Lectures on Landau Theory of Phase Transitions

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1 Goals of these Lectures

Phase transitions are ubiquitous in nature. Examples include a magnets, liquid crystals, superconductors, crystals, amorphous equilibrium solids, and liquid condensation. These transitions occur between equilibrium states as functions of temperature, pressure, magnetic field, *etc.*; and define the nature of the matter we deal with on a day to day basis. Understanding how to predict and describe both the existence of these transitions, as well as their character and consequences for everyday phenemena, is one of the more important roles of statistical and condensed matter physics.

In this brief set of Lectures I propose to outline one of the basic theoretical tools for describing phase transitions, the **Landau Theory of Phase Transitions**. This was developed by Landau in the 1940's, originally to describe superconductivity. The procedure is general, and is one of the most useful tools in condensed matter physics. Not only can we use Landau Theory to describe and understand the nature of phase transitions among ordered (and disordered) states, but we can use it as a starting point for understanding the behavior of ordered states. These lectures are designed to establish the following broad brush strokes:

1. Very few phase transitions can be calculated exactly: nonetheless, there is still much that can be understood without having to solve the entire problem. These kinds of questions (order of phase transitions, hydrodynamics and elasticity, fluctuations) are the domain of Landau theory.

2. I will present (some of) the problems of phase transitions, and introduce Landau Theory as a way of understanding the behavior (but not the *existence*) of phase transitions.

3. We will explore, through examples, the profound implications of symmetry for the nature of ordered states and their associated transitions.

4. We will see how to use the nature of the *order parameter* to understand deformations in a broken symmetry state: this often goes by the name of *generalized elasticity*, and incorporates elasticity of solids, Frank elasticity in nematic liquid crystals, the deformation energy of smectic liquid crystals and membrane systems, sound waves in fluids, *etc.*

5. Landau theory is a *mean field theory*, in the sense that the system is assumed to be adequately described by a single macroscopic state.

6. We will use Landau free energy functionals to calculate observable quantities such as structure factors; identify the breakdown of Landau theory due to fluctuations.

7. We will examine some interesting paradigms whereby the qualitative nature of phase transitions, such as the *order* of the phase transition, is altered by fluctuation effects and the coupling of different degrees of freedom.

Along the way we will learn how to follow our noses and construct proper free energy functionals on symmetry grounds; pick up some calculational tools; and examine some fundamental ideas in statistical mechanics.

2 Phase Transitions

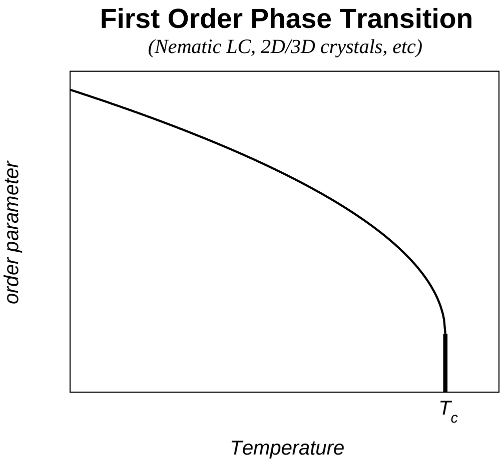
A phase transition occurs when the equilibrium state of a system changes qualitatively as a function of externally imposed constraints. These constraints could be temperature, pressure, magnetic field, concentration, degree of crosslinking, or any number of other physical quantities. In the following I only consider a transition as a function of temperature, but note that the idea is, of course, more general than that (physicists strive to be as general as possible!). In any of these transitions there is some quantity that can be observed to change qualitatively as a function of temperature. In many cases more than one quantity can be observed, but it is quite obvious that something is happening. This quantity will be taken later to be the order parameter of the phase transition.

2.1 Examples

1. **Crystals:** In a transition to a crystalline solid a disordered liquid with non apparent structure undergoes a transition to a structure with long range periodic order, usually in three dimensions. This is most easily parametrized by the mass density, $\rho(\mathbf{r})$:

$$\rho(\mathbf{r}) = \bar{\rho} + \sum_{\mathbf{q}\in\mathbf{G}} \left[\rho(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{r}} + c.c\right], \tag{1}$$

where $\bar{\rho}$ is the mean density and $\{\mathbf{G}\}$ is the set of reciprocal lattice vectors that characterize the crystal structure. The Fourier modes refer to density modulations with wavenumber $q = 2\pi/\lambda$, with wavelength λ. The complex conjugate is added to retain a real number for the mass density. Upon cooling a liquid into a crystal the object that distinguishes the crystal from the liquid is the set of wavevectors $\{\rho(\mathbf{G})\}$, which appear as Bragg peaks in a scattering experiment. Usually these Fourier modes grow discontinuously from zero, in what is called a **first order phase transition:**



2. **Nematic Liquid Crystals:** The *isotropic-nematic* transition occurs in melts (or solutions) of rigid rod-like molecules. At high temperatures (or dilute concentrations) the rods are isotropically distributed, and upon cooling an orientational interaction which is a combination of enthalpic and excluded volume effects encourages the rods to spontaneously align along a particular direction, denoted the **director**, $\hat{\boldsymbol{n}}$. A scalar measure of the order is the anisotropy of the distribution of rods,

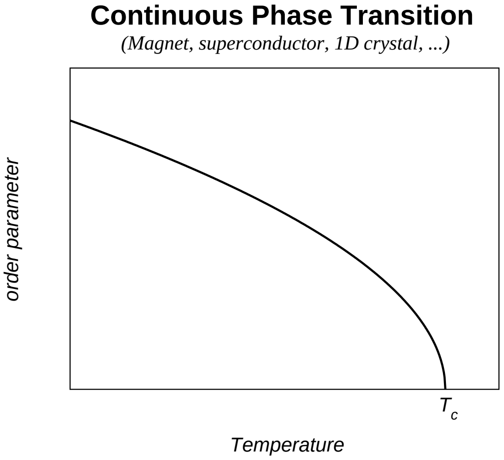
$$\langle P_2(\cos\theta)\rangle = \langle \cos^2\theta - \tfrac{1}{3}\rangle, \tag{2}$$

where the average $\langle\cdot\rangle$ is taken over the equilibrium distribution for all rods in the system, and θ is the angle with respect to some fixed direction. Like 2D crystallization, the isotropic-nematic is a first order transition, with a discontinuity in $\langle P_2(\cos\theta)\rangle$ at the transition temperature T_{IN}. Since "up" and "down" are the same for such a system (in liquid crystals the rodlike molecules are typically symmetric under reflection through the long axis), the order parameter is symmetric under $\cos\theta \to -\cos\theta$.

3. **Magnets:** In a ferromagnet an assembly of magnetic spins undergoes a spontaneous transition from a disordered phase with no net magnetization to a phase with a non-zero magnetization. The order parameter is thus the magnetization,

$$\mathbf{M} = \frac{1}{N}\sum_i \langle \mathbf{S}_i \rangle, \tag{3}$$

   where the average is an equilibrium average over all spins $\mathbf{S}_i$ in the system. Unlike the nematic liquid crystal, the ferromagnetic phase transition is a **continuous phase transition**, in which the magnetization grows smoothly from zero below a critical temperature T_c (often called the *Curie Temperature*, after its discoverer).



Continuous Phase Transition

(Magnet, superconductor, 1D crystal, ...)

4. **One Dimensional (layered) Crystals:** In a one dimensional crystal, or a layered system, a one-dimensional modulation develops spontaneously below the critical temperature. Examples include block-copolymers, which can phase separate into layers of A and B material, to relieve chemical incompatibility but maintain the connectivity constraint; helical magnets which develop a pitch as the spin twists; cholesteric phases which develop a twisted nematic conformation; and smectic phases in thermotropic liquid crystals and lyotropic surfactant solutions. In this case the order parameter is the Fourier mode of the relevant degree of freedom:

$$\psi(\mathbf{r}) = \bar{\psi} + \psi(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{r}} + c.c. \tag{4}$$

   This transition is predicted by Landau (mean field) theory to be continuous, but it is believed to be first order in physical situations, due to fluctuation effects. Hopefully we will get this far!

5. **Phase Separation:** Finally, one of the most common phase transitions from every day life is phase separation, which makes it necessary to shake the salad dressing. In this case the order parameter is the deviation of the local composition from the mean value. Usually this is a first order phase transition, but if the concentration is just right the system can be taken through a *critical point*, or continuous phase transition. This system is equivalent to liquid-liquid or liquid-gas phase separation, in which case the order parameter is a density difference instead of a composition difference.

2.2 Statistical Mechanics and Phase Transitions

One of the uses of statistical mechanics (aside from helping us to understand nature) is to calculate fundamental properties of matter, including phase transitions. In principle, this is a remarkably simple task, thanks to Boltzmann. All of the statistical information of a system is encoded in the *Partition Function*, $\mathcal{Z}$:

$$\mathcal{Z} = \sum_{\mu} e^{-\mathcal{H}[\mu]/k_B T}, \tag{5}$$

where μ refers to all the microstates of the system (*e.g.* all possible configurations spins in a magnet) and $\mathcal{H}[\mu]$ is the Hamiltonian (energy). Boltzmann proved that the (Helmholtz) free energy is given by

$$F = -k_B T \ln \mathcal{Z}. \tag{6}$$

If we can calculate the free energy F we can then calculate all desired thermodynamic quantities by appropriate derivatives.[*] Unfortunately, the free energy can only be evaluated for a few systems, notably the Ising Model (spins which can point up or down, and interact with each other by a very simple interaction, $\mathcal{H} = -J\sum_{ij} S_i S_j$). More often than not we are faced with an impossibly difficult calculation.

In the case of phase transitions, perhaps we can get away with a less rigorous calculation. A clue is the very nature of a phase transition: at a phase transition a system undergoes a *qualitative* change, and develops some order where there was none before. Hence the system does not vary smoothly as a function of (for example) temperature. This means that the free energy $F(T)$ is, mathematically, a *non-analytic* function of temperature. This is of fundamental importance in the theory of phase transitions, and forms the starting point of rigorous studies. A non-analytic function is one for which some derivatives are undefined at certain points, or *singularities.* Phase transitions are points (in the parameter space of field variables such as temperature, pressure, magnetic field) or sets of points which are singularities in the free energy. *The free energy, and hence the behavior of a thermodynamic system, behaves non-smoothly as it is taken through a phase transition.*

It's interesting to try and understand how to get non-analytic behavior out of a sum of exponentials, each of which is separately analytic at any finite temperature:

$$F = -k_B T \ln\left[\sum_{\mu} e^{-\mathcal{H}[\mu]/k_B T}\right]. \tag{9}$$

The existence of singularities in F is a direct result of the *thermodynamic limit*, that is, the presence of an essentially infinite number of degrees of freedom in a thermodynamic system. Possible singularities we can imagine in F are discontinuities in the first derivative, $\partial F/\partial T$,

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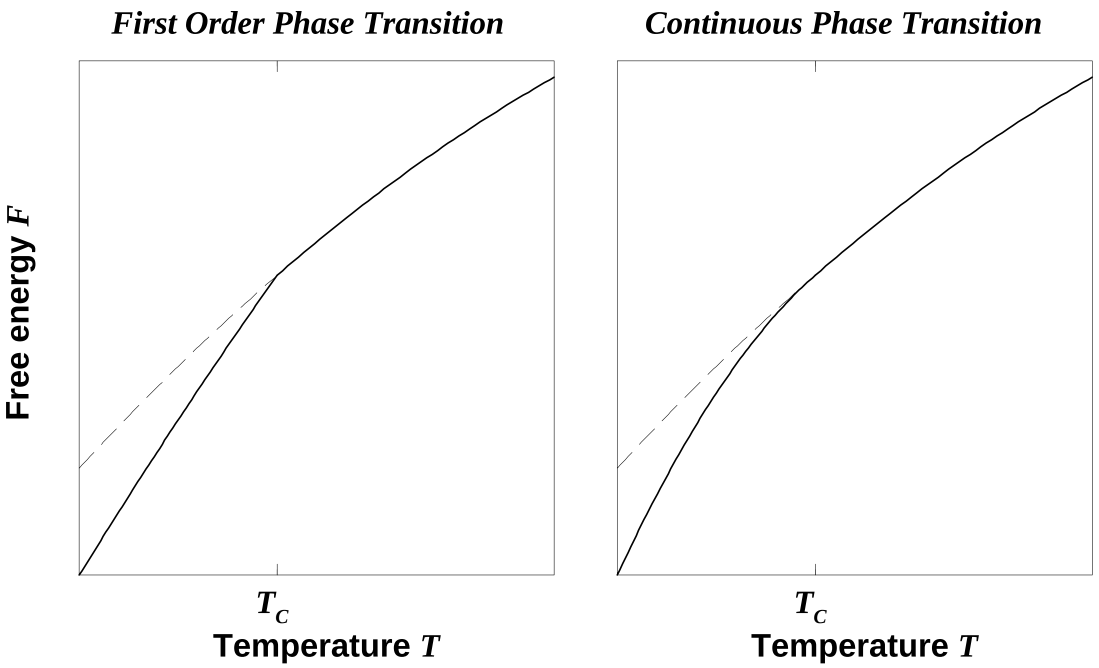
[*] For example, the magnetization can be determined by

$$M = -\left.\frac{\partial F}{\partial h}\right|_{h=0}, \tag{7}$$

where an additional symmetry-breaking field has been added to the system Hamiltonian. For any system, it's only a matter of cleverness to determine the extra field to add to "extract" the desired order parameter by a suitable derivative. In this case the field enters as

$$\mathcal{H}[S] \rightarrow \mathcal{H}[S] - h\sum_i S_i. \tag{8}$$

or in higher order derivatives $\partial^2 F/\partial T^2, \partial^3 F/\partial T^3, \ldots$. These two cases define, respectively, first order or continuous (often termed "second order") phase transitions.



From the theory of analytic functions we are familiar with the fact that a surprising amount of information is contained in singularities: witness the Cauchy Integral Theorem. So, if we can somehow come to grips with a singularity in the free energy, even in just a qualitative way, then perhaps some progress can be made in understanding the physics of phase transitions. This is the goal of Landau Theory.

3 Landau Theory: Fundamentals

3.1 The Recipe

Landau made a series of assumptions to approximate the free energy of a system, in such a way that it exhibits the non-analyticity of a phase transition and turns out to capture much of the physics. There are essentially four steps in this procedure: we will visit these steps first, and then explore them again in terms of the partition function.

1. *Define an order parameter ψ:* For a given system an order parameter must be constructed. This is a quantity which is zero in the disordered phase and non-zero in the ordered phase. Examples include the magnetization in a ferromagnet, the amplitudes of the Fourier modes in a crystal, and the degree of orientation of a nematic liquid crystal.

2. *Assume a free energy functional:* Assume the free energy is determined by minimizing the following functional

$$\tilde{F} = F_0(T) + F_L(T, \psi), \tag{10}$$

where F_0 is an analytic (smooth) function of temperature, and $F_L(T, \psi)$ contains all the information about dependence on the order parameter ψ.

3. *Construction of $F_L(\psi)$:* The Landau Functional is assumed to be an analytic (typically polynomial expansion) function of ψ that obeys all possible symmetries associated with ψ; this typically includes translational and rotational invariance, and other "internal" degrees of dicatated by the nature of the order parameter. This is the most important part of the theory, wherein most of the physics lies.

4. *Temperature Dependence:* It is assumed that all the non-trivial temperature dependence resides in the lowest order term in the expansion of $F_L(T, \psi)$, typically of the form

$$F_L[T, \psi] = \int dV \left[\tfrac{1}{2}a_0(T - T_*)\psi^2 + \ldots\right] \tag{11}$$

Since F_L is constructed as an expansion, there will be other unknown constants. In a physical system these constants have temperature dependence, but if these dependences are smooth then they have negligible effect near the phase transition. This is rigorous for a continuous phase transition, and an approximation for a first order phase transition.

Upon constructing the Landau functional, and minimizing it over ψ as a function of temperature, the nature of the phase transition may be determined. The system at this level is specified as having a uniform, or mean, state; hence Landau theory is really a mean field theory. However, the resulting approximate free energy is a natural starting point for examining fluctuation effects.

3.2 Relation to Statistical Mechanics

To understand what's going on, let's reexamine statistical mechanics. The free energy is given by

$$e^{-F/k_BT} = \sum_{\mu} e^{-\mathcal{H}[\mu]/k_BT}. \tag{12}$$

Landau's assumption is that we can replace the entire partition function by the following,

$$e^{-F/k_BT} \simeq e^{-F_0/k_BT} \int \mathcal{D}\psi\, e^{-F_L[T,\psi]/k_BT}, \tag{13}$$

where the integral $\int \mathcal{D}\psi$ is a *functional integral* over all degrees of freedom associated with ψ, instead of an integral over all microstates. For example, if ψ is the mean magnetization, a given value for the magnetization can be determined by many different microstates. It is assumed that all of this information is contained in F_L. This is a non-trivial assumption which can nonetheless be proven for certain systems. The conversion of the degree of freedom from μ to ψ is known as *coarse-graining*, and is at the heart of the relationship between statistical mechanics and thermodynamics. The next step is to minimize $F_L[T, \psi]$, giving:

$$e^{-F/k_BT} \simeq e^{-F_0/k_BT} e^{-\min_{\{\psi\}} F_L[T,\psi]/k_BT}. \tag{14}$$

This is tantamount to performing a saddle point approximation to the function integral in Eq. (13).

Here's a more formal rationalization:

$$e^{-F/k_BT} = \sum_{\mu} e^{-\mathcal{H}[\mu]/k_BT} \qquad \text{exact Partition Function} \tag{15a}$$

$$= \sum_{\mu} \int \mathcal{D}\psi\, \delta[\psi - \langle\mu\rangle] e^{-\mathcal{H}[\mu]/k_BT} \qquad \text{introduce } \psi \text{ as an average over } \mu \tag{15b}$$

$$= \int \mathcal{D}\psi \sum_{\mu} \delta[\psi - \langle\mu\rangle] e^{-\mathcal{H}[\mu]/k_BT} \qquad \text{interchange limits} \tag{15c}$$

$$\simeq \int \mathcal{D}\psi\, g(\psi) e^{-\mathcal{H}[\psi]/k_BT} \tag{15d}$$

- $g(\psi)$ represents the degeneracy of ψ (number of microstates)
- $\mathcal{H}[\mu] \to \mathcal{H}[\psi]$ is generally incorrect, but illustrates the idea.

$$= \int \mathcal{D}\psi\, e^{-[\mathcal{H}[\psi] - k_BT \ln g(\psi)]/k_BT} \tag{15e}$$

$$\Rightarrow \; F \simeq \min_{\psi} \left[\mathcal{H}[\psi] - k_BT \ln g(\psi)\right]. \qquad \text{saddle point approximation} \tag{15f}$$

Now, the free energy of a system is given by

$$F = E - TS. \tag{16}$$

Hence $\ln g(\psi)$ is essentially the entropy of the system. To rationalize the assumed form of the temperature dependence of $F_L[T,\psi]$, we write:

$$\frac{F}{\text{Volume}} \simeq E_0 \underbrace{-E_*\psi^2}_{\text{attraction}} + \ldots - T[S_0 \quad \underbrace{-a\psi^2 + \ldots}_{\text{reduction due to ordering}} \quad] \tag{17a}$$

$$= F_0 + a(T - \tfrac{E_*}{a})\psi^2 + \ldots \tag{17b}$$

We assume there is some "attraction" neccessary to induce order in the system, but this occurs at the expense of reducing the entropy; this, in principle, is contained in the degeneracy $g(\psi)$. The competition of these effects leads to a phase transition.

In a physical system, the steps between Eq. (15c) and Eq. (15d) is exceedingly difficult, since the relationship between ψ and μ is often not simple, and usually a different functional form than the appearance of μ in the original Hamiltonian $\mathcal{H}[\mu]$. Hence this procedure should be considered a cartoon; in reality, $\mathcal{H}[\psi]$ and $g[\psi]$ are inextricably and inseparably bound into $F_L[\psi]$.[†]

4 Examples

To make this discussion concrete and useful we must examine some physical systems. We will do this in order of complexity, and gradually introduce important concepts and generalizations as they appear.

[†] In the case of polymer blends, where the Hamiltonian is given by $\mathcal{H} = -\sum_{\alpha,\beta} \phi_\alpha V_{\alpha\beta} \phi_\beta$, where ϕ_α denote the mean fractions of species $\alpha = A, B, C, \ldots$ in the blend and $V_{\alpha\beta}$ is a matrix of Flory interaction parameters, the reduction above is essentially correct! This is the RPA (Random Phase Approximation).

4.1 Ising Magnet

Order Parameter—The Ising Model consists of spins which can only point up or down. At high temperatures the spins are disordered, and at low temperatures the spins spontaneously choose whether to point up or down. The order parameter is the mean value of the spins,

$$M = \langle S_i \rangle_{i+\Lambda} \tag{18}$$

where the average is within a region Λ about a given spin. Λ is the *coarse graining length.* To describe local ordering Λ should be much larger than a lattice spacing a, and to adequately describe spatial fluctuations (later), Λ should be much smaller than the system size. Since there are generally 10^7 orders of magnitude to deal with in a particular system, this separation of length scales isn't a problem. For most calculations we don't need to specify the value of Λ, but it becomes important when we consider non-uniform terms (later) or the renormalization group (much later!).

Symmetries—The only symmetry which is relevant for M is that up and down are identical states, related by a rotation of the sample by π. Since we assume the system is rotationally invariant (for example, it isn't in a magnetic field), the free energy in the absence of a field should be invariant under $M \to -M$. Note that this does *not* mean that the spins themselves, or indeed the order parameter, is the same under a flip. This is an important distinction.

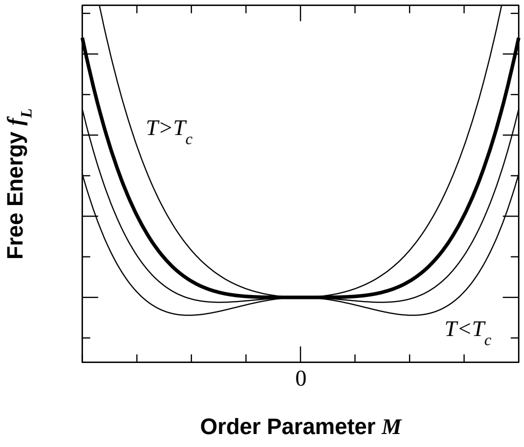
Free Energy—The free energy consistent with this symmetry is

$$f_L \equiv \frac{F_L}{\text{Volume}} = \tfrac{1}{2}a(T-T_c)M^2 + \tfrac{1}{4}\,cM^4 + \ldots \tag{19}$$

Higher order terms M^{2n} are possible, but we will see that they are not necessary to describe the transition. As a function of temperature, this free energy has minima at

$$M = \begin{cases} 0 & (T > T_c) \\ \pm\sqrt{\frac{a(T_c-T)}{c}} & (T < T_c) \end{cases} \tag{20}$$

for temperatures $T < T_c$. This is a **continuous transition**, since the magnetization grows smoothly from zero. We shall see that this is a feature of all free energies which, by symmetry, have only even powers of the order parameter.



Thermodynamics—Upon minimizing the free energy, the free energy as a function of temperature is now:

$$F = \begin{cases} F_0(T) & (T > T_c) \\ F_0(T) - V\tfrac{1}{2}\dfrac{a|T_c-T|^2}{c} & (T < T_c) \end{cases} \tag{21}$$

(V is the volume). Hence, we see that $\partial F/\partial T$ vanishes at the critical point, while the second derivative has a discontinuity:

$$\left.\frac{\partial^2 F}{\partial T^2}\right|_{T_c^+} - \left.\frac{\partial^2 F}{\partial T^2}\right|_{T_c^-} = \frac{a}{c}\,V. \tag{22}$$

Hence this is a second order phase transition. This is related to the heat capacity:

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_V = -T\left.\frac{\partial^2 F}{\partial T^2}\right|_V. \tag{23}$$

Thus, for the magnet there is a discontinuity (a step decrease) in the heat capacity given by $\Delta C_V = -VTa/c$.

The Landau free energy has two free parameters, a and c. In principle, these can be determined by comparison with experiment from the shape of $M(T)$ and the heat capacity jump.

4.2 Heisenberg Ferromagnet

Order Parameter—In the Heisenberg ferromagnet (in, say, 3D), the spin can point anywhere in space. Hence the magnetization is a vector, defined in the same was as for the Ising Model:

$$\mathbf{M} = \langle \mathbf{S}_i \rangle_{i+\Lambda} \tag{24}$$

Symmetries—In the magnetic state the system spontaneously chooses a direction in which to point. In isolation this direction is entirely arbitrary. Hence, the system is rotationally symmetric with respect to any angle of rotation. Any free energy must be invariant under

$$\mathbf{M} \longrightarrow \mathsf{R}\cdot\mathbf{M}, \tag{25}$$

where R is a rotation matrix. If $\mathbf{M}$ is the only order parameter in the problem, and space is isotropic, then any free energy must only depend on the invariant $\mathbf{M}\cdot\mathbf{M}$. Under a rotation this invariant transforms as

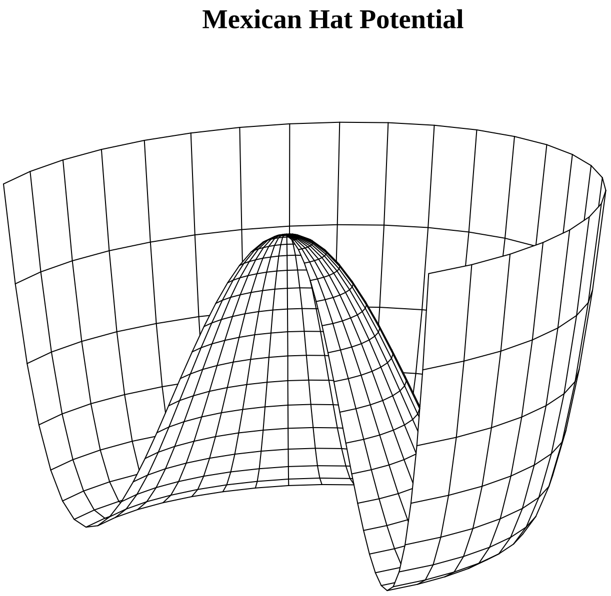
$$\mathbf{M}\cdot\mathbf{M} \rightarrow \mathbf{M}\cdot\mathsf{R}^T\cdot\mathsf{R}\cdot\mathbf{M} = \mathbf{M}\cdot\mathbf{I}\cdot\mathbf{M} = \mathbf{M}\cdot\mathbf{M}, \tag{26a}$$

where we used the fact that $\mathsf{R}^T\cdot\mathsf{R}$ is the identity matrix $\mathbf{I}$, for any proper rotation.

Free Energy—The free energy consistent with this symmetry is

$$f_L \equiv \frac{F_L}{\mathrm{V}} = \tfrac{1}{2}a(T-T_c)\mathbf{M}\cdot\mathbf{M} + \tfrac{1}{4}\,c\,(\mathbf{M}\cdot\mathbf{M})^2 + \ldots \tag{27}$$

Odd order terms are not allowed by symmetry. Hence, like the Ising Magnet, the Heisenberg Magnet has a second order transition. The primary difference between the two systems is that, while the Ising magnet breaks up-down symmetry, the Heisenberg magnet *breaks rotational symmetry:* $\mathbf{M}$ can point anywhere in space. The free energy surface is often called the “wine bottle” or “Mexican hat” potential. Below the Curie temperature T_c the system rolls to the bottom of the wine bottle.



Once the system has broken symmetry, the further behavior at a given temperature (under, say, the action of a small perturbing field) is much different than that of the Ising magnet. While the Ising magnet can change only its magnitude, the Heisenberg magnet can change both magnitude and direction. From the shape of the potential we can see that changes in magnitude run up the side of the wine bottle, while changes in direction run around the bottom of the wine bottle and cost no energy! Hence the response, and elasticity, of the broken symmetry state is dominated by the "soft" modes around the wine bottle. This is a general feature of all systems which spontaneously break continuous symmetries, including the big bang! It is arguably one of the most important principles in the universe. The curvature up the side of the wine bottle is often called a "mass", and in the context of the big bang may have something to do with real physical mass.

4.3 Nematic Liquid Crystals

The Isotropic-Nematic transition is an excellent example because, in addition to telling us about the liquid crystal system, it contains many general features of first order phase transitions (liquid-gas, liquid-crystal, etc).

Order Parameter—In nematic liquid crystals, rodlike molecules develop an orientation in space, along an arbitrary direction called the director, $\hat{\boldsymbol{n}}$. We have already mentioned that a useful scalar order parameter for this transition is the average $\langle P_2(\cos\theta)\rangle$. However, this is not a useful order parameter since it is not obvious how to deal with the rotational symmetry. It is more useful to consider the mean of the orientation vectors $\hat{\boldsymbol{\nu}}_i$ for all rods. Since rods are assumed to have up-down symmetry (*i.e.* they look the same [unlike magnetic spins]), the order parameter itself must be invariant under $\hat{\boldsymbol{\nu}} \to -\hat{\boldsymbol{\nu}}$. Hence we need something quadratic in $\hat{\boldsymbol{\nu}}$. We will use the following *tensor* order parameter,

$$Q_{\alpha\beta} = \langle \nu_\alpha \nu_\beta - \tfrac{1}{3}\delta_{\alpha\beta}\rangle_\Lambda, \tag{28}$$

where $\delta_{\alpha\beta}$ is the identity tensor. As before, this is defined within a volume of order Λ^3, much larger than a molecular volume. For an isotropic distribution of rods all orientations are uncorrelated, so that $\langle \nu_\alpha \nu_\beta \rangle$ vanishes unless $\alpha = \beta = x, y, z$, in which case all directions are equally probable, $\nu_\alpha \nu_\alpha = \frac{1}{3}$. Hence, Q vanishes in the isotropic state and is non-zero in the nematic state.

Note that the *trace* of Q, defined as the sum of all diagonal elements, vanishes:

$$\mathrm{Tr}\,\mathsf{Q} \equiv \sum_\alpha Q_{\alpha\alpha} = \langle \widehat{\boldsymbol{\nu}} \cdot \widehat{\boldsymbol{\nu}} - \tfrac{1}{3} \cdot 3 \rangle = 0. \tag{29}$$

Hence, although Q has three eigenvalues, only two are independent because of the trace condition. The most general form of Q is:

$$\mathsf{Q} = \begin{pmatrix} -\frac{1}{3}S_1 + S_2 & 0 & 0 \\ 0 & -\frac{1}{3}S_1 - S_2 & 0 \\ 0 & 0 & \frac{2}{3}S_1 \end{pmatrix} \equiv S_1(\widehat{\boldsymbol{n}}\,\widehat{\boldsymbol{n}} - \tfrac{1}{3}\mathbf{I}) + S_2(\widehat{\boldsymbol{m}}\,\widehat{\boldsymbol{m}} - \widehat{\boldsymbol{l}}\,\widehat{\boldsymbol{l}}). \tag{30}$$

If $S_2 = 0$ the system is uniaxial, with principal axis of alignment $\widehat{\boldsymbol{n}}$, and $S_1 = \langle P_2(\cos\theta)\rangle$. For $S_2 \neq 0$ the system is biaxial, with $\widehat{\boldsymbol{m}}$ and $\widehat{\boldsymbol{l}}$ the major and minor axes of alignment in the plane normal to $\widehat{\boldsymbol{n}}$. Note that $\widehat{\boldsymbol{l}} = \widehat{\boldsymbol{n}} \times \widehat{\boldsymbol{m}}$, so there are two independent axes (hence biaxial).

Symmetries—There are two relevant symmetries to think of for the order parameter.

1. (Lack of) inversion symmetry. Consider a uniaxial state:

   $$\mathsf{Q} = \begin{pmatrix} -\frac{1}{3}S_1 & 0 & 0 \\ 0 & -\frac{1}{3}S_1 & 0 \\ 0 & 0 & \frac{2}{3}S_1 \end{pmatrix} \quad \text{(prolate uniaxial)} \tag{31}$$

   Under inversion,

   $$-\mathsf{Q} = \begin{pmatrix} \frac{1}{3}S_1 & 0 & 0 \\ 0 & \frac{1}{3}S_1 & 0 \\ 0 & 0 & -\frac{2}{3}S_1 \end{pmatrix} \quad \text{(oblate uniaxial).} \tag{32}$$

   Hence the degree of order is qualitatively different under $\mathsf{Q} \to -\mathsf{Q}$, and odd invariants are allowed in the free energy.

2. In a homogeneous isolated system the direction of nematic order is arbitrary; that is, the system and therefore the free energy is rotationally invariant. Q behaves like a tensor under rotation, because it is a dyad of unit vectors which rotate as usual. Hence an arbitrary rotation, for which

   $$Q_{\alpha\beta} \longrightarrow R_{\alpha\lambda} R_{\beta\rho} Q_{\lambda\rho}, \tag{33}$$

   must leave the free energy invariant. For a 3D tensor Q, there are two non-trivial invariants (corresponding to the two independent eigenvalues), $\mathrm{Tr}\,\mathsf{Q}^2$ and $\mathrm{Tr}\,Q^3$. Under a rotation,

$$\begin{aligned}
\mathrm{Tr}\,\mathsf{Q}\cdot\mathsf{Q} = Q_{\alpha\beta}\,Q_{\beta\alpha} &\to R_{\alpha\lambda}\,R_{\beta\rho}\,Q_{\lambda\rho}\,R_{\beta\mu}R_{\alpha\nu}\,Q_{\mu\nu} && \text{(34a)}\\
&= (\mathsf{R}^T\mathsf{R})_{\nu\lambda}\,(\mathsf{R}^T\mathsf{R})_{\mu\rho}\,Q_{\lambda\rho}\,Q_{\mu\nu} && \text{(34b)}\\
&= \delta_{\nu\lambda}\,\delta_{\mu\rho}Q_{\lambda\rho}Q_{\mu\nu} && \text{(34c)}\\
&= Q_{\nu\mu}Q_{\mu\nu} && \text{(34d)}\\
&= \mathrm{Tr}\,\mathsf{Q}\cdot\mathsf{Q}, && \text{(34e)}
\end{aligned}$$

and similarly for any power $\mathrm{Tr}\,\mathsf{Q}^n$.

Free Energy—Respecting the invariants, the free energy is

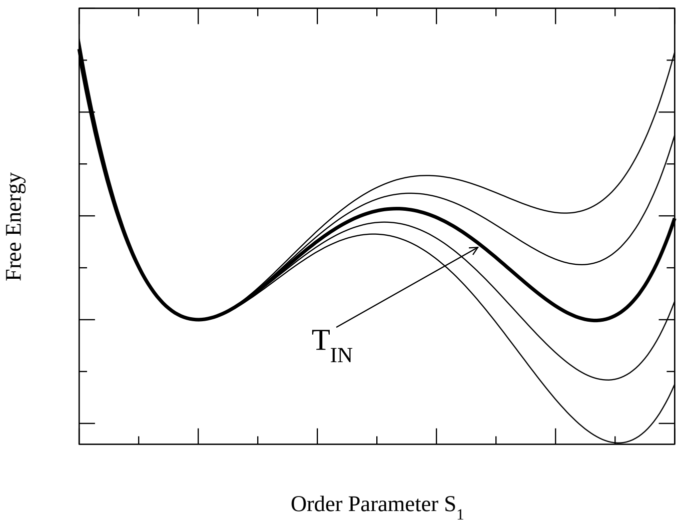
$$f_L = \tfrac{1}{2}\,a\,(T-T_*)\;\mathrm{Tr}\,\mathsf{Q}^2 + \tfrac{1}{3}\,b\,\mathrm{Tr}\,\mathsf{Q}^3 + \tfrac{1}{4}\,c\left(\mathrm{Tr}\,\mathsf{Q}^2\right)^2. \tag{35}$$

We can now insert the general form of Q, Eq. (30), into the free energy, and minimize over S_1 and S_2. We need to compute quantities such as

$$\begin{aligned}
\mathrm{Tr}\,\mathsf{Q}^2 &= S_1^2\,\mathrm{Tr}\left(\widehat{\boldsymbol{n}}\widehat{\boldsymbol{n}} - \frac{1}{3}\boldsymbol{I}\right)^2 + 2S_1S_2\,\mathrm{Tr}\left(\widehat{\boldsymbol{n}}\widehat{\boldsymbol{n}} - \frac{1}{3}\boldsymbol{I}\right)\cdot\left(\widehat{\boldsymbol{m}}\widehat{\boldsymbol{m}} - \widehat{\boldsymbol{l}}\,\widehat{\boldsymbol{l}}\right) + S_2^2\,\mathrm{Tr}\left(\widehat{\boldsymbol{m}}\widehat{\boldsymbol{m}} - \widehat{\boldsymbol{l}}\,\widehat{\boldsymbol{l}}\right)^2\\
&= \tfrac{1}{3}S_1^2\,\mathrm{Tr}[\widehat{\boldsymbol{n}}\widehat{\boldsymbol{n}} + \tfrac{1}{3}\boldsymbol{I}] - \tfrac{2}{3}\,S_1S_2\,\mathrm{Tr}\left(\widehat{\boldsymbol{m}}\widehat{\boldsymbol{m}} - \widehat{\boldsymbol{l}}\,\widehat{\boldsymbol{l}}\right) + S_2^2\,\mathrm{Tr}[\widehat{\boldsymbol{m}}\widehat{\boldsymbol{m}} + \widehat{\boldsymbol{l}}\,\widehat{\boldsymbol{l}}] && \text{(36a)}\\
&= \tfrac{2}{3}\,S_1^2 + 2\,S_2^2, && \text{(36b)}
\end{aligned}$$

using properties of unit vectors and the orthonormal system $\{\widehat{\boldsymbol{n}},\widehat{\boldsymbol{m}},\widehat{\boldsymbol{l}}\}$. The free energy reduces to (up to algebraic errors!)

$$f_L = \underbrace{\tfrac{1}{3}a(T-T_*)\,S_1^2 + \tfrac{2}{27}b\,S_1^3 + \tfrac{1}{9}c\,S_1^4}_{F_1} + \underbrace{S_2^2\left[a(T-T_*) - \tfrac{4}{3}b\,S_1 + \tfrac{2}{3}c\,S_2^2\right] + c\,S_2^4}_{F_2}. \tag{37}$$



Thermodynamics In principle we must look for minima of f_L as a function of S_1 and S_2. F_1 gives, for $S_2 = 0$, a minima at $T > T_*$ for bS_1 negative, due to the cubic term. This will make the term in square brackets in F_2 positive, so the system is stable against S_2 becoming non-zero, and is in fact a uniaxial state. So, we consider $S_2 = 0$ and minimize over S_1:

$$\left.\frac{\partial F_1}{\partial S_1}\right|_{S_2=0} = 0 \longrightarrow S_1^* = \begin{cases} 0 \\ \dfrac{1}{4c}\left[-b \pm \sqrt{b^2 - 24ac}\right]. \end{cases} \tag{38}$$

By inspection, we take the root with the largest magnitude; now we must change the temperature until the free energy at S_{1*} vanishes, at which point the system makes a first order phase transition to the nematic state. (Somewhat tedious) algebra gives:

$$S_{1*} = -\frac{b}{6c}, \qquad \Delta T = T_{IN} - T_* = \frac{b^2}{27ac}. \tag{39}$$

If want a prolate uniaxial state we must have S_1 positive, in which case we must choose $b < 0$. Conventionally, then, the Landau Free energy for a nematic liquid crystal is usually written as $f_L = \ldots - \frac{1}{3}\, b \,\mathrm{Tr}\,\mathsf{Q}^3 + \ldots$, with $b > 0$. We'll continue here, however, with a general b. Substituting into the free energy, we find

$$f = f_0 + \begin{cases} 0 & (T > T_{IN}) \\ \frac{1}{2}a(T - T_*)S_{1*}^2 + \ldots & (T \leq T_{IN}). \end{cases} \tag{40}$$

The free energy is continuous at T_{IN}, but has a kink. This kink is related to the entropy change, for we can calculate

$$\frac{S}{V} = -\frac{\partial f}{\partial T} = -\frac{\partial f_0}{\partial T} + \begin{cases} 0 & (T > T_{IN}) \\ \frac{\partial}{\partial T}\left\{\frac{1}{2}a(T - T_*)S_{1*}^2 + \ldots\right\} & (T \leq T_{IN}). \end{cases} \tag{41}$$

Hence the entropy change upon cooling through the transition temperature is

$$\Delta S = S_{T=T_{IN}^-} - S_{T=T_{IN}^+} = -\frac{b^4}{729\, a\, c^3} \tag{42}$$

The entropy of the system decreases, which is the latent heat $L = T_{IN}\Delta S$ liberated upon cooling into the nematic state.

Notes:

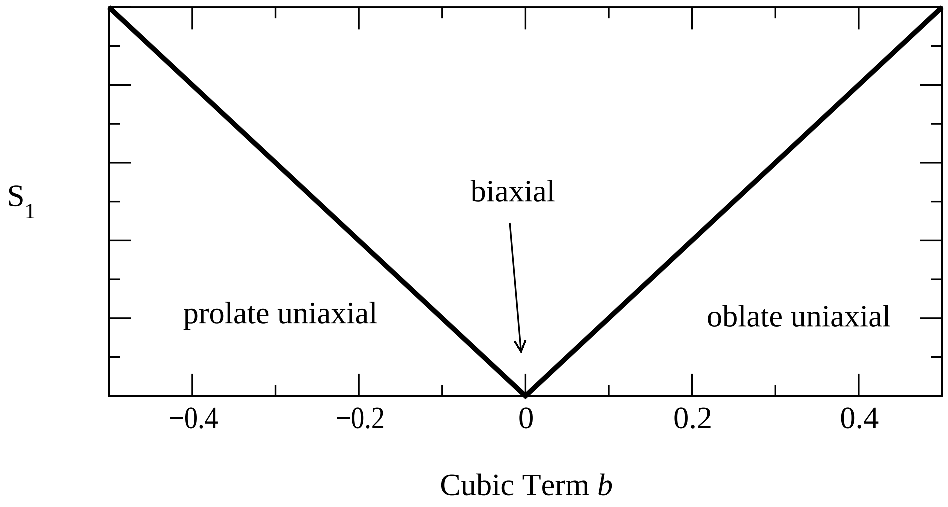
1. Like the magnet, the liquid crystal spontaneously breaks rotational symmetry, with a direction (director) $\hat{\boldsymbol{n}}$ chosen at random by the system.
2. The Landau free energy for a first order transition is not strictly correct just below the transition, since the order parameter grows from a finite value. Hence all results can only be qualitative at best, even within mean field theory. Conversely, the Landau energy for a second order transition is exact, within mean field theory, close to the transition.
3. There are three parameters, a, b, c, T_*, which can be fitted from experiment by measuring, for example, $T_{IN}, S_{1*}, \Delta T$, and the latent heat. ΔT can be measured from light scattering far above T_{IN}.

4. Other mean field first order phase transitions also typically have a cubic term (*e.g.* most crystal phases).

Biaxial Phases—Consider the case where the cubic term vanishes, $b = 0$. One could imagine such a system by, for example, mixing molecules of different shapes. In this case the free energy is all even terms in S_1 and S_2:

$$f_L = \tfrac{1}{3}a(T - T_*)\,S_1^2 + \tfrac{1}{9}c\,S_1^4 + S_2^2\left[a(T - T_*) + \tfrac{2}{3}c\,S_2^2\right] + c\,S_2^4. \tag{43}$$

This is thus a *second order* phase transition, and it turns out to have both S_1 and S_2 non-zero, so it is a biaxial phase transition. There have been very few examples of biaxial phases; one can see that the chemistry has to be very special for such a phase.



4.4 Crystal Systems

With crystal systems we will round off the most common set of classical phase transitions. In this case the order parameter is the density (or modulation of some other quantity, such as composition, charge, *etc)*)

$$\rho(\mathbf{r}) = \bar{\rho} + \sum_{\mathbf{q}\in\mathbf{G}}\left[\rho(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{r}} + c.c\right], \tag{44}$$

The Landau free energy is usually expanded in the Fourier coefficients of the density, $\rho(\mathbf{q})$. Note that these are *complex numbers*, and hence contain phase information. In particular, note that $\rho^*(\mathbf{q}) = \rho(-\mathbf{q})$, which can be seen by taking the complex conjugate of $\rho(\mathbf{r})$, which must be the same thing as $\rho(\mathbf{r})$ (a real number).

4.4.1 Lamellar Systems

Lamellar systems are one-dimensional crystals, and include magnetic systems, smectic liquid crystals, and lamellar block copolymers. A wavevector is assumed, $\mathbf{q} = 2\pi\widehat{\boldsymbol{n}}/\lambda$, pointing in a direction $\widehat{\boldsymbol{n}}$ with wavelength λ.

Order Parameter—The order parameter is taken to be the single Fourier mode $\rho(\mathbf{q})$. Other harmonics will be stabilized at lower temperatures. This is an assumption, and in some cases one could have, due to the microscopic physics, a coincidence of transition temperatures for several harmonics.

Symmetries—The only relevant symmetry is translational invariance. Although we will see that the lamellar state breaks translational invariance, the lamellae can be slid anywhere, and the high temperature state has no preferred point of reference. Under translation $\mathbf{r} \to \mathbf{r}+\mathbf{a}$, the density transforms to

$$\rho(\mathbf{r}) \to \rho(\mathbf{r}+\mathbf{a}) = \bar{\rho} + \sum_{\mathbf{q}\in\mathbf{G}} \left[\rho(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{r}-i\mathbf{q}\cdot\mathbf{a}} + c.c\right]. \tag{45}$$

Hence we have $\rho(\mathbf{q}) \to \rho(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{a}}$. That is, all Fourier modes pick up a phase shift. For the free energy to possess translational invariance, there can be no dependence on the complex phase of the Fourier modes.

Free Energy—So, we now expand in a single Fourier mode. The lowest order expansion of the Landau free energy is

$$\begin{aligned} f_L &= \frac{1}{2}a(T-T_c)\rho_{\mathbf{q}}\rho_{-\mathbf{q}} + \frac{1}{4}b\left(\rho_{\mathbf{q}}\rho_{-\mathbf{q}}\right)^2 && (46a)\\ &= \frac{1}{2}a(T-T_c)\left|\rho_{\mathbf{q}}\right|^2 + \frac{1}{4}b\left|\rho_{\mathbf{q}}\right|^4. && (46b) \end{aligned}$$

Since the free energy only depends on the modulus of $\rho(\mathbf{q})$, there is no dependence on the phase. There is no cubic term, since we always assume an analytic expansion of the free energy, which precludes terms like $|\rho(\mathbf{q})|^{3/2}$. Hence, one-dimensional crystals are, within mean field theory, continuous transitions, with spontaneously broken translational symmetry. That is, the direction is arbitrary, as is the phase of the lattice. We will see later that this transition is ripe for all sorts of interesting fluctuation effects.

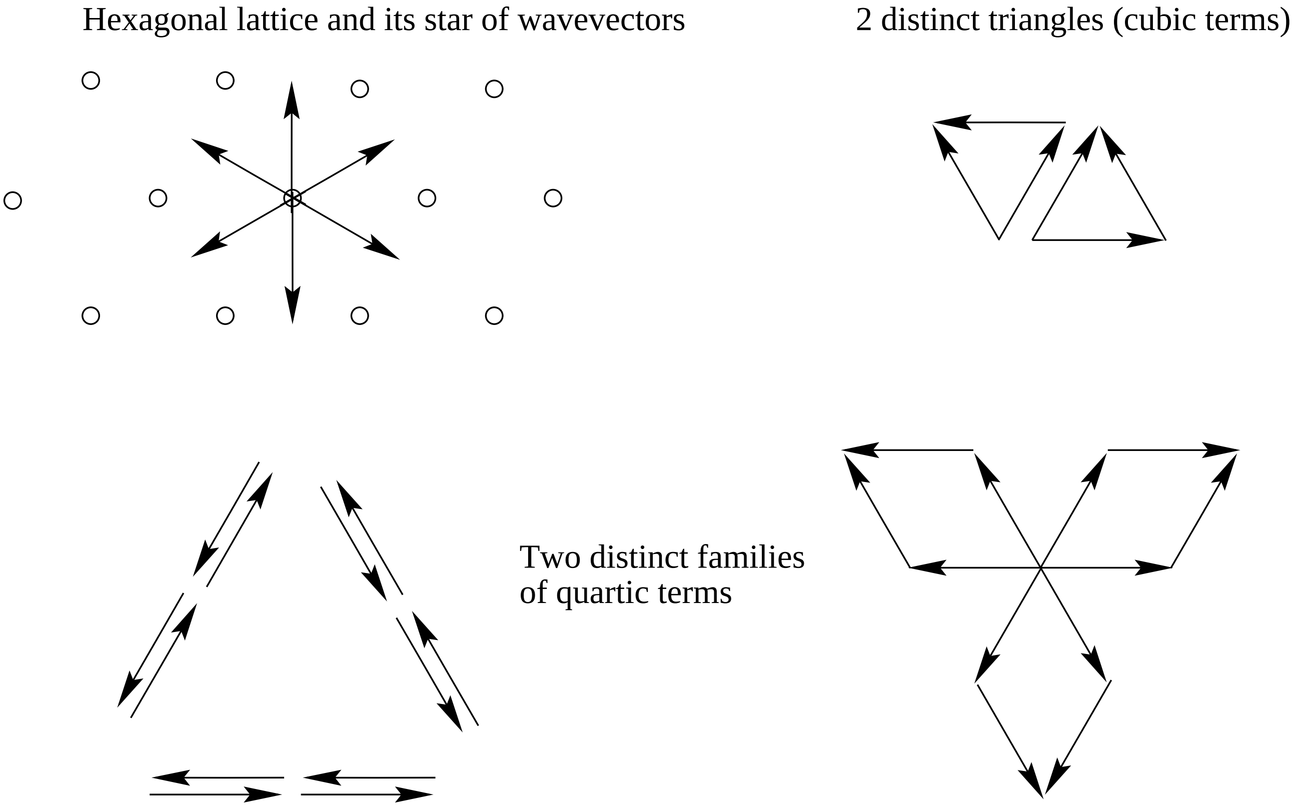
4.4.2 Two and Three Dimensional Crystals

Order Parameter— Consider first a 2-dimensional hexagonal crystal. In this case there are three wavevectors in the first harmonic $\mathbf{G}_* = \{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3\}$, of equal magnitude and at relative angles of 60° and 120° degrees. They form a *star* of wavevectors. The Landau free energy for the transition to a hexagonal crystal must thus be expanded in this star:

$$\rho(\mathbf{r}) = \bar{\rho} + \sum_{\mathbf{q}\in\mathbf{G}_*} \left[\rho(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{r}} + c.c\right], \tag{47}$$

Free Energy—As with the lamellar crystal, the free energy must be constructed so that it is translationally invariant, and doesn't depend on the absolute position of the lattice. Consider the transformation of the following terms under a translation, $\mathbf{r} \to \mathbf{r}+\mathbf{a}$:

$$\begin{aligned} \rho_{\mathbf{k}_1}\rho_{\mathbf{k}_2} &\longrightarrow \rho_{\mathbf{k}_1}\rho_{\mathbf{k}_2}\, e^{-i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{a}} && (48a)\\ \rho_{\mathbf{k}_1}\rho_{\mathbf{k}_2}\rho_{\mathbf{k}_3} &\longrightarrow \rho_{\mathbf{k}_1}\rho_{\mathbf{k}_2}\rho_{\mathbf{k}_3}\, e^{-i(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\cdot\mathbf{a}} && (48b)\\ \rho_{\mathbf{k}_1}\rho_{\mathbf{k}_2}\rho_{\mathbf{k}_3}\rho_{\mathbf{k}_4} &\longrightarrow \rho_{\mathbf{k}_1}\rho_{\mathbf{k}_2}\rho_{\mathbf{k}_3}\rho_{\mathbf{k}_4}\, e^{-i(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\cdot\mathbf{a}} && (48c) \end{aligned}$$



We can have quadratic terms in the free energy for combinations of Fourier modes for which $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{0}$, cubic terms for combinations for which which $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = \mathbf{0}$, and quartic terms for combinations for which $\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4 = \mathbf{0}$. Note that these are vector sums of the allowable wavevectors in the star for the relevant crystal, in this case the hexagonal crystal. Hence it's easiest to find which terms are allowed by constructing the allowable triangles (for the cubic terms) and quadrangles (for the quartic terms) from the star of wavevectors.

Hence we have the following terms in the free energy:

$$\rho_1\rho_{-1}, \rho_2\rho_{-2}, \rho_3\rho_{-3}, \qquad \text{3 quadratic terms} \tag{49a}$$

$$\rho_1\rho_{-2}\rho_3, \rho_{-1}\rho_2\rho_{-3} \qquad \text{2 distinct triangles} \tag{49b}$$

$$\rho_1\rho_2\rho_{-1}\rho_{-2} \cdots \qquad \text{3 open quadrangles} \tag{49c}$$

$$\rho_1\rho_{-1}\rho_1\rho_{-1} \cdots \qquad \text{3 double quadratic terms.} \tag{49d}$$

Now, we assume a symmetry between all three wavevectors, since the system is rotationally invariant. That is, we'll assume the magnitude of each Fourier mode is the same:

$$\rho_1 = \psi e^{i\phi_1}, \quad \rho_2 = \psi e^{i\phi_2}, \quad \rho_3 = \psi e^{i\phi_3}, \tag{50}$$

where ψ is the magnitude and ϕ_i are arbitrary (so far) phase factors.

Hence all three quadratic terms must be equivalent, and have the same coefficient in the free energy. Similarly, all three cubic terms are the same, so they must have the same coefficient. However, the two classes of quartic terms are distinctly different, and each can, potentially, have its own separate coefficient. So, we are led to the following free energy:

$$f_L = \tfrac{1}{2}a\,(T - T_*)\,\psi^2 + \tfrac{1}{3}b\,\psi^3\cos\left(\phi_1 - \phi_2 + \phi_3\right) + \tfrac{1}{4}(c_1 + c_2)\psi^4. \tag{51}$$

In a purely phenomenological approach we might as well set $c_1 + c_2 = c$, another arbitrary constant[‡]. In some systems (notably block copolymers) c_1 and c_2 can be calculated from "first principles", assuming Gaussian chains. The phase factors are chosen to minimize the free energy: choosing $\phi_1 - \phi_2 + \phi_3 = 0$ gives the largest magnitude for the cosine, so the cubic term can then contribute to the free energy for a non-zero ψ (note that the sign of ψ doesn't have any physical significance). Note that the phase factors cannot be determined to any more precision: higher order terms in the free energy lead to a unique determination of the relative phases.

Notes—

1. All real three dimensional crystals have first order phase transitions because "triangles" can be made. Note that a 2D square lattice has, within mean field theory, a continuous phase transition!
2. One expects single-starred crystals (*i.e.* square instead of rectangular, hexagonal instead of rhombic) to appear from the melt, since these will typically be triggered by the first length scale which becomes unstable. For deeper quenches, or strong first order phase transitions, other harmonics develop.
3. By counting the number of triangles, essentially, one can make a very beautiful and general argument that most simple substances should become BCC crystals immediately from the melt[§]. This simple rule is obeyed astonishingly often!
4. An excellent example of this approach combined with a derivation of the Landau coefficients is Leibler's treatment of microphase separation in block copolymers[¶]. He predicted the stability of BCC, hexagonal, and lamellar phases from a single-star theory. Enlarging the theory to include the second star (harmonic) can predict the stability of the Gyroid phase[‖]

[‡] For higher order terms the different classes of pentangles, sextangles, *etc* could have different phase factors, in which case the corresponding coefficients should be kept distinct.

[§] S. Alexander and J. McTague, "Should all crystals be bcc? Landau theory of solidification and crystal nucleation", *Phys. Rev. Lett.* **41** (1978) 702-705

[¶] L. Leibler, "Theory of Microphase Separation in Block Copolymers", *Macromolecules* **13** (1980) 1602-1617

[‖] S. T. Milner and P. D. Olmsted, "Analytical weak-segregation theory of bicontinuous phases in diblock copolymers", *J. Phys. II (France)* **7** (1997) 249-255.

5 Smectic Liquid Crystals

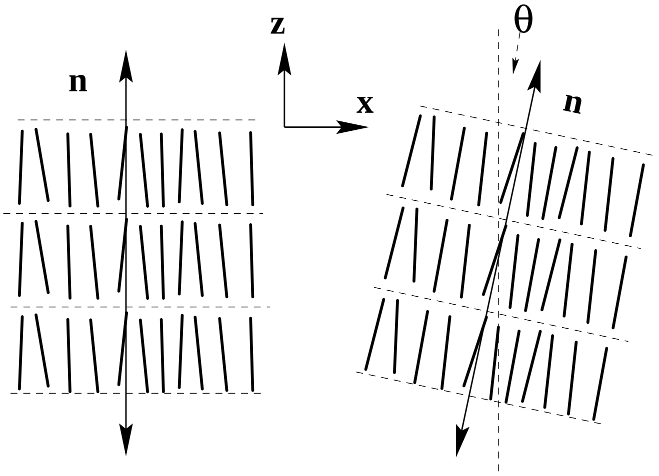
5.1 Mean Field Theory of the Nematic-Smectic–A transition

A thermotropic smectic liquid crystal has the symmetry of a one-dimensional lamellar crystal, but suffers the complications of occuring out of a nematic phase which has broken rotational symmetry. In the smectic–A phase the rodlike molecules are, on average, parallel to the layer normals. Hence the director, $\widehat{\boldsymbol{n}}(\mathbf{r})$, is parallel to the layer normal.

Order Parameter—The order parameter of the smectic transition is taken to be the Fourier component of the fundamental harmonic of the one-dimensional crystal; *i.e.* we expand the density as

$$\rho(\mathbf{r}) = \bar{\rho} + \left\{\psi e^{-iq\,\widehat{\boldsymbol{n}}\cdot\mathbf{r}} + \psi^{*} e^{iq\,\mathbf{n}\cdot\mathbf{r}}\right\}, \tag{52}$$

where $\widehat{\boldsymbol{n}}$ is both the director and the definition of the layer normals.



Symmetries— The layers can be oriented in any direction, as long as the director is also pointing in that direction. Hence any smectic free energy that we write down must be invariant under simultaneous rotations of the layers and the director. Under a uniform rotation of a smectic system about the $\widehat{\boldsymbol{y}}$ axis by an angle θ, the director changes:

$$\widehat{\boldsymbol{n}} \longrightarrow \widehat{\boldsymbol{n}}' = \widehat{\boldsymbol{n}} + \delta\widehat{\boldsymbol{n}} = \widehat{\boldsymbol{n}} - \theta\,\widehat{\boldsymbol{x}}. \tag{53}$$

Hence the smectic order parameter changes according to:

$$\psi \longrightarrow \psi e^{iq\,\theta x} = \psi e^{-iqx\,\delta n_x}. \tag{54}$$

Any free energy we write down my respect this symmetry (rotational invariance).

Free Energy—Now we write down the free energy. First we consider a uniform amplitude of the density modulation ψ. Since a smectic is a one-dimensional crystal, we can reproduce what we had before:

$$f_{L,hom} = \tfrac{1}{2}\,a(T - Tc)\;|\psi|^2 + \tfrac{1}{4}\,c\;|\psi|^4. \tag{55}$$

To this we add the energy of deformation of the director fluctuations, the Frank Free Energy:

$$f_N = \tfrac{1}{2}K_1\;(\boldsymbol{\nabla}\cdot\delta\widehat{\boldsymbol{n}})^2 + \tfrac{1}{2}K_2\;(\widehat{\boldsymbol{n}}\cdot\boldsymbol{\nabla}\times\delta\widehat{\boldsymbol{n}})^2 + \tfrac{1}{3}K_3\;|\widehat{\boldsymbol{n}}\times(\boldsymbol{\nabla}\times\delta\widehat{\boldsymbol{n}})|^2, \tag{56}$$

where K_1, K_2, K_3 penalize, respectively, splay, bend, and twist fluctuations.

Finally, we can consider an envelope of spatial modulations in the magnitude of the density modulation, $\psi(\mathbf{r})$. These fluctuations, in the smectic state, correspond to phonons. If we consider the rigid body rotation above, transverse spatial derivatives of ψ pick up a term from the director rotation:

$$\underbrace{\partial_x\psi(\mathbf{r}) \longrightarrow}_{\text{(rotate about }\widehat{\boldsymbol{y}})} (\partial_x\psi)\, e^{-iq\,x\delta n_x} + iq\,\delta n_x\,\psi(\mathbf{r})\, e^{-iq\,x\delta n_x}. \tag{57}$$

Since the free energy must be invariant under a rigid body rotation, such spatial derivatives must not contribute to the free energy. Hence the free energy of deforming the order parameter is

$$f_{L,def} = \tfrac{1}{2}\,g_{\|}\,\left|\widehat{\boldsymbol{n}}\cdot\boldsymbol{\nabla}\,\psi\right|^2 + \tfrac{1}{2}\,g_{\perp}\,\left|\left(\boldsymbol{\nabla}_{\perp} - iq\delta\widehat{\boldsymbol{n}}\right)\,\psi\right|^2. \tag{58}$$

The additional term in parentheses in the second terms subtracts off the unwanted irrelevant term. This derivative is often called a *covariant derivative*, and has an analogy in superconductivity, in which the superconductor is analogous to the smectic order parameter and the vector potential is analogous to the director fluctuations. This is an example of a *gauge field theory*, which arises when the relevant order parameter has a local internal symmetry (the smectic order parameter is a complex number with a phase, corresponding to a $U(1)$ symmetry, which can vary from point to point). There have been many interesting fruits born out of this analogy between smectics and superconductors! In electrodynamics there is a gauge symmetry (the vector potential $\mathbf{A}$ is defined only up to an additive irrotational vector field $\boldsymbol{\nabla}\,\Theta$), while in the smectic liquid crystal the gauge is actually fixed because of the presence of a director in the nematic state.

5.2 Free Energy and Superconducting Analogy

To compare the liquid crystals and superconductors, let's look at the free energies. For the liquid crystal we have

$$f_{NA} = \tfrac{1}{2}a\,|\psi|^2 + \tfrac{1}{4}c\,|\psi|^4 + \tfrac{1}{2}\,g_{\|}\,\left|\widehat{\boldsymbol{n}}\cdot\boldsymbol{\nabla}\,\psi\right|^2 + \tfrac{1}{2}\,g_{\perp}\,\left|\left(\boldsymbol{\nabla}_{\perp} - iq\delta\widehat{\boldsymbol{n}}\right)\,\psi\right|^2 + \tfrac{1}{2}\,K\,\left(\nabla_{\alpha}\delta\hat{n}_{\beta}\right)^2, \tag{59}$$

where we have used the so-called one-constant approximation $K_1 = K_2 = K_3 \equiv K$.

For a superconductor, we'll take the order parameter to be ψ again. Landau postulated that this is a complex number, and in fact it turns out to be closely related to the wavefunction for Cooper pairs of electrons (which is a complex number). The physics of electrons is invariant under a *local* change in the phase of the wavefunction, $\psi(r) \to \psi(r)e^{i\phi(r)}$. This transformation is in fact the gauge invariance which gives rise to the electromagnetic field, and we usually write

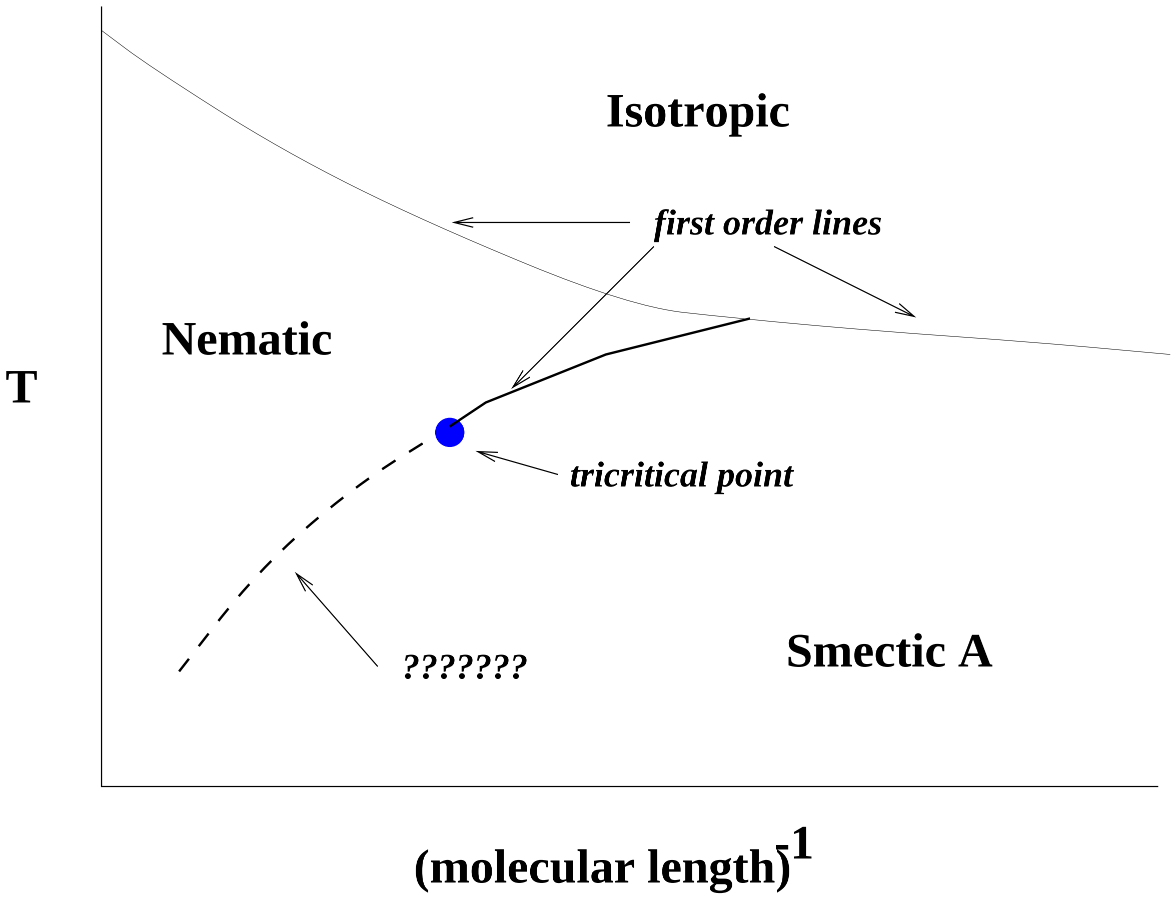
$$\psi(r) \to \psi(r)e^{i2e\int_{\mathbf{r}_0}^{\mathbf{r}}\mathbf{A}\cdot d\mathbf{r}'}, \tag{60}$$

where $\mathbf{A}$ is the electromagnetic vector potential (this funny phase factor gives rise to the Aharonov-Bohm effect), in units where the speed of light is unity. There is a 2 here because the wavefunction is for a pair of electrons. Now, we can write down the free energy for a superconducting transition, exactly as for the smectic. When it comes to writing the gradient terms we must "subtract" off this arbitrary phase, which can't change the physics, so gradient operators generally enter as $\hbar\boldsymbol{\nabla} - i2e\mathbf{A}$. Finally, there is a free energy associated with gauge field fluctuations: the energy in the magnetic field is $\mathbf{B}\cdot\mathbf{B}/8\pi$. Writing $\mathbf{B} = \boldsymbol{\nabla}\times\mathbf{A}$, we have, for the superconducting free energy,

$$f_{sup} = \tfrac{1}{2}a\,|\psi|^2 + \tfrac{1}{4}c\,|\psi|^4 + \tfrac{1}{2}\,g\,\left|\left(\boldsymbol{\nabla} - i\frac{2e}{\hbar}\mathbf{A}\right)\,\psi\right|^2 + \frac{c^2}{8\pi}\,|\boldsymbol{\nabla}\times\mathbf{A}|^2\,. \tag{61}$$

Hence, aside from the fact that the liquid crystal is anisotropic, and the coupling of $\mathbf{A}$ to the gradient terms is slightly different in tensorial nature to the coupling of $\delta\widehat{\boldsymbol{n}}$, the transitions "should" be qualitatively the same. Just as a superconductor expels magnetic flux, a liquid crystal expels (it turns out) both twist and bend director fluctuations. For example, it was realized that the analog of the Abrikosov vortex phase of Type II superconductors should exist in liquid crystals, and this was subsequently predicted and then found experimentally: the "twisted grain boundary (TGB) phase" in cholesteric smectics.

The phase diagram of a smectic looks something like the following:



The nematic phase intervenes when the molecules are anisotropic enough, and otherwise the system can go directly from the isotropic to the smectic phase. One can show quite generally that the following term, which couples liquid crystalline order to density,[**]

$$f_{\psi Q} = Q_{\alpha\beta}\,\nabla_{\alpha}\rho\,\nabla_{\beta}\rho \tag{62}$$

[**] Can you show that this term is allowed by symmetry?

leads (via nematic fluctuations) to an effective quartic term in the smectic free energy of the form $-\chi\psi^4$, where χ is the susceptibility for fluctuations around the nematic phase. Hence, it is likely that for molecular parameters with a narrow nematic range, for which the susceptibility χ is large, the total quartic term in the smectic free energy is negative, leading to a first order phase transition. For parameters with a wide nematic range the $N-A$ transition is expected, within mean field theory, to be a continuous transition. In the next section we will see that this does not, generally, survive inclusion of fluctuations.

5.3 Fluctuations and the *Halperin-Lubensky-Ma* Effect.

In the region of the smectic transition both ψ and $\delta\widehat{\boldsymbol{n}}$ are fluctuating. If we consider a fluctuation in which a smectic blob appears in the nematic, there are two relevant length scales:

$$\xi_{\parallel,\perp} = \sqrt{\frac{g_{\parallel,\perp}}{a}} \qquad (\psi \text{ healing length}) \tag{63}$$

$$\lambda = \sqrt{\frac{K}{g_{\parallel,\perp} q_0^2 |\psi|^2}} \qquad (\text{bend and twist penetration lengths}) \tag{64}$$

The Frank constant K is proportional to the magnitude of the nematic order parameter Q, so λ is large when the nematic phase has a large range and smaller when the nematic range is smaller. Hence we expect two regimes:

$$\kappa \equiv \frac{\lambda}{\xi} \begin{cases} < \dfrac{1}{\sqrt{2}} & (\text{Type I}) \\ > \dfrac{1}{\sqrt{2}} & (\text{Type II}) \end{cases} \tag{65}$$

In the Type I case the director fluctuation (or magnetic field) decays quickly compared to the smectic order parameter, and the system can efficiently expel twist (or magnetic field). This corresponds to the Meissner phase in superconductors. In the Type II case the twist can penetrate a longer distance while order parameter has healed, and can in fact penetrate easier. This corresponds to the Abrikosov vortex phase in superconductors.

If we consider fluctuations in the nematic phase, in the Type I limit we can safely assume that ψ is uniform relative to director fluctuations (since ψ varies much more smoothly). To examine the smectic transition in this limit, then, we consider small (uniform) fluctuations in ψ, and integrate out the director fluctuations. Hence:

$$\mathcal{Z} = \int \mathcal{D}\delta\widehat{\boldsymbol{n}}\,\mathcal{D}\psi\, e^{\{\int d^3r f_{NA}/k_BT\}} \tag{66}$$

$$\simeq \int \mathcal{D}\delta\widehat{\boldsymbol{n}}\,\mathcal{D}\psi \exp\left\{-\frac{V}{k_BT}\left[\tfrac{1}{2}a\,|\psi|^2 + \tfrac{1}{4}c\,|\psi|^4\right] + \right. \tag{67}$$

$$\left. \tfrac{1}{k_BT}\int d^3r \left\{\tfrac{1}{2}\,g_\perp\,\left|\left(\boldsymbol{\nabla}_\perp - iq_0\delta\widehat{\boldsymbol{n}}\right)\,\psi\right|^2 + \tfrac{1}{2}\,K\,\left(\nabla_\alpha\delta\widehat{n}_\beta\right)^2\right\}\right\}, \tag{68}$$

$$\simeq \int \mathcal{D}\psi e^{-Vf_{0NA}[\psi]/k_BT} \int \delta\widehat{\boldsymbol{n}} e^{-F_{nem}/k_BT} \tag{69}$$

where f_{0NA} is the free energy in the absence of director fluctuations, and

$$F_{nem} = \tfrac{1}{2}\int d^3r\,\left\{g_\perp q_0^2|\psi|^2|\delta\widehat{\boldsymbol{n}}|^2 + K\,\left(\nabla_\alpha \delta\hat{n}_\beta\right)^2\right\}. \tag{70}$$

The director fluctuation integral is Gaussian, and can be done without too much trouble. In Fourier space, $\delta\widehat{\boldsymbol{n}}(r) = \sum_{\mathbf{q}} \delta\widehat{\boldsymbol{n}}(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}$, we can write

$$F_{nem} = \tfrac{1}{2}\sum_{\mathbf{q}}\left[g_\perp q_0^2|\psi|^2| + Kq^2\right]|\delta\widehat{\boldsymbol{n}}(\mathbf{q})|^2\,. \tag{71}$$

The director integral is a Gaussian integral for each Fourier mode, giving (up to factors of 2π)

$$\int \delta\widehat{\boldsymbol{n}} e^{-F_{nem}/k_BT} \simeq \prod_{\mathbf{q}}\left[g_\perp q_0^2|\psi|^2| + Kq^2\right]^{-\frac{1}{2}\,2} \tag{72}$$

(a power of $\frac{1}{2}$ for each independent mode of $\delta\widehat{\boldsymbol{n}}$). Hence the effective free energy for the smectic transition is

$$\mathcal{Z} = \int \mathcal{D}\delta\widehat{\boldsymbol{n}}\,\mathcal{D}\psi\, e^{\{\int d^3r \hat{f}_{NA}/k_BT\}} \tag{73}$$

$$\Longrightarrow \hat{f}_{NA} = f_{0NA} + k_BT\sum_{\mathbf{q}}\ln\left[g_\perp q_0^2|\psi|^2 + Kq^2\right] \tag{74}$$

This integral can be done ($\sum_{\mathbf{q}} \to 1/(2\pi)^3\int d^3q$), and expanded in the order parameter ψ. Note that it can't be expanded first because the integrand is non-analytic at $\psi = 0$. The result is

$$\hat{f}_{NA} = f_{0NA} + a_1|\psi|^2 - \frac{1}{6\pi}\left(\frac{g_\perp q_0^2|\psi|^2}{K}\right)^{3/2} + a_2\psi^4 + \dots \tag{75}$$

Hence, there is a cubic term induced in the magnitude of ψ. This leads to a very weak fluctuation-induced first order transition. This seems to have been verified experimentally (most people agree).

In the case of Type II systems, where director and order parameter fluctuations (or magnetic field and superconducting order parameter), a renormalization group type of treatment is necessary. It is believed that the first order transition remains, but results are inconclusive. In any case if it remains first order it is VERY weak!

5.4 Layered liquids and the *Brazovskii* effect

To be added!