phases of liquid crystals and their transitions

Term paper for PHYS 569

Xiaoxiao Wang

Abstract

A brief introduction of liquid crystals and their phases is provided in this paper. Liquid crystal is a state of matter which has intermediate prosperities between liquid and crystalline solid. Its phases are characterized by their space and point group symmetry. We'll give a description of the symmetry and characteristics of different phase types of liquid crystals. And then talk about their phase transition. In particular, we'll talk about some interesting theoretical and experimental results for N-I, N-S_A and S_A-S_C transition.

1. Introduction of liquid crystal

Homogeneous, isotropic liquid has short-range order but no long-range order. It is invariant under arbitrary rotations and translations, thus possesses $T(3) \times O(3)$ symmetry. On the other hand, crystalline solid has long-range positional and rotational order, which results in much lower symmetry. Liquid crystal is a state of matter which has symmetry and mechanical properties that are intermediate between those of a crystalline solid and an isotropic liquid. Their positional order is either fully or partially lost while some degree of orientation order is still maintained.



Fig. 1 Schematic arrangement of molecules in crystalline solid, liquid crystal and isotropic liquid respectively (by Singh and Dunmur[1],p.2)

The liquid crystals can be derived either from the rod-shaped molecules (i.e., one axis is much longer than the other two) which are called "calamitics", or from disc-like molecules (i.e. one molecular axis is much shorter than the other two), which are referred to as "discotics". We'll limit our discussion to calamitics in the rest of this paper. Furthermore, Calamitics can generally be divided into two phases, nematic and smectic phase.



2. Liquid crystal phases

Nematic phase

At high temperatures, thermal fluctuations dominate the system. The axes of the anisotropic molecules are randomly oriented and their centers of mass are randomly distributed. When the isotropic liquid is cooled, the first phase that emerges is the nematic phase. The nematic phase is the simplest liquid crystal phase with least order and highest symmetry. In this phase, the molecules tend to align along a particular direction denote by a unit vector **n**, called the director, while the molecules' centers of mass are still isotropically distributed (Fig. 3(b)). Therefore the translational symmetry T(3) maintains, but the rotational symmetry group $D_{\infty h}$ or a biaxial symmetry group D_{2h} . Nematic phases with higher rotational symmetry such as hexagonal, cubic and so on are also theoretically possible. <u>Smectic phase</u>

If the temperature continues cooling down, the translational symmetry may lose in one dimension, one obtains stacks of two dimensional liquid. Such stratified systems are called smectics (Fig. 3(c), (d)). The interlayer spacing of smectics is welled defined, which is essentially the rod length. The rods can move like liquid or rotate about one axis within each layer. In addition, the interlayer attractions are weak, and there are no correlations of the positions of the molecules from one layer to the next.

Smectics can be characterized by its periodicity in one direction of space, and its point group symmetry. In principle, an infinite number of smectic phases are possible, as no point group is forbidden. However, we only know a finite number of smectics, indicated as S_A, S_B, S_C...S_I. They differ from each other in the orientation of the preferred directions of the molecules with respect the layer normal and the distribution of the centers of the molecules within the layer.

(a) The simplest smectic phase is the smectic A (S_A) which has symmetry of $T(2) \times D_{\infty}$. That is, in this phase, the average molecular orientation is perpendicular to the liquid layers; within each layer the center of mass of molecules are distributed randomly(Fig. 3(c)). Thus the structure may be defined as orientationally ordered fluid on which is superimposed a one dimensional density wave. The smectic layer spacing can be evaluated by small angle x-ray scattering (SAXS) experimentally.

(b) When temperature is further decreased, the S_A phase will transform in to a phase possessing even lower symmetry. The breaking of D symmetry may lead to the appearance of tilting of molecules relative to the smectic layers. The phase thus derived is called smectic C (S_C) which possess the symmetry T(2)×C_{2h}. It has a lower symmetry compared to the S_A phase. The tilted molecules pick a special direction in the smectic plane, i.e., their projections in the xy-plane align along a common direction denoted by a unit vector **c**, called the **c**-director (Fig. 3(d)), just like the molecules in a nematic,. While in S_A phase, the distribution of the molecules' projections in xy-plane is an isotropic liquid.

(c) Apart from what is mentioned above, there are several smectic phases in which the molecules inside the layer have effective rotational symmetry around their long axes and are arranged in a hexagonal (S_B) or pseudo hexagonal (S_F , S_G , S_I , S_J) manner. In a S_B phase, the molecules are normal to the layer plane, whereas in other phases they are tilted.



(d)

Fig. 3 Schematic representation of the position and orientation of anisotropic molecules in (a) the isotropic, (b) the nematic, (c) the smectic-A, and (d) the smectic-C phases. (c) and (d) also show the arrangement of molecules in the smectic planes in the S_A and S_C phases (by Chaikin and Lubensky[4], P.62)

3. Nematic-Isotropic phase transition

Experiments show that the transition between nematic phase and isotropic liquid is of first order. It is a relatively weak transition thermodynamically compared to solid-nematic transition. The heat of transition is only 1kJ/mol. The entropy and volume change involved in this transition are much less than the corresponding values for the solid-nematic transition [1].

A lot of theories have been developed in several directions to describe the nematic phase and N-I phase transition. Among them, the most widely used approach is a phenomenological model proposed by de Gennes based on the Laudau's general description of phase transition, the so called Laudau-de-Gennes (LDG) theory [7].

The basic idea of LDG theory is to expand the Laudau free energy [6] in powers of the order parameters and its spatial variations near the phase transition point, and find the minima of the free energy with respect to order parameter at each temperature and pressure. Let's now talk about it briefly

<u>Order parameter</u>

From previous discussion, we know that different liquid crystal phases are characterized by their symmetry. The transition between different phases involves the breaking of some symmetry. Therefore, the phase transitions can be described in terms of order parameters. In principle, order parameter Q are defined in such a way that

(a) Q=0, in the more symmetric (less ordered) phase

(b) $Q\neq 0$, in the less symmetric (more ordered)phase

Good examples are magnetization as order parameter in ferromagneticparamagnetic transition (see lecture notes).

Experimental measurements find that the significant difference between the isotropic liquid at high temperature and the liquid crystalline phase lies in their macroscopic tensor properties. Therefore, we can use the macroscopic properties, such as diamagnetic susceptibility, the refractive index, the dielectric permittivity and so on, as the tensor order parameters (Here we follow Chaikin and Lubensky[4], P. 39).

A tensor order parameter can be defined in the following way. Suppose some field \mathbf{h} is applied to the system, the resulting response \mathbf{A} of the system is give by

$$A_{\alpha} = T_{\alpha\beta} h_{\beta}$$

where $T_{\alpha\beta}$ is a symmetric tensor, i.e., $T_{\alpha\beta} = T_{\beta\alpha}$, and h_{β} and A_{α} represent, respectively, the component of **h** and **A** in a given coordinate system. **T** can be diagonalized in a properly chosen coordinate system:

$$\mathbf{T} = \begin{pmatrix} T_1 & 0 & 0 \\ 0 & T_2 & 0 \\ 0 & 0 & T_3 \end{pmatrix}$$

The diagonal elements depend on temperature. Imposing the condition $\sum_{i=1}^{3} T_i = T$,

the elements T_i can be expressed as

$$T_{1} = \frac{1}{3}T(1 - Q_{1} + Q_{2})$$
$$T_{2} = \frac{1}{3}T(1 - Q_{1} - Q_{2})$$
$$T_{3} = \frac{1}{3}T(1 + 2Q_{1})$$

i.e., the tensor T can be expressed as

$$T_{\alpha\beta} = T(Q_{\alpha\beta} + \frac{1}{3}\delta_{\alpha\beta})$$

where the tensor Q having elements $Q_{\alpha\beta}$ is identified as the tensor order parameter,

$$Q = \begin{pmatrix} -\frac{1}{3}(Q_1 - Q_2) & 0 & 0 \\ 0 & -\frac{1}{3}(Q_1 + Q_2) & 0 \\ 0 & 0 & \frac{2}{3}Q_1 \end{pmatrix}$$

In the isotropic phase $Q_1 = Q_2 = 0$. In an anisotropic phase of uniaxial symmetry only one order parameter $Q_1 \neq 0$ (and $Q_2 = 0$) is required. A biaxial symmetry requires Q_2 is also not zero. Obviously both of them depend on the temperature.

Consider a Cartesian coordinate system with basis vectors $\overline{e_{\alpha}}$. The elements of this diagonal representation are $\overline{Q_{\alpha\beta}}$. We make an arbitrary rotation of Q to a coordinate system with basis vectors e_{α} to get general expression for the tensor order parameter. The elements $Q_{\alpha\beta}$ of the tensor Q with respect to new coordinate system are given by

$$Q_{\alpha\beta} = -\frac{1}{3}(Q_1 - Q_2)(e_\alpha \cdot \overline{e_1})(e_\beta \cdot \overline{e_1}) - \frac{1}{3}(Q_1 + Q_2)(e_\alpha \cdot \overline{e_2})(e_\beta \cdot \overline{e_2}) + \frac{2}{3}Q_1(e_\alpha \cdot \overline{e_3})(e_\beta \cdot \overline{e_3})$$

This is the general expression of the tensor order parameter for a biaxial phase. In uniaxial nematic, the direction of unique axis give by the director **n** coincide with one of the basis vectors of Cartesian coordinate system in which Q is diagonal. Here $\vec{n} = \vec{e_3}$ or $\vec{n} = -\vec{e_3}$; i.e. $Q_2 = 0$. Now $Q_{\alpha\beta}$ reduces to

$$Q_{\alpha\beta} = -\frac{1}{3}Q_1(e_\alpha \cdot \vec{e_\gamma})(e_\beta \cdot \vec{e_\gamma}) + Q_1(e_\alpha \cdot \vec{n})(e_\beta \cdot \vec{n})$$
$$= -\frac{1}{3}Q_1\delta_{\alpha\beta} + Q_1(e_\alpha \cdot \vec{n})(e_\beta \cdot \vec{n})$$

Here we have used the relation $(e_{\alpha} \cdot \overline{e_{\gamma}})(e_{\beta} \cdot \overline{e_{\gamma}}) = \delta_{\alpha\beta}$. Thus the expression for the tensor

order parameter Q for a uniaxial nematic is given by $Q_{\alpha\beta} = Q_1(n_{\alpha}n_{\beta} - \frac{1}{3}\delta_{\alpha\beta})$

The order parameter Q_1 is temperature dependent and describes the orientational order. As a convention, Q_1 is usually written as S(T) [2], with

$$\mathbf{S}(T) = \frac{1}{2} \left\langle 3\cos^2 \theta_i - 1 \right\rangle = 2\pi \int_0^{\pi} \mathbf{P}_2(\cos\theta) f(\theta) \sin\theta d\theta$$

The brackets denote a statistical average over an ensemble of molecules with their individual long molecular axis deviating from the director **n** by an angle θ_i . $P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$ is the Legendre polynomial of the second order. $f(\theta, \varphi)d\Omega$ is the probability of finding the molecular axis **a** within a solid angle $d\Omega = \sin\theta d\theta d\varphi$ about the direction (θ, φ) . Because the directions +**a** and -**a** are equivalent in the

nematic bulk, $f(\theta, \varphi) = f(\pi - \theta, \varphi)$. Obviously $0 \le \theta < \pi$, and $f(\theta, \varphi)$ does not depend on φ . The function $f(\theta, \varphi) = f(\theta)$ is normalized:

$$\oint f(\theta, \varphi) d\Omega = 2\pi \int_0^{\pi} f(\theta) \sin \theta d\theta = 1$$

In the isotropic phase with a random distribution of θ_i , all orientations have equal probabilities; hence $f(\theta, \varphi) = \frac{1}{4\pi}$, and results in S=0. For perfectly aligned molecules,

$$f(\theta) = \frac{1}{4\pi} \delta(\theta)$$
, thus S=1. The scalar S, first introduced by Tsvetkov [8], can be taken

as the modulus of the order parameter; it is often referred to as the scalar order parameter that describes the degree of orientational order. Experimentally, S can be extracted from NMR (Nuclear Magnetic Resonance) data (see [6], P. 43 for details).

By this definition, the diagonal elements of the tensor order parameter is

$$Q_{xx} = Q_{yy} = -\frac{1}{3}S \text{ and } Q_{zz} = \frac{2}{3}S.$$

LDG theory

Various experimental measurements indicate that in the nematic phase, the order parameter decreases continuously as the temperature is raised while drops abruptly to zero at the NI transition temperature [1]. Near the transition point, the free energy density can be written as (here we closely follow the deviation given by Kleman and Lavrentovich [2])

$$g(p,T,Q) = g_0(p,T,0) + \frac{1}{2}A(T)Q_{\alpha\beta}Q_{\beta\alpha} - \frac{1}{3}B(T)Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \frac{1}{4}C(T)Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\delta}Q_{\delta\alpha} + \cdots$$

where $g_0(p,T,0)$ is the free energy for a given temperature and pressure of the state with Q=0. The simplest possible form of A(T) is a linear one: $A(T) = a(T - T^*)$, a>0, Furthermore, we assume that a, B and C are temperature independent positive constants.

Substitute the order parameter $Q_{\alpha\beta} = S(n_{\alpha}n_{\beta} - \frac{1}{3}\delta_{\alpha\beta})$ into g, we get

$$\Delta g = g(p,T,Q) - g_0(p,T,0) = \frac{1}{3}a(T-T^*)S^2 - \frac{2}{27}Bs^3 + \frac{1}{9}CS^4 + \cdots$$

which should be minimized with respect to S,

$$\frac{dg}{dS} = 0 = a(T - T^*)S - \frac{1}{3}BS^2 + \frac{2}{3}CS^3 + \cdots$$

It has the following solutions near the transition point

 $S_{iso} = 0$ (the isotropic phase)

$$S_{nem} = \frac{B}{4C} \left[1 + \sqrt{1 - \frac{24a(T - T^*)C}{B^2}} \right] > 0 \text{ (the nematic phase)}$$

The third solution is

$$S_{3} = \frac{B}{4C} \left[1 - \sqrt{1 - \frac{24a(T - T^{*})C}{B^{2}}} \right]$$

should be discarded. It corresponds either to an energy maximum, or, at temperatures $T < T^*(S_3 < 0)$, to a local minimum which is not achieved.

The transition temperature T_c and the corresponding value S_c are derived from the condition that the free energy densities of the two phases are equal, $g(S \neq 0) = g_0$ and the condition of stability $\partial g / \partial S = 0$

$$T_c = T^* + \frac{B^2}{27aC}$$
$$S_c = B/3C$$

There is another important temperature T^{**} below which the solution $S_{nem}>0$ gives a local minimum of the free energy density and the nematic phase is therefore metastable (Fig. 4).

$$\mathbf{T}^{**} = T_c + \frac{B^2}{216aC}$$

When B=0, $T_c = T^* = T^{**}$, this becomes a second order phase transition, in which the order parameter S is continuous at transition point.



Fig. 4 Free energy density vs scalar order parameter (by Kleman and Lavrentovich [2])

Experiments found that $S\approx 0.3$ at the transition point, increasing to values of $S\approx 0.6$ far above T_c [9]. Below is a typical experimental figure shows the temperature dependence of S.



Fig. 5 Typical illustration of the temperature dependence of the scalar nematic order parameter S for PAA (p-azoxyanisole). (Data after Ref. [9])

The above development is physically appealing and mathematically convenient. However, the problem associated with this LDG theory is that the coefficients appearing in the expansion are phenomenological. They are assumed to be analytic functions of p, T, which, in reality, may not be true. Also the dependence of the transition on the molecular properties and molecular interactions is not determined in this theory.

In order to solve these problems, many other works have been proposed. Examples are the famous Maier-Saupe theory [10] which attributes the formation of the ordered phase to the anisotropic attractive interaction among molecules, the van der Waals type theories, as well as Singh and others' works [1] which are based on the density functional approach. We won't go into much detail here.

4. Nematic-Smectic A phase transition

More efforts have been made on developing the theory of NS_A transition than any other smectic transition. Despite of that, the situation remains very complicated with a lot of unsolved questions. In the following analysis, we'll see that it is somewhat similar to the superconducting normal transition.

We extend the Landau-de Gennes theory for the NI transition to the NS_A transition as follows (follow [2]).

Again, we start by defining an order parameter for the smectic A phase. The order parameter of the S_A phase must have two components:

(a) A nematic component, with amplitude S and phase n

In Nematic-Smectic A transition, S reaches its maximum value precisely at the transition point. We can assume that the nematic phase is well ordered just above T_c and that S is approximately 1. Also, S is almost temperature independent in the smectic phase immediately below T_c .

(b) A component relating to the modulation of matter density along the z-axis

$$\rho = \sum \rho_{\rm k} \exp(-i\vec{k} \cdot \vec{z})$$

where $\vec{k} = m \frac{2\pi}{d_0} \vec{v}$, m is an integer, **v** is a unit vector normal to the layers, and d₀ is the

smectic layer spacing. Define $q_0 = \frac{2\pi}{d_0}$ as the wave vector.

Consider a slight deformation of smectic, which is described by a displacement field $\vec{u} = u\vec{z}$. The material that was at \vec{r}' is now at \vec{r} , with $\vec{r}' = \vec{r} - \vec{u}$. Hence, the density at \vec{r} can be written as

$$\rho(\vec{r}) = \sum_{k} \rho_{k} \exp\left[-i\vec{k} \cdot (\vec{r} - \vec{u})\right] = \rho_{0} + \rho_{1} \exp\left[-i\vec{q}_{0} \cdot (\vec{r} - \vec{u})\right] + \cdots$$
$$= \rho_{0} + \rho_{1} \exp(i\varphi) \exp\left[-i\vec{q}_{0} \cdot \vec{r}\right] + \cdots$$

where we have introduced the phase $\varphi = \overrightarrow{q_0} \cdot \overrightarrow{u}$. This phase is a degeneracy parameter varying in a range $[0,2\pi]$. It describes all possible positions of the smectic phase with respect to a reference smectic $\varphi = 0$. Therefore, the smectic order parameter that describes the modulation of matter density along z-axis is a complex number:

$$\psi = \psi_0 \exp i\varphi$$

Let us first consider this order parameter only. The expansion of the free energy density is

$$f_{S_A} = \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2M_{\parallel}} \left| \frac{\partial \psi}{\partial z} \right|^2 + \frac{1}{2M_{\perp}} \left| \nabla_{\perp} \psi \right|^2 + \cdots$$

where $\alpha = a(T - T_c)$; the positive coefficients α , β , M_{\parallel} and M_{\perp} all depends on

temperature;
$$\nabla_{\perp} = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, 0)$$
, $|\nabla_{\perp}\psi|^2 = \left|\frac{\partial\psi}{\partial x}\right|^2 + \left|\frac{\partial\psi}{\partial y}\right|^2$. The coefficients $\frac{1}{M_{\parallel}}$ and

 $\frac{1}{M_{\perp}}$ describe the anisotropic rigidity of the smectic phase for the deformation along

the normal and in the layers. There are no odd terms in the free energy density, so that the transition can be second order. The most important feature is the the gradient terms, which indicates that ψ can vary with space.

The director $\vec{n}_0 = (0,0,1)$ may have fluctuations $\vec{\delta n} = (\delta n_x, \delta n_y, 0)$, $\vec{n} = \vec{n}_0 + \vec{\delta n}$.

This leads to the fluctuations of ψ .

Under simultaneous rotations of the director \mathbf{n} and the normal \mathbf{v} to the layers, Laudau free energy of the smectic phase must be invariant:

$$\vec{n} = (\delta n_x, \delta n_y, 1), \quad \vec{v} = \left(-\frac{\partial u}{\partial x}, -\frac{\partial u}{\partial y}, 1\right)$$

These variables are regarded as independent here. Under the rotation by a small angle $\theta \ll 1$, the director tilt $\vec{\delta n}$ is equivalent to the displacement of layers $u = \theta x = -x \vec{\delta n_x}$ along the z-axis, which is further equivalent to a phase change $\varphi \rightarrow \varphi - q_0 x \vec{\delta n_x}$, so that $\psi \rightarrow \psi_0 \exp(i\varphi) \times \exp(-iq_0 x \vec{\delta n_x})$ and

$$\frac{\partial}{\partial x}\psi \rightarrow \left(\frac{\partial}{\partial x} - iq_0 \delta n_x\right)\psi$$

The free energy density with the correct gradient term is, thus,

$$f_{S_A} = \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2M_{\parallel}} \left| \frac{\partial \psi}{\partial z} \right|^2 + \frac{1}{2M_{\perp}} \left| (\nabla_{\perp} - iq_0 \vec{\delta n}) \psi \right|^2$$

The total free energy density is obtained by adding to f_{S_A} the deformation of the nematic director, i.e. the Frank-Oseen energy:

$$f_{FO} = \frac{1}{2}K_1(div\vec{n})^2 + \frac{1}{2}K_2(\vec{n} \cdot curl\vec{n})^2 + \frac{1}{2}K_3(\vec{n} \times curl\vec{n})^2$$

where K_1 , K_2 and K_3 are elastic constants of splay, twist, and bend deformations, respectively. For small director distortions in the vicinity of the transition, the total energy density is

$$f_{tot} = \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2M_{\parallel}} \left| \frac{\partial \psi}{\partial z} \right|^2 + \frac{1}{2M_{\perp}} \left| (\nabla_{\perp} - iq_0 \vec{\delta n}) \psi \right|^2$$
$$+ \frac{1}{2} K_1 (div\vec{n})^2 + \frac{1}{2} K_2 (\vec{n} \cdot curl\vec{n})^2 + \frac{1}{2} K_3 (\frac{\partial}{\partial z} \vec{\delta n})^2$$

de Gennes pointed out that , the total free energy density is analogous to the Ginzburg-Landau functional describing a superconductor-normal metal phase transition:

$$f_{\sup er} = f_{normal} + \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{\hbar^2}{4m} \left(-i\nabla - 2e\frac{\vec{A}}{\hbar c} \right) \psi \Big|^2 + \frac{(curl\vec{A})^2}{8\pi} - \frac{\vec{H_0} \cdot curl\vec{A}}{4\pi} + \frac{1}{4\pi} \left(-i\nabla - 2e\frac{\vec{A}}{\hbar c} \right) \psi \Big|^2 + \frac{(curl\vec{A})^2}{8\pi} - \frac{\vec{H_0} \cdot curl\vec{A}}{4\pi} + \frac{1}{4\pi} \left(-i\nabla - 2e\frac{\vec{A}}{\hbar c} \right) \psi \Big|^2 + \frac{(curl\vec{A})^2}{8\pi} - \frac{\vec{H_0} \cdot curl\vec{A}}{4\pi} + \frac{1}{4\pi} \left(-i\nabla - 2e\frac{\vec{A}}{\hbar c} \right) \psi \Big|^2 + \frac{(curl\vec{A})^2}{8\pi} - \frac{\vec{H_0} \cdot curl\vec{A}}{4\pi} + \frac{1}{4\pi} \left(-i\nabla - 2e\frac{\vec{A}}{\hbar c} \right) \psi \Big|^2 + \frac{(curl\vec{A})^2}{8\pi} - \frac{(curl\vec{A})^2}{4\pi} + \frac{1}{4\pi} \left(-\frac{1}{4\pi} + \frac{1}{4\pi} \right) \frac{(curl\vec{A})^2}{4\pi} + \frac{1}{4\pi} \left(-\frac{1}{4\pi} + \frac{1}{4\pi} + \frac{1}{4\pi} \right) \frac{(curl\vec{A})^2}{4\pi} + \frac{1}{4\pi} \left(-\frac{1}{4\pi} + \frac{1}{4\pi} + \frac{1}{4\pi} + \frac{1}{4\pi} \right) \frac{(curl\vec{A})^2}{4\pi} + \frac{1}{4\pi} \left(-\frac{1}{4\pi} + \frac{1}{4\pi} + \frac{1}{4\pi} + \frac{1}{4\pi} + \frac{1}{4\pi} \right) \frac{(curl\vec{A})^2}{4\pi} + \frac{1}{4\pi} \left(-\frac{1}{4\pi} + \frac{1}{4\pi} + \frac{1}{4$$

with $\vec{A} \leftrightarrow \delta \vec{n}$. The superconductor's order parameter ψ is the wave function of the coherent ensemble of Cooper pairs. Therefore, we can expect that the results for N-S_A transition are similar to that of superconductor-normal metal transition.

Let's minimize the total free energy with respect to ψ^*

$$\alpha \psi + \beta |\psi|^2 \psi - \frac{1}{2M_{\parallel}} \left(\frac{\partial \psi}{\partial z}\right)^2 - \frac{1}{2M_{\perp}} \left((\nabla_{\perp} - iq_0 \vec{\delta n}) \right)^2 \psi = 0$$

This gives two coherence lengths:

$$\xi_{\parallel} = \frac{1}{\sqrt{2|\alpha|M_{\parallel}}}$$
 and $\xi_{\perp} = \frac{1}{\sqrt{2|\alpha|M_{\perp}}}$

For T>T_c, these lengths are the sizes of the smectic clusters in the nematic bulk. As, $T \rightarrow T_c$, the coherence lengths diverge. At T<T_c, these lengths are those along which a strong perturbation of the amplitude of the order parameter relaxes.

Minimize f_{tot} with respect to $\vec{\delta n}$ will give us the penetration length of splay, twist or bend

$$\lambda_1 = \frac{1}{q_0} \sqrt{\frac{M_{\parallel} K_1 \beta}{|\alpha|}} \quad \text{and} \quad \lambda_{2,3}^{\parallel,\perp} = \frac{1}{q_0} \sqrt{\frac{M_{\parallel,\perp} K_{2,3} \beta}{|\alpha|}}$$

Many high resolution heat capacity and X-ray studies have been devoted to the N-S_A transition. Most of the focus has been on the critical exponents. The most extensively measured critical exponents are α , γ , ξ_{\parallel} , ξ_{\perp} . They are the critical exponents of the singular part of the specific heat, the susceptibility, parallel correlation length and perpendicular correlation length, respectively. Typical values are $\gamma \approx 1.3$ -1.5, $\xi_{\parallel} \approx 0.57$ -0.75, $\xi_{\perp} \approx 0.45$ -0.60 (see [6], P. 519 for details). Below is experimental results got by Davidov and Safinya, et al in 1979 [5].



Fig. 6 Left: Longitudinal and transverse correlation lengths as function of reduced temperature. Right: Susceptibility as a function of reduced temperature, which yields $\gamma = 1.26 \pm 0.06$ [5]

5. N-S_C transition and S_A-S_C transition

In S_C phase, the director is tilted by an angle compared to the S_A phase. The tilt of an individual molecule can be described by a vector with an amplitude θ_i and azimuthal tilt direction φ_i . The average molecular tilt over an ensemble of molecules can be expressed by

$$\theta = \left\langle \theta_i \begin{pmatrix} \cos \varphi_i \\ \sin \varphi_i \end{pmatrix} \right\rangle$$

The amplitude of the tilt θ is depends on temperature, pressure and so on and is considered to be the order parameter for phase transition. In the low temperature range of the S_C phase, the typical value of θ is in the order of 25° - 35° [3].

 S_C materials are generally divided into two groups: those transform to S_A phase at high temperature, and those transform to nematic or isotropic phase at high temperature. The S_A - S_C transition is (most often) of second order and can be described by a Landau theory. The calculation is similar to what we did before. In the second case, a first order transition is usually observed, where the order parameter vanishes discontinuously at the transition temperature.



Fig. 7 Typical dependence of the director tilt angle on reduced temperature for a second order $S_c^*-S_A^*$ and a first order $S_c^*-N^*$ phase transition. (Taken from Dierking[3], P.12)

In the S_A - S_C transition, when temperature decreases, the tilt angle increases from $\theta = 0$ (S_A) to $\theta > 0$ (S_C), the smectic layer spacing d thus decreases. This can be observed by SAXS experiments. From X-ray measurements we can obtain the tilt angle by comparing of the layer spacing in S_A and S_C .



Fig. 8 Dependence of the smectic layer spacing d on reduced temperature across the S_A - S_C transition, obtained from SAXS experiments. (It's a second order transition). (Taken from Dierking[3], P.13)

6. Conclusion

In this paper, we talked about general types of liquid crystal phases. We use Laudau-de-Gennes (LDG) theory to explain N-I, N-S_A, N-S_C and S_A-S_C phase transitions. Some experimental results are also presented.

Liquid crystal is a subject with intensive experimental and theoretical studies due to its meaning to fundamental physics research as well as its wide application. However, many aspects of it still remain to be discovered or solved.

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