Liquid Crystal Colloids: Functionalization of Inclusions and Continuum

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Support of the EC under the Marie Curie project ACTOIDS is acknowledged. The contents reflect only the author’s views and not the views of the EC.
Outline

@ introduction
@ theory and modeling
@ functionalization of inclusions: role of shape, Janus surface anchoring profile, topological charge, surface structure
@ functionalization of continuum: material activity and confinement
@ conclusion
**Introduction - Colloids: Assembly**

Various types of materials and (self)assembly:

**Droplets: Phase separation**

![Image of droplets phase separation](image)


**Droplets: Surface trapping**

![Image of droplets surface trapping](image)


**Solid beads: Optical tweezers**

![Image of optical tweezers](image)


**Solid beads: Electrophoresis**

![Image of electrophoresis](image)

Introduction - Nematodynamics & Activity

Materials have internal motility (e.g. swarms of bacteria):

- Nematodynamics

Design flow states
Bio-patterns

Kibble mechanism; Defect dynamics

Dombrowski et al, PRL 2004
Dreyfus et al, Nature 2005

FIG. 1. Bioconvection in a sessile drop of diameter 1 cm. Top: images 5 min apart show the traveling-wave bio-Boycott convection that appears first at the drop edge. Bottom: images 2 min apart show self-concentration seen from above, beginning as vertical plumes which migrate outward.
Order parameter tensor:

\[ Q_{ij} = \frac{S}{2} (3n_in_j - \delta_{ij}) + \frac{P}{2} (e_i^{(1)} e_j^{(1)} - e_i^{(2)} e_j^{(2)}) \]

I. Equilibrium physics of static NLC

\[ F = \frac{1}{2} L \int_{LC} \left( \frac{\partial Q_{ij}}{\partial x_k} \right) \left( \frac{\partial Q_{ij}}{\partial x_k} \right) dV \]
\[ + \int_{LC} \left( \frac{1}{2} A Q_{ij} Q_{ji} + \frac{1}{3} B Q_{ij} Q_{jk} Q_{ki} + \frac{1}{4} C (Q_{ij} Q_{ji})^2 \right) dV \]
\[ + \frac{1}{2} W \int_{Surf.Col.} (Q_{ij} - Q_{ij}^0) (Q_{ji} - Q_{ji}^0) dS \]

Numerical relaxation on cubic mesh:

- **Euler-Lagrange equations**
  \[ \frac{d}{dx_k} \frac{\partial F}{\partial Q_{ij}} - \frac{\partial F}{\partial Q_{ij}} = u_{ij}^{(bulk)} = 0 \]
  \[ \frac{\partial F}{\partial Q_{ij}} \cdot \nu_k = u_{ij}^{surf.} = 0 \]

- **Relaxation algorithm**
  \[ \gamma \frac{d Q_{ij}}{dt} = u_{ij} \]

- **Equilibrium order parameter tensor profile**

5 degrees of freedom: director, degree of order, secondary director, biaxallity

II. Nematodynamics + Activity

Hybrid Lattice Boltzmann algorithm: finite differences for Q dynamics and LB for Navier-Stokes flow dynamics.

\[
(\partial_t + \vec{u} \cdot \nabla)Q - S(W, Q) = \Gamma H + \lambda \Delta \mu Q
\]

Material derivative \(\text{LC alignment in flow (tumbling/aligning)}\)

\[
\rho (\partial_t + u_\beta \partial_\beta) u_\alpha
\]

\[
= \partial_\beta (\Pi_{\alpha\beta}) + \eta \partial_\beta (\partial_\alpha u_\beta + \partial_\beta u_\alpha + (1 - 3\partial_\rho P_0) \partial_\gamma u_\gamma \delta_{\alpha\beta})
\]

Stress tensor \(\text{viscosity possible compressibility}\)

Distribution functions \(f_i\):

\[
\rho = \sum_i f_i, \quad \rho u_\alpha = \sum_i f_i e_{i\alpha},
\]

Streaming and collision:

\[
f_i(x + e_i \Delta t, t + \Delta t) - f_i(x, t) = \frac{1}{2} \Delta t [C_{f_i}(x, t, \{f_i\}) + C_{f_i}(x + e_i \Delta t, t + \Delta t, \{f_i\})]
\]

\[
C_{f_i}(x, t, \{f_i\}) = -\frac{1}{\tau_f} (f_i(x, t) - f_i^{\text{eq}}(x, t, \{f_i\})) + p_i(x, t, \{f_i\})
\]

Numerical parameters and characteristics:

- coupled cubic mesh (10nm and 100nm)
- parallel multi-thread computer code
- typical number of mesh points:
  few 100 x few 100 x few 100 = few $10^7$ (max: 600 x 600 x 600 = $2 \times 10^8$)
- basic parameter values: $\xi_N = 6.63$nm, $S_{\text{bulk}} = 0.533$, strong surf. anchor.

Nematodynamics vs equilibrium static nematic:

- memory requirements increase by $\sim 10x$
- evaluation time increases by $\sim 10$-100x; (for equal number of evaluation steps)
- crucial coupling of LC and LB time scale (stability)
- activity is effectively introduced by single phenomenological parameter in stress tensor
  \[ \Pi_{\alpha\beta} = \Pi_{\alpha\beta}^{\text{passive}} + \Pi_{\alpha\beta}^{\text{active}} \]
  \[ \Pi_{\alpha\beta}^{\text{active}} = \zeta \Delta \mu Q_{\alpha\beta} \]
  (can be switched-off to yield passive nematodynamics)
Particle shape - ellipsoids

Ellipsoidal particles can break symmetry of the director:

parallel inclination

anti-parallel inclination
Janus particles

Functionalization of particles by surface anchoring design

- Gold deposition
- Planar anchoring
- DMOAP hometropic surfactant

Crossed polars
Opt. microsc.
Retardation plate
Janus particles

Bistability in (meta)stable particle orientations

Energy minima can be tuned by relative surface anchoring strengths.

Possible application: light shutter
"Higher-order" Janus particles

Particles with homeotropic/planar surface patches:

Structure: tiles of director corresponding to relevant surface patches.

Controllable torques and equilibrium orientation.

(e) Free energy ($10^5 kT$) vs. Symmetry axis angle (°)
By generalizing topological anchoring profile, spherical particles with higher-than-one topological charge can be designed:
Topological charge 2 particles

Two possible compensations:

Bonuses: director is analytically given at the particle surface hence it changes can be analytically followed along the full loop.
**Tuning interparticle potential**

Elastic dipoles and quadrupoles

\[
V_{PP}(\mathbf{R}) = \frac{1}{R^8} (1 - 3 \cos^3 \theta)
\]

\[
V_{CC}(\mathbf{R}) = \frac{1}{R^8} (9 - 90 \cos^2 \theta + 105 \cos^4 \theta)
\]

**I. Particle shape / director symmetry**

![Graph showing force vs. distance for different W values.]

\[ F \propto 1/R^n \]

fit for \( W = 10^{-2} \text{ J/m}^2 \): \( n = 2.02 \)

fit for \( W = 10^{-2} \text{ J/m}^2 \): \( n = 2.1 \)

**II. Confinement**

\[ \nabla^2 n_\mu = 0 \]

\[ n_\mu = \sum_n \sin \left( \frac{n\pi z}{h} \right) \left[ A_n I_n \left( \frac{n\pi}{h} \rho \right) + B_n K_n \left( \frac{n\pi}{h} \rho \right) \right] \]

\[ K_n(x) = \sqrt{\frac{\pi}{2x}} e^{-x} \]
Active flow profiles in planar nematic cell with thickness of 2 μm. 2D in-plane flow profiles:

\[
\begin{align*}
\zeta &= 0.2 \\
\zeta &= 0.3 \\
\zeta &= 0.4
\end{align*}
\]
3D flow profiles are found.

\[ \zeta = 0.001 \quad \text{inplane} \]

\[ \zeta = 0.01 \]

\[ \zeta = 0.1 \]

\[ \text{helical} \]

Activity

Flow can be steared by designing 3D profile of nematic director. Alternatively, orientation can be controlled by imposing flow profile.

--> full backflow coupling between Q and u.
Active liquid crystal colloids

Mechanisms for steering material flow via backflow coupling:

In-situ assembly of microfluidic elements:
Conclusions

Functionalization of particles: shape, surface anchoring, surface profile, topological charge

Functionalization of bulk: activity, flow steering, confinement, colloids

Future work: dynamics and photonics of colloidal structures, active materials.