

Complex Disordered Systems

Anisotropy and orientational order

Francesco Turci

What are Liquid Crystals?

- Intermediate phases between **liquids** and **crystals**
- Exhibit **orientational order** without full positional order
- Formed by **anisotropic particles** (rods, ellipsoids, plates)
- Key property: **decoupling** of orientational and translational degrees of freedom

Types of Order

Positional order: Regular arrangement of particle positions (lattice)

Orientational order: Angular alignment of particles

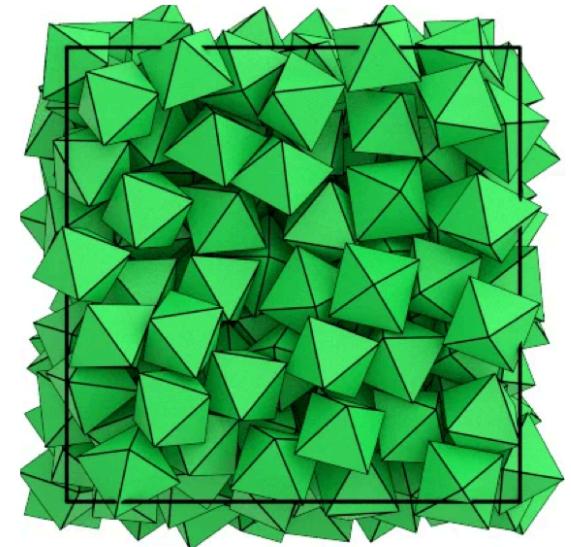
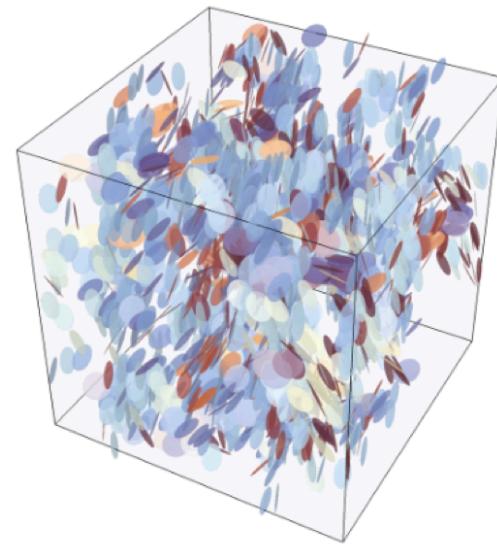
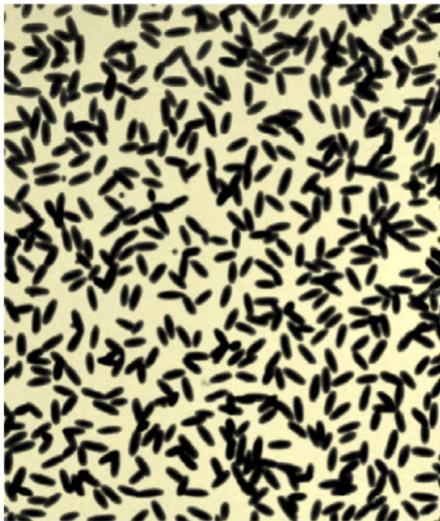
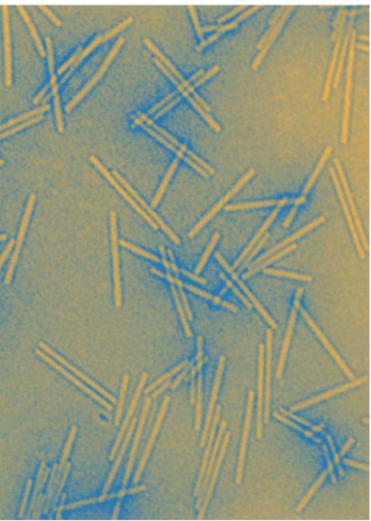
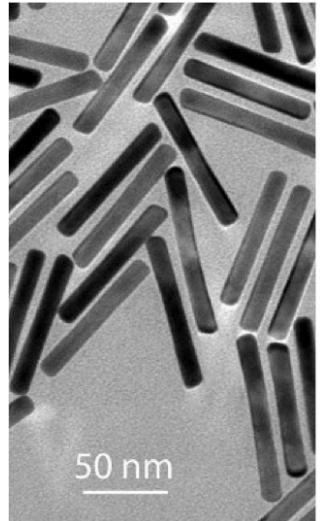
Phase	Positional	Orientational
Crystal	Yes (3D)	Yes
Liquid	No	No
Liquid Crystal	Partial/No	Yes

The strength of the ordering is determined by the **decay** of correlation functions:

- in liquids we have at best short range order (exponential decay of the oscillations in the $g(r)$)
- in crystals we have long-range order — correlations do not decay (sharp Bragg peaks in $S(\mathbf{k})$ and $g(r)$); this order is only disrupted by defects (dislocations, grain boundaries) on macroscopic scales

Anisotropic Particles

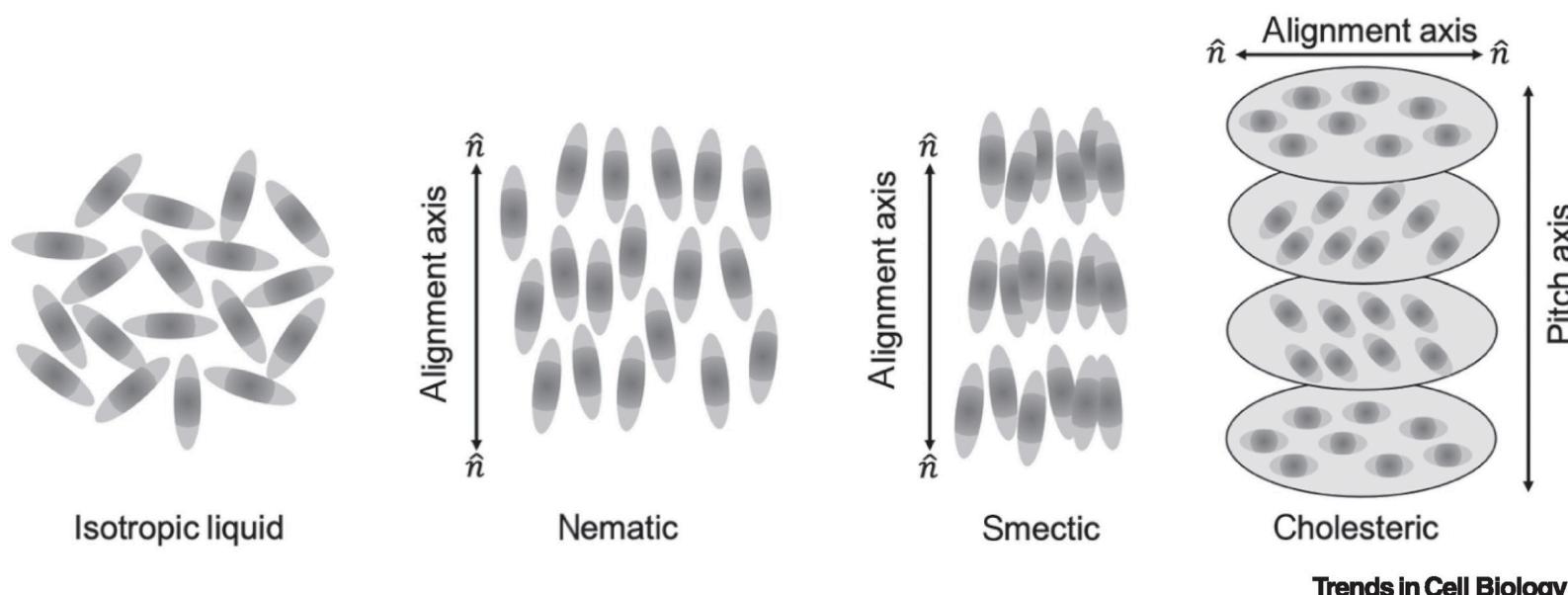
Many natural and artificial systems have anisotropy



Golden nanorods, tobacco virus rods , ellipsoidal silica-coated hematite particles, hard platelets in the isotropic phase, and an arrangement of hard octahedra

Liquid Crystal Phases

- **Isotropic fluid:** No long-range order (like normal liquids)
- **Nematic phase:** Orientational order, no positional order.
 - Particles align along a common direction: the **director \mathbf{n}**
- **Smectic phase:** Layered structure with orientational order
 - Positional order in 1D (layers)
 - Liquid-like within layers
- **Columnar phase:** Particles stack into columns
 - 2D positional order
- **Crystal:** Full 3D positional + orientational order
- **Chiral nematic (Cholesteric):** Director forms a helix

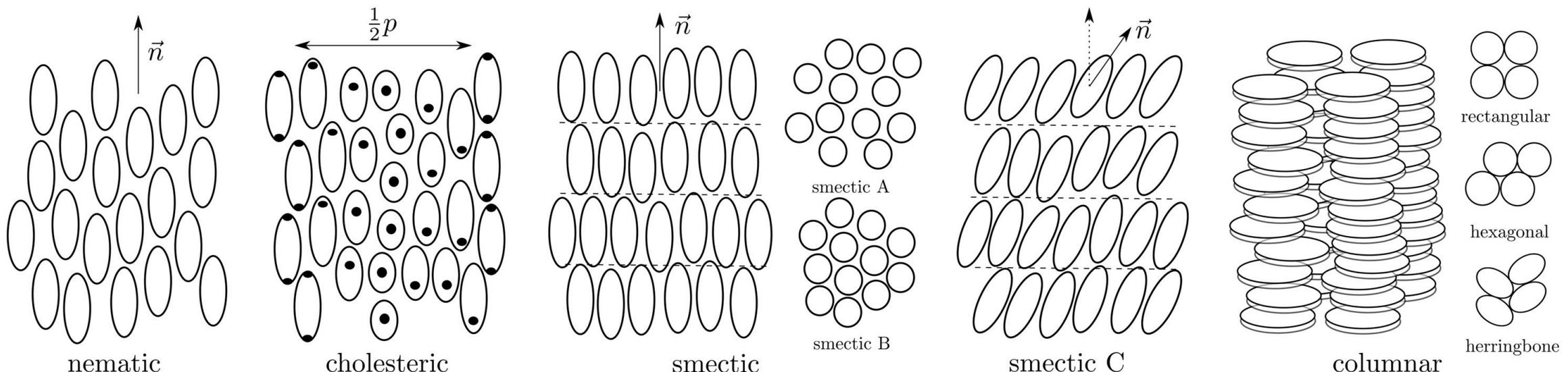


Different liquid crystalline phases, from Doostmohammadi and Ladoux, Trends in Cell Biology (2002)

Trends in Cell Biology

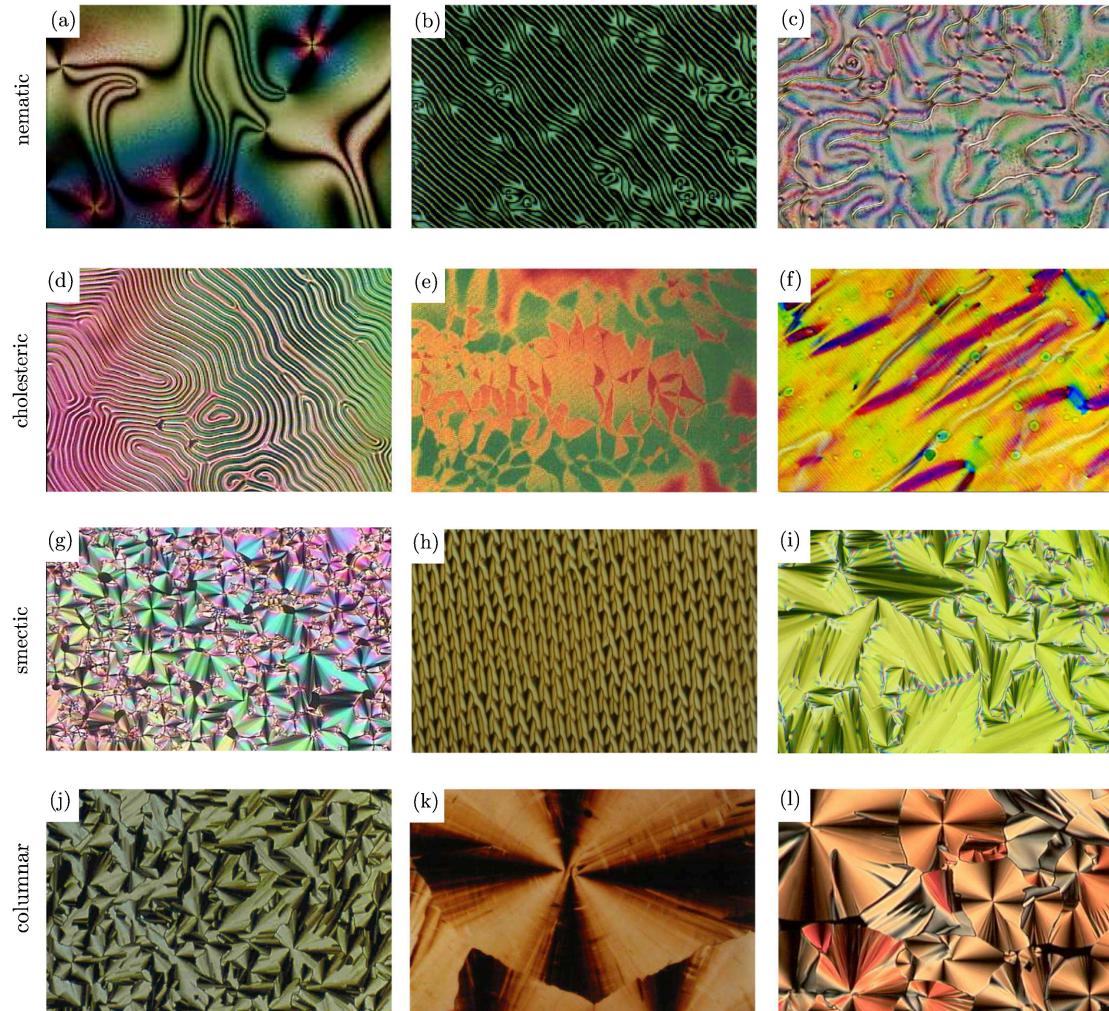
Phase Comparison

Phase	Positional Order	Orientational Order
Isotropic	No	No
Nematic	No	Yes (long-range)
Smectic	Yes (1D: layered)	Yes
Columnar	Yes (2D: columns)	Yes
Cholesteric	No	Yes (helical)
Crystal	Yes (3D: lattice)	Yes



Orientation and order in various phases, from Andrienko, Journal of Molecular Liquids (2018)

Phase Comparison: Textures and Defects



Examples of phases/textures: (a) Nematic with surface point defects. (b) Thin nematic film on isotropic substrate. (c) Thread-like nematic texture. (d) Cholesteric fingerprint (helical axis in plane). (e) Short-pitch cholesteric (standing helix) with vivid colors. (f) Long-range cholesteric DNA alignment in a magnetic field. (g, h) Focal conic textures of chiral smectic A. (i) Focal conic texture of chiral smectic C. (j) Hexagonal columnar spherulitic texture. (k) Rectangular discotic phase. (l) Hexagonal columnar phase. From Andrienko, Journal of Molecular Liquids (2018)

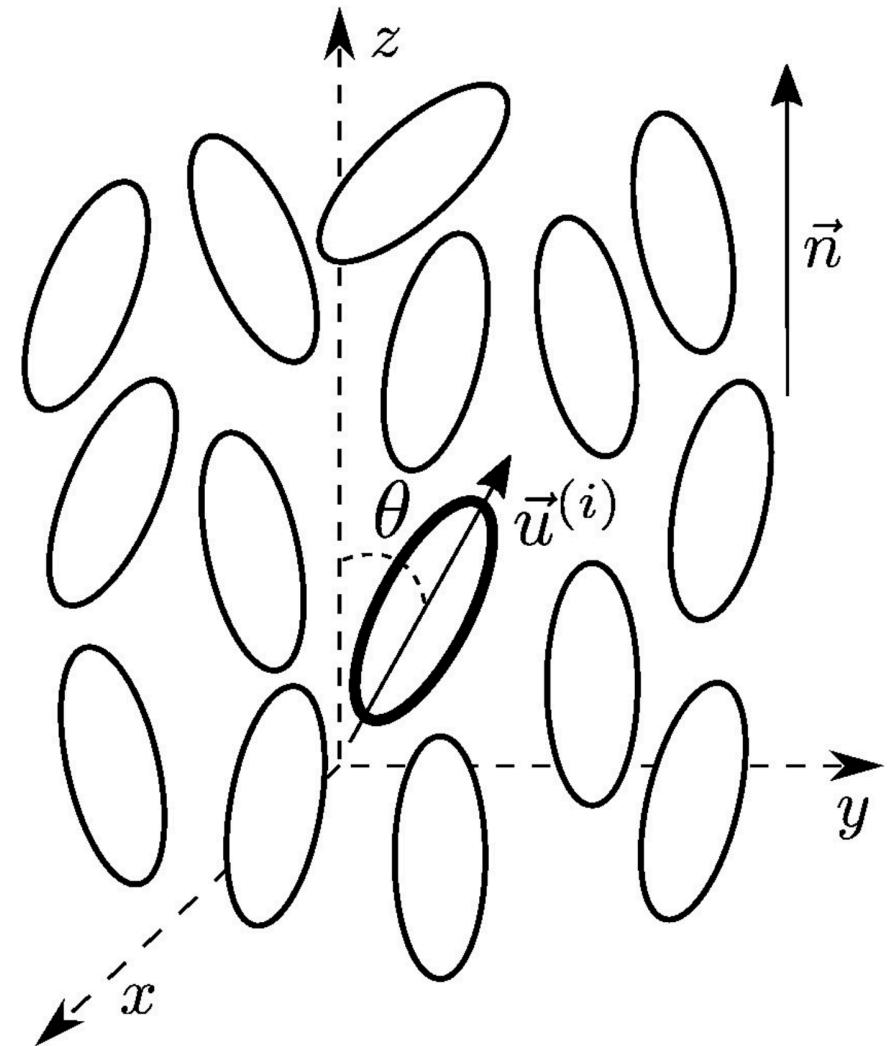
Orientation and director

- Orientation of a rigid rod is described by a **unit vector \mathbf{u}** along its long axis
- The particles are head-tail symmetric, so they have a centre of symmetry
- Because \mathbf{u} and $-\mathbf{u}$ are equiprobable, on average

$$\langle \mathbf{u} \rangle = 0$$

- Vectorial order parameter is zero. The next non-trivial invariant is a **second rank tensor**

Tensor	Rank	Example order parameter
Scalar	0	Scalar nematic S (degree of alignment), e.g., $S = \langle P_2(\cos \theta) \rangle$
Vector	1	Polarization or magnetization vector \mathbf{P} / \mathbf{M} (polar order)
Second-rank tensor	2	Matrices, Alignment tensor Q_{ij} (nematic order)
Third-rank tensor	3	Octupolar / tetrahedral order T_{ijk}



The local orientation vector of a molecule \mathbf{u} and the director \mathbf{n}

The Nematic Order Parameter

For **head-tail symmetric** rods, we cannot simply average orientations.

Instead, construct the **alignment tensor**

$$\mathbf{Q} = \frac{d}{2} \left\langle \mathbf{u}_i \otimes \mathbf{u}_i - \frac{1}{d} \mathbf{I} \right\rangle$$

- we make it **traceless** by removing the identity
- we make it include quadratic combinations (it is as **second moment**, essentially the covariances)
- \otimes is the outer product, giving a $d \times d$ matrix:

$$\mathbf{u} \otimes \mathbf{u} = \begin{pmatrix} u_1 u_1 & u_1 u_2 & \cdots & u_1 u_d \\ u_2 u_1 & u_2 u_2 & \cdots & u_2 u_d \\ \vdots & \vdots & \ddots & \vdots \\ u_d u_1 & u_d u_2 & \cdots & u_d u_d \end{pmatrix}$$

where d is dimensionality, \mathbf{u}_i is the unit orientation vector. For us, $d = 2, 3$

Extracting Order

- Diagonalisation: it extracts the invariants (the properties that do not change wrt a coordinate change or rotations)
- **Largest eigenvalue** → scalar order parameter \mathcal{S}
- **Corresponding eigenvector** → director \mathbf{n}

$$\mathcal{S} \in [0, 1]$$

- $\mathcal{S} = 0$: isotropic (random orientations)
- $\mathcal{S} = 1$: perfect nematic order (all aligned)

 Caution

The nematic order parameter \mathcal{S} should not be confused with the entropy S .

2D Nematic Order Parameter

In two dimensions, the director is simply characterised by the angle ψ expressed as

$$\psi = \frac{1}{2} \operatorname{atan2}(\sin 2\theta_i, \cos 2\theta_i).$$

and the nematic order parameter is simply

$$S = \sqrt{\langle \cos 2\theta_i \rangle^2 + \langle \sin 2\theta_i \rangle^2}$$

3D Nematic Order Parameter

In 3D, choosing coordinates along director \mathbf{n} :

$$\mathcal{S} = \frac{1}{2} \langle 3 \cos^2 \theta_i - 1 \rangle$$

where θ_i is angle between particle i and director.

This uses the **Legendre polynomial** $P_2(\cos \theta)$ to enforce head-tail symmetry.

- Lowest nontrivial rotationally-invariant scalar that is even under $\mathbf{n} \rightarrow -\mathbf{n}$

n	Legendre polynomial $P_n(x)$	Head-tail symmetric?
0	$P_0(x) = 1$	Yes (even: $P_0(-x) = P_0(x)$)
1	$P_1(x) = x$	No (odd: $P_1(-x) = -P_1(x)$)
2	$P_2(x) = \frac{1}{2}(3x^2 - 1)$	Yes (even: $P_2(-x) = P_2(x)$)
3	$P_3(x) = \frac{1}{2}(5x^3 - 3x)$	No (odd: $P_3(-x) = -P_3(x)$)
4	$P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$	Yes (even: $P_4(-x) = P_4(x)$)

Landau-de Gennes mean field theory

Using the tensorial order parameter one can express a Landau theory of the isotropic-to-nematic transition (the simplest form of orientational order appearing in liquid crystals).

Leveraging that \mathcal{S} is an eigenvalue of \mathbf{Q} , i.e. $\mathbf{Q}\mathbf{n} = S\mathbf{n}$ we have

$$\mathbf{Q} = \mathcal{S} \left(\mathbf{n} \otimes \mathbf{n} - \frac{1}{d} \mathbf{I} \right)$$

If we choose z to be the axis along the director \mathbf{n} then explicitly

$$\mathbf{Q} = \mathcal{S} \begin{pmatrix} -\frac{1}{3} & 0 & 0 \\ 0 & -\frac{1}{3} & 0 \\ 0 & 0 & \frac{2}{3} \end{pmatrix}$$

Landau-de Gennes mean field theory

We want to characterise the deviations from the director's orientation.

We can think of compiling a **probability distribution** $p(\Omega)$ of finding a rod with pair of polar angles $\Omega = (\theta, \phi)$ in a coordinates system with polar axis along \mathbf{n} .

- Note: the nematic phase has **cylindrical symmetry** around \mathbf{n}
- Hence, we have no dependency in the azimuthal angle ϕ but only on θ .

So, by definition of an average, the orientational order parameter reads

$$\mathcal{S} = \frac{3}{2} \left\langle (\mathbf{u} \cdot \mathbf{n})^2 - \frac{1}{3} \right\rangle = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle = \langle P_2(\cos \theta) \rangle \quad (1)$$

$$= 2\pi \int_0^\pi P_2(\cos \theta) p(\theta) \sin \theta d\theta \quad (2)$$

where we used the Jacobian in spherical coordinates.

Landau-de Gennes mean field theory

The phenomenological Landau-de Gennes approach is to construct a **generic free energy density** as an expansion in scalar combinations of the tensor \mathbf{Q} (of which \mathcal{S} is an example)

$$f = f_0 + \frac{A}{2} Q_{ij} Q_{ji} - \frac{B}{3} Q_{ij} Q_{jk} Q_{ki} + \frac{C}{4} (Q_{ij} Q_{ij})^2$$

or in more compact form

$$f = f_0 + \frac{A}{2} \operatorname{tr} \mathbf{Q}^2 - \frac{B}{3} \operatorname{tr} \mathbf{Q}^3 + \frac{C}{4} (\operatorname{tr} \mathbf{Q}^2)^2$$

- Notice that all the indices are contracted!
- A, B, C are phenomenological constants (and cannot be immediately linked to microscopic properties of the anisotropic particles)

Landau-de Gennes mean field theory

According to our earlier 3D definitions

$$\text{Tr}(\mathbf{Q}^2) = \frac{2}{3}S^2 \quad , \quad \text{Tr}(\mathbf{Q}^3) = \frac{2}{9}S^3$$

So

$$f = f_0 + \frac{A}{2} \text{tr } \mathbf{Q}^2 - \frac{B}{3} \text{tr } \mathbf{Q}^3 + \frac{C}{4} (\text{tr } \mathbf{Q}^2)^2$$

becomes

$$f = f_0 + \frac{A}{3}S^2 - \frac{2B}{27}S^3 + \frac{C}{9}S^4$$

Landau-de Gennes theory result

- We can use the Landau phase transition approach.
- We can **expand** A, B, C around a reference temperature T^* :

- $A(T) = a(T - T_*) + \dots$
- $B(T) = b + \dots$
- $C(T) = c + \dots$, with $a, b, c > 0$ to preserve the most relevant terms.

and obtain

$$f - f_0 = \frac{a}{3} (T - T^*) S^2 - \frac{2b}{27} S^3 + \frac{c}{9} S^4.$$

The cubic term implies that there is a **temperature range** where **two minima coexist**:

- $S_1 = 0$: isotropic
- $S_2 > 0$: nematic

First order phase transition. The cubic terms prevents the free energy from having an inflection at $S = 0$ (the free energy never gets truly flat)

Landau-de Gennes theory result

```
Python Code ↻ Start Over ▷ Run Code
```

```
1 T = 1.01 # working temperature
2 Tni = 1.0 #transition temperature
3 a = 1.0
4 b = 5.0
5 c = 3.0
6 T_star = Tni-b**2/(27*a*c)
7 # Order parameter range
8 S = np.linspace(0, 1, 200)
9 # Free energy density (setting f_0 = 0)
10 f = (a/3) * (T - T_star) * S**2 - (2*b/27) * S**3 + (c/9) * S**4
11 plot(S,f)
```

The transition temperature is

$$T_{NI} = T^* + \frac{b^2}{27ac}$$

while T^* is a material dependent temperature, identifying instability (spinodal).

Aside : constrained optimisation with Lagrange multipliers

Many physics problems can be cast in terms of constrained optimisation

Area	Problem	Constraint
Mechanics	Minimize action $S = \int L dt$	Energy conservation
Thermodynamics	Maximize entropy S	Fixed total energy E
Electromagnetism	Minimize energy	Gauss's law $\nabla \cdot \mathbf{E} = \rho/\epsilon_0$
General Relativity	Minimize Einstein-Hilbert action	Metric signature constraint
Liquid Crystals	Minimize Frank energy	Director normalization $\ \mathbf{n}\ = 1$
Statistical Mechanics	Maximize partition function	Micro/Gran/canonical ensembles
Optics	Minimize optical path (Fermat)	Snell's law at interfaces

Method: Use **Lagrange multipliers** λ to convert constrained into unconstrained problem:

$$\mathcal{L} = f(\mathbf{x}) - \lambda g(\mathbf{x})$$

then solve $\nabla \mathcal{L} = 0$.

Geometrical understand of Lagrange multipliers

- Take a function $f(x, y)$.
- A constraint is expressed by fixing the value of a second function $g(x, y) = c$
- We want to find the extrema of $f(x, y)$ subject to the constraint $g(x, y) = c$: It has to be a curve
- This means find the extremal values of f on the curve $\mathcal{C} : g(x, y) = c$
- We could parametrise \mathcal{C} but we can also simply think in terms of its geometrical features.

Take the example of a minimum: - at every point of \mathcal{C} there is a tangent vector \vec{t} - we want to find the points on \mathcal{C} where f is minimal. This means that *changes of f along \mathcal{C}* are minimal. - we can calculate such changes as the projection of the local gradient with the tangent vector and state that

$$\vec{\nabla}f \perp \vec{t}$$

- Notice that, by definition, the

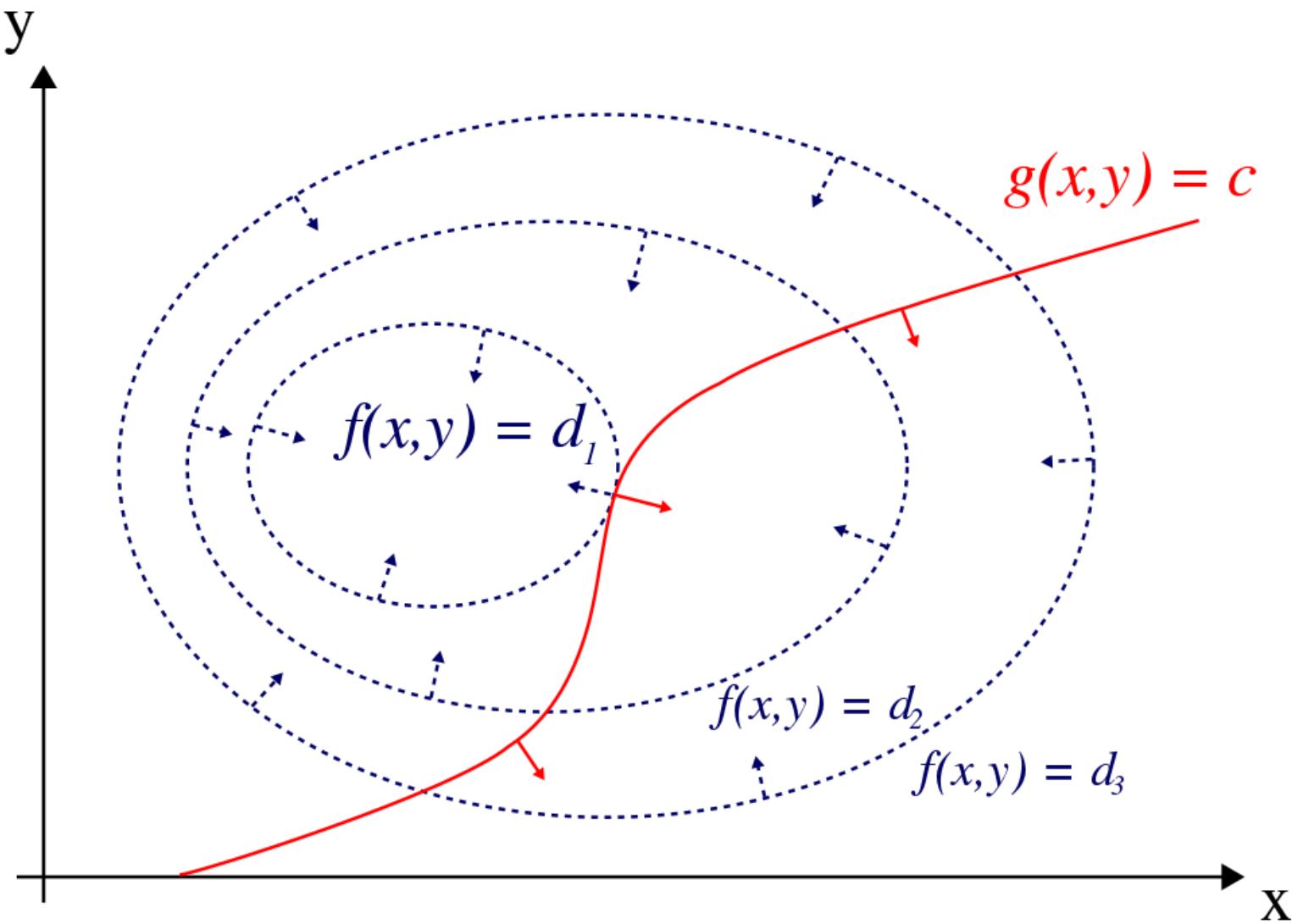
$$\vec{\nabla}g \perp \vec{t}$$

- So we are simply saying that

$$\vec{\nabla}f \parallel \vec{\nabla}g \rightarrow \vec{\nabla}f = \lambda \vec{\nabla}g$$

for some scalar λ

Example



Generalise to many variables: Example of probabilities

Discrete case: Find extremum of entropy

$$S = - \sum_i p_i \ln p_i$$

with constraints

$$\sum_i p_i = 1 \quad \sum_i p_i E_i = \langle E \rangle$$

Using Lagrange multipliers:

$$\mathcal{L} = - \sum_i p_i \ln p_i - \lambda_1 \left(\sum_i p_i - 1 \right) - \lambda_2 \left(\sum_i p_i E_i - \langle E \rangle \right)$$

Setting $\frac{\partial \mathcal{L}}{\partial p_i} = 0$:

$$-\ln p_i - 1 - \lambda_1 - \lambda_2 E_i = 0 \quad \Rightarrow \quad p_i = \exp(-\lambda_2 E_i - \lambda_1 - 1)$$

This is the **Boltzmann distribution**: $p_i \propto \exp(-\beta E_i)$ with $\beta = \lambda_2$.

Continuous Limit

Replace sums with integrals. Let $p_i \rightarrow p(x)$ where x is a continuous variable.

Constraints become:

$$\int p(x)dx = 1, \quad \int p(x)E(x)dx = \langle E \rangle$$

Entropy functional:

$$S[p] = - \int p(x) \ln p(x) dx$$

Lagrangian:

$$\mathcal{L} = - \int p(x) \ln p(x) dx - \lambda_1 \left(\int p(x)dx - 1 \right) - \lambda_2 \left(\int p(x)E(x)dx - \langle E \rangle \right)$$

Functional derivative $\frac{\delta \mathcal{L}}{\delta p(x)} = 0$:

$$-\ln p(x) - 1 - \lambda_1 - \lambda_2 E(x) = 0 \quad \Rightarrow \quad p(x) = \exp(-\beta E(x) - c)$$