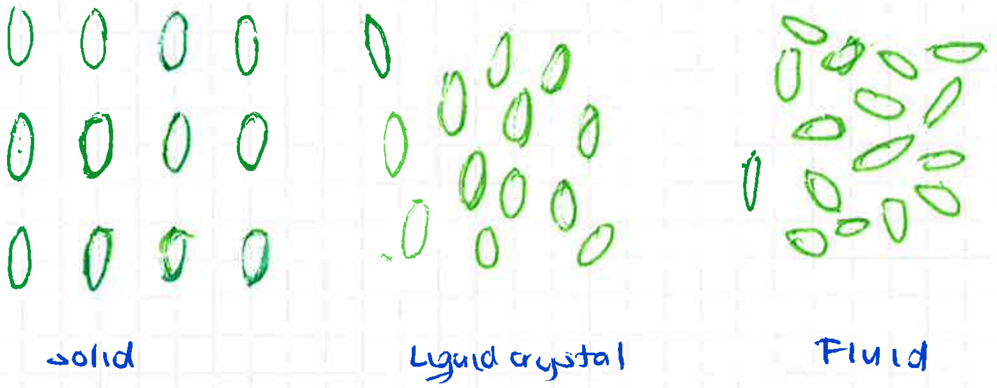
Lecture 11 Liquid crystals

The history of liquid crystals starts in Prague 1888, at the laboratory of Friedrich Reinitzer in the Institute of plant physiology.

He was studying the melting behavior of cholesterol and made the following observations:

→ At low temperatures cholesterol forms a solid
→ At 145.5C it melted into a liquid of a "pearly milkiness" appearance
→ At 178.5C the liquid turned clear

In collaboration with Friedrich Ostwald they developed the idea that the transition from complete order to complete disorder occurs in "stages".



A liquid can be moved in space in any of 3 directions ($\hat{x}, \hat{y}, \hat{z}$) or a combination of them, and by any displacement, resulting in a state indistinguishable from the original one.

For a solid (crystal) this symmetry only exists for displacements equal to the lattice spacing. So in the solid the three continuous translational symmetries are broken.

Likewise in a fluid there are 3 angles of continuous rotational symmetry (turning around its axis, in latitud, and longitude). In crystallization all 6 degrees of freedom (3 translational and 3 rotational) are lost). Their symmetries are all broken at the same temperature. Similarly, they are typically liberated at once as the solid melts.

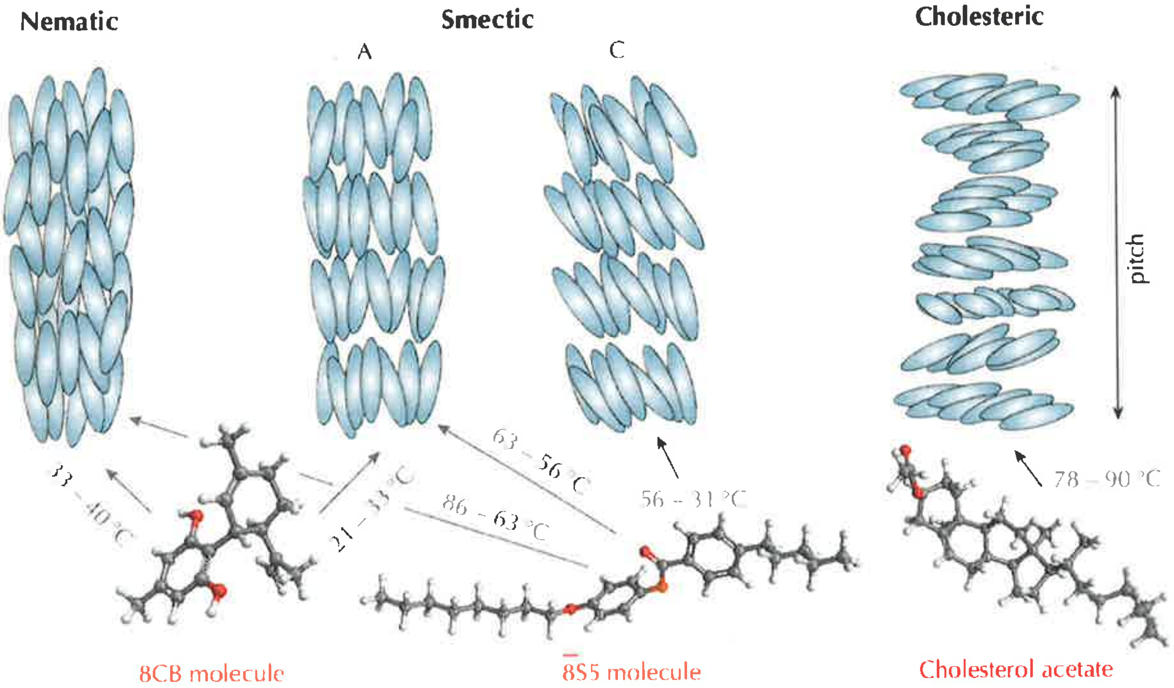
However a rod-like material does something radically different. It moves from complete order (solid) to complete disorder (fluid) by first freezing three spatial degrees of freedom, and the one that allows molecules to spin around their long axis, but keeping two of the rotational angles restricted. In this intermediate state all the molecules point with their long axis in the same direction, but they are now free to move spatially to any place in the fluid. This intermediate "semimelted" phase is termed a liquid crystal! This term was coined given that like a normal liquid its molecules can move into any position, so it flows, but like a crystal it can be further melted into complete disorder.

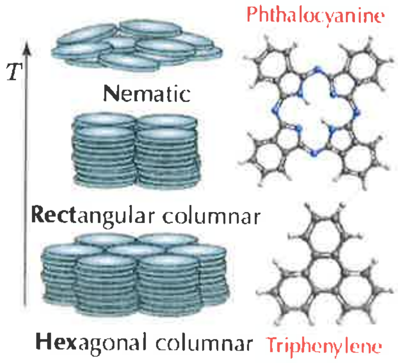
Video: Cholesterol liquid crystal.

To emphasize the intermediate nature of liquid crystals, the term mesophase has been introduced, but we will follow the standard practice to use the generally accepted name liquid crystal.

The three most common mesophases are
- *nematic: molecules have an average orientation but no positional order.
- *smectic: molecules form layers with the average orientation of the molecules parallel to the normal to the layers
- *cholesteric: the orientation rotates in a plane along the axis perpendicular to the planes.

There are far more liquid crystal phases than these, but these are the most common ones.



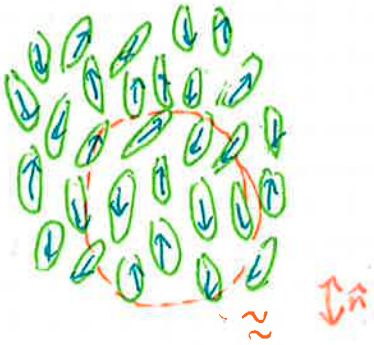


~~To~~
Materials that have molecular shape anisotropies form liquid crystals.

We will focus our discussion on the nematic phase since the discussion of this phase is a natural route to introducing the director field $\hat{n}$ which characterizes the orientational order.

In the nematic phase there is only orientational order of the molecules, this means that the molecules point in a particular direction, which is denoted by $\hat{n}$, a unit vector called the director.

We think of the director as a continuum field, obtained by coarse-graining over elements which are large enough that the average is well defined, but small enough compared to the outer scale at which the director field varies.



on average we have as many molecules up as down so we have the symmetry $\hat{n} \leftrightarrow -\hat{n}$

that's why we represent $\hat{n}$ by a director ↕

(in contrast to a vector ↑)

The theory around liquid crystals was largely inspired by ideas from superconductivity and the Ising model for magnetization. Both of these systems exhibit phase transitions as a function of temperature.

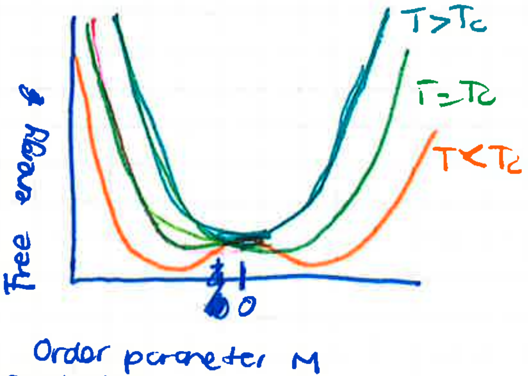
In superconductors below a critical temperature electrons pair up and fall into an ordered collective state that carries electric current without resistance. Like all phase transitions, the superconductive transition also changes the symmetry of the material at the bulk level. At high temperatures, thermal fluctuations are enough to excite electrons out of their special cooperative state, into a more disordered normal state. Similarly at high temperatures in a liquid crystal thermal motion maintains long range randomness in the orientational direction of molecular rods. At the macroscopic level, the material is a normal fluid, with no preferred orientation over normal distances - however as temperature is lowered, thermal fluctuations become weaker and local interactions ~~that~~ between rods that tend to align them are able to drive a transition in the entire system. In the resultant nematic phase of a liquid crystal, a preferred orientation appears at the bulk level. There is ~~now~~ still no spatial order so the system is still a fluid in terms of its propensity to flow, but it possesses a strong long-range orientational order.

The identification of the analogue similarities between these transitions is due to Pierre de Gennes. His approach to describing the nematic transition was based in the Landau-Ginzburg theory of phase transitions. The key ideas behind this theory can be understood qualitatively and pictorially:

① Identify a quantity, let us call it S, a property of each point in space that describes how well ordered the material is in its vicinity. This quantity is called an order parameter.
→ for liquid crystals this is the nematic order parameter,
$S=0$ disordered state
$S=1$ ~~ordered state~~ perfectly ordered nematic state

② Identify an 'energy landscape' in which this parameter changes. The system will tend to move from "high places" to "low places", where 'place' refers to a value of S, under the jostling of a thermal environment.

③ The landscape itself is allowed to shift as the temperature changes. valleys at one temperature can become hills at another and vice-versa. If the order parameter value corresponding to a valley bottom shifts then so will the emergent value of the order itself.



A local maximum of the free energy appears for $T<T_c$ at $S=0$.

Otherwise for $T>T_c$ there is a local maximum at $S=0$.

In the analogy to superconductors:
Slow changes in nematic direction are enough to scatter light through its changing degree of alignment with the light polarization. The spatial domains that seemed to have formed were made of "particle orientation".

The formal argument:

At any point in the liquid there is a preferred direction of orientation of the molecules
→ Macroscopic state of the system can be specified by a director $\hat{n}(\underline{r})$ at each point r. This director has the preferred orientation of the molecules.

→ In a complete equilibrium state $\hat{n} = \text{constant}$. Inhomogeneous distributions $\hat{n}(\underline{r})$ describe various deformational states of the liquid crystal

→ If a macroscopic deformation $\hat{n}(\underline{r})$ varies slowly through the body, the characteristic dimensions of the deformation are large compared to molecular dimensions.
⇒ The derivatives of $\hat{n}(\underline{r})$ with respect to the coordinates are thus small quantities of an order that increases with that of the derivative, so the ~~total~~ total free energy of the deformed liquid crystal (at a given temperature):

$$F_b = \int F\,dV \qquad \text{(free energy of distortions of the director field}$$

we can expand the free energy density in powers of the derivatives $\hat{n}(\underline{r})$

This expansion of F can contain only scalar combinations of the components of the vector $\hat{n}$ and its derivatives.

There are only two scalar combinations linear in the first derivatives

$$\left.\begin{array}{ll} \nabla\cdot\hat{n} & \text{divergence of } \hat{n} \quad \text{(true scalar)} \\ \nabla\cdot(\nabla\times\hat{n}) & \text{pseudoscalar} \end{array}\right\}$$

when integrated over the bulk each reduces to a surface integral or is not allowed by symmetry
→ linear terms are irrelevant or forbidden

True scalars quadratic in the first derivatives can be found by taking the rank-four tensor $\frac{\partial n_k}{\partial x_i}\frac{\partial n_l}{\partial x_m}$ and forming invariants from it by contraction with pairs of suffixes

or multiplication by components of the vector $\hat{n}$. Following this produces the following invariants can be found:

$$(\nabla\cdot\hat{n})^2 \longrightarrow (\text{splay})^2$$

$$(\hat{n}\cdot\nabla\times\hat{n})^2 \rightarrow (\text{twist})^2$$

$$(\hat{n}\times(\nabla\times\hat{n}))^2 \rightarrow (\text{bend})^2$$

Using these 3 invariants quadratic in the derivatives we can write the free energy as:

$$F = \frac{1}{2}K_1(\nabla\cdot\hat{n})^2 + \frac{1}{2}K_2(\hat{n}\cdot\nabla\times\hat{n})^2 + \frac{1}{2}K_3(\hat{n}\times(\nabla\times\hat{n}))^2$$

Frank free energy

These terms are the first non-trivial terms in a gradient expansion of the variations that are consistent with $\hat{n} \Leftrightarrow -\hat{n}$ symmetry. As mentioned this expansion relies on the ~~variations on $\hat{n}$ being~~ spatial variations in $\hat{n}$ being on scales much larger than the length of molecules.

† K's are called classic elastic constants, they are 3 independent effective constants, which depend on the precise molecular details.

Since F has dimensions of energy/volume (energy density), the dimensions of the K's is energy per length (i.e force). We expect them to be in the order of $O(K) \simeq \frac{U}{a} \sim \frac{K_B T}{a}$ with $a \simeq 1\,nm$ the typical molecular length. With this $O(K) \simeq 4\,pN$, consistent with the order of magnitude of typical elastic constants.

Given the order of magnitude and the fact that $\hat{n}$ typically varies on scales much larger than a, the Frank distortion energy is small compared to the total energy of the system. Just as bending distortions are the low energy deformations of a thin rod, director distortions are the low energy distortions of the nematic phase.

Splay, twist and bend distortions

The 3 fundamental deformations of a nematic are splay, twist and bend. Each corresponding to one of the K's. We will consider below the cases where only one of the K's contributes to F, i.e. pure splay ($K_1 \neq 0$), pure twist ($K_2 \neq 0$), pure bend ($K_3 \neq 0$).

Splay K_1

$\hat{n} = (\cos\phi, \sin\phi, 0)$

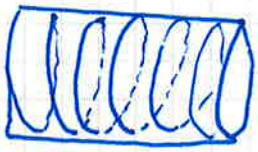
$\hat{n} = \hat{r}$ in cylindrical coord.

directors are radial from center

$$F_d = \frac{K_1}{2r^2}$$

energy density diverges at the origin as a result of a defect being present.

Twist K_2



$\hat{n} = (\cos\theta(z), \sin\theta(z), 0)$

Director rotates in a chiral fashion

$$F_d = \frac{1}{2} K_2 (\theta'(z))^2$$

this term is finite, there is no defect thence no singularity.

Bend K_3

$\hat{n} = (-\sin\phi, \cos\phi, 0)$

$\hat{n} = \phi$ in cylindrical coordinates

Director is ⊥ to the radial vector from center

$$F_d = \frac{K_3}{2r^2}$$

Energy density configuration diverges as in the case of splay.

Equilibrium solutions

The Frank energy density is zero when the director field is uniform. In practice this is impossible due to the boundary conditions, we always have defects.

The problem of finding the equilibrium configuration is equivalent to minimizing the free energy $F_T = \int d^3\underline{r}\, F$ subject to the constraint that $\hat{n}$ is a unit vector.

In the energy minimum the variation of the energy is zero for all types of variations, so the equations determining the equilibrium configuration are:

$$\delta F = 0 \quad \text{for variations } \delta\underline{n} \text{ such that } |\underline{n} + \delta\underline{n}|^2 = 1$$

A way to treat general situations is to allow the variations $\delta\underline{n}$ to be arbitrary by imposing the constraint $|\underline{n}|^2 = 1$ by a Lagrange multiplier.

Imposing the constraint via Lagrange multiplier means that we allow for arbitrary variations $\delta\underline{n}$ of the augmented variational problem:

$$\delta \int d^3\underline{r}\, [F(\underline{n}) + \lambda(\underline{n} \cdot \underline{n} - 1)] = 0$$

Variations $\delta\lambda(\underline{r})$ of λ immediately lead to the constraint $|\underline{n}|^2 = 1$ everywhere:

$$\delta_\lambda \int d^3r\, \lambda(\underline{r})(|\underline{n}|^2 - 1) = \int d^3r\, \delta\lambda(\underline{r})(|\underline{n}|^2 - 1) = 0$$

since $\delta\lambda(\underline{r})$ is arbitrary: $|\underline{n}|^2 = 1 \;\; \forall \underline{r}$, which gives the constraint.

Variation with respect to $\underline{n}$:

Second term of integrand $\quad \delta(\lambda(\underline{n} \cdot \underline{n} - 1)) = \lambda\delta(\underline{n} \cdot \underline{n}) = \lambda(2\underline{n} \cdot \delta\underline{n})$

For the first term of the integrand:

$$\delta F = \frac{\partial F}{\partial n_j}\delta n_j + \frac{\partial F}{\partial(\partial_i n_j)} \underbrace{\delta(\partial_i n_j)}_{\delta(\partial_i n_j) = \partial_i(\delta n_j)}$$

$$\Rightarrow \delta F = \frac{\partial F}{\partial n_j}\delta n_j + \frac{\partial F}{\partial(\partial_i n_j)} \partial_i(\delta n_j)$$

So we have:

$$\int d^3\underline{r} \left[\frac{\partial F}{\partial n_j}\delta n_j + \frac{\partial F}{\partial(\partial_i n_j)} \partial_i(\delta n_j) + 2\lambda n_j \delta n_j\right] = 0$$

$$\Rightarrow \int d^3\underline{r} \left(\frac{\delta F}{\delta \underline{n}} + 2\lambda \underline{n}\right)\cdot \delta\underline{n}(\underline{r}) = 0 \quad (*)$$

where $\frac{\delta F}{\delta \underline{n}}$ is a functional derivative since $\underline{F}$ depends on the whole function $\underline{n}(\underline{r})$

Along standard analysis lines it can be written as:

$$\int d^3\underline{r}\ \frac{\delta F}{\delta \underline{n}}\cdot \delta\underline{n}(\underline{r}) = \int d^3\underline{r}\left[\frac{\partial F}{\partial n_j}\delta n_j + \frac{\partial F}{\partial(\nabla_i n_j)}\nabla_i \delta n_j\right]$$

$$\underset{\text{integration by parts}}{=} \int d^3\underline{r}\left[\frac{\partial F}{\partial n_j} - \nabla_i\left(\frac{\partial F}{\partial(\nabla_i n_j)}\right)\right]\delta n_j$$

It is customary to call the functional derivative of the Frank free energy the molecular field $\underline{h}$:

$$\underline{h} = -\frac{\delta F_T}{\delta \underline{n}} \Rightarrow h_j = -\frac{\partial F}{\partial n_j} + \nabla_i\left(\frac{\partial F}{\partial(\nabla_i n_j)}\right)$$

With this notation we can write the equilibrium equation (*) as:

$$\underline{h} = 2\lambda\underline{n}$$ and by projecting the eq onto $\underline{n}$ we see that:

$$\lambda = \frac{1}{2}\underline{n}\cdot\underline{h}$$ so the equilibrium equations can be summarized by:

$$\underline{h} - \underline{n}(\underline{n}\cdot\underline{h}) = 0$$

Switching the director field. The Frédericks transition

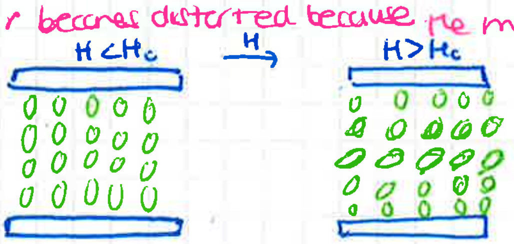
Liquid crystals typically have an anisotropic magnetic susceptibility and electric polarizability. The magnetic and electric contributions to the free energy are:

$$F_M = -\frac{1}{2}\mu_0 \chi_a (\hat{n}\cdot\underline{H})^2$$ Magnetic case

$$F_E = -\frac{1}{2}\varepsilon_0 \varepsilon_a (\hat{n}\cdot\underline{E})^2$$ electrical case

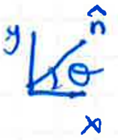
where χ_a and ε_a measure the magnetic & electric anisotropies.

The Frédericks transition is the transition from the undistorted state to the one where the director becomes distorted because the molecules prefer to orient parallel to the field.



bending distortion at $H > H_c$

where H is a magnetic field



For the coordinates sketched in the figure above we have:

$$\hat{n} = (\cos\theta(y), \sin\theta(y), 0) \quad , \underline{H} = (H, 0, 0)$$

The director is anchored in the normal direction at the plates, so we have the B-C:

$$\theta(y=0) = \theta(y=d) = \pi/2$$

For this case the total free energy (per unit area) is the sum of the Frank distortion energy + magnetic term:

$$\frac{F}{\text{area}} = \frac{1}{2}\int_0^d dy \Big[\underbrace{(K_1\cos^2\theta + K_3\sin^2\theta)\left(\frac{d\theta}{dy}\right)^2}_{\text{elastic terms which raise the energy if the director changes orientation}} - \underbrace{\mu_0 \chi_a H^2 \cos^2\theta}_{\text{magnetic term which lowers the energy if the molecules orient with the field}} \Big]$$

For small distortions, i.e $\theta \simeq \frac{\pi}{2}$ bend effects dominate the elastic energy

For large distortions, i.e $\theta \sim 0$ splay deformations dominate

To determine the onset of the Freedericksz transition we start by writing $\theta = \frac{\pi}{2} + \Delta\theta$, just above the threshold $\Delta\theta$ will be small (deviations in the angle will be small). Thus for determining the onset we analyze the free energy to quadratic order in $\Delta\theta$. To this order the energy is:

$$\frac{F}{\text{area}} = \frac{1}{2}\int_0^d dy \left[K_3\left(\frac{d\Delta\theta}{dy}\right)^2 - \mu_0\chi_a H^2 (\Delta\theta)^2 \right] \quad (**)$$

We can analyze the onset by allowing for a sum of Fourier modes that satisfy the B-C $\Delta\theta(0) = \Delta\theta(d) = 0$. Based on this we can anticipate that the mode that becomes unstable first is a sine mode

$$\Delta\theta(y) = A_1 \sin\left(\frac{\pi y}{d}\right)$$ and subs this in the expression (**) we get:

$$\frac{F}{\text{area}} = \frac{d}{4}\left[K_3\left(\frac{\pi}{d}\right)^2 - \mu_0\chi_a H^2 \right] A_1^2$$

For small magnetic fields the elastic term dominates, so the energy of this mode is higher than the energy ($F=0$) of the undistorted state with $\theta = \pi/2$. However as H increases beyond a critical value:

$$H_c = \frac{\pi}{d}\left(\frac{K_3}{\mu_0\chi_a}\right)^{1/2}$$

the energy of the distorted mode is negative, so lower than the undistorted state. So H_c is the critical field for the magnetic Fréedericks transition in this particular configuration.

This analysis illustrates that it's possible to measure the Frank elastic constants from the critical field (H_c) we can switch the B-C or configuration to measure other K's.

Topological defects in the director orientation

When we considered the cases of pure splay and bend we noticed there is a divergence of the elastic energy at the origin. Both of these cases are examples of topological defects, which naturally occur in liquid crystals.

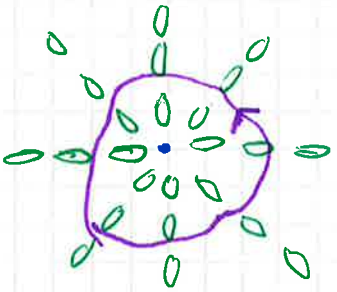
Defects cannot be undone by continuous transformations or deformations of the director field. Defects can annihilate or move to a boundary and disappear, but they can't suddenly disappear in the bulk. They can form and annihilate in pairs. Their existence and interactions often govern most of the long time and long-range dynamics.

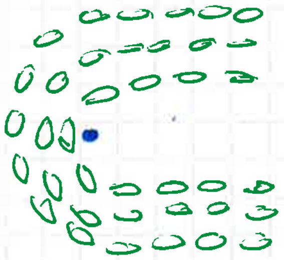
We will call a disclination a discontinuity in the orientation. For any path c along a closed contour encircling a disclination we have that:

$$\oint_c d\theta = 2\pi s \quad , s = \pm\frac{1}{2} , \pm 1 , \dots$$

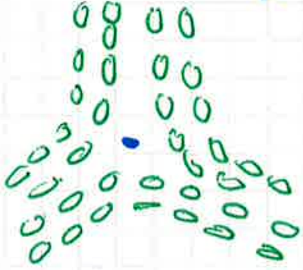
because of the $\hat{n} \Leftrightarrow -\hat{n}$ symmetry of a nematic, continuity of the director field requires that when we follow a closed path around a defect, the director angles at the beginning and end of the path are the same up to a multiple of π.

We can classify any defect by its topological winding numbers.





$s = \frac{1}{2}$

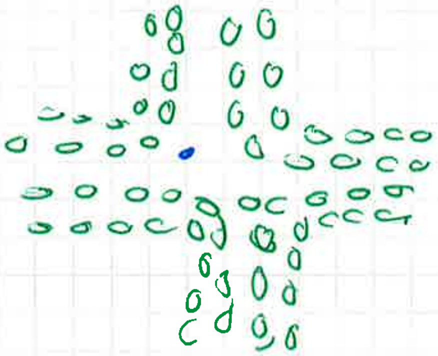


$s = -\frac{1}{2}$

$\oint d\theta = 2\pi$

direction of increasing θ is counterclockwise.

$s = 1$



$s = -1$