

Complex Disordered Systems

Maier-Saupe Theory, Lebwohl-Lasher Model, Frank Elasticity, Topological Defects

Francesco Turci

Aside: Functional Derivatives

- Functional derivative is the extension of ordinary derivative to functionals (functions of functions)
- A general formulation (that you may have already seen) starts from an **action functional** $S[\phi]$:

$$S[\phi] = \int \mathcal{L}(\phi(x), \phi'(x), x) dx$$

\mathcal{L} is the **Lagrangian function**: e.g. x is space, $\phi(x)$ a field defined over space (e.g. density)

- Perturb $S[\phi]$ by an amount ϵ with an arbitrary function $\eta(x)$ vanishing at the boundaries

$$S[\phi + \epsilon\eta] = \int \mathcal{L}(\phi + \epsilon\eta, \phi' + \epsilon\eta', x) dx$$

Expanding to first order in ϵ :

$$S[\phi + \epsilon\eta] \approx S[\phi] + \epsilon \int \left[\frac{\partial \mathcal{L}}{\partial \phi} \eta + \frac{\partial \mathcal{L}}{\partial \phi'} \eta' \right] dx$$

Aside: Functional Derivatives

Integrating by parts the second term:

$$\int \frac{\partial \mathcal{L}}{\partial \phi'} \eta' dx = \left[\frac{\partial \mathcal{L}}{\partial \phi'} \eta \right]_{\text{boundary}} - \int \frac{d}{dx} \left(\frac{\partial \mathcal{L}}{\partial \phi'} \right) \eta dx$$

Since $\eta(x)$ vanishes at the boundaries, the first term drops out, giving:

$$\delta S = \int \left[\frac{\partial \mathcal{L}}{\partial \phi} - \frac{d}{dx} \left(\frac{\partial \mathcal{L}}{\partial \phi'} \right) \right] \eta(x) dx$$

If we want $S[\phi]$ to be stationary with respect to arbitrary perturbations $\eta(x)$, then $\delta S = 0$ for all $\eta(x)$.

This leads to the **Euler-Lagrange equation**:

$$\frac{\partial \mathcal{L}}{\partial \phi} - \frac{d}{dx} \left(\frac{\partial \mathcal{L}}{\partial \phi'} \right) = 0$$

which defines the functional derivative as

$$\frac{\delta S}{\delta \phi(x)} = \frac{\partial \mathcal{L}}{\partial \phi} - \frac{d}{dx} \left(\frac{\partial \mathcal{L}}{\partial \phi'} \right)$$

Maier-Saupe Theory of Nematic Liquid Crystals

- We saw the Landau-de Gennes free energy for nematic liquid crystals.

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

- phenomenological (the coefficients are results of a perturbation)
- based on symmetries only (rotational invariance, head-tail symmetry)
- no molecular basis
- The **Maier-Saupe theory** is a simple alternative **microscopic** mean-field theory that gives us a more physical insight.
- The idea is to construct the free energy as we have done in various prior cases by identifying:
 - an entropic contribution
 - an energetic contribution

As for the Landau-de Gennes theory, we will focus on :

- angular deviations θ from the director and their probability distribution $p(\theta)$
- a scalar orientational order parameter \mathcal{S}

Maier-Saupe Theory of Nematic Liquid Crystals

Energetic Contribution

- We assume molecules interact with an angular potential that depends on their orientations

$$V(\Omega_i, \Omega_j) = -u P_2(\mathbf{u}_i \cdot \mathbf{u}_j)$$

We can average over all possible orientations of molecule j to get the mean-field potential felt by molecule i :

$$U_i^{\text{mf}}(\Omega) = \rho \int V(\Omega, \Omega') p(\Omega') d\Omega' = -u S P_2(\mathbf{u}_i \cdot \mathbf{n})$$

where we have defined the scalar order parameter

$$S = \int P_2(\mathbf{u} \cdot \mathbf{n}) p(\Omega) d\Omega$$

and identified the director \mathbf{n} and the energetic **coupling** u .

So we can average the mean-field potential over all orientations of molecule i to get the average interaction energy per molecule (and divide by 2 to avoid double counting):

$$U^{\text{mf}} = -\frac{u}{2} S^2$$

In essence, we get a potential that aligns molecules with the director, and that is quadratic to reflect head-tail

Maier-Saupe Theory of Nematic Liquid Crystals

Entropic contribution

The second contribution is **entropic** in nature.

Use orientational distribution function $p(\Omega)$ and (as in Landau-de Gennes) and assume uniaxial symmetry around the director \mathbf{n} , i.e. $p(\Omega) \sim p(\theta)$.

The usual Gibbs (or Shannon) entropy functional $-k_B \int p(\Omega) \ln p(\Omega) d\Omega$ contributes to the free energy as

$$f_{\text{entropy}} = k_B T \int_0^\pi p(\theta) \ln(4\pi p(\theta)) \sin \theta d\theta$$

where 4π and $\sin \theta d\theta$ come from normalization over solid angle.¹

1. Check that for the isotropic distribution $p(\theta) = 1/4\pi$ the entropy is zero.

Maier-Saupe Theory of Nematic Liquid Crystals

Together we, have the Maier-Saupe free energy functional per molecule

$$f = f_0 - u \frac{S^2}{2} + k_B T \int_0^\pi p(\theta) \ln(4\pi p(\theta)) \sin \theta d\theta$$

The only constraint is normalization of $p(\theta)$:

$$\int_0^\pi p(\theta) \sin \theta d\theta = 1$$

where the $\sin \theta$ comes from the solid angle element.

Introduce the Lagrange multiplier λ to enforce the constraint and minimize the functional and set the variation to zero:

$$\delta \left[f + \lambda \left(\int_0^\pi p(\theta) \sin \theta d\theta - 1 \right) \right] = 0$$

The functional derivative yields (check!):

$$\frac{\delta f}{\delta p(\theta)} + \lambda \sin \theta = 0$$

Maier-Saupe Theory of Nematic Liquid Crystals

Remember that - by **definition** -

$$S = \langle P_2(\cos \theta) \rangle = \int_0^\pi P_2(\cos \theta) p(\theta) \sin \theta d\theta$$

So

$$\frac{\delta S^2}{\delta p} = 2S P_2(\cos \theta) \sin \theta$$

So when calculating the partial derivative we have

$$\frac{\delta f}{\delta p} = -uS P_2(\cos \theta) \sin \theta + k_B T (\ln(4\pi p(\theta)) + 1) \sin \theta$$

and hence, after simplifying $\sin \theta$, our Lagrange equation reads

$$-uS P_2(\cos \theta) + k_B T (\ln(4\pi p(\theta)) + 1) + \lambda = 0$$

Its solution yields

$$p(\theta) = \frac{1}{Z} \exp(\lambda P_2(\cos \theta)) = \frac{1}{Z} \exp\left(\frac{uS}{k_B T} P_2(\cos \theta)\right)$$

where the partition function Z ensures normalization.

Self-consistency in the Maier-Saupe Result

The solution is said to be **self-consistent** because $p(\theta)$ depends on S , which in turn depends on $p(\theta)$.

The self-consistency condition is

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

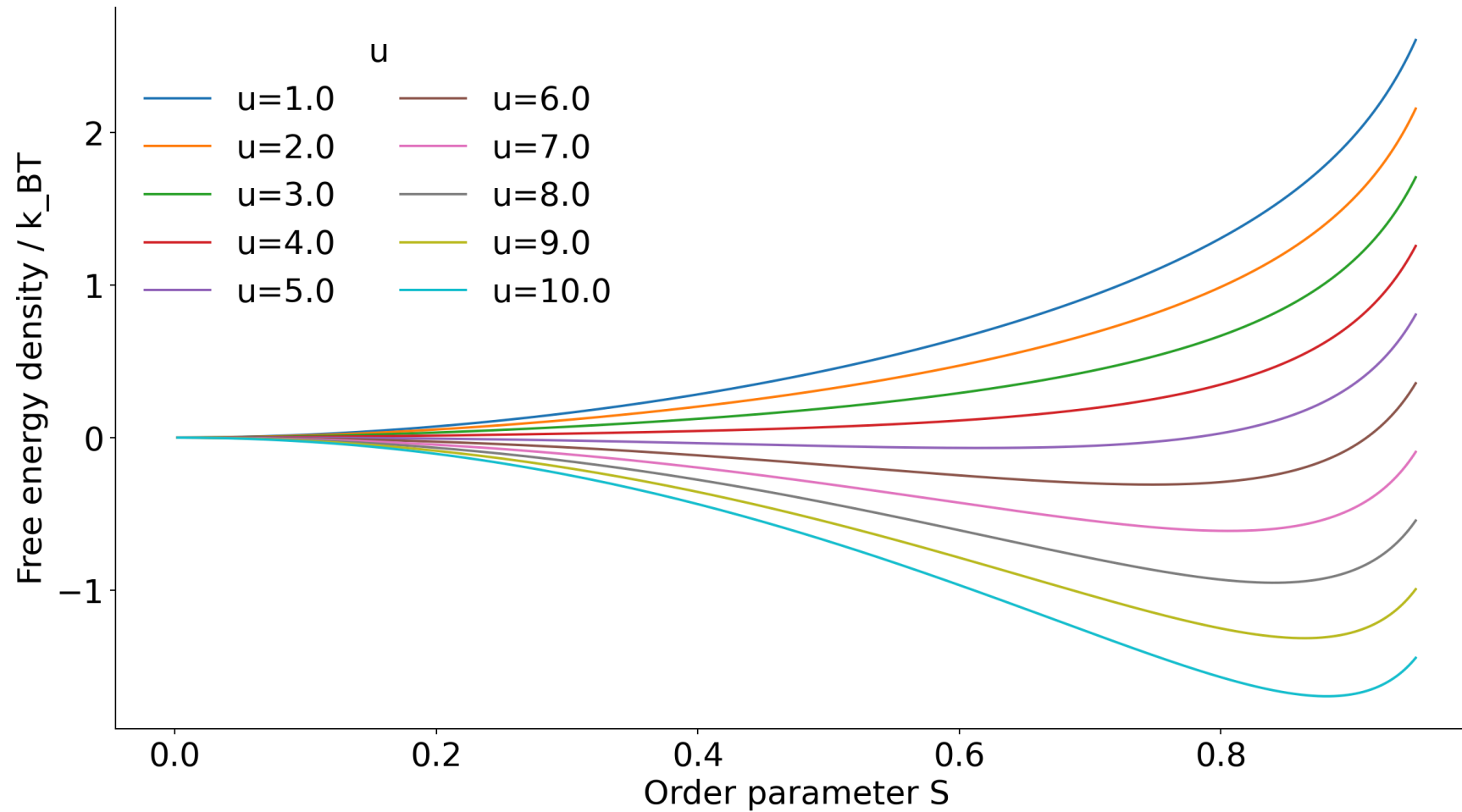
where $p(\theta)$ itself depends on S :

$$p(\theta) = \frac{1}{Z} \exp \left(\frac{uS}{k_B T} P_2(\cos \theta) \right)$$

This equation must be solved for S at each temperature T .

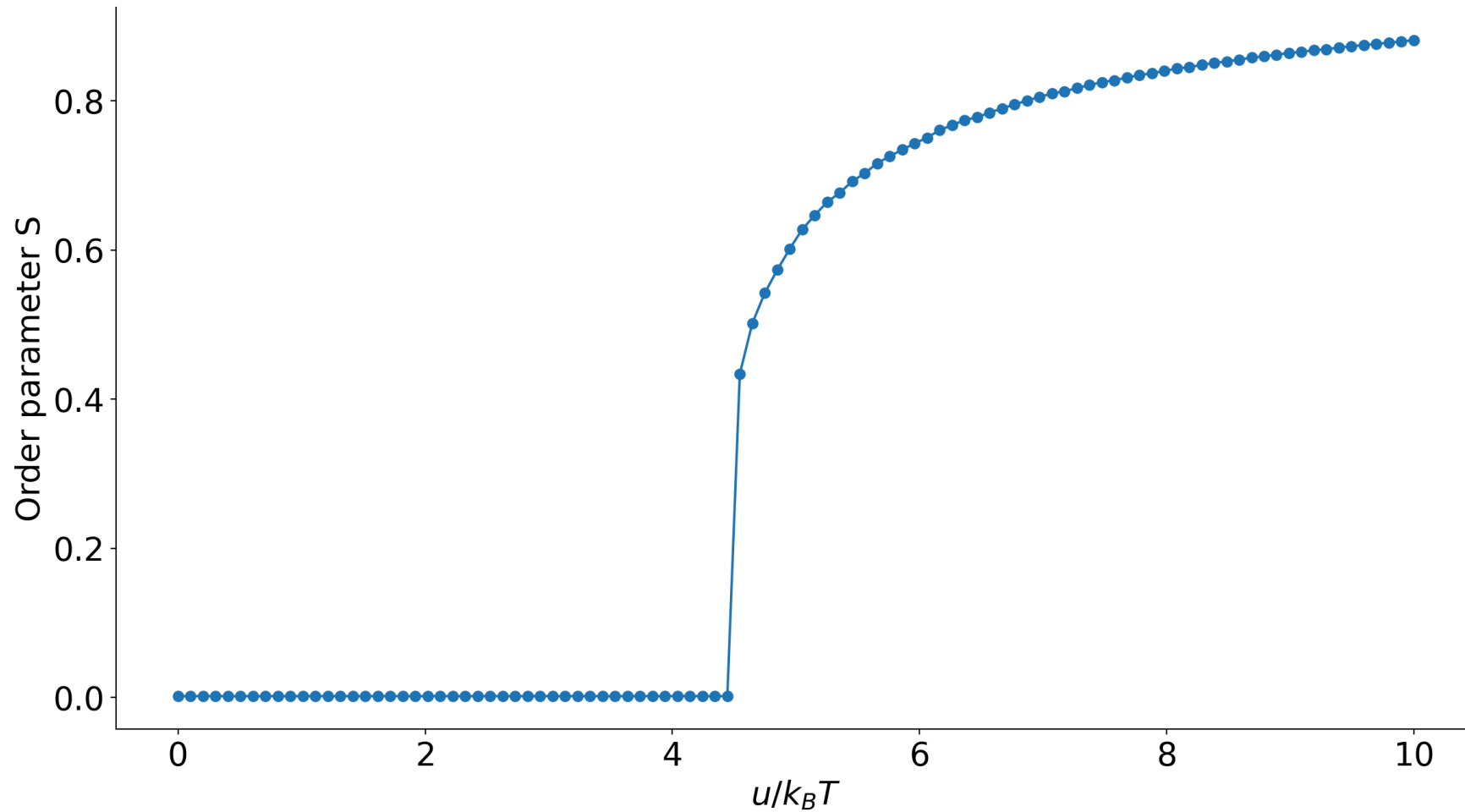
In general, this requires a **numerical** solution (see problem classes for a special case where we can make progress analytically).

Maier-Saupe: Numerical Solution



 [Play with the numerical solution](#)

Maier-Saupe: Numerical Solution



The resulting phase transition is weakly first order with a discontinuous jump in S at the transition temperature. $u/k_B T \approx 4.55$.

Quick comparison Maier-Saupe vs Landau-de Gennes

- Both theories predict a first-order isotropic-nematic phase transition with a discontinuous jump in the order parameter S .
 - Landau-de Gennes is phenomenological, Maier-Saupe is microscopic.
 - Maier-Saupe provides a molecular basis for the coefficients in Landau-de Gennes
 - Both theories can be extended to include spatial variations in the order parameter and director field, leading to descriptions of defects and elasticity in nematic liquid crystals.
 - Maier-Saupe requires self-consistency requirement, while Landau-de Gennes is often simpler to analyze analytically: (slightly) harder numerics.
 - Easier to cast Maier Saupe onto a lattice model (Lebwohl-Lasher).
- What about **hard rods** ? Can we get nematic order from purely entropic effects?

Simple lattice model: Lebwohl-Lasher

- A way to construct a Maier-Saupe-like model on lattice.
- Vectors on a lattice represent the orientations of molecules.
- Nearest-neighbor interactions favor alignment of neighboring vectors.

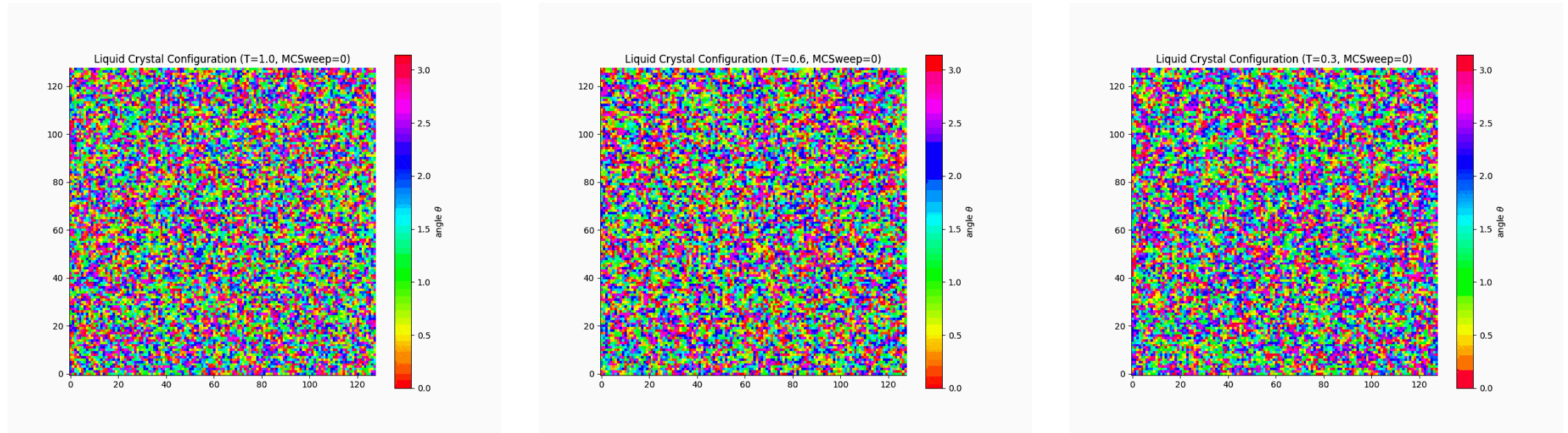
In 2D

$$H = -\epsilon \sum_{\langle i,j \rangle} \left[\frac{3}{2} \cos^2 (\theta_i - \theta_j) - \frac{1}{2} \right]$$



Demonstration in class

Simple lattice model: Lebwohl-Lasher



in 2d the transition is **rounded**, not true first order (Kosterlitz-Thouless only quasi long range order) due to a key theorem due to **Mermin and Wagner** which states that

(Mermin-Wagner theorem) Continuous symmetries **cannot be spontaneously broken** at finite temperature in systems with sufficiently short-range interactions in dimensions $d \leq 2$.

Long-range fluctuations are favoured in $d \leq 2$.

Here the continuous symmetry is the rotational invariance of the director field in the plane.

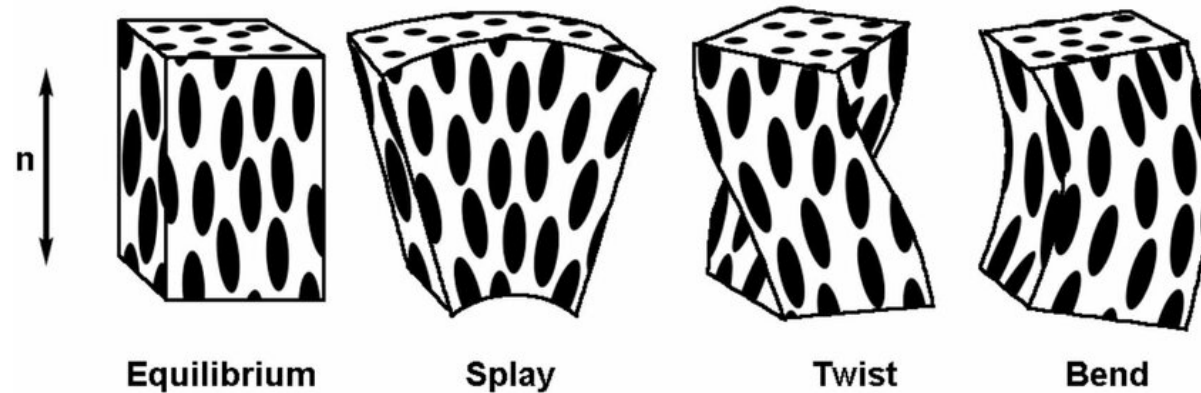
Continuum limit and Frank elasticity

Charles Frank (1958, of our Frank lecture theatre) developed a continuum theory to describe the elastic properties of nematic liquid crystals.

The Frank free energy density describes the cost of spatial variations in the director field $\mathbf{n}(\mathbf{r})$:

$$f_{\text{Frank}} = \frac{1}{2}K_1(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}K_2(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{1}{2}K_3(\mathbf{n} \times \nabla \times \mathbf{n})^2$$

- K_1 : **splay** elastic constant
- K_2 : **twist** elastic constant
- K_3 : **bend** elastic constant

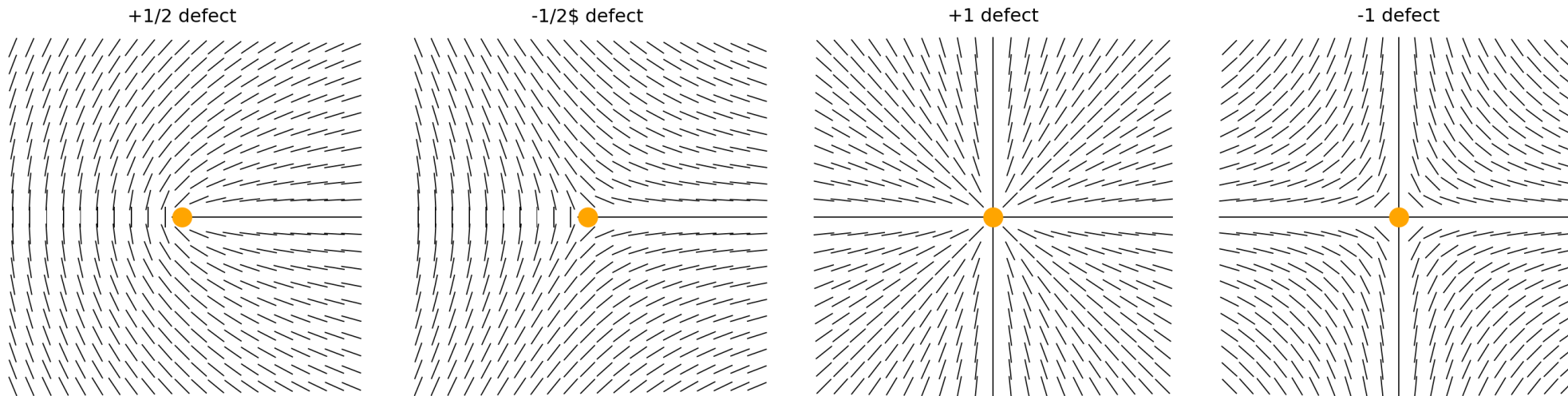


Pure splay, twist and bend compared to equilibrium from Binder et al. J. Phys. Mater. (2020)

With this free energy, one can model large-scale deformations and **defects** in nematic liquid crystals.

Topological Defects in Nematic Liquid Crystals

- We are working in the continuum with a director field $\mathbf{n}(\mathbf{r})$ that describes the local average orientation of molecules.
- In this framework, defects are **singularities** of the field, called **disclinations**
- Examples in 2D:



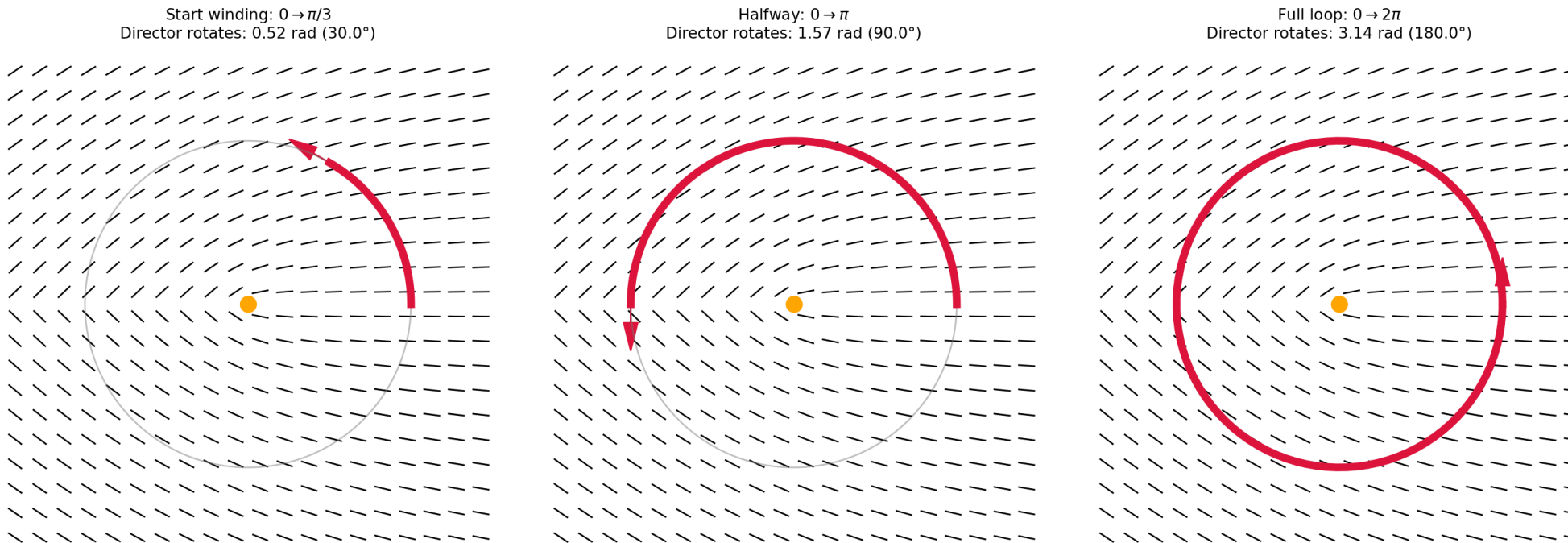
- These singularities cannot be removed by any smooth deformation of the field: they are **topologically protected**.
- To make them vanish, one needs oppositely signed defects to bring together so that they **annihilate** each other.
- At finite temperature, defects are spontaneously created/annihilated.

Topological Charge of a Defect

- The topological charge (or winding number) s of a defect quantifies how many times the director field rotates by 2π when encircling the defect once.

$$\Delta\theta = 2\pi s$$

For example, a charge of $s = 1/2$ is a rotation by π is performed when going around the defect once.



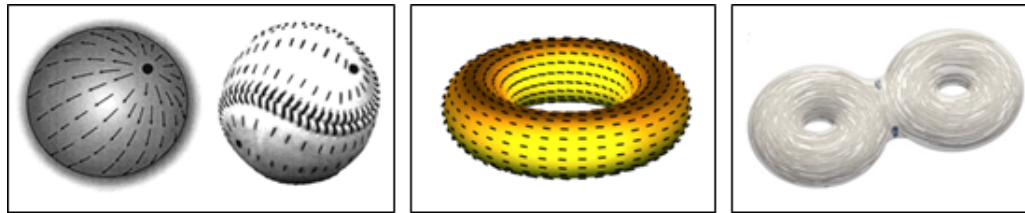
Conservation of Topological Charge

- Topological charge is **conserved**: the total charge in a closed system remains constant over time.
- Defects can be created or annihilated only **in pairs** of opposite charge (e.g., $+1/2$ and $-1/2$).
- The **topology** of the space imposes such constraints of conservation via the *Poincaré-Hopf theorem*, which states

The total topological charge of the defects in a field confined to a compact space is equal to the Euler characteristic of that space

In practice:

- On a plane (Euler characteristic = 1), the total topological charge must sum to 1.
- On a sphere (Euler characteristic = 2), the total topological charge must sum to 2.
- On a torus (Euler characteristic = 0), the total topological charge must sum to 0. → in periodic systems the total charge must be zero.
- This imposes constraints on the dynamics and interactions of defects.

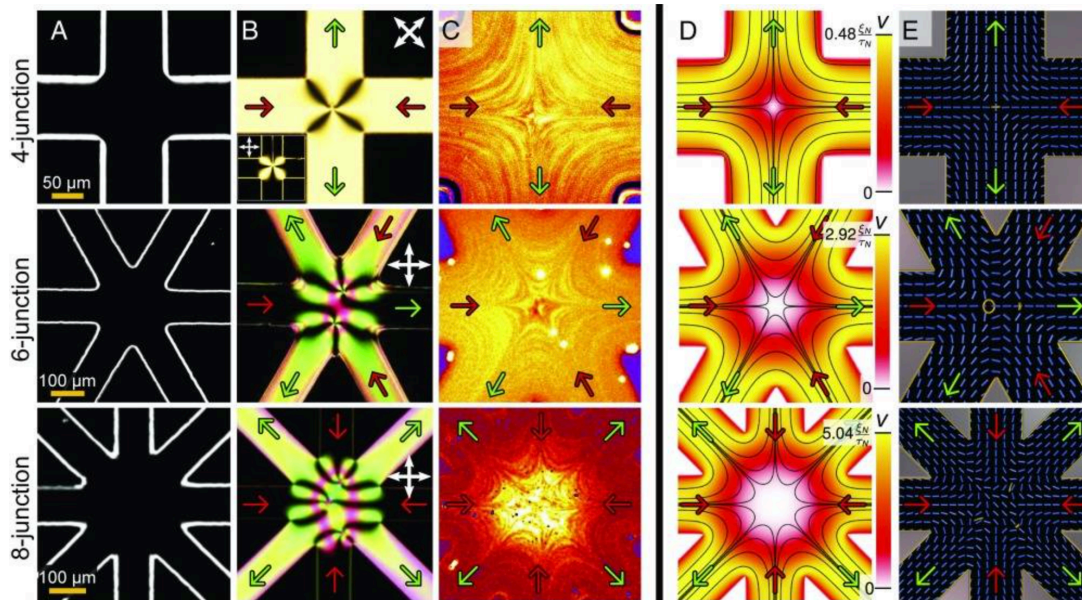


Director fields on a sphere, on a torus and a double torus. The number of handles (the genus g) determines the Euler characteristic $\chi = 2 - 2g$. From Nelson (2002)

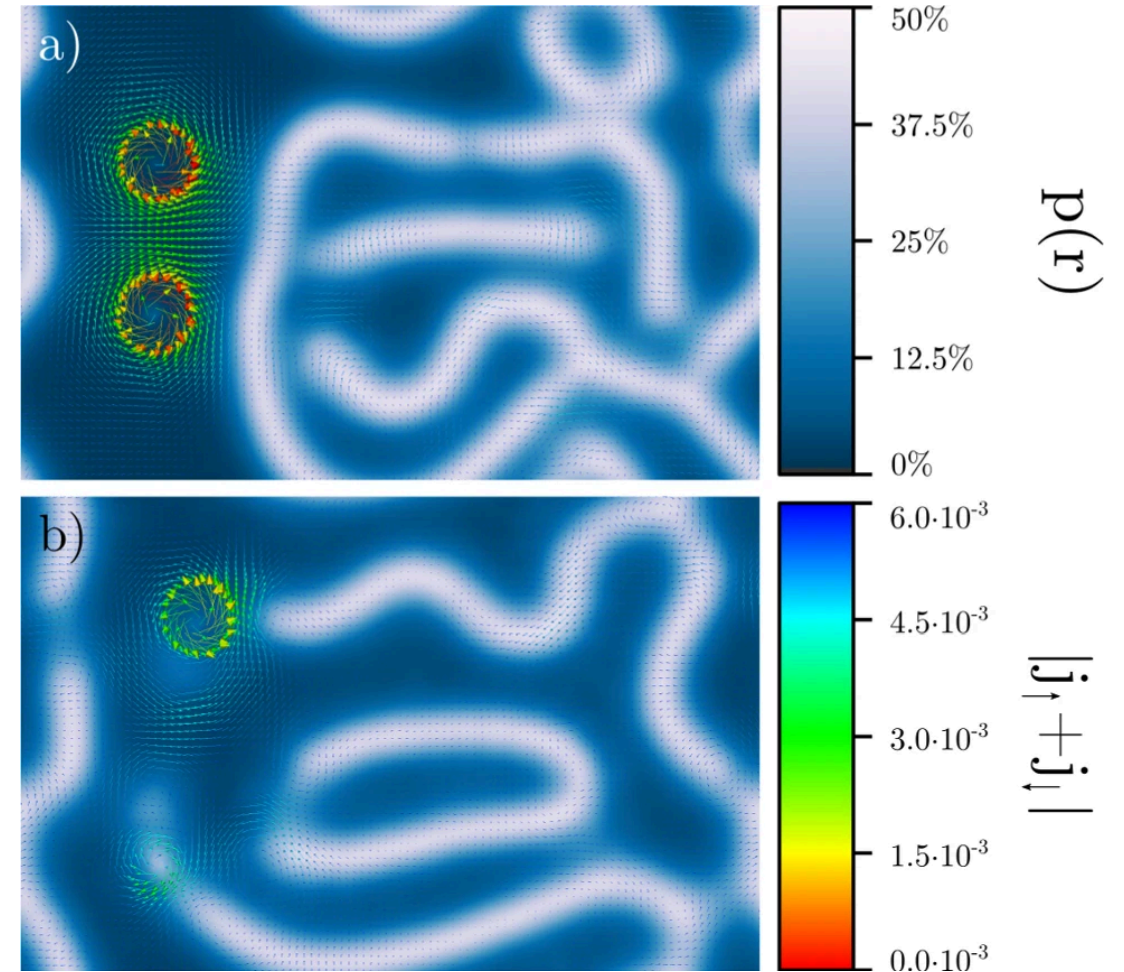
Topological defects

Analogies well-beyond liquid crystals:

- vortices in superfluids and superconductors
- dislocations in crystals
- electromagnetic field configurations
- flow fields microfluidic junctions



Topological defects in microfluidic devices



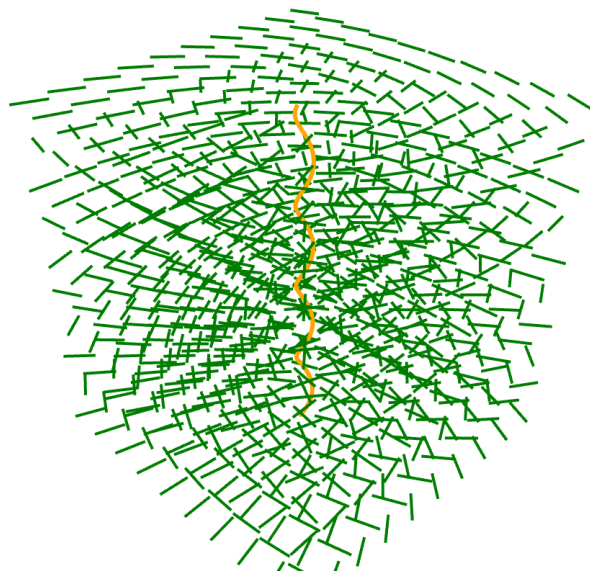
Vortex anti-vortex pair in a superfluid (a) initial configuration and (b) after relaxation. From Magierski, *Eur Phys J* (2024)

Defects in 3 Dimensions

- In 3D the disclinations become **lines**
- The director field wraps around the line defect in a similar way as in 2D.
- The classification of disclination in 3D involves the rotation group $SO(3)$ (that generalises the construction we have seen in two dimensions) and are more complex in general. They include
 - lines
 - closed loops
 - point-like features (hedgehogs and monopoles)
 - complex textures.

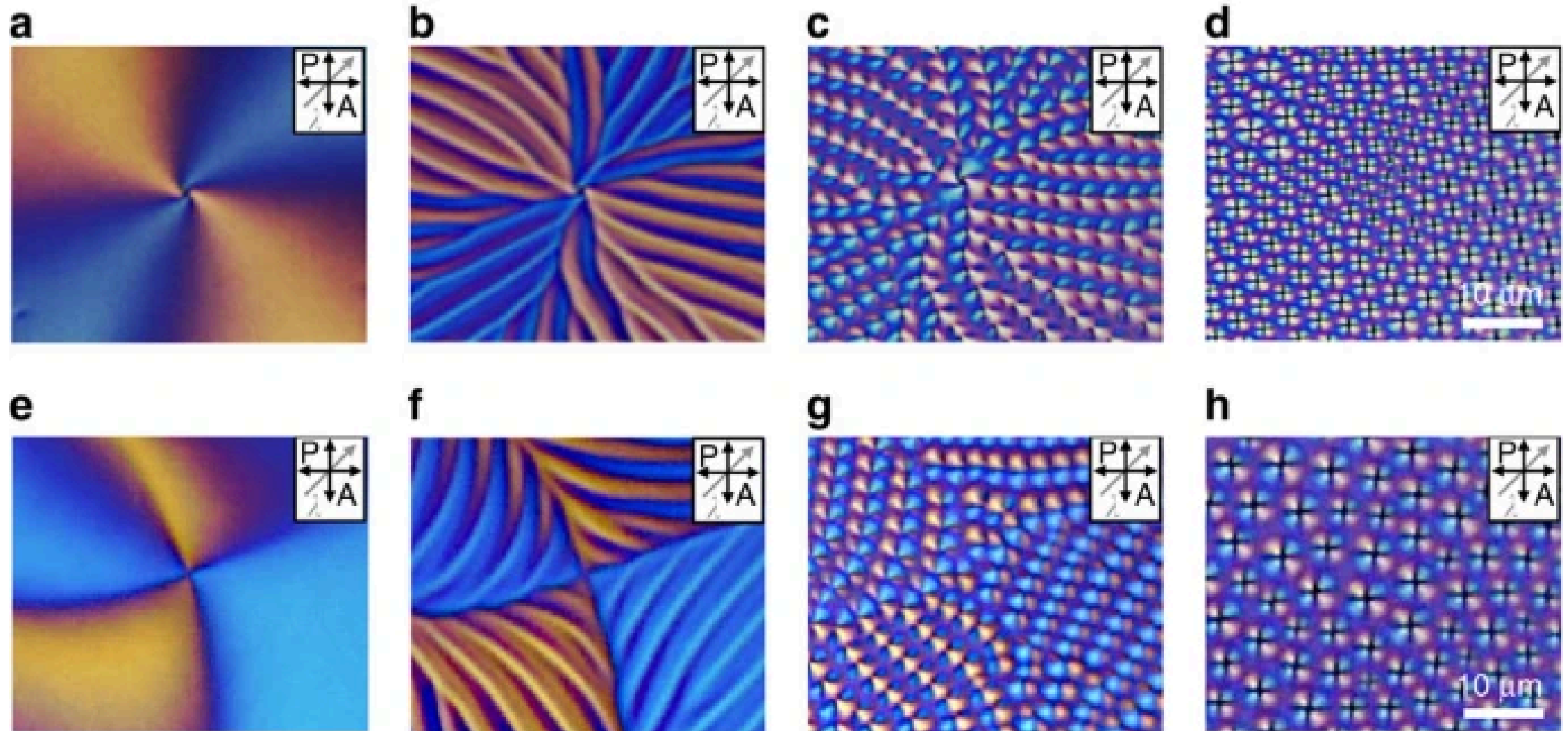
3D Twisting Nematic Disclination Line

Helical Disclination Core



Defects and Phase Transitions

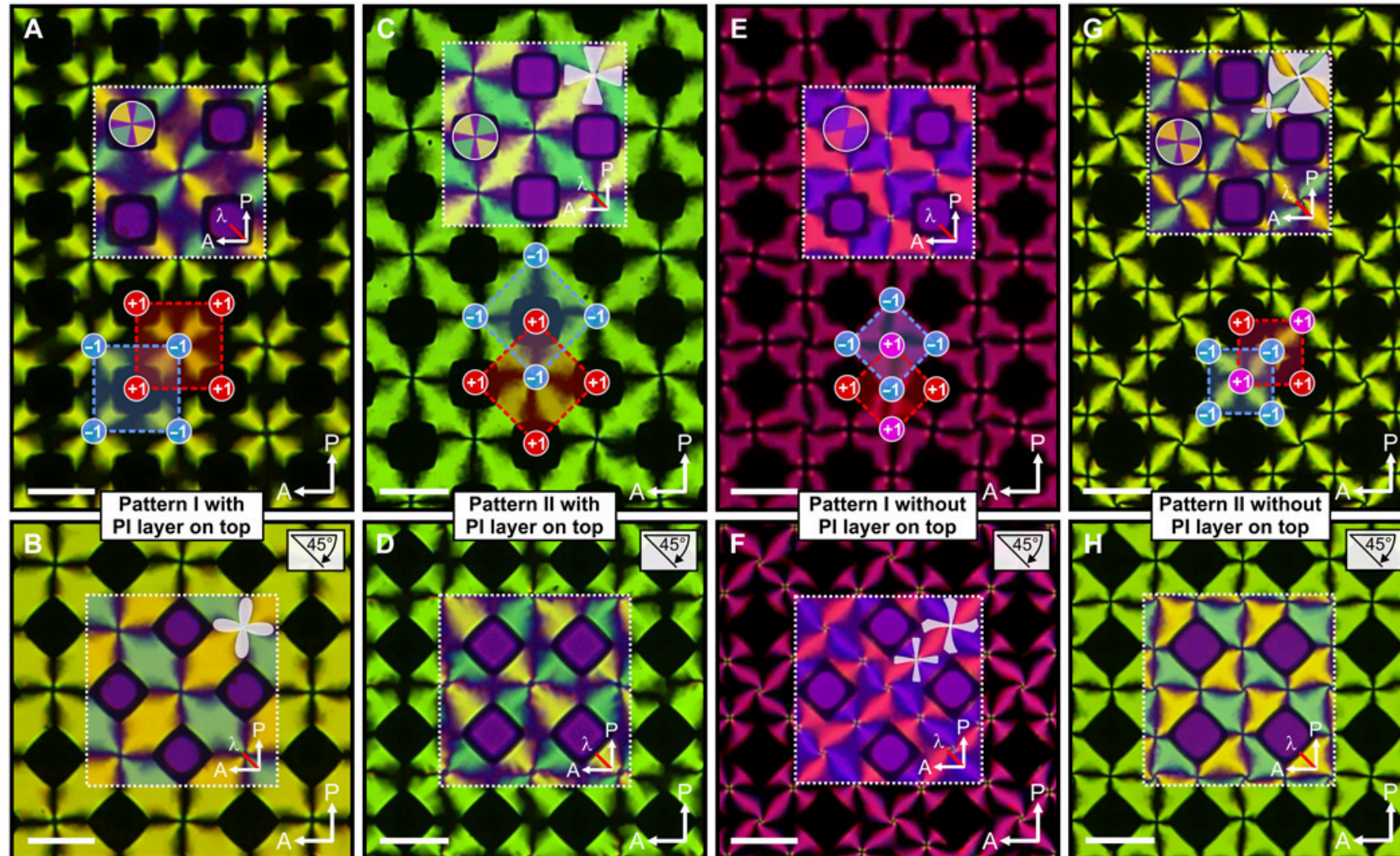
Defects control the stability and dynamics of nematic liquid crystals and drive the phase transitions between phases.



Defect formation and nematic to smectic phase transition via defect branching, Gim et al Nature Communications (2017)

Complex Dislocation Patterns

Example from Kim et al Science Advances (2018)



Liquid-crystals defects created and controlled by external forces (air pillars through a substrate).