x},t) = \begin{cases} \mathbf{0}, & |\boldsymbol{x}| < R(t), \\ \dfrac{[\![v]\!] R^2(t)\dot{R}(t)\boldsymbol{x}}{v^+|\boldsymbol{x}|^3}, & |\boldsymbol{x}| > R(t), \end{cases}} \qquad [\![v]\!] > 0.$$

On the interface $|\boldsymbol{x}| = R(t)$:

$$\boldsymbol{u}^-(\boldsymbol{x},t)\cdot\mathbf{m}(\boldsymbol{x},t) = -\frac{[\![v]\!]\dot{R}(t)}{v^+}$$

For a *shrinking drop*, $V = -\dot{R} > 0$ and

$$\boldsymbol{u}^-\cdot\mathbf{m} = [\![v]\!]V/v^+ < V.$$

The theory therefore predicts that a liquid particle on the interface experiences a backflow. (An experimental backflow measurement can therefore be used to estimate $[\![v]\!]/v^+$.)

## Pressure field

Isotropic phase ($|\boldsymbol{x}| < R(t)$):

$$\boxed{\begin{aligned} p^+(t) = \frac{\upsilon^-}{\upsilon^+}\bigg\{p_\infty + \Psi_0 + \frac{[\![\upsilon]\!]}{\upsilon^+\upsilon^-}\bigg\{R(t)\ddot{R}(t) + \bigg(2 - \frac{[\![\upsilon]\!]}{2\upsilon^+}\bigg)\dot{R}^2(t)\bigg\} \\ + \frac{4[\![\upsilon]\!](\mu_1 + \mu_4)\dot{R}(t)}{\upsilon^+ R(t)}\bigg\} \\ + \frac{\langle\!\langle\upsilon\rangle\!\rangle[\![\upsilon]\!]\dot{R}(t)}{\upsilon^+\upsilon^+}\bigg\{\frac{4(\lambda_1 + \lambda_5)}{R^2(t)} - \frac{\dot{R}(t)}{\upsilon^+}\bigg\} - \frac{\lambda_9\dot{R}(t)}{\upsilon^+\upsilon^+} \end{aligned}}$$

Nematic phase ($|\boldsymbol{x}| > R(t)$):

$$\boxed{p(\boldsymbol{x},t) = p_\infty - \frac{\kappa}{|\boldsymbol{x}|^2} + \frac{[\![\upsilon]\!]}{\upsilon^+\upsilon^-|\boldsymbol{x}|}\bigg\{\dot{\overline{R^2(t)\dot{R}(t)}} - \frac{[\![\upsilon]\!]R^4(t)\dot{R}^2(t)}{\upsilon^+|\boldsymbol{x}|^3}\bigg\}}$$

## Normal configurational momentum balance

$$\boxed{\begin{aligned}&\frac{1}{\upsilon^-}\left(\frac{[\![\upsilon]\!]}{\upsilon^+}\right)^2\Bigg\{\underbrace{R\ddot{R}+\frac{3\dot{R}^2}{2}}_{\text{inertia}}+\underbrace{\frac{4\upsilon^-(\mu_1+\mu_4)\dot{R}}{R}}_{\text{bulk rheology}}+\underbrace{\frac{2\upsilon^-(\lambda_1+\lambda_5)\dot{R}}{R^2}}_{\text{interfacial rheology}}\Bigg\}\\ &\qquad+\frac{\lambda_9\dot{R}}{(\upsilon^+)^2}=\Psi_0-\frac{2\sigma}{R}+\frac{\kappa}{R^2}-\frac{[\![\upsilon]\!]}{\upsilon^+}(\Psi_0+\overbrace{p_\infty}^{\substack{\text{ambient}\\\text{pressure}}})\end{aligned}}$$

Compare: $\boxed{\beta_3\dot{R}=\Psi_0-\frac{2\sigma}{R}+\frac{\kappa}{R^2}}$

- For common nematics (such as PAA, MBBA, and 5CB):

$$\boxed{\frac{[\![\upsilon]\!]}{\upsilon^+}\sim 10^{-3}}$$

- Equilibria are influenced by the ambient pressure.
- Dynamics are influenced by inertia and rheological properties.

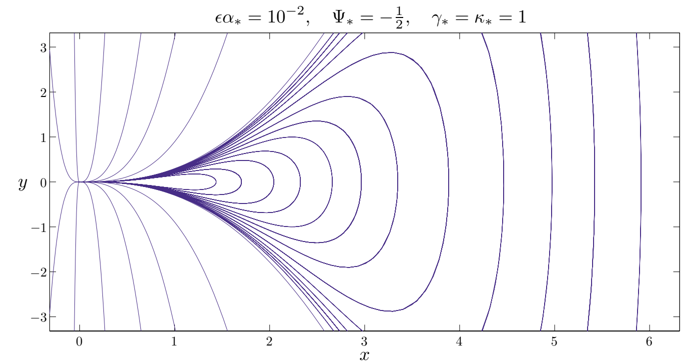
# Hamiltonian case

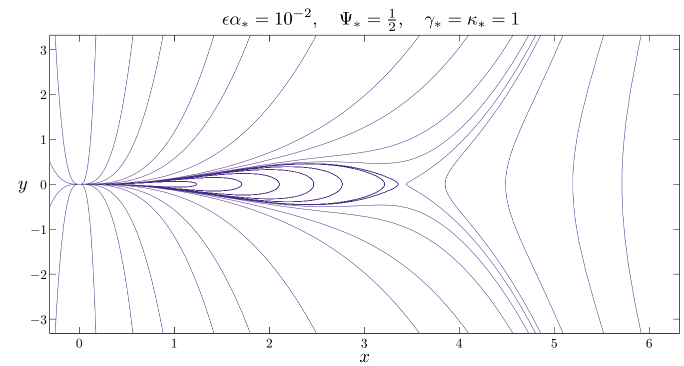
$$\epsilon\alpha_*\left\{r\ddot{r} + \frac{3\dot{r}^2}{2}\right\} = \Psi_* - \frac{2\gamma_*}{r} + \frac{\kappa_*}{r^2}$$

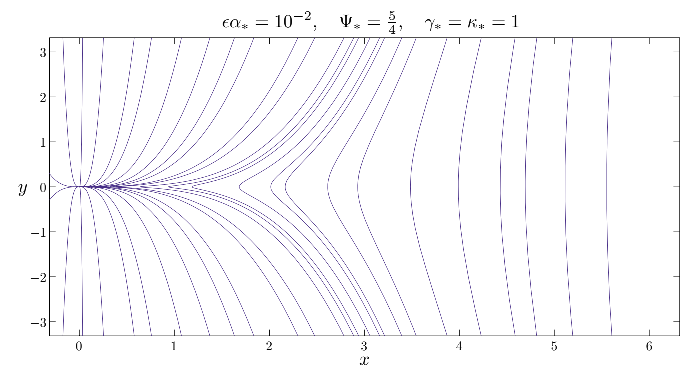
$$x = r, \qquad y = \epsilon\alpha_* r^3 \dot{r}$$

$$H(x,y) = \frac{y^2}{2\epsilon\alpha_* x^3} - \frac{\Psi_* x^3}{3} + \gamma_* x^2 - \kappa_* x$$

$$\dot{x} = \frac{\partial H(x,y)}{\partial y}, \qquad \dot{y} = -\frac{\partial H(x,y)}{\partial x}$$



## Conclusions

- The Ericksen–Leslie theory has been extended to acount for transformations between the isotropic and uniaxial nematic phases of a liquid crystal.
- The theory models phase interfaces as sharp nonmaterial surfaces that are endowed with energy and capable of sustaining stress.
- The theory has been applied to a problem involving the evolution of an isotropic drop, yielding results qualitatively consistent with observations and valid at submicron scales.
- Of key importance in the theory is an additional evolution equation for the interface: this equation expresses the notion of configurational momentum balance.
- Configurational forces arise naturally in problems involving the generation and growth of defects. The approach taken in this work applies to a wide variety of applications involving processes in novel material systems.

## Work in progress

- How does the ambient pressure $p_\infty$ influence stability?
- How do the bulk and interfacial viscosities influence growth?
- What is the correct phase-field regularization of the theory?
  - J. L. Ericksen. Liquid crystals with variable degree of orientation. *Archive for Rational Mechanics and Analysis* **113** (1990), 97–120.

## Future work

- Numerical simulations
  - Three-dimensional instabilities and pattern-formation ...
  - Interactions between interfaces and other defects ...