### Liquid Crystals: Lecture 3 Dynamics

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Support: NSF

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Boulder School for Condensed Matter and Materials Physics, Soft Matter In and Out of Equilibrium, 6-31 July, 2015

#### Outline

- **D**ynamics of director realignment
  - Anisotropy of viscosity
  - Response to ON and OFF field
  - Coupling of director reorientation and flow
- □ Statics of colloids in nematic LC
  - Levitation
- **D**ynamics of colloids in nematic LC
  - Brownian motion
  - LC-enabled electrokinetics
  - Living liquid crystals

#### Anisotropic viscosity

Miezowicz experiments (Nature **136**, 261 (1935); Nature, **158**, 27 (1946)): Fix the director and create shear flow to measure the effective viscosities; the results depend on how the flow, director and velocity gradient are oriented wrt each other



#### Anisotropic viscosity

$$\sigma_{ij} = \alpha_1 n_i n_j n_k n_l A_{kl} + \alpha_2 n_j N_i + \alpha_3 n_i N_j + \alpha_4 A_{ij} + \alpha_5 n_j n_p A_{pi} + \alpha_6 n_i n_p A_{pj}$$
$$\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \qquad A_{ij} = A_{ji} = \frac{1}{2} \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \quad \mathbf{N} = \frac{d\hat{\mathbf{n}}}{dt} - \left[ \mathbf{w} \times \hat{\mathbf{n}} \right] \quad \mathbf{w} = \frac{1}{2} \nabla \times \mathbf{v}$$

Viscous stress tensor depends not only on the velocity gradients, but also on the rotation of the director; six viscosity coefficients, five of which are independent; for small distortions, only the three Miezowicz coefficients are relevant

Director dynamics caused by the field and elasticity is described by balance of torques:

$$\begin{bmatrix} \hat{\mathbf{n}} \times \mathbf{h} \end{bmatrix} - \begin{bmatrix} \hat{\mathbf{n}} \times (\gamma_1 \mathbf{N} + \gamma_2 \mathbf{A} \cdot \hat{\mathbf{n}}) \end{bmatrix} = 0 \qquad \gamma_1 = \alpha_3 - \alpha_2 \qquad \gamma_2 = \alpha_6 - \alpha_5$$
  
Molecular field  $h_i = \mu_0^{-1} \chi_a (n_j B_j) B_i - \frac{\partial f_{FO}}{\partial n_i} + \frac{\partial}{\partial x_j} \left[ \frac{\partial f_{FO}}{\partial (\partial n_i / \partial x_j)} \right]$ 

Molecular field and director are parallel in equilibrium

#### **Splay Frederiks Transitions**



#### Dynamics of Frederiks transition

$$K\frac{\partial^2\theta}{\partial z^2} + \varepsilon_0\varepsilon_a E^2\theta = \gamma_1\frac{\partial\theta}{\partial t}$$

Very strong field: 
$$\theta \propto \exp(t / \tau_{on})$$

$$\tau_{on} \approx \frac{\gamma_1}{\varepsilon_0 \varepsilon_a E^2} \cong 0.2 \,\mu \text{s} \quad (E = 10^8 \,\text{V/m}; \, \gamma = 0.1 \,\text{Pa} \times \text{s})$$

~10 ns: Takanashi et al Jpn. J. Appl. Phys. 37, 2587 (1998)



The active field-on time could be fast, but the passive field-off time is several orders of magnitude slower. Practical solution: Synthesis of materials with low viscosity; reduction of cell thickness.

#### Nanosecond electro-optic switching



Degree of nematic ordering is never perfect; scalar order parameter is less than 1. Electric field can be used to modify the order parameter without realigning the director





$$\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} < 0$$

Electro-optic switching of a NLC with response time <100 ns to both <u>field on</u> and <u>field off</u> driving

V. Borshch et al, PRL **111**, 107802 (2013)

#### Flow causes director reorientation: Thermal expansion experiment



Young Ki Kim, Bohdan Senyuk et al, Nature Comm. 3, 1133 (2012)

### Flow causes director reorientation: Thermal expansion experiment

#### Thermally expanding state

Density changes with time:

$$\frac{\partial \rho}{\partial t} = -\rho \nabla \cdot \mathbf{v}$$



$$\rho = \rho_0 \left( 1 - \beta \xi t \right)$$

Expansion coeff

Rate of T change

$$v_x \propto \beta \xi x$$
  
Re =  $\rho dv_x / |\alpha_2| \sim 10^{-6}$   
 $\alpha_2 = -0.3 \text{ kg m}^{-1} \text{ s}^{-1}$ 

no-slip,  $v_x = 0$ , and no-penetration,  $v_z = 0$ , at the walls z = 0, d; Stokes eq yields the velocity profile:

$$v_{x} \approx 6\beta\xi x \frac{z}{d} \left(1 - \frac{z}{d}\right)$$
$$K_{3} \frac{\partial^{2}\theta}{\partial z^{2}} + \alpha_{2} \frac{\partial v_{x}}{\partial z} = 0$$

$$\theta(z) = \beta \xi x z \frac{(-\alpha_2)}{K_3} \left(1 - \frac{z}{d}\right) \left(1 - \frac{2z}{d}\right)$$

9 Young Ki Kim, Bohdan Senyuk et al, Nature Comm. 3, 1133 (2012)

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- Dynamics of colloids in nematic LC
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  - LC-enabled electrokinetics
  - Living liquid crystals

### Colloid in isotropic fluid: sedimentation, **Brownian motion**, electrophoresis

Gravity vs. Brownian motion determines the probability of finding the particle at height z:  $p(z) = \exp\left(-m^*gz / k_BT\right)$ Gravitation length:  $z_{gr} = \frac{3k_BT}{4\pi R^3 g \Lambda \rho}$ 

Lekkerkerker HNW & Tuinier R (2011) Colloids and the Depletion Interactions (Springer).

Colloid: a particle no larger than gravitation length,  $R \le z_{or}$ ; typically <1 µm

Electrophoresis: Motion of a charged particle in a fluid under the action of a (uniform) electric field:  $\mathbf{v} = \mu \mathbf{E}$ 



This work: What would happen in a LC?



#### Particles in LC

The director tries to follow an "anchoring direction", say, normal to the interface; the resulting distortion competes with the uniform director away from the particle



#### 2D .....and 3D Microscopy



Perpendicular anchoring, bipolar director distortions

Tangential anchoring, Quadrupolar director distortions



Vertical cross-section of the cell, 3D fluorescence confocal polarizing microscopy; density of glass is 2.5 higher than density of LC, thus the sphere is expected to be seen at the bottom, not in the middle

Pishnyak et al, PRL 99 (2007)

#### LC-enabled levitation



Gravity force:  $F_{gr} = \frac{4}{3} \pi R^3 \Delta \rho g$ Elastic dipole-wall repulsion  $F_{repulsion} \approx A^2 \pi K \frac{R^4}{z^4}$  $E_{repulsion} \approx 2 \times 10^{-19} \text{ J} \approx 50 k_B T \text{ for } R=1 \text{ } \mu \text{m}$ 

The bigger the particle the higher it levitates in a LC,



Vertical cross-section of the cell, 3D microscopy

$$z_{elastic} \approx \left(\frac{KR}{\Delta \rho g}\right)^{1/4}$$

totally different from the isotropic fluid:

$$z_{gr} = \frac{3k_B T}{4\pi R^3 g \Delta \rho}$$

Pishnyak et al, PRL 2007; 2011

#### Brownian motion is anisotropic



Displacements: zero on average

$$\left< \Delta x \right> = 0; \left< \Delta y \right> = 0$$





MSD at long timescales: follows Einstein-Smoluchowski law derived for isotropic fluids

$$\left\langle \Delta x \right\rangle^2 = 2 D_{\parallel} \tau; \left\langle \Delta y \right\rangle^2 = 2 D_{\perp} \tau$$

but reflecting anisotropy  $D_{\parallel} \neq D_{\perp}$ (Loudet, Hanusse, Poulin, *Science* (2004)) What would happen at time scales shorter than the director relaxation time?

$$\tau_d \sim \gamma R^2 / K \sim (0.1 - 1) \,\mathrm{s}$$

#### Brownian motion is anomalous at short $\boldsymbol{\tau}$

0



Anomalous diffusion in N

Special LC: Zero birefringence and high viscosity,

Normal diffusion in Isotropic

Anomalous diffusion in N:



Turiv et al, *Science* **342**, 1351 (2013)

#### Brownian motion at short time scales

Subdiffusion through internal memory



$$\tau \sim \tau_d \sim \gamma d^2 / \pi^2 K \sim (0.1 - 10) \mathrm{s}$$

Superdiffusion: Fluctuations of the neighborhood









Irrelevant fluctuations

Turiv et al, *Science* **342**, 1351 (2013)

#### Electrophoresis in isotropic melt of LC



#### Electrophoresis in liquid crystal







Strongly nonlinear dependence

$$v = \mu E \pm \beta E^2$$

#### ODL, Lazo, Pishnyak, Nature 467, 947 (2010)

#### AC electrophoresis of spheres in N

### Alternating current (AC) driving



$$\left\langle v \right\rangle_{p>0} = \left\langle \mu E + \beta E^2 \right\rangle = + \left\langle \beta E^2 \right\rangle$$
$$\left\langle v \right\rangle_{p<0} = \left\langle \mu E - \beta E^2 \right\rangle = - \left\langle \beta E^2 \right\rangle$$





ODL, Lazo, Pishnyak, Nature 467, 947 (2010)

What is the mechanism?

...Maybe we could understand better by considering first how electrophoresis works in isotropic fluid

#### Electrokinetics: Classic linear, isotropic fluid

Electrophoresis: Motion of a charged particle in a fluid under the action of a (uniform) electric field.  $\mathbb{E} \rightarrow$ 

The system is electroneutral, but the charges are separated in space, thanks to dissociation of surface groups at the solid-fluid interface The electric field creates a torque on electric double layer, accelerating  $\mathbf{v}$ counter-ions relative to charges at the surface, until the motion is stabilized by the viscous torque, leading to electrophoresis (solid is free to move) or electro-osmosis (solid is immobilized); linear dependence of velocity on the electric fields

#### Problems:

- Only DC can carry the particles; AC produces no net displacement
- Electrode blocking and degradation
- □ Steady flows are difficult to maintain
- Only charged particles can be moved
- □ Motion limited by the field direction
- No vortices

#### Induced charge electrokinetics, isotropic fluids



Dukhin, Murtsovkin, 1970-, 80-, 90-ies; Squires, Bazant, *J. Fluid Mech.* **509**, 217 (2004): Electric field brings electric charges to the polarizable surface and then acts on the induced charge to move it around the sphere:

$$u_{fluid} \propto \rho E \propto (aE) E \propto E^2$$

Charge separation is induced by the field; the same field drives these separated charges; hence Inducedcharge electro-osmosis with velocities proportional to the square of the field



Squires, Bazant, *J. Fluid Mech.* (2006): Broken symmetry of particle leads to asymmetry of flows that enables an induced charge electrophoresis (ICEP); O. Velev et al, PRL 100, 058302 (2008)

$$v_{ep} \propto (aE) E \propto E^2$$

## Charge separation as a necessary condition of electrokinetics

Isotropic electrolyte: Charges are separated thanks to the properties of the particles (electric double layer around a dielectric particle as in linear electrokinetics or induced charge around polarizable particle in nonlinear electrokinetics); the isotropic electrolyte serves to supply the counterions

Liquid crystal electrolyte: Charges are separated in the electrolytic medium regardless of the properties of the particle (that can be dielectric, metal, fluid, etc). Mechanism of charge separation is rooted in anisotropy of electric conductivity and director distortions

#### Anisotropic conductivity: Carr-Helfrich effect of anomalous field orientation



Carr (1969); Helfrich (1969): fluctuative misalignment and conductivity anisotropy separate charges that create a torque acting to realign the director parallel to the original electric field, i.e. in an "anomalous fashion" from the point of view of dielectric anisotropy.

What would happen when the LC is already **predistorted**?

### Colloidal sphere: A source of permanent director distortions



... these distortions separate charges in presence of the electric field



Because ions prefer to move along the director rather than perpendicular to it, positive charge accumulates on left, negative on right. Thus the charges are separated. ... these distortions separate charges in presence of the electric field



Because ions prefer to move along the director rather than perpendicular to it, positive charge accumulates on left, negative on right. Thus the charges are separated.

## ... these separate charges are driven the electric field, which means electro-osmosis!



Because ions prefer to move along the director rather than perpendicular to it, positive charge accumulates on left, negative on right. Thus the charges are separated. The field drives ionic flows ... the flow pattern does not depend on field polarity...



Reversing field polarity reverses the charges but does not change the direction of flows, which is determined by the product of the induced charge and the electric field, thus

 $\rho \propto E$   $u \propto \rho E \propto E^2$ 

#### ... but depends on director gradients



Because ions prefer to move along the director rather than perpendicular to it, positive charge accumulates on left, negative on right.

Tangential surface anchoring; negative charge on left, positive on right; direction of flows is opposite to the particle above!



E

#### Velocity field around Si spheres in N



 $3.0\,\mu\text{m/s}$ 

Normal surface anchoring; flows towards the sphere

Tangential surface anchoring; flows away from the sphere, as expected. The flow pattern is vortex-like despite the fact that the field is uniform; can be used for mixing

F



 $E = 40 \text{ mV/}\mu\text{m}$  f = 5 Hz  $\Delta \varepsilon < 0.001$   $\eta_{\parallel} = 54 \text{ mPa} \cdot \text{s}$   $\eta_{\perp} = 78 \text{ mPa} \cdot \text{s}$ Lazo et al, *Nature Comm.* **5**, 5033 (2014)

# Broken symmetry of director distortions: pumping!

Broken fore-aft symmetry of director should lead to pumping of LC around immobilized particles and electrophoresis of free particles -E



## Broken symmetry of director distortions: pumping around immobilized sphere



Asymmetric director, immobilized sphere: asymmetric flows and pumping along the xaxis:

$$Q_x(x) = \frac{2}{3} h \int_{-y_0}^{y_0} u_x(x, y) dy$$



 $h = 60 \ \mu \text{m} \ 2a = 50 \ \mu \text{m} \ E = 40 \ \text{mV}/\mu \text{m} \ f = 5 \ \text{Hz} \ \Delta \varepsilon < 0.001 \ \eta_{\parallel} = 54 \ \text{mPa} \cdot \text{s} \ \eta_{\perp} = 78 \ \text{mPa} \cdot \text{s}$ 

### Broken symmetry: electrophoresis of free particles



Asymmetric director, free particle: Unidirectional ACdriven electrophoresis with





#### Induced charge and electrokinetic velocities-?

$$\hat{\mathbf{n}} = (n_x, n_y) = (1, \varphi)$$

$$J_i = \sigma_{ij} E_j = (\sigma_\perp \delta_{ij} + \Delta \sigma n_i n_j) E_j ;$$

$$div \mathbf{J} = 0; \quad \varepsilon \varepsilon_0 div \mathbf{E} = \rho$$

$$\rho(x, y) = -\frac{\varepsilon \varepsilon_0 \Delta \sigma}{\sigma} \frac{\partial \varphi}{\partial y} E_x$$



$$f = \rho E$$
 vs  $f_{drag} = \eta u / R^2$ 

$$|u| \approx \frac{\varepsilon \varepsilon_0}{\eta} \frac{\Delta \sigma}{\sigma} R E_x^2$$

Lazo et al, *Nature Comm.* **5**, 5033 (2014)

#### Velocity field around Si spheres in N



$$\frac{\left|u^{LC}\right|}{\left|u_{water}\right|} \approx \frac{\varepsilon_{LC} \eta_{water} a}{\varepsilon_{water} \eta_{LC} \lambda_{D}} \sim 10^{2} - 10^{3}$$

EO velocity around a glass sphere in LC is much higher than in water; because the charges are separated over distances ~*a* (*length scale of distortions*) rather than over the Debye length

## What you have learned so far about colloids in LCs...

- LC enables levitation of (large) colloidal particles
- Diffusion: Anomalous with sub- and super-diffusive regimes
- □ LC-enabled electrokinetics, can move uncharged particles, pump LC around immobilized particles and can be steadily driven by an AC field
- Mechanisms of LC-enabled separation of charges rooted in anisotropy of electric conductivity and director distortions

#### Examples of active fluids



Narayan, Ramaswamy, Menon, *Science* (2007): Active granular rods with disclinations and giant number fluctuations

Sanchez, Dogic et al, *Nature* (2012): Active microtubules with flows and disclinations



Review: Marchetti et al RMP (2013)

Activity of building units/consumption and dissipation of energy make the nematic "active", very different from the normal nematic that is uniform at equilibrium

#### Living Liquid Crystals

 $\Box$  Living liquid crystals=*Chromonics*+*B*. *Subtilis* 



Chromonics

Bacillus subtilis

Motivation: The system allows one to control orientational order and activity separately

- Orientational order modifies bacterial behavior
- Bacterial activity modifies orientational order

Collaboration with Igor Aranson at Argonne Natl Lab

#### Living LC: Individual bacteria follow $\hat{\mathbf{n}} = const$

Low concentration of bacteria (c<10<sup>14</sup> /m<sup>3</sup>)



Bacteria swim along the director, similar to observations by T. Galstian et al, Mol. Cryst. Liq. Cryst (2013) and N. Abbott et al, Soft Matter (2014); I. Smalyukh et al PRE 78 030701 (2008) show that the rod like bacteria orient along the director

## Living LC: Individual bacteria follow distorted director

Isotropic tactoids

...bacteria follow distorted director of the chromonic N around isotropic tactoids



Rate  $\frac{1}{4}$ 

#### Cargo transport



Bacteria move parallel to the director; if there is an obstacle, bacteria push it forward along the director;

the "cargo transport" effect is impossible in an isotropic fluid, as the bacterium simply pushes the colloid to the side, or swims around

A. Sokolov et al, Phys Rev E **91**, 013009 (2015)

### Living LC: Individual bacteria distorts LC









Flagella rotation:16 Hz Body rotation: *f*=2.5 Hz

The rotation is fast enough to make the Ericksen number larger than 1

 $Er = \eta_{eff} frh / K \sim 10$ 

implying that the director is distorted by moving flagella

#### Living LC: Individual bacteria melt LC

Moving bacterium can also change the scalar order parameter, melting the material and forming isotropic droplets-tactoids in its wake ("Wilson chamber")



Rate  $\frac{1}{2}$ 

### Living LC: Collective effects, Bend stripes

No oxygen; equilibrium state of uniform director

Added oxygen; director undulations

Higher concentration of bacteria ( $c_B \sim 10^9 / \text{cm}^3$ )





Oxygen supplied from the left hand side

### Living LC: Collective effects, Bend stripes



High concentration of bacteria, addition of oxygen: periodic undulations with a characteristic spatial scale that depends on  $c_B$ , amount of oxygen, etc.



Oxygen supplied from the left hand side, rate 100

#### Bending: Activity vs Elasticity

Spatial scale: balances viscous shear (bacterial) and elastic (LC) torques



## Higher activity: Bend stripes replaced by disclination pairs



As activity increases, the uniform state (1) undulates, then (2) nucleates disclination pairs Similar 2 stage scenario is seen in numerical simulations of active matter: Thampi et al, EPL (2014); Shi, Ma, Nature Comm (2013)



#### What have you learned

- □ LC: anisotropic viscosity
- □ Flow realigns director, director realignments cause flow
- □ LC-enabled electrokinetics:
  - Anisotropy of conductivity separated charges in a distorted LC; bulk charge driven by the electric field leads to electro-osmosis and electrophoresis with velocities growing as the square of applied field;
  - Broken symmetry of the LC director distortions produce unidirectional AC-driven pumping around immobilized particles or unidirectional AC-driven electrophoresis of free particles
- □ Living LCs:
  - Non-uniform director guide bacteria along predesigned trajectory
  - Bacteria can transport cargo when placed in the LC
  - Activity increase cause two-step transition: first to banding/stripe instability, then to topological turbulence with nucleating and annihilating pairs of disclinations