Mesoscopic Simulation of Flowing Topological Composite Materials

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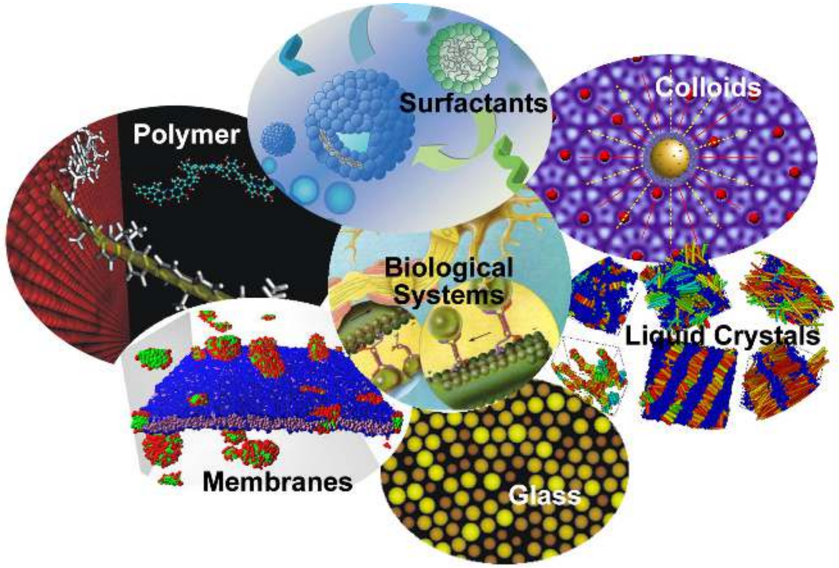
Outline

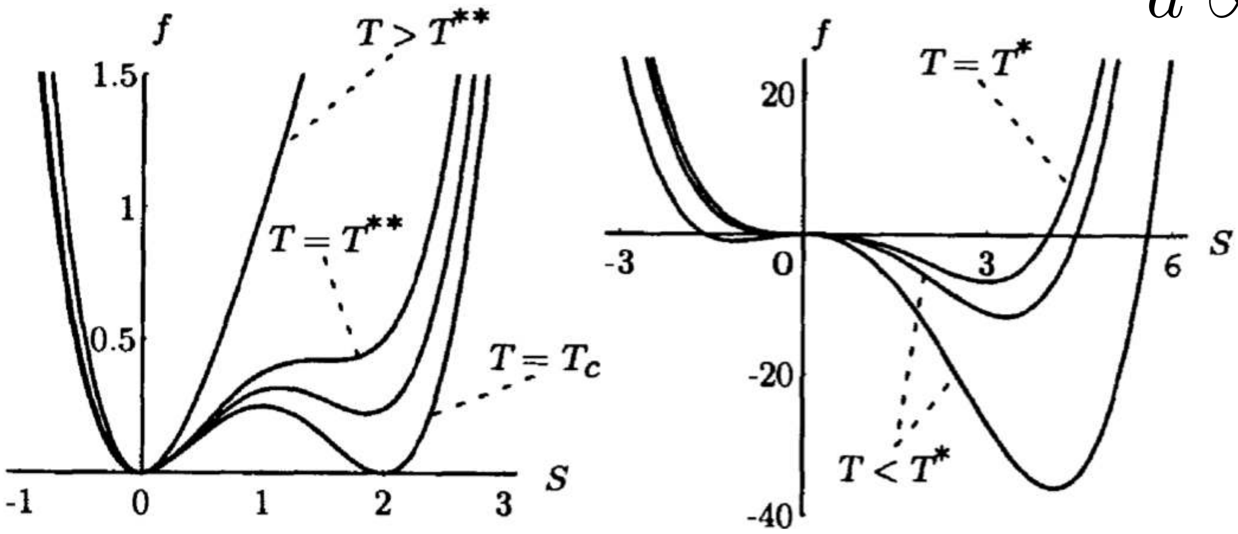


- Soft condensed matter
  - easily ***deformed by thermal fluctuations***
  - ***self-organisation*** into ***mesoscopic*** structures
  - ***macroscopic behaviour*** depends on ***mesoscopic structures***
- **Landau models** for phase transitions and complex fluids
- **Lattice-Boltzmann** simulation method
- **Microfluidics** of **nanoparticle-liquid crystal composite materials**

Landau Theory 1st Order Phase Transition

- **Scalar order parameter** $S \in \mathbb{R}$ measures "the order"
- **Free energy functional** $\mathcal{F}[S] = \int d^3x \left\{ aS^2 - bS^3 + cS^4 \right\}$

$$a \propto (T - T_*)$$

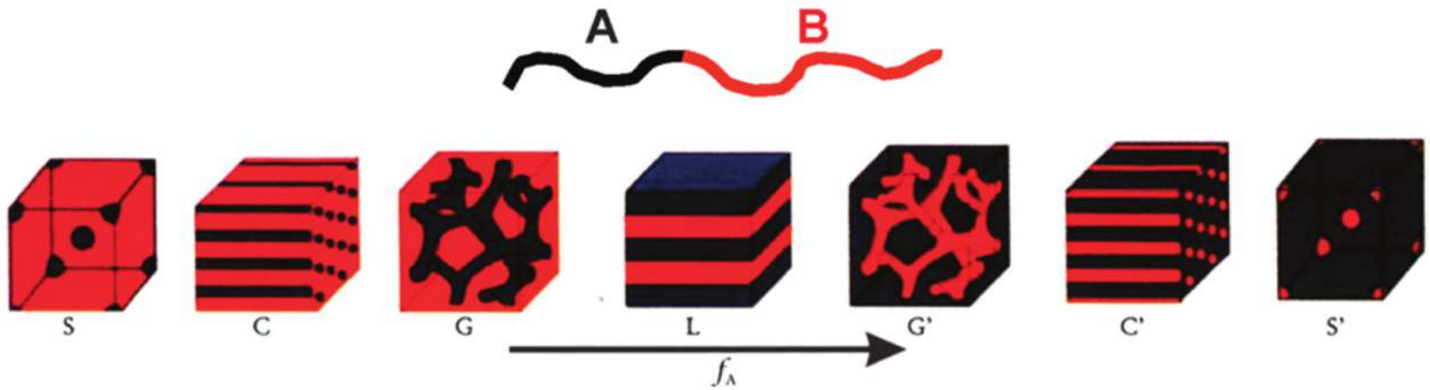


T^*, T^{**} limits of metastability for supercooling and superheating

Discontinuous change of S at T_c

Binary Fluid: Order Parameter

- **Phase-separating** binary liquid: phase *A, B, e.g.* block-copolymers



- **Scalar order parameter** $\phi = \rho_A - \rho_B$ density difference between the two phases

- **Free energy functional**

$$\mathcal{F}[\phi] = \int d^3x \left\{ \frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 + \frac{\kappa}{2}\left(\vec{\nabla}\phi\right)^2 \right\}$$

a, b Landau parameters

κ related to surface tension

Binary Fluid: Dynamics

- **OP dynamics**: advection-diffusion equation

$$\partial_t \phi + \vec{\nabla} \cdot (\vec{u}\, \phi) = M\, \nabla^2 \frac{\delta \mathcal{F}}{\delta \phi} = M\, \nabla^2\, \mu$$

μ chemical potential

M mobility coefficient

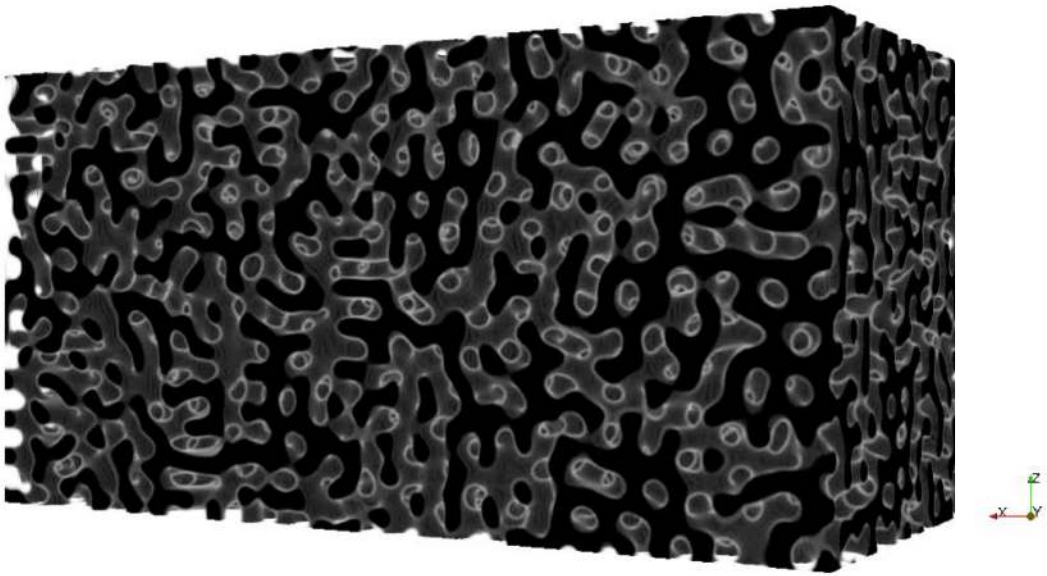
- **HD**: Navier-Stokes equation $\partial_t\, u_\alpha + (u_\beta \nabla_\beta) u_\alpha = \partial_\beta\, \sigma_{\alpha\beta}$

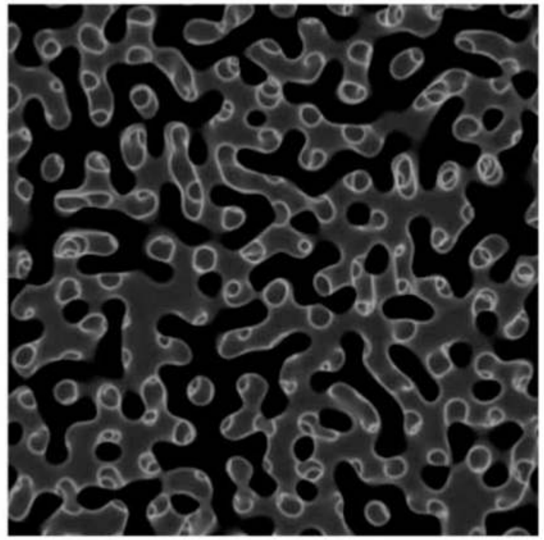
- **Stress tensor** in NSE

$$\sigma_{\alpha\beta} = -p\delta_{\alpha\beta} + \eta(\partial_\alpha u_\beta + \partial_\beta u_\alpha) - P^{chem}_{\alpha\beta}$$

$$P^{chem}_{\alpha\beta} = \kappa(\partial_\alpha \phi)(\partial_\beta \phi)$$ chemical pressure due to composition

Binary Fluid in Shear Flow

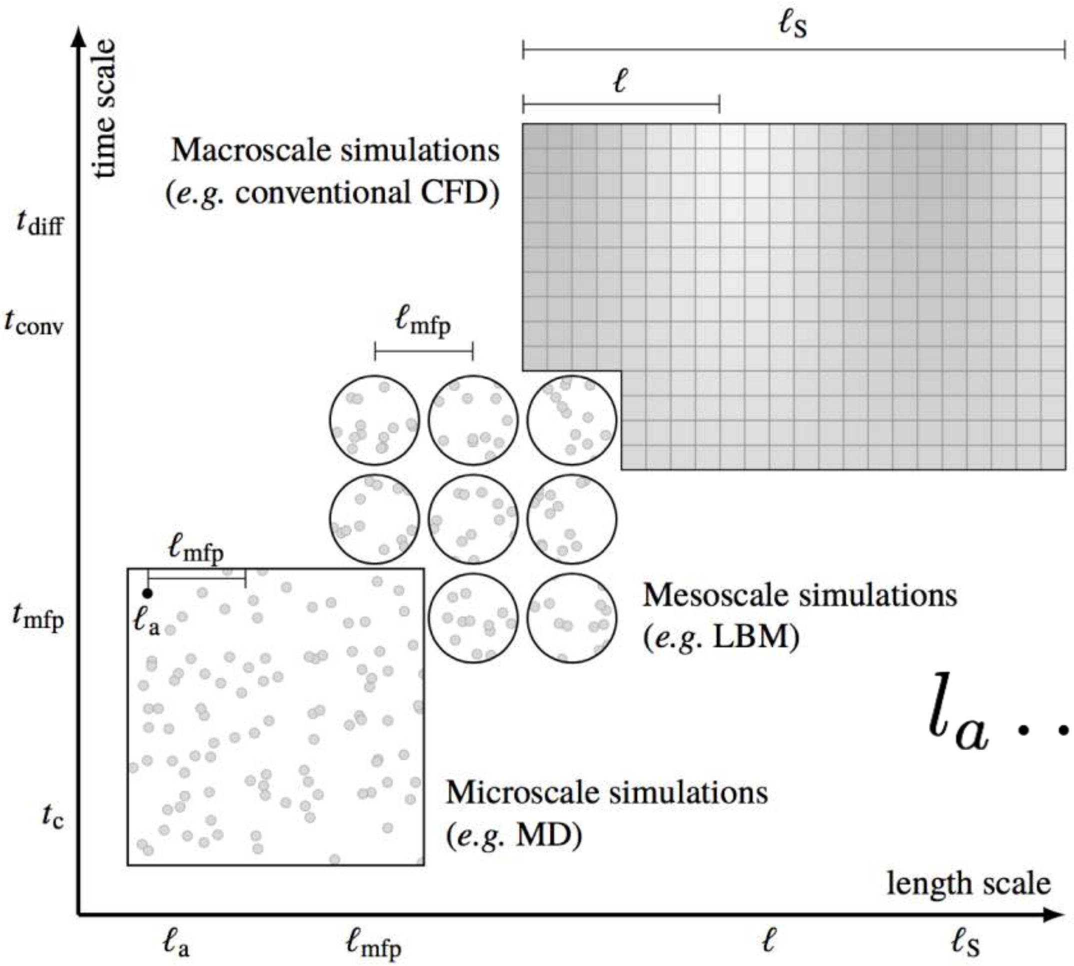




3D: undergoes ordering

2D: forms fluctuating lamellae with spatial heterogeneities

Mesoscopic Simulation Methods



l_s . . . system size

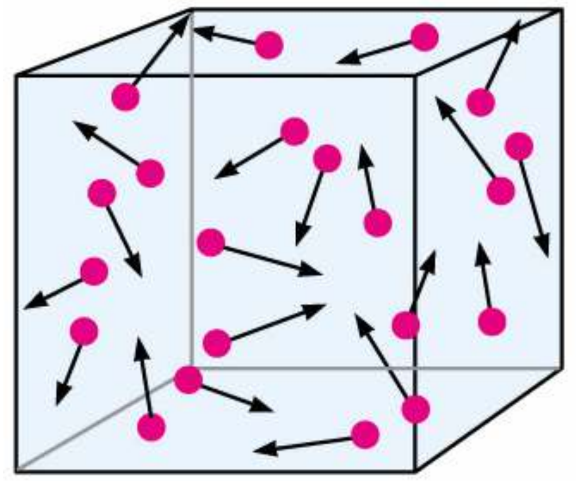
l . . . typical length scale
e.g. gradient

l_{mfp} . . . mean free path

l_a . . . size of atom or molecule

Recent review: Ulf Schiller, Timm Krüger, Oliver Henrich,
Mesoscopic Modelling and Simulation of Soft Matter,
Soft Matter **14**, 9 (2018)

Lattice Boltzmann Method



Probability density function

$$f(\mathbf{r}, \mathbf{p}, t)$$

Kinetic Theory: Boltzmann Equation

$$\partial_t f + \mathbf{u} \cdot \partial_{\mathbf{r}} f + \mathbf{F} \cdot \partial_{\mathbf{p}} f = \Omega[f]$$

Density $$\rho(\mathbf{r}, t) = \int f(\mathbf{r}, \boldsymbol{\xi}, t)\, d^3\xi$$

Momentum $$\rho(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t) = \int \boldsymbol{\xi}\, f(\mathbf{r}, \boldsymbol{\xi}, t)\, d^3\xi$$

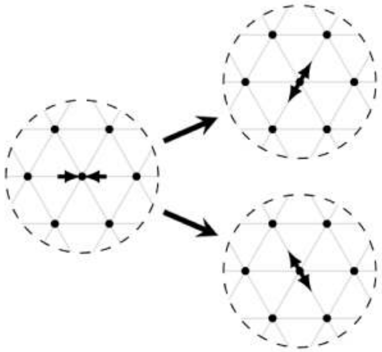
Energy $$\rho(\mathbf{r}, t)e(\mathbf{r}, t) = \int |\boldsymbol{\xi} - \boldsymbol{u}(\mathbf{r}, t)|^2\, f(\mathbf{r}, \boldsymbol{\xi}, t)\, d^3\xi$$

Lattice Boltzmann Method

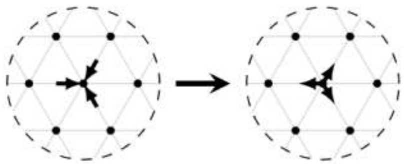
Discretisation of **time**, **configuration** AND **momentum** space

Lattice Gas Cellular Automata

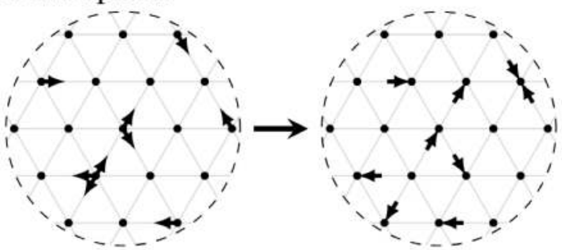
simplified collision rules reproduce HD



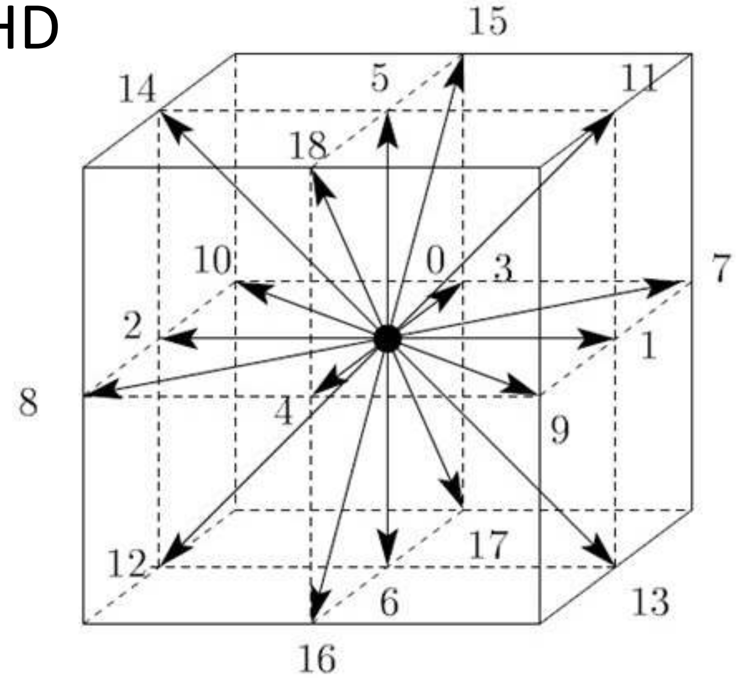
(a) Two-particle collision; the resolution is chosen randomly from the two options



(b) Three-particle collision



(c) Streaming



U.Frisch, B.Hasslacher, Y.Pomeau, *Phys. Rev. Lett.* **56**, 1505 (1986)

Discrete lattice velocities $\mathbf{c}_i$

D3Q19: $i = \{0, \ldots, 18\}$

Lattice Boltzmann Method

Lattice Boltzmann equation: for every discrete velocity $\mathbf{c}_i$

$$f_i(\mathbf{r} + \mathbf{c}_i, t + \Delta t) = f_i(\mathbf{r}, t) + \Omega_i[\{f, f_i^{eq}\}]$$

Continuous analogue of

$$\partial_t f + \mathbf{u} \cdot \partial_{\mathbf{r}} f + \mathbf{F} \cdot \partial_{\mathbf{p}} f = \Omega[f]$$

Collision operator

$$\Omega[\{f_i, f_i^{eq}\}] = \frac{1}{\tau_f}(f_i^{eq} - f_i)$$

$\tau_f \propto \nu$ viscosity

P. Bhatnagar, E. Gross , M. Krook, "A model for collision processes in gases", *Phys. Rev.* **94**, 511 (1954)

Equilibrium distribution

$$f_i^{eq} = \omega_i \, \rho \left(1 + \frac{\mathbf{c}_i \cdot \mathbf{u}}{c_s^2} + \frac{(\mathbf{c}_i \cdot \mathbf{u})^2}{2c_s^4} - \frac{\mathbf{u}^2}{2c_s^2}\right)$$

Lattice Boltzmann Method

1. **Collision** step $f_i^*(\mathbf{r},t) = f_i(\mathbf{r},t) + \Omega_i[\{f, f_i^{eq}\}]$

2. **Streaming** step $f_i(\mathbf{r}+\mathbf{c}_i, t+\Delta t) = f_i^*(\mathbf{r},t)$

or combined $f_i(\mathbf{r}+\mathbf{c}_i, t+\Delta t) = f_i(\mathbf{r},t) + \Omega_i[\{f, f_i^{eq}\}]$

From **distributions** $f_i(\mathbf{r},t)$ to **macroscopic observables**

Density $\rho = \sum_i f_i$

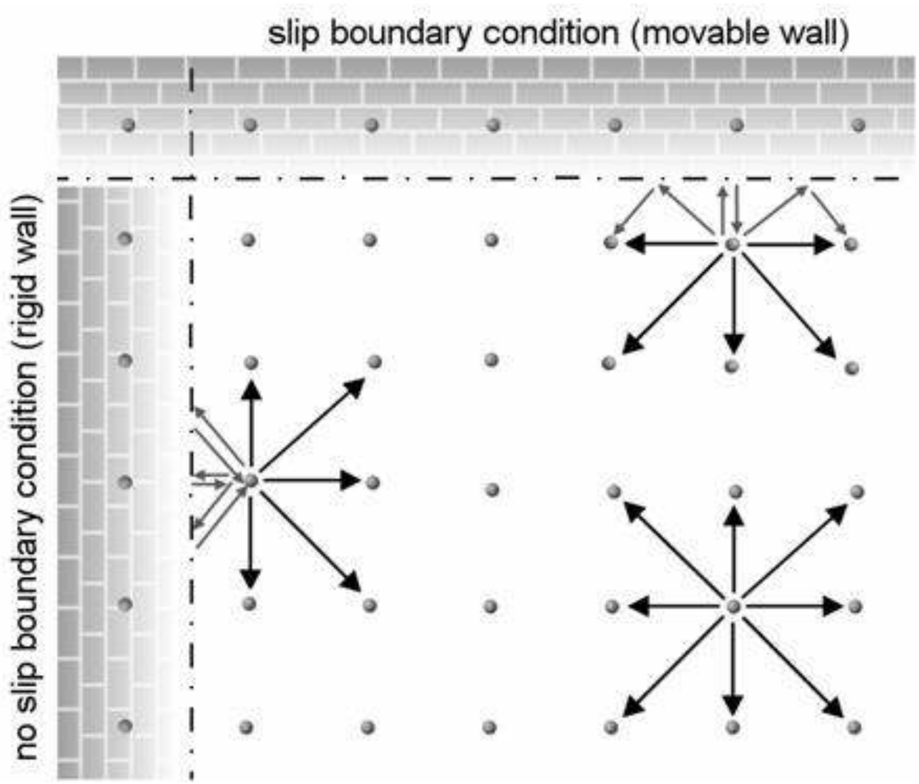
Momentum $\rho\, u_\alpha = \sum_i c_{i,\alpha}\, f_i$

Stress $\sigma_{\alpha\beta} = \sum_i c_{i,\alpha} c_{i,\beta}\, f_i$

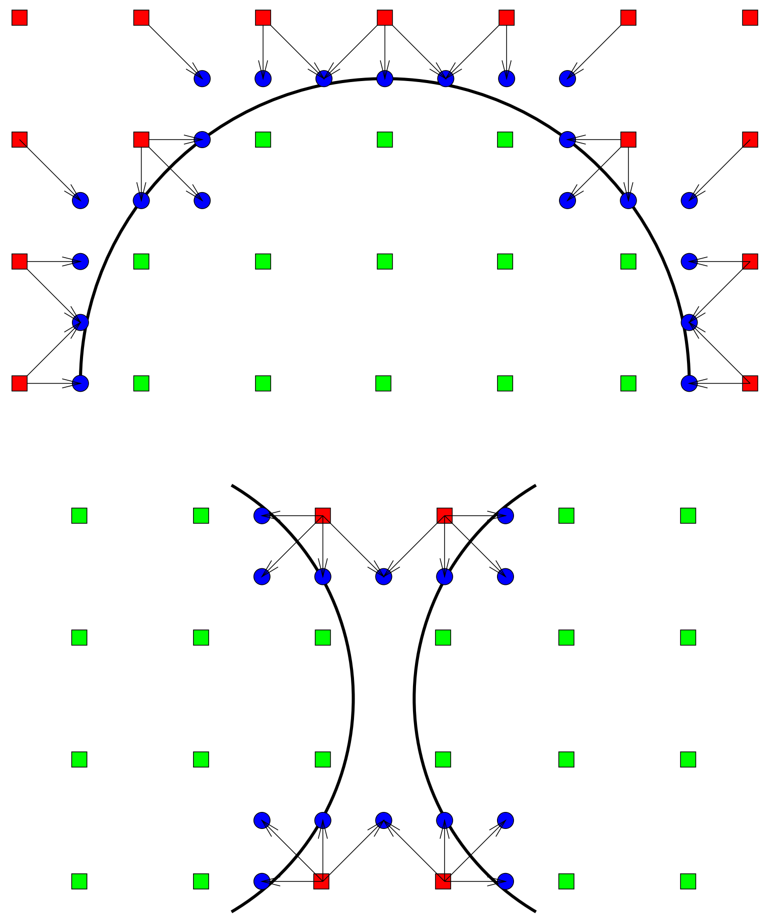
Lattice Boltzmann Method

(Relatively) simple boundary conditions

Walls



Particles

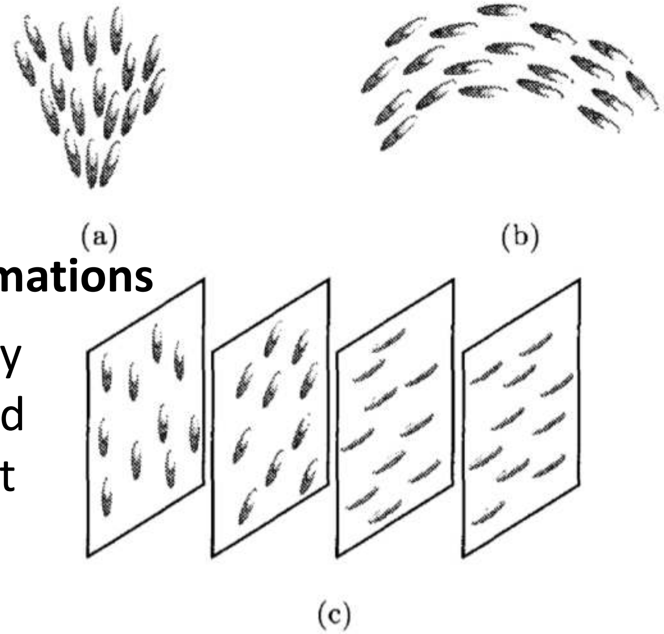


Mesoscopic Description of LCs

- **Unit vector**, aka 'director' $\vec{n} = (n_x, n_y, n_z)$
- **Scalar order parameter** $S \in [0, 1]$
- **Tensor order parameter** $Q_{\alpha\beta} = S\left(n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta}\right)$

Deformations

a) splay
b) bend
c) twist



Landau-de Gennes Free Energy Functional

$$\mathcal{F} = \int d^3r \left(\frac{A_0}{2}\left(1 - \frac{\gamma}{3}\right) Q_{\alpha\beta}^2 - \frac{A_0\gamma}{3} Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \frac{A_0\gamma}{4}(Q_{\alpha\beta}^2)^2 + \frac{K}{2}\left\{(\partial_\alpha Q_{\alpha\beta})^2 + (\varepsilon_{\alpha\mu\nu}\partial_\mu Q_{\nu\beta} + 2q_0 Q_{\alpha\beta})^2\right\} - \frac{\epsilon_a}{12\pi} E_\alpha Q_{\alpha\beta} E_\beta \right)$$

Bulk terms — $A_0 \ldots$ Bulk free energy constant

Elasticity terms — $\gamma \ldots$ Temperature

Coupling to external field — $K \ldots$ Elastic constant

Mesoscopic Description of LCs

EOM of the Q-tensor order parameter (finite difference)

$$(\partial_t + u_\alpha \partial_\alpha)\mathbf{Q} - \mathbf{S}(\{\partial_\beta u_\gamma\}, \mathbf{Q}) = \Gamma\, \mathbf{H}$$

Advection — Order-flow coupling — Molecular field

Molecular field $\mathbf{H} = -\frac{\delta \mathcal{F}}{\delta \mathbf{Q}} + \mathbb{1}/3 Tr \frac{\delta \mathcal{F}}{\delta \mathbf{Q}}$ Rotational diffusion constant Γ

Order-flow coupling

$$\mathbf{S}(\mathbf{W}, \mathbf{Q}) = (\xi \mathbf{A} + \mathbf{\Omega})(\mathbf{Q} + \frac{\mathbb{1}}{3}) + (\mathbf{Q} + \frac{\mathbb{1}}{3})(\xi \mathbf{A} - \mathbf{\Omega}) - 2\xi(\mathbf{Q} + \frac{\mathbb{1}}{3}) Tr(\mathbf{QW})$$

Navier-Stokes & continuity equation (lattice-Boltzmann)

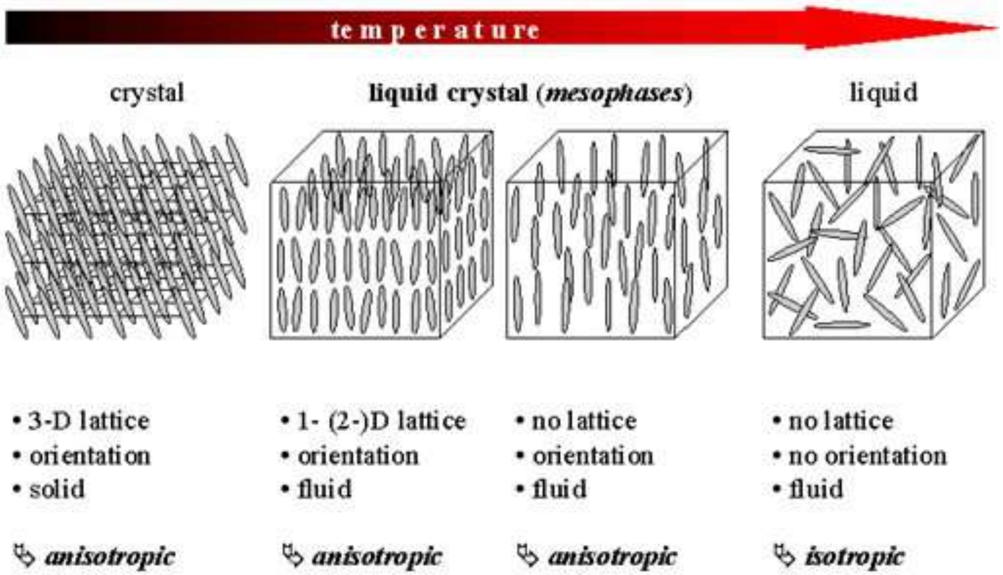
$$\rho\left(\partial_t u_\alpha + u_\beta \partial_\beta u_\alpha\right) = \partial_\beta\left(\sigma^s_{\alpha\beta} + \sigma^a_{\alpha\beta}\right) \quad \partial_\alpha u_\alpha = 0$$

$$\begin{aligned}\sigma^s_{\alpha\beta} \;=\; & -P_0 \delta_{\alpha\beta} + \eta\, \partial_\beta \{\partial_\alpha u_\beta + \partial_\beta u_\alpha\} - \xi H_{\alpha\gamma}\left(Q_{\gamma\beta} + \frac{1}{3}\delta_{\gamma\beta}\right) \\ & -\xi \left(Q_{\alpha\gamma} + \frac{1}{3}\delta_{\alpha\gamma}\right) H_{\gamma\beta} + 2\xi \left(Q_{\alpha\beta} + \frac{1}{3}\delta_{\alpha\beta}\right) Q_{\gamma\nu} H_{\gamma\nu} \\ & -\partial_\alpha Q_{\gamma\nu} \frac{\delta \mathcal{F}}{\delta \partial_\beta Q_{\gamma\nu}}\end{aligned}$$

$$\sigma^a_{\alpha\beta} = Q_{\alpha\gamma} H_{\gamma\beta} - H_{\alpha\gamma} Q_{\gamma\beta}$$

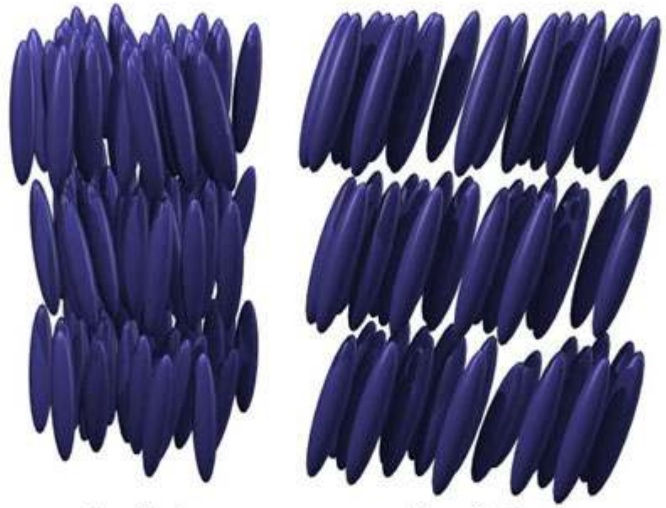
Liquid Crystal Mesophases

Solid, liquid crystal, liquid

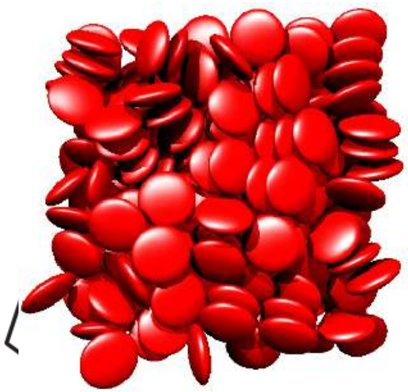


Nematic

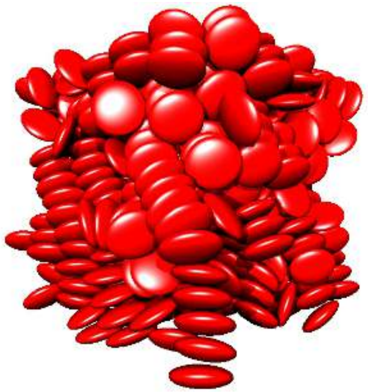
Smectic A & C



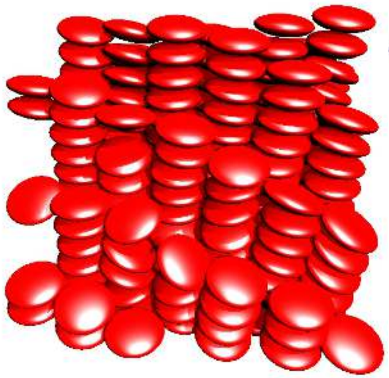
Isotropic

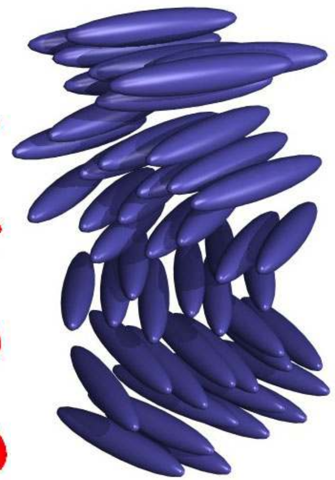


Nematic



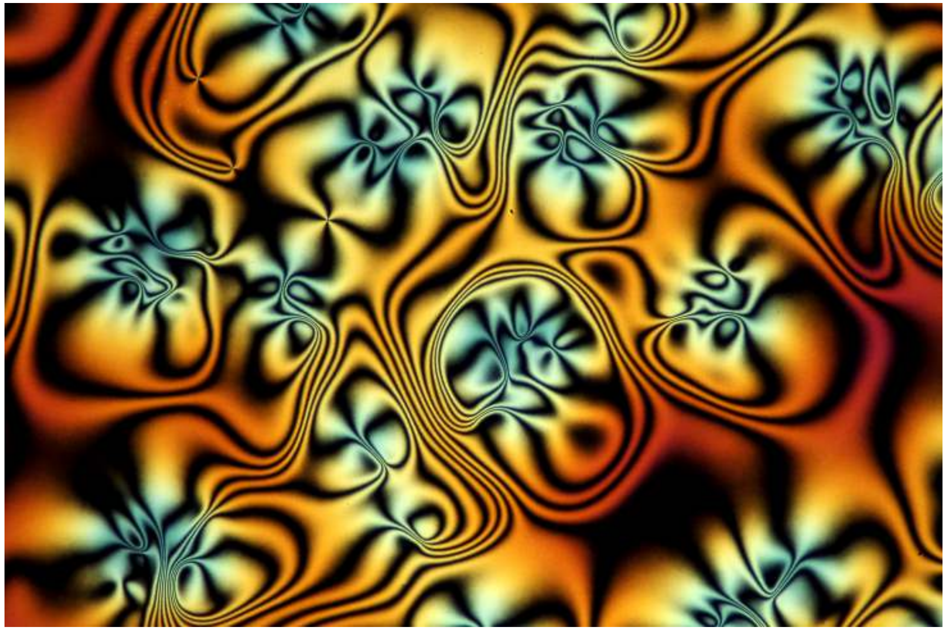
Columnar



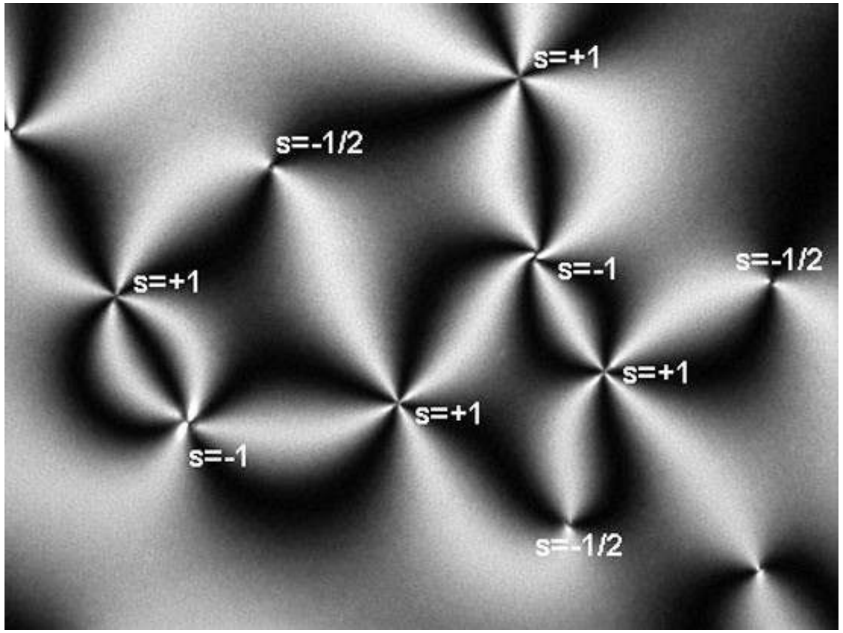


Cholesteric

Liquid Crystals: Topological Defects



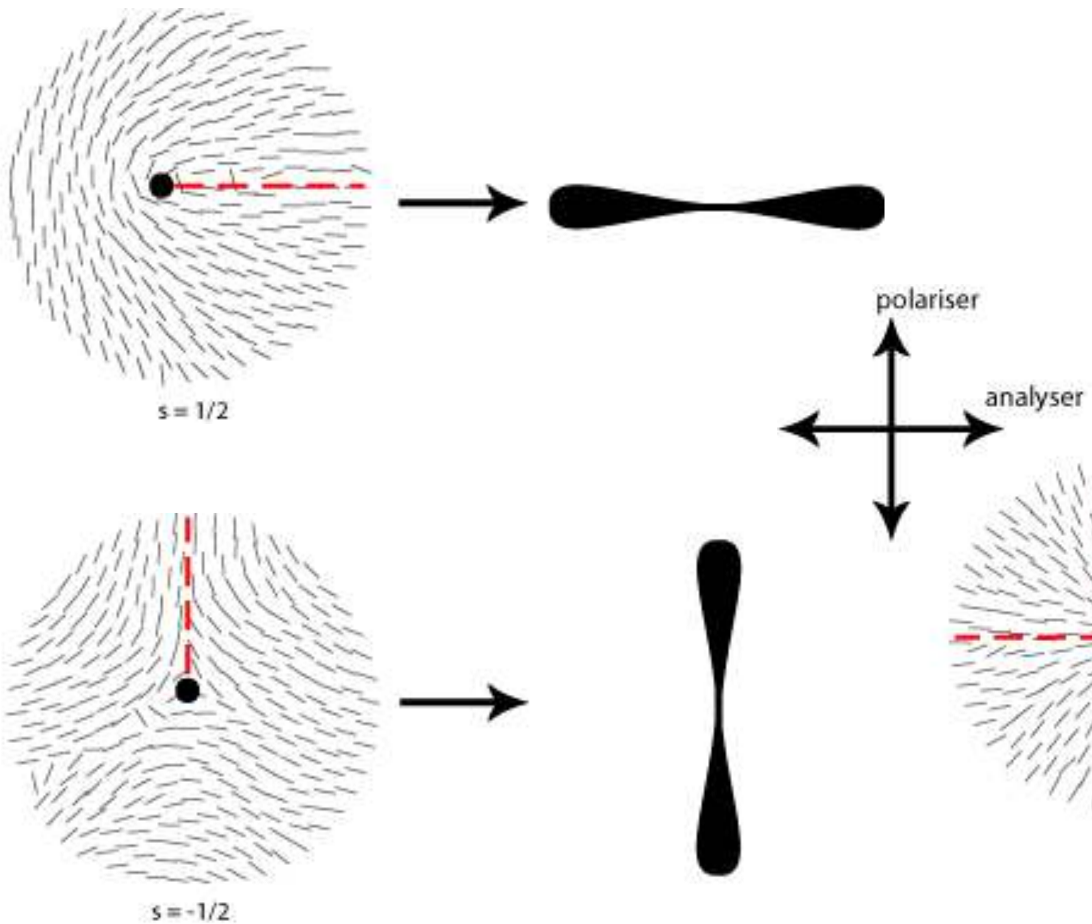
'**Schlieren**' texture in nematic liquid crystals under **crossed polarisers**

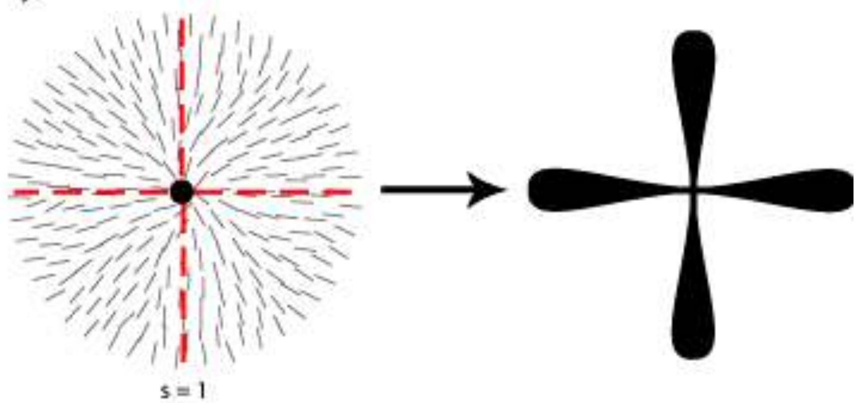


Defects carry a **topological charge**

Liquid Crystals: Topological Defects

Local order structure and appearance in **polarised light microscopy**





Liquid Crystals and Colloids

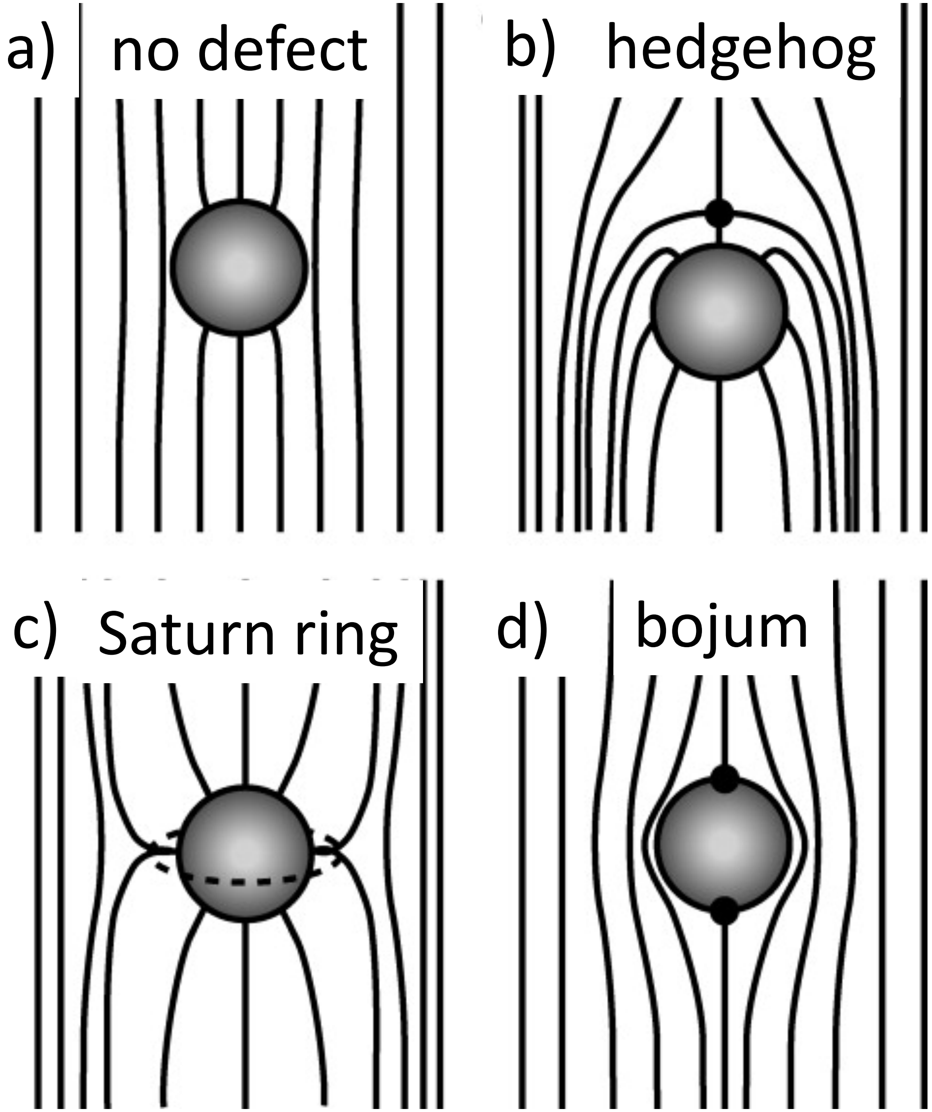
- **Anchoring** (preferred orientation) of the LC on the **particle surface**

- Free energy functional

$$\mathcal{F} = \int d^3r\,(f_{LdG} + f_s)$$

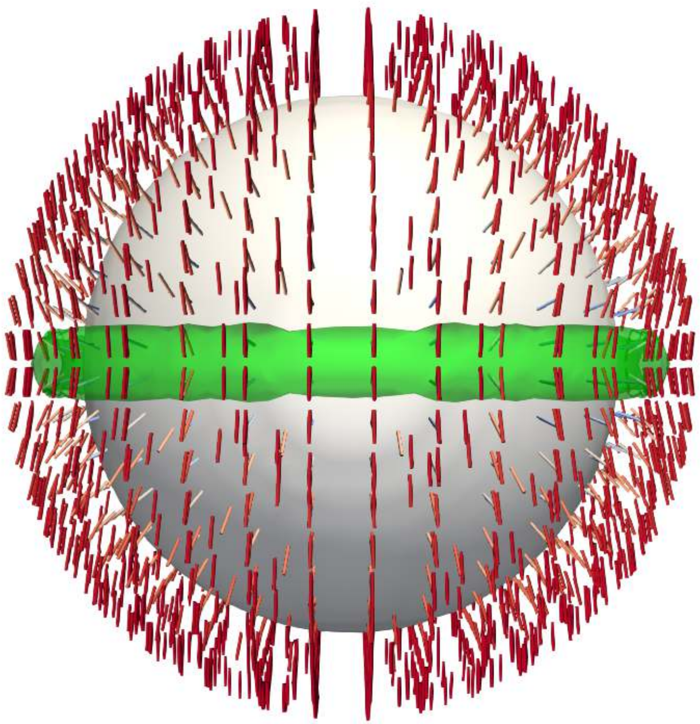
$$f_s = w(Q_{\alpha\beta} - Q^0_{\alpha\beta})^2$$

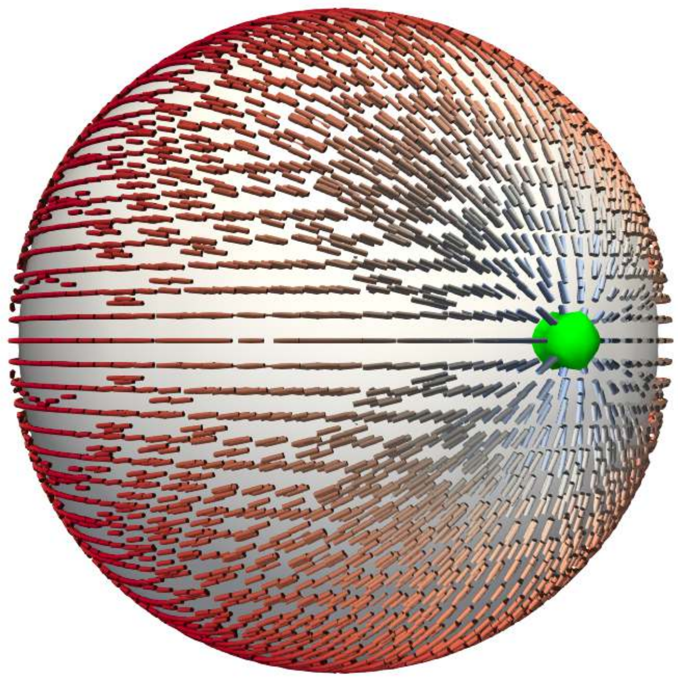
a) weak normal
b) very strong normal
c) normal
d) planar degenerate



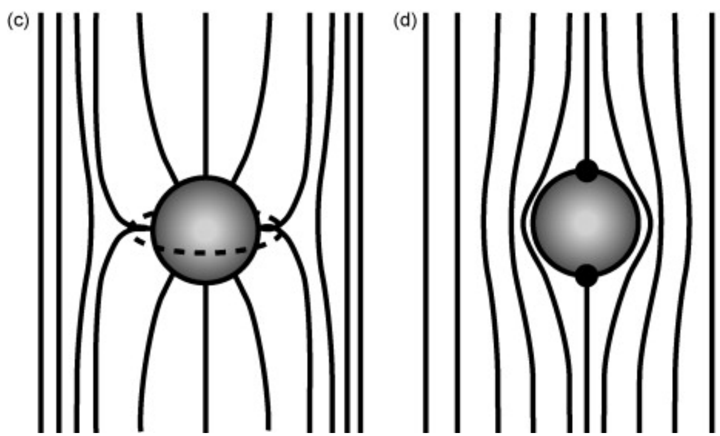
T. Yamamoto et al., *Colloids Surf. A* **334**, 155 (2009)

Liquid Crystals and Colloids





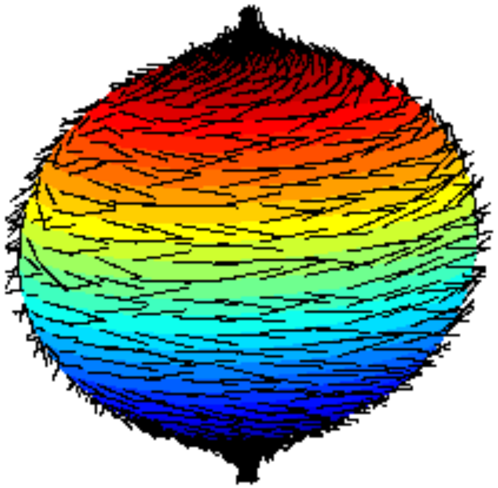
Normal anchoring
Saturn ring defect



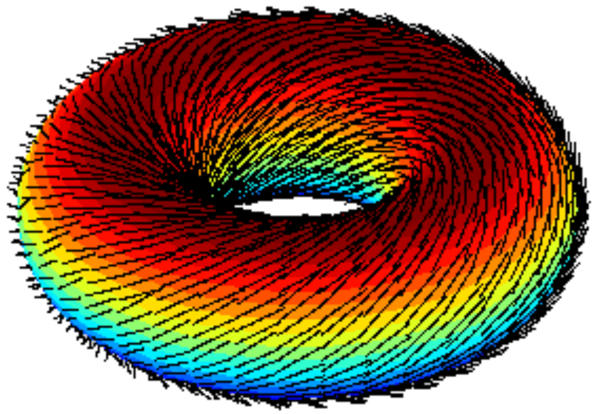
Planar degenerate anchoring
bojum defect

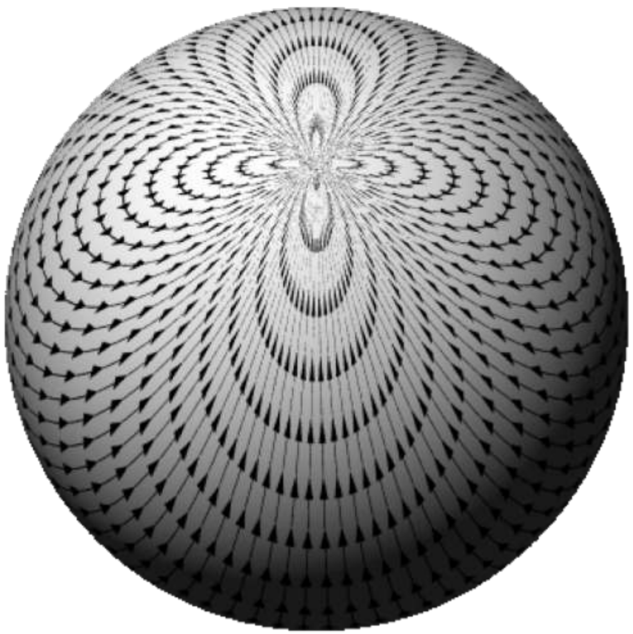
Liquid Crystals and Colloids

Hairy ball or **hedgehog theorem** *(Henri Poincaré, late 19th century)*



no non-vanishing continuous tangent vector field on even-dimensional *n*-spheres





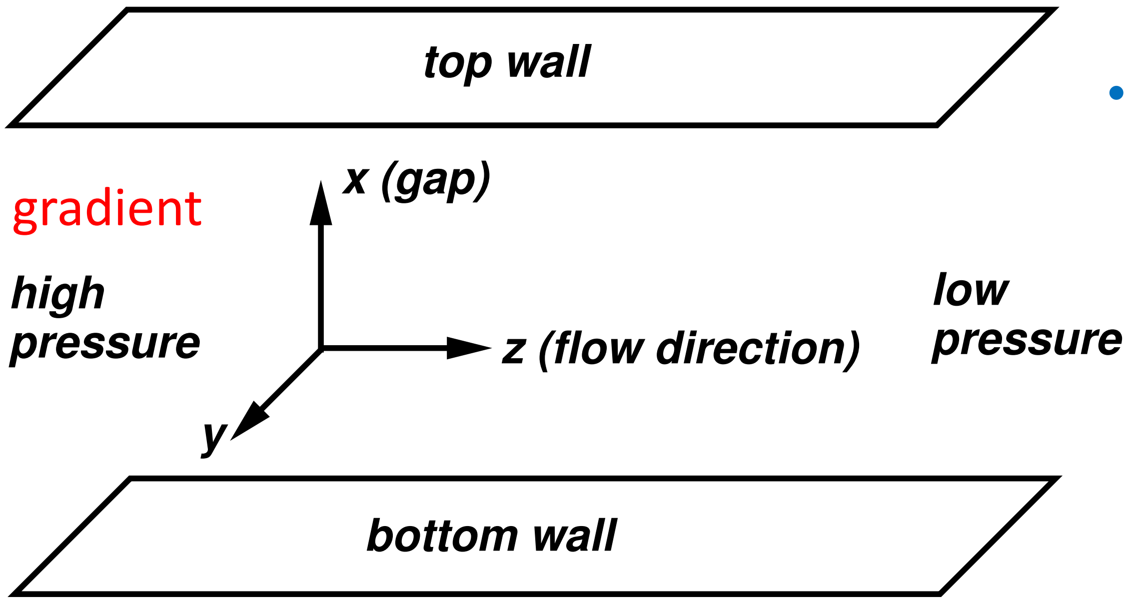
Colloid-LC Composite Material in Flow

Multidimensional parameter space

Particles:

- Volume fraction
- Anchoring type: normal, planar
- Anchoring strength: strong, weak

Pressure gradient

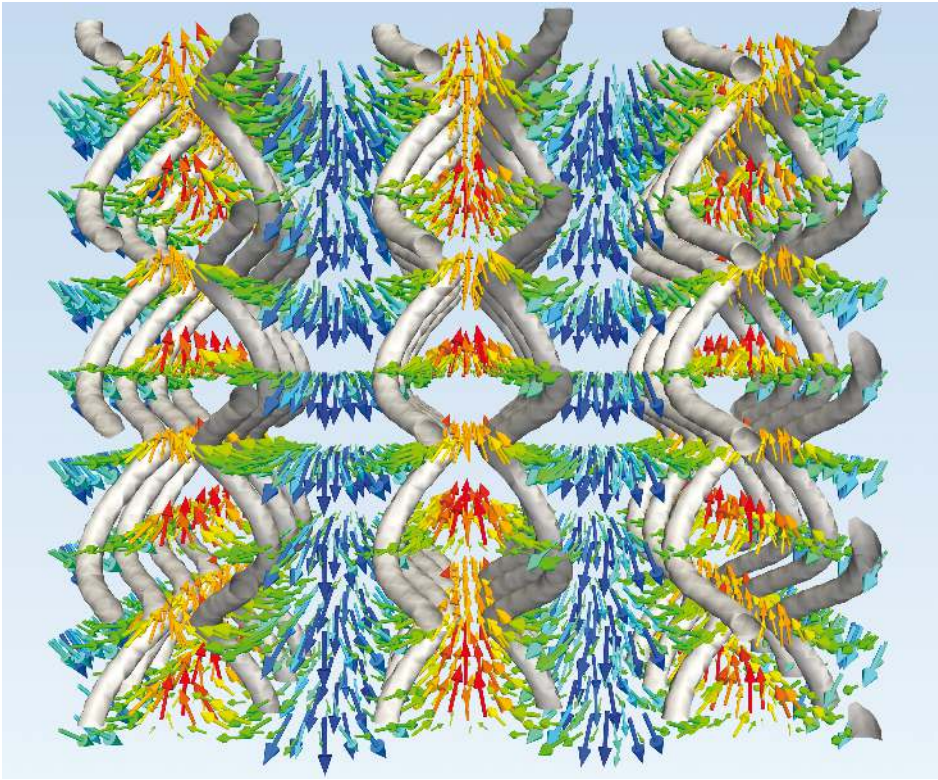


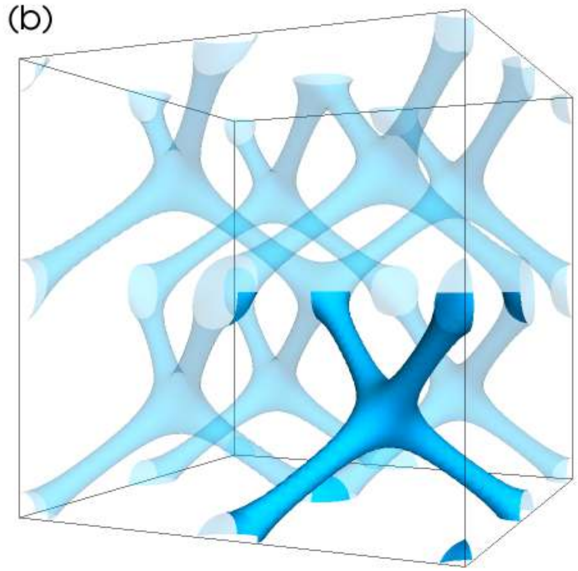
Walls:

- Anchoring type: normal, planar, hybrid
- Anchoring strength: strong, weak

Summary

- Thermodynamically consistent Landau models for complex fluids
- Mesoscopic lattice-Boltzmann simulation method
- Microfluidic flow of LC composite materials





Flow around disclination or defect lines in a cholesteric Blue Phase II (above)

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archer

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