The Nematic to Smectic-A Phase Transition in Liquid Crystals

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Abstract

Perhaps the most interesting phase transition studied in liquid crystals is the nematic to smectic-A phase transition. Here we begin with a discussion of the mean field approach to the phase transition and move on to a continuum model which turns out to be almost analogous to the Landau-Ginzburg model of conventional superconductors. The analog is then stretch the utmost leading to the startling result of finding a new phase of matter called the Twist Grain Boundary phase.

1 Introduction

From a naïve point of view, the term *liquid crystal* seems to be an oxymoron. How can a substance be both a liquid and a crystal at the same time? The answer, of course, is that a liquid crystal is neither a liquid nor a crystal but is some mixture of both. Even considering such a mixture requires the relaxation of the constraint that a phase of matter must be either a solid or a liquid. However, by doing so, we open up a door to very rich systems with a large wealth of interesting phenomena.

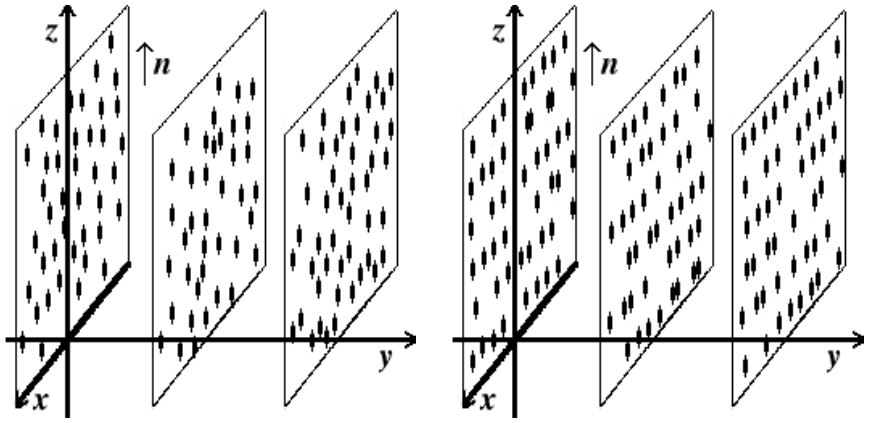
Let us then begin by considering a general system of atoms, each of which exhibit discrete rotational symmetry that depends roughly on the angular momentum of their valence electrons. When a collection of these atoms is cooled from a liquid state, they undergo a phase transition and lose continuous translational symmetry. Because of the discrete symmetry of the atoms it is then hard to imagine any other state besides a discrete lattice after the phase transition. In other words, a collection of discretely symmetrical objects have no choice other than to be in a liquid state or a crystal state.

If we are then to relax the constraint that matter must exist in either a liquid or solid state, we must consider a collection of objects that exhibit some kind of continuous symmetry. This sounds like a rather difficult task as all of matter is composed of atoms which, as we already said, are discretely symmetric. However, if we take a few steps back and consider the gross properties of large molecules, we can to a rough approximation consider them to be modeled by a suitable smooth geometric object[1]. Many polymers then fit into this class of objects and although this approximation seems to be rather crude, it turns out to be enormously powerful.

Consider a collection of ellipsoidal objects or rods whose length is much greater than width. At high temperatures, these objects will be in a liquid state which we shall define as a state with no order of any kind. As we cool the system down, there comes a point at which continuous rotational symmetry is broken yet continuous translational symmetry remains. Suddenly a large number of the ellipsoidal objects point in the same direction! They are still free to move around as they wish, but there orientation is now fixed. Such a phase of matter no longer satisfies our definition of a liquid and gains the new title of a *Nematic Liquid Crystal* and we shall denote the alignment direction of the ellipsoids by $\hat{\mathbf{n}}$, called the *director*. An example of this is displayed in Figure 1.

Not stopping at just a loss of orientational order we continue to cool the system down. As these objects are cylindrically symmetric, we must ask the question, what does cylindrical symmetry imply when we lose translational order? Imagine a cylindrically symmetric state of matter. This state must remain the same through any rotation about the $\hat{\mathbf{z}}$ direction, must be invariant under a $\hat{\mathbf{z}} \to -\hat{\mathbf{z}}$ transformation but contain no other symmetries. Sounds very much like a 2D liquid, but, as we are in 3D, perhaps a stack of 2D liquid sheets would be a better description? This turns out to be exactly the case and our system

[1] A classic case of modeling a horse as a sphere.



(a) Nematic (b) Smectic

Figure 1: An example of a nematic and smectic liquid crystal. Note: the use of vertical planes is purely instructive so that the smectic layers in (b) are co-planer with the xy-plane.

of oriented ellipsoids becomes layered with the nematic director $\hat{\mathbf{n}} = \hat{\mathbf{z}}$ giving the normal to the smectic layer and ellipsoids free to move within each layer but unable to travel between layers. This new phase of matter was given the name of a *Smectic A Liquid Crystal* and is depicted in Figure 1.

Not surprisingly, the geometrical approximation we have made sometimes breaks down. The clearest example of this is when the constituent molecules of the system are chiral. This means that if we place a mirror through the molecule's middle, the image in the mirror is chemically different and so has a different structure than the actual other half of the molecule (see Figure2). Notice that this only really occurs in three dimensions and that the real half of the molecule is generally rotated with respect to the mirror image otherwise a rotation of the image would bring the molecule back to its original state. This has remarkable consequences on a macroscopic scale as the effects of this rotation or twist are seen quite dramatically.

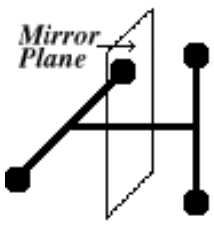


Figure 2: A chiral molecule.

Consider again a collection of ellipsoidal objects but let this collection, upon closer inspection, contain chiral molecules. As we cool down from the liquid state, we find that again orientational order is broken but something else also occurs. The alignment of the ellipsoids is no longer the same throughout the system but instead varies along one direction in a helical pattern(see Figure 3.). This interesting phase is called a *Cholesteric Liquid Crystal.* The pitch of the helix is on the order

of optical wavelengths lending very dynamical responses to beams of light and explains why cholesteric liquid crystals are used quite frequently in the design of flat panel displays.

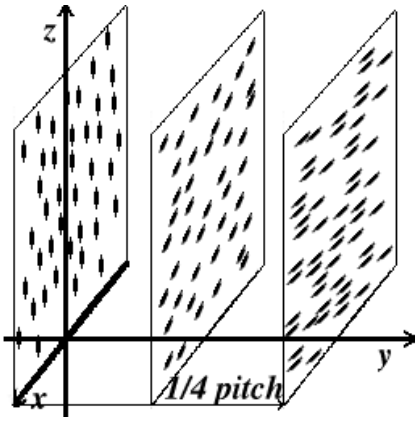


Figure 3: An example of a cholesteric liquid crystal.

Cooling further, the system undergoes another phase transition into again a layered smectic state. It may now be in a state very similar to the smectic A called the smectic A* which although similar in symmetry, contains some form of rotatory power[1][2].

The main goal of this paper is to investigate the phase transition from the Nematic to smectic A mesophases and the corresponding phase transition with chiral molecules. As we shall see, the N-S_A phase transition is quite surprisingly analogous to the normal metal to superconducting phase transition. This analogy was not quite complete before 1988, and in the pursuit of improving it, we shall follow Renn and Lubensky[3] by considering a system of chiral molecules near the same phase transition and will discover a new phase of matter called the *Twist Grain Boundary* phase or TGB.

2 Order Parameters

To begin to describe the N-S_A phase transition, we need to obtain parameters that are zero in the more random phases and take on non-zero values in the new phase. To begin to study the nematic phase, define $\hat{\mathbf{a}}_j$ to be the orientation of the major axis of the j^{th} ellipsoid. We can then count how many ellipsoids are pointing in some general direction, $\hat{\mathbf{c}}$, and define the function

$$f(\hat{\mathbf{c}}) = \frac{1}{N}\sum_{j=1}^{N}\delta(\hat{\mathbf{c}} - \hat{\mathbf{a}}_j), \tag{2.1}$$

which gives the orientational distribution of all of the ellipsoids in the system. If we single out one particular direction, such as the director $\hat{\mathbf{n}}$ in the nematic phase, we can characterize the vector $\hat{\mathbf{c}}$ by the usual polar and azimuthal angles, (θ, ϕ) with respect to that direction so that $f(\hat{\mathbf{c}}) = f(\theta, \phi)$.

[2]For a more in depth discussion on liquid crystals, there is an excellent book by de Gennes and Prost[1] that both introduces the subject and provides a relatively complete reference. For a broader perspective of liquid crystals in soft condensed matter see Chaiken and Lubensky[2]. Harris, Kamien and Lubensky also provide an interesting discussion on molecular chirality[3].

Although $f(\theta,\phi)$ describes the orientational degrees of freedom well, it perhaps contains too much information and we should hunt for a simpler parameter to define the nematic phase. Expanding f in a series of spherical harmonics,

$$f(\theta,\phi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} b_{\ell m} Y_{\ell m}(\theta,\phi), \tag{2.2}$$

we can then search for a particular harmonic to define the nematic phase. Since the nematic phase is cylindrically symmetric, f must be independent of ϕ so that $b_{\ell m} = 0$ for $m \neq 0$. Further, f should not change under the transformation $\hat{\mathbf{z}} \to -\hat{\mathbf{z}}$ or $(\theta,\phi) \to (\pi-\theta,\phi)$, so $b_{\ell m} = 0$ for ℓ odd[3]. Finally, since the liquid phase has $f(\theta,\phi) = Y_{00}(\theta,\phi)$, we define the nematic phase order parameter by the next available harmonic

$$S = \sqrt{\frac{4\pi}{5}} \int d\Omega \; f(\theta,\phi) Y_{20}^*(\theta,\phi) = \frac{1}{2}\left\langle (3\cos^2(\theta) - 1) \right\rangle_f, \tag{2.3}$$

where the factor of $\sqrt{\frac{4\pi}{5}}$ is used so that if $f(\theta,\phi) = \frac{1}{4\pi}(\delta(\theta) + \delta(\pi-\theta))$, the ideal nematic phase, $S = 1$. In other words, we are searching for this harmonic amongst the distribution function $f(\theta)$ (see Figure 4. for a plot).

Along a similar path, we can define an order parameter for the smectic phase. Instead of looking at the conformation of all the ellipsoids, we begin with the positional distribution or density

$$\rho(\mathbf{r}) = \frac{1}{N} \sum_{j=1}^{\infty} \delta(\mathbf{r} - \mathbf{r}_j), \tag{2.4}$$

where $\mathbf{r}_j$ is the center of mass position of the j^{th} ellipsoid. Again we can expand this function and search for a harmonic to characterize a smectic,

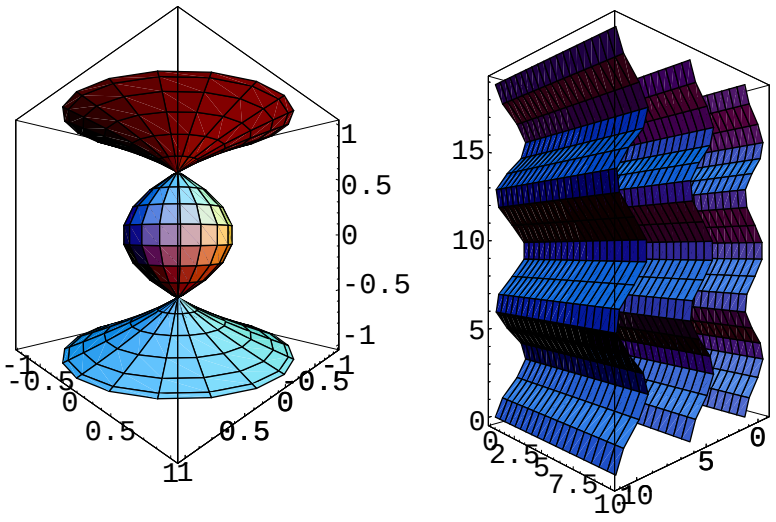
$$\rho(\mathbf{r}) = \int_{-\infty}^{\infty} \frac{d^3k}{(2\pi)^3} \; \rho(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{2.5}$$

If the z-axis defines the normal to each layer in the smectic, then liquid-like behaviour within a layer dictates that $\rho(k_x,k_y,k_z) = 0$ for all nonzero k_x,k_y. Further, the periodicity of the smectic layers limites k_z to $\frac{2n\pi}{a}$ where a is the layer spacing. We must also include the symmetry $\rho(x,y,z) = \rho(x,y,-z)$ so that odd terms must be eliminated. With all this in mind (2.5) can be reorganized into

$$\rho(\mathbf{r}) = \sum_{n=0}^{\infty} 2(\rho(k) + \rho^*(k)) \cos(nq_0 z), \tag{2.6}$$

where $q_0 = \frac{2\pi}{a}$ and we have arbitrarily set the origin on one of the layers. This function completely conforms to the symmetry of a smectic A liquid crystal and

[3]Spherical harmonics have the symmetry $Y_{\ell m}(\theta,\phi) = (-1)^{(\ell+m)} Y_{\ell m}(\pi-\theta,\pi+\phi)$.



(a) Nematic (b) Smectic

Figure 4: The nematic order parameters searches for (a) within the angular distribution function $f(\theta, \phi)$ while the smectic order parameter searches for (b) within the density $\rho(\mathbf{r})$.

is a constant in the nematic phase. Hence, we once again pick out the first non-zero harmonic to be our order parameter

$$\rho_1 = \int d^3r \ \rho(\mathbf{r}) \cos(q_0 z) = \big\langle \cos(q_0 z) \big\rangle, \tag{2.7}$$

where we have used the subscript '1' just to denote that it is the first harmonic (other harmonics have been investigated[1]).

3 Mean Field Description of the N-S_A Phase Transition

Given the above definitions for the two order parameters, we are now in a position to develop the mean field predictions for the N-S_A phase transition. Having two order parameters, however, complicates matters so we proceed cautiously.

Pretending that the smectic phase exists independently of the nematic phase, we can write down a naïve free energy as a power law in ρ_1. Keeping in mind that a transformation $\rho_1 \to -\rho_1$ merely shifts the origin from one layer to

another, we omit odd terms from the free energy and obtain

$$L_S(\rho_1) = \frac{1}{2}r\rho_1^2 + \frac{1}{4}u_0\rho_1^4 + \frac{1}{6}v\rho_1^6. \tag{3.1}$$

The coefficient, r, in the first term varies with temperature in the usual manner as $r \sim T - T_{LS}$. The temperature, T_{LS}, is the obscure temperature at which a 2^{nd} order liquid-smectic phase transition would occur as we have neglected the nematic phase. According to de Gennes[1], the coefficient u_0 is always positive and we may initially neglect the third term.

To evaluate the effects of the nematic phase on the smectic free energy, let us denote S_0 as the nematic order parameter without the interaction of ρ_1. Then in the presence of ρ_1, we can write the free energy contribution as the old nematic free energy plus the response of S to the field ρ_1^2

$$L_N(S) = L_N(S_0) + \frac{1}{2\chi}\delta S^2 - C\rho_1^2\delta S, \tag{3.2}$$

where $\delta S = S - S_0$ and we are evaluating the response of S to ρ_1^2 instead of ρ_1 since as stated previously, we omit odd terms in ρ_1. As anticipated in its definition, if we take $\delta L_N/\delta S = 0$ we find that $\chi \sim \delta S/\delta(\rho_1^2)$ is the response of S to a ρ_1^2 variation[4]. According to de Gennes[1], χ is large near the liquid-nematic transition but small at lower temperatures since S_0 stabilizes away from the phase transition.

We are now in a position to combine the two free energies. First we minimize (3.2) with respect to δS and obtain

$$\delta S = C\chi\rho_1^2 \quad \rightarrow \quad L_N = L_N(S_0) - 2C^2\chi\rho_1^4. \tag{3.3}$$

Then we add this new term to (3.1) and arrive at the mean field description of the N-S_A phase transition

$$L_{NS_A} = L_N(S_0) + \frac{1}{2}r\rho_1^2 + \frac{1}{4}u\rho_1^4 + \frac{1}{6}v\rho_1^6, \tag{3.4}$$

where $u = u_0 - 2C^2\chi$. For large χ, i.e. the N-S_A phase transition is near the liquid-nematic phase transition, u is negative! Hence our mean field theory predicts a tricritical result and we can immediately draw the phase diagram as depicted in Figure 5. We also see that any other competing order parameter, such as ρ_2, S_2, etc. would produce a similar tricritical behaviour.

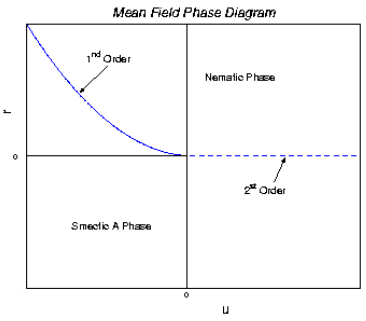


Figure 5: N-S_A phase diagram.

[4]The reader may be more familiar with the analogous case of $\chi_T \sim \frac{\partial M}{\partial H}$ in a magnetic system.

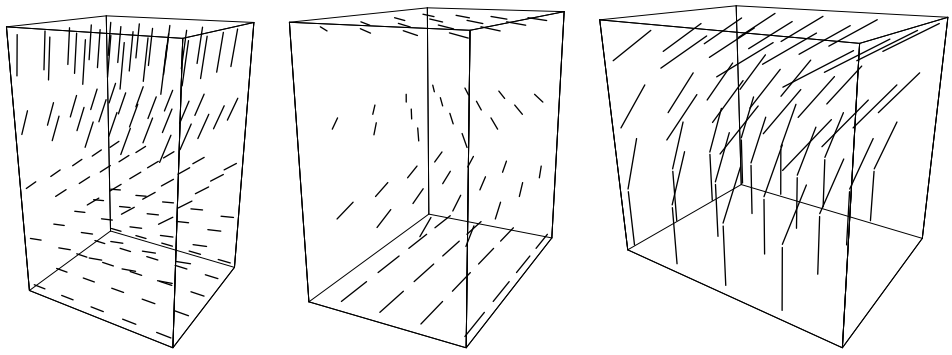
4 The Frank-Oseen Elasticity Theory of Nematics

If we are to deepen our understanding of the N-S_A phase transition, we must begin to incorporate fluctuations. However, due to the physical nature of our system, fluctuations cause various stresses and strains and it is imperative that we develop a theory of elasticity before we continue.

If we compute the director, $\hat{\mathbf{n}}$ by taking the average over a small region of the system, we will find that it varies from place to place. How it varies will give us an idea of how the system fluctuates and hence we can gain a knowledge of the stresses involved. Rather than deriving the result (a nice derivation can be found in de Gennes[1]), we state without proof the Frank-Oseen distortion free energy for nematics:

$$F_d = \int d^3r \ \frac{1}{2}K_1(\nabla\hat{\mathbf{n}})^2 + \frac{1}{2}K_2(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2 + \frac{1}{2}K_3(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2. \qquad (4.1)$$

The three terms in this equation represent three different independent types of stress that can be applied to the system. K_1 refers to a *splay* or growth, K_2 refers to a *twist* and K_3 refers to a *bend* (see Figure 6.). Any stress applied to the system should increase the free energy so that K_1, K_2 and K_3 are all positive.



(a) Splay (b) Twist (c) Bend

Figure 6: Depiction of the three independent distortions. (a) represents splay or divergence, (b) represents a twist similar to a cholesteric liquid crystal and (c) represents a bending of the director. Note: in all cases the ellipsoids are free to move throughout the box and the layered appearance of these diagrams is merely instructive.

5 The Continuum Theory and an Analog of Type II Superconductors

In mean field theory, we have been able to describe the N-S_A phase transition through the order parameter ρ_1. If fluctuations are to be included, we will have to let $\rho_1 \to \rho_1(\mathbf{r})$. However, this is not enough! ρ_1 measures the first harmonic and if we let the layer distance fluctuate, we most certainly have to include higher harmonics. It sounds like a rather onerous task to include the higher harmonics, but in fact we can do so in a simple way. Suppose that we increase the layer spacing by δa, then if we relax the constraint that ρ_1 has to be real, we could simply change the phase of ρ_1 and define a new order parameter:

$$\frac{2\pi}{a+\delta a} z \approx q_0 z - q_0 \frac{z}{a}\delta a \to \tilde{\rho}_1 = \rho_1 e^{-iq_0 \frac{z}{a}\delta a}. \tag{5.1}$$

In other words, this particularly simple distortion of the layer is well described by a U(1) transformation. Hence, if ρ_1 fluctuates locally, to first order we could define a layer displacement field $u(\mathbf{r})$, which was $\frac{z}{a}\delta a$ in the previous example, and create a new order parameter through

$$\psi(\mathbf{r}) = \rho_1(\mathbf{r}) e^{-iq_0 u(\mathbf{r})}. \tag{5.2}$$

Ignoring the distortion free energy of the nematic phase for the moment, we can now simply write down a free energy functional that describes the the N-S_A transition based on our mean field theory

$$L_S[\psi] = \int d^3r \ \frac{1}{2}r|\psi|^2 + \frac{1}{4}u|\psi|^4 + \frac{1}{6}v|\psi|^6 + \frac{1}{2}C_{\|}\left|\frac{\partial\psi}{\partial z}\right|^2 + \frac{1}{2}C_{\perp}|\nabla_{\perp}\psi|^2, \tag{5.3}$$

where $\nabla_{\perp} = (\partial/\partial x, \partial/\partial y)$. Notice the explicit anisotropy in the gradient terms that fundamentally represents the existence of the smectic layers.

The question is, how do we include the elastic effects of the nematic phase? Let us first note that the gradients terms in (5.3) were taken with respect to the director assuming $\hat{\mathbf{n}} = \hat{\mathbf{z}}$. If $\hat{\mathbf{n}}$ is allow to fluctuate, then we have to alter the gradients based on its deviation which we shall define as $\delta\mathbf{n}_{\perp} = \hat{\mathbf{n}} - \hat{\mathbf{z}}$. If we are only concerned with fluctuation to first order, $\delta\mathbf{n}_{\perp}$ lies in the (x,y)-plane and we can write the director $\hat{\mathbf{n}}(\mathbf{r}) \approx (\delta n_x(\mathbf{r}), \delta n_y(\mathbf{r}), 1)$. About a point $\mathbf{r_0}$ we can then define a plane, or smectic layer, by $\hat{\mathbf{n}}(\mathbf{r}_0)\cdot\mathbf{r} \approx const$ so that small changes in z are described by

$$dz = -\delta n_x(\mathbf{r}_0)dx - \delta n_y(\mathbf{r}_0)dy \equiv du, \tag{5.4}$$

and so locally u is described by

$$u = -\delta n_x(\mathbf{r}_0)x - \delta n_y(\mathbf{r}_0)y + const. \tag{5.5}$$

The order parameter then transforms under a fluctuation in the director by $\psi \to \psi e^{+iq_0\delta\mathbf{n}_{\perp}\cdot\mathbf{r}_{\perp}}$ and so the perpendicular gradient changes by

$$\nabla_{\perp} \to \nabla_{\perp} - iq_0\delta\mathbf{n}_{\perp}. \tag{5.6}$$

An alert reader will at this point notice that in a sense, we have just used minimal coupling to include the effects of $\delta\mathbf{n}_\perp$ on our complex order parameter!

Now that we understand the effects of a fluctuation in all relevant parameters of our system, we are able to put everything together and obtain the free energy functional for the N-S_A phase transition (with $u > 0$):

$$L_N S_A[\psi] = \int d^3r \ \frac{1}{2}r|\psi|^2 + \frac{1}{4}u|\psi|^4 + \frac{1}{2}C_\parallel \left|\frac{\partial\psi}{\partial z}\right|^2 + \frac{1}{2}C_\perp|(\nabla_\perp - iq_0\delta\mathbf{n}_\perp)\psi|^2 + \frac{1}{2}K_1(\nabla\delta\mathbf{n}_\perp)^2 + \frac{1}{2}K_2(\hat{\mathbf{z}}\cdot\nabla\times\delta\mathbf{n}_\perp)^2 + \frac{1}{2}K_3\left(\frac{\partial}{\partial z}\delta\mathbf{n}_\perp\right)^2. \quad (5.7)$$

Although this is a rather complicated equation, we can gain some insight by noticing that it is remarkably similar to the Landau-Ginzburg functional describing the normal metal to superconductor phase transition

$$L_{NMSC} = \int d^3r \ \frac{1}{2}r|\Delta|^2 + \frac{1}{4}u|\Delta|^4 + \frac{1}{2m}\left|\left(\hbar\nabla - i\frac{q}{c}\mathbf{A}\right)\Delta\right|^2 + \frac{1}{16\pi\mu}(\nabla\times\mathbf{A})^2. \quad (5.8)$$

This resemblance is simply amazing and unexpected. From it, the following analogy may lend some insight into the N-S_A phase transition:

Liquid Crystal	*Superconductor*	
ψ	Δ	superconductor gap
$\delta\mathbf{n}_\perp$	$\mathbf{A}$	Magnetic vector potential
$C_\parallel, C_\perp$	m^{-1}	inverse mass of cooper pairs
q_0	q/c	charge of cooper pairs
K_1	$1/\mu$	inverse magnetic permittivity
Frank-Oseen elastic energy		Magnetic energy

Figure 7: Analogy of the N-S_A phase transition to the normal metal to superconductor phase transition

Despite the closeness of the analogy, there are basically two differences between smectics and superconductors. Although the vector potential is analogous to $\delta\mathbf{n}_\perp$, the particular gauge we are using has $\delta\mathbf{n}_z = 0$. This gauge has a very real meaning, we are considering only small fluctuations of $\hat{\mathbf{n}}$ away from $\hat{\mathbf{z}}$. Should we consider another gauge, such as $\nabla\cdot\delta\mathbf{n}_\perp = 0$, i.e., the Coulomb gauge, we would get very different physical results. Hence (5.7) is not gauge invariant! The other major difference is that the smectic phase is not isotropic which distinguishes it quite remarkably from the superconductor phase.

What the analogy does tell us is that smectics can be divided up into two types (both experimentally verified[1])

1. The *Meisner effect* for type I superconductors states that such superconductors expel magnetic fields. In the case of smectics, smectics should expel bend and twist.

2. Type II superconductors develop vortices with a circulation quantized in units of 2π. The analog in smectics are dislocations which cause the vector field u to be non-analytic at such abrupt changes in the smectic layering.

6 Critical Behaviour at the N-S_A Phase Transition

Let us consider the nature of the critical exponents and the order of this phase transition with the help of our analogy. Experimentally, we can determine the behaviour K_2 and K_3 with temperature near the phase transition and so it behooves us to use this information as a key into the scaling behaviour of our system. It turns out[4] that

$$\delta K_2 \sim \frac{\xi_\perp^2}{\xi_\parallel} \quad \text{and} \quad \delta K_3 \sim \xi_\parallel, \tag{6.1}$$

where $K_i = K_{0i} + \delta K_i$ and K_{0i} is the value of K_i away from the phase transition. Hence, this allows us to determine the behaviour of the correlation lengths experimentally.

Mean field theory predicts that

$$\xi_\parallel \sim t^{-\frac{1}{2}} \quad \text{and} \quad \xi_\perp \sim t^{-\frac{1}{2}}, \tag{6.2}$$

both above and below the phase transition. However, this makes no sense physically since smectics are not isotropic. We expect that

$$\xi_\parallel \sim t^{-\nu_\parallel} \quad \text{and} \quad \xi_\perp \sim t^{-\nu_\perp} \tag{6.3}$$

with $\nu_\parallel \neq \nu_\perp$ and experiment shows this, but is it predicted by a more elaborate theory? Using various renormalisation group approaches, one can hunt for an anisotropic fixed point. Unfortunately, such attempts have failed in either finding such a fixed point or finding one whose anisotropy is close to that expected experimentally[1]. Other approaches have also been used such as the dislocation unbinding picture. Here dislocations are invented and there effects are extrapolated to the elastic coupling constents. Unfortunately, at least a simple application of this leads to an isotropic result[1]. It seems that theory then has yet to predict adequate critical exponents for this phase transition.

What about the order of the phase transition? Experiment seems to agree with mean field theory in that for $u > 0$ the phase transition is second order and for $u < 0$ it is first order. Our analogy with superconductors tells us that if the

smectic is type I then fluctuations will cause the $u > 0$ portion of the tricritical behaviour to be first order instead of second order. Hence all smectics must be type II! This turns out to be mostly correct but some type I smectics have been found.

7 Twist Grain Boundaries

We concluded at the end of the previous section that smectics are generally analogous to type II superconductors. Hence, they must contain dislocations of some sort. Upon investigating further, Renn and Lubensky[5] discovered a new phase by studying the organization of dislocations with chiral molecules called the *Twist Grain Boundary* phase. Recall the effect of chiral molecule on the nematic phase. In that phase, the director was not constant but rotated in a helical pattern in one direction. However, once the cholesteric phase is cooled through a phase transition into a smectic A* the director is again fixed as the layers are flat planes unable to rotate. This need for rotation must cause a lot of stress on the smectic layer and where one finds stress, so should one find dislocations if they are to occur. Based on this simple description we expect the TGB phase, if it existes, to be something like Figure 8. It turns out, around the same time but independently of Renn and Lubensky's predictions, Goodby *et al.*[6] discovered that this phase in fact does exist. Hence, the prediction of the TGB phase represents a remarkable achievement for the superconductor analogy.

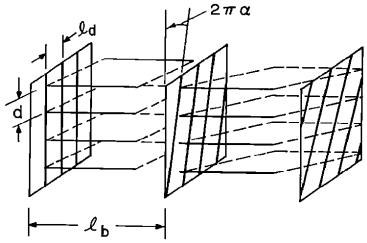


Figure 8: TGB Phase. Taken from[5]

Why were Renn and Lubensky led to study chiral molecules in this phase transition? Perhaps because they noticed in our superconducting analogy, that the twist term contains $\nabla \times \delta\mathbf{n}_\perp$ which is the analog of the magnetic field in a superconductor. Chiral molecules have the same effect as a twist as can be seen by comparing Figures 3 and 6 so that cholesteric liquid crystals are the analog of a normal metal in an external magnetic field. Therefore, if one is to find dislocations (which were not found prior to 1988 but predicted by our superconducting analogy) chiral molecules were the place to search. This is further evidence of the power of the superconducting analogy.

8 Conclusion

In studying the nematic to smectic-A phase transition, we began with a mean field approach. It was found that the quartic term in the Landau free energy was less than zero if the N-S_A phase transition was too close to the liquid-nematic

phase transition. This forces the need for a quantic term driving the phase transition tricritical. This tricritical behaviour is seen experimentally in most liquid crystals so that the mean field phase diagram is essentially correct.

Going beyond mean field theory, fluctuations were included and a continuum theory was established. It was found that this theory bears a very close resemblance to the Landau-Ginzburg theory of the normal metal to superconductor phase transition. The main differences turned out to be that the liquid crystal was not "gauge invariant" and that the anisotropy of the smectic phase had no analog in a superconductor. Despite these differences, the analogy led us to conclude that there are two types of smectics, corresponding to the two types of superconductors. With type I superconductors, fluctuations should drive the second order phase transition predicted by mean field theory into a first order transition. Since, we experimentally find that this phase transition is indeed second order, we concluded that most smectics should be analogous to type II superconductors where such fluctuations are not present.

Type II smectics should then exhibit dislocations as they are analogous to the vortices found in type II superconductors. Prior to 1988 such dislocations were not found but the analogy led Renn. and Lubensky to study chiral molecules and introduce a new liquid crystal phase called a twist grain boundary phase. This phase, being a mixture of a cholesteric liquid crystal and a smectic liquid crystal, included dislocations and hence completed the superconductor analogy.

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