

4.5 The first-order nematic-to-isotropic transition

As discussed in Chapter 2, liquid crystals are composed of long, barlike molecules. In the isotropic fluid phase, the orientations and positions of the molecules are random. In the nematic phase, the positions of the molecules are still random, but their long axes are oriented on the average along a particular direction specified by a unit vector \mathbf{n} called the director, as shown in Fig. 4.5.1. Thus, the nematic phase is characterized by broken rotational but not translational symmetry. It is, therefore, tempting to associate the order parameter with the unit vector \mathbf{v}^α which points along the long axis of molecule α located at position \mathbf{x}^α . However, since the nematic molecules either have a center of inversion or, if they do not, they have equal probability of pointing parallel or anti-parallel to any given direction, both \mathbf{v}^α and $-\mathbf{v}^\alpha$ contribute to the order. Thus any order parameter must be even in \mathbf{v}^α . Since a vector order parameter is insufficient, we can try a second rank tensor. We require the order parameter to be zero in the high-temperature isotropic phase. A symmetric traceless tensor will yield zero when averaged over directions, so we construct the order parameter from the symmetric traceless tensor formed from \mathbf{v}^α . Let

$$Q_{ij} = \frac{V}{N} \sum_{\alpha} (v_i^\alpha v_j^\alpha - \frac{1}{3} \delta_{ij}) \delta(\mathbf{x} - \mathbf{x}^\alpha), \quad (4.5.1)$$

where v_i^α is the i th component of \mathbf{v}^α . The factor of V/N is introduced in the definition of Q_{ij} to make it unitless as is conventionally done. Let \underline{Q} be the tensor with components Q_{ij} . Note that $\text{Tr} \underline{Q} = 0$ since \mathbf{v}^α is a unit vector. In the ordered state $\langle \underline{Q} \rangle$ is not zero. In a coordinate system with one axis along the direction of molecular alignment, the matrix $\langle \underline{Q} \rangle$ is diagonal:

$$\langle \underline{Q} \rangle = \begin{pmatrix} \frac{2}{3}S & 0 & 0 \\ 0 & -\frac{1}{3}S + \eta & 0 \\ 0 & 0 & -\frac{1}{3}S - \eta \end{pmatrix}. \quad (4.5.2)$$

If η is nonzero, \underline{Q} is *biaxial*, and there are two, rather than one, preferred directions. Except in exceptional cases, nematic liquid crystals are uniaxial so that $\eta = 0$. In this case,

$$\langle Q_{ij} \rangle = S(n_i n_j - \frac{1}{3} \delta_{ij}), \quad (4.5.3)$$

where the unit vector \mathbf{n} , called the Frank director, specifies the direction of the principal axis of $\langle Q_{ij} \rangle$. From Eq. (4.5.1)

$$S = \frac{1}{2} \langle 3(\mathbf{v}^\alpha \cdot \mathbf{n})^2 - 1 \rangle = \frac{1}{2} \langle (3 \cos^2 \theta^\alpha - 1) \rangle, \quad (4.5.4)$$

where θ^α is the angle between the molecular axis and the director \mathbf{n} .

We are now in a position to construct a Landau free energy for a nematic liquid crystal. The free energy density f must be invariant under all rotations. \underline{Q} transforms like a tensor under the rotation group. f must, therefore, only be a function of the scalar combinations $\text{Tr} \langle \underline{Q} \rangle^p$, $p = 2, 3, \dots$ that are invariant under rotations. The term with $p = 1$ is just the trace of $\langle \underline{Q} \rangle$ and is by definition zero.

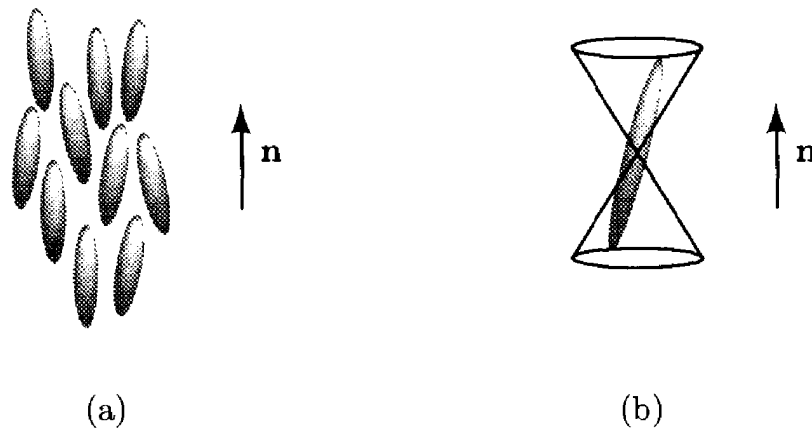


Fig. 4.5.1. (a) Schematic representation of barlike molecules in the nematic phase. They are oriented on the average along the director \mathbf{n} . The direction of each molecule is effectively confined to lie within a cone, as shown in (b), rather than being free to choose any solid angle.

Thus, there is no term linear in $\langle \underline{Q} \rangle$ in the free energy. To fourth order in \underline{Q} , we therefore have

$$\begin{aligned} f &= \frac{1}{2}r\left(\frac{3}{2}\text{Tr}\langle \underline{Q} \rangle^2\right) - w\left(\frac{9}{2}\text{Tr}\langle \underline{Q} \rangle^3\right) + u\left(\frac{3}{2}\text{Tr}\langle \underline{Q} \rangle^2\right)^2, \\ &= \frac{1}{2}rS^2 - wS^3 + uS^4. \end{aligned} \quad (4.5.5)$$

In general, there should be two fourth-order terms proportional, respectively, to $(\text{Tr}\langle \underline{Q} \rangle^2)^2$ and $\text{Tr}\langle \underline{Q} \rangle^4$. However, for 3×3 symmetric traceless tensors, they are strictly proportional, and we need only include the $(\text{Tr}\langle \underline{Q} \rangle^2)^2$ term. As before, r is positive at high T and negative at low T . We choose

$$r = a(T - T^*). \quad (4.5.6)$$

u and w are independent of temperature.

The free energy of Eq. (4.5.5) differs from that of the Ising model by the presence of the third-order term $-wS^3$. If the order parameter for the nematic phase were a vector (as might be imagined if the constituent molecules lacked inversion symmetry) rather than a tensor, then odd order terms would be prohibited in the free energy by rotational symmetry. However, the rodlike molecules have a quadrupolar rather than a dipolar symmetry, and the order parameter is a tensor for which rotational invariance does not rule out the odd terms. Note that the quadrupole symmetry is also reflected in the form of the order parameter in Eqs. (4.5.3) and (4.5.4). f is sketched as a function of S for various values of T in Fig. 4.5.2. Note that the cubic term leads to an asymmetry in f as a function of S and the emergence of a secondary minimum at finite S . The value of f at this minimum is greater than zero at high temperature but becomes equal to zero at a critical temperature T_c that is greater than the temperature T^* at which the extremum at the origin develops negative curvature. Since f is less than zero at the secondary minimum for all $T < T_c$, there is a phase transition with a

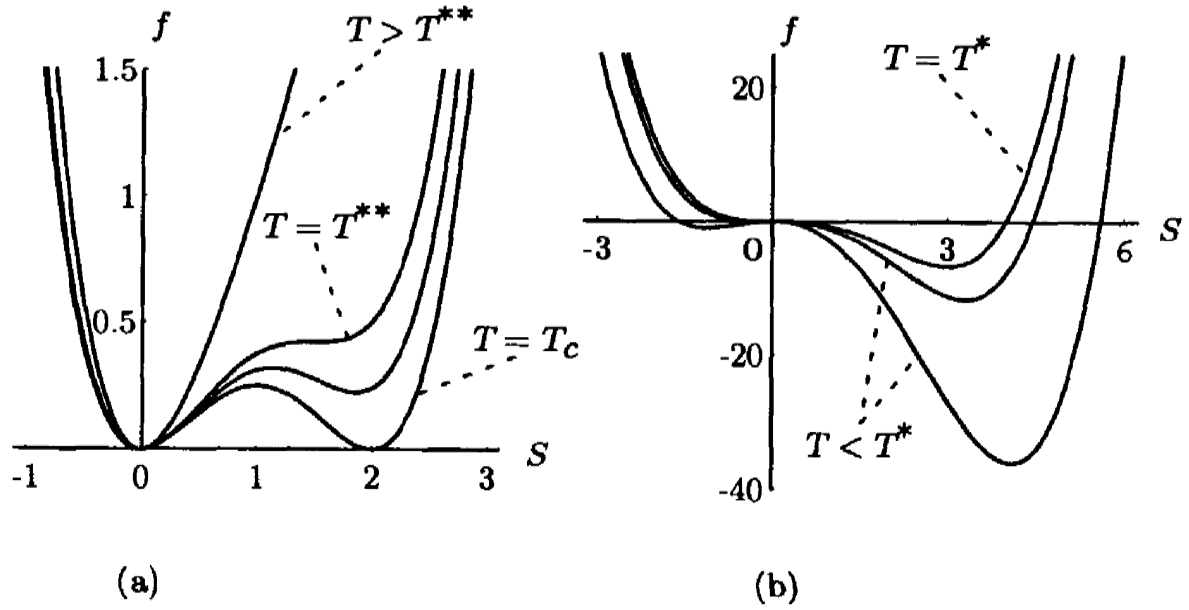


Fig. 4.5.2. Free energy density f as a function of order parameter S for different T for the isotropic-nematic transition. The transition is first order. Note the limits of metastability for supercooling (T^*) and superheating (T^{**}).

discontinuous change in S at T_c , i.e. there is a first-order transition at T_c . T^* is the *limit of metastability* of the isotropic phase since, for $T^* < T < T_c$, the origin is still a local minimum even though it is not a global minimum. The limit of metastability of the nematic phase occurs at the temperature T^{**} at which the secondary minimum disappears on heating.

The first-order transition temperature T_c and the value S_c of S at T_c are calculated by requiring that f be an extremum with respect to S in equilibrium and that the free energies of the disordered and ordered phases be equal at the transition. The latter condition implies that the isotropic and nematic phases can coexist at the transition temperature. If other variables, such as pressure or density, were included in our treatment, the two phases would coexist along a line rather than at a single point. The equations determining T_c and S_c are, therefore,

$$\frac{\partial f}{\partial S} = (r - 3wS + 4uS^2)S = 0 \quad (4.5.7)$$

$$f = \left(\frac{1}{2}r - wS + uS^2\right)S^2 = 0. \quad (4.5.8)$$

Thus,

$$S_c = \frac{w}{2u}, \quad r_c = a(T_c - T^*) = \frac{w^2}{2u}. \quad (4.5.9)$$

Since the transition is first order, there is an associated latent heat. The entropy per unit volume of the disordered phase is zero in mean-field theory, whereas that of the nematic phase is negative. This result can be obtained from the free energy of the nematic phase, which to lowest order in $r - r_c$ is

$$f = \frac{1}{2}(r - r_c)S_c^2 = \frac{1}{2}(r - r_c)(w/2u)^2. \quad (4.5.10)$$

The entropy density in the nematic phase (relative to that of the isotropic phase) is then

$$s = -\frac{\partial f}{\partial T} = -\frac{1}{2}aS_c^2 = -\frac{1}{2}a(w/2u)^2. \quad (4.5.11)$$

There are, of course, other contributions to the entropy not included in the present model that ensure that the total entropy is always positive. The latent heat absorbed in going from the nematic to the isotropic phase is thus

$$q = -T_c s = \frac{1}{2}aT_c(w/2u)^2. \quad (4.5.12)$$

The molecules comprising nematic liquid crystals (called *nematogens*) are anisotropic diamagnets. Typically they have lower energy when they are aligned with their long axis parallel to the magnetic field. The interaction Hamiltonian is

$$\begin{aligned} H_{\text{ext}} &= - \int d^d x \chi_a Q_{ij} H_i H_j, \\ &= -\frac{3}{2} \int d^d x \chi_a H^2 S, \end{aligned} \quad (4.5.13)$$

where χ_a is the difference in the magnetic susceptibility of a nematic molecule for directions parallel and perpendicular to its long axis and \mathbf{H} is the external magnetic field along \mathbf{n} . Thus $h = (3/2)\chi_a H^2$ is the field conjugate to S . The susceptibility associated with S can be calculated as before. It satisfies

$$\chi = \frac{\partial S}{\partial h} = (r - 6wS + 12uS^2)^{-1}. \quad (4.5.14)$$

χ appears to diverge at $T = T^*$ as temperature is lowered in the isotropic phase. The first-order phase transition at $T_c > T^*$ cuts off this divergence as shown in Fig. 4.5.3. T^* is thus the limit of metastability of the isotropic phase. To find the limit of metastability (T^{**}) of the nematic phase, we calculate the temperature at which $\chi^{-1} = 0$ in the free energy minimum with $S > 0$. S satisfies the equation of state [Eqs. (4.5.7)] as before, and

$$r^{**} = a(T^{**} - T^*) = \frac{9w^2}{16u}. \quad (4.5.15)$$

Note that $T^{**} - T_c = w^2/(16au) > 0$ as necessary.

A general phenomenon associated with first-order transitions is the presence of hysteresis in cycling through the transition and the related effects of superheating and supercooling. Thermodynamically the transition should occur at T_c . However, the high temperature phase with $S = 0$ is stable against small fluctuations until the temperature T^* is reached on cooling. Between T_c and T^* , the ordered phase will only occur if there is a sufficiently large fluctuation. Below T^* the system is unstable against infinitesimal fluctuations into the ordered state. Thus, on cooling, the actual transition to the low-temperature ordered phase will occur at some temperature between T_c and T^* depending on the particular sample and the experimental conditions. Similar arguments show that, on heating, the

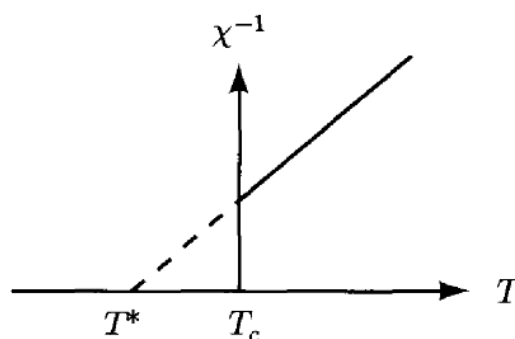


Fig. 4.5.3. χ^{-1} for a first-order transition. In mean-field theory, this function extrapolates to zero at the limit of metastability T^* .

transition from the ordered to the high temperature phase will occur between T_c and T^{**} .

The example of the isotropic-to-nematic transition is representative of phase transitions in which the order parameter possesses a third-order invariant. One expects in general that such transitions will be first order. Though the above Landau theory correctly predicts qualitative properties of first-order transitions, it certainly cannot make detailed quantitative predictions. This is because the order parameter is not zero at the transition. One is not justified, therefore, in truncating the power series expansion of f at fourth order. Even in mean-field theory, higher order terms in this expansion will lead to corrections both to T_c and S_c . If, however, the transition is nearly second order, as would be the case if the predicted value of $T_c - T^*$ is small, the truncated model is a reasonable approximation.

4.6 Multicritical points

The phase transitions discussed in Secs. 4.4 and 4.5 occurred in response to changes in a single variable, the temperature T , when the external ordering field (i.e., field conjugate to the order parameter) is zero. Thus, the phase diagram for these systems can be drawn on the temperature axis alone with a critical point separating the high-temperature disordered phase from the low-temperature ordered phase. In systems where there is more than one non-ordering field (such as pressure and temperature), phase diagrams become multidimensional, and there can occur critical points that can be reached only by fixing two or more non-ordering fields. In this section, we will consider a few of these *multicritical points*.

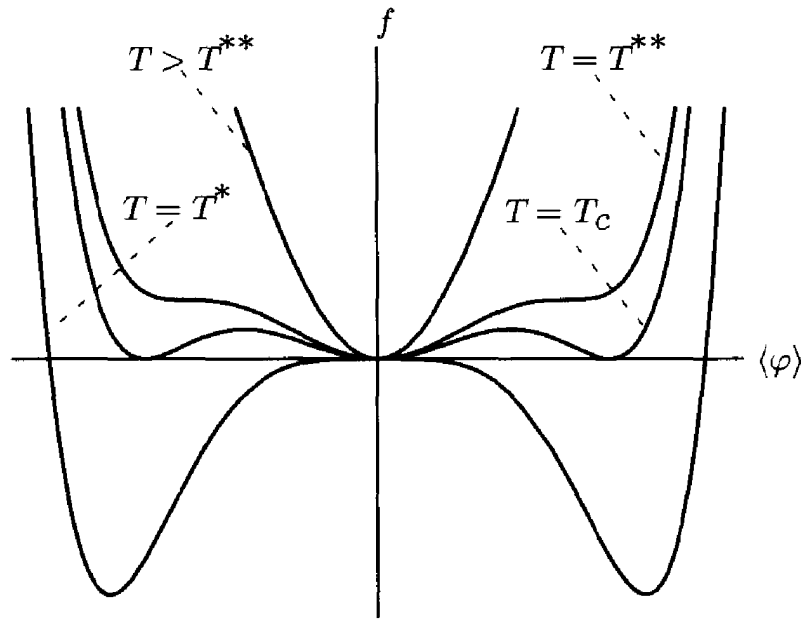


Fig. 4.6.1. f for a ϕ^6 potential [Eq. (4.6.1)] with u_4 negative. There is a first-order transition at $T = T_c$. T^{**} and T^* are, respectively, the limits of metastability on heating and cooling.

1 Tricritical points

In the preceding section, we found that third-order invariants lead to first-order transitions. First-order transitions can also occur if symmetry prohibits odd-order terms. Consider the following Landau free energy:

$$f = \frac{1}{2}r\phi^2 + u_4\phi^4 + u_6\phi^6, \quad (4.6.1)$$

where $r = a(T - T^*)$. If u_4 is positive, the sixth-order term can be neglected in the vicinity of the predicted second-order transition. If, on the other hand, u_4 is negative, the sixth-order term is required to maintain stability. In this case, secondary minima symmetrically placed about $\phi = 0$ develop as T is lowered, as shown in Fig. 4.6.1. When the free energies of the secondary minima with $\phi \neq 0$ pass through zero, there is a first-order transition as in the isotropic-to-nematic example.

When $u_4 > 0$, the mean-field transition temperature is the same as for the ϕ^4 -model of Sec. 4.4, i.e., $r_c = 0$ and $T_c = T^*$. When $u_4 < 0$, however, the first-order transition temperature is determined by the conditions $f(r_c, \phi) = 0$ and $\partial f(r_c, \phi)/\partial \phi = 0$ just as for the nematic liquid crystal. This leads to

$$r_c = a(T_c - T^*) = \begin{cases} 0 & \text{if } u_4 > 0; \\ \frac{1}{2}|u_4|^2/u_6 & \text{if } u_4 < 0. \end{cases} \quad (4.6.2)$$

The phase diagram described by this equation in the $r - u_4$ plane is shown in Fig. 4.6.2. The line of second-order transitions for $u_4 > 0$ is called a *lambda* line. (It was first observed at the normal-to-superfluid transition in liquid helium mixtures; see Fig. 4.6.7. The superfluid transition is often referred to as a λ

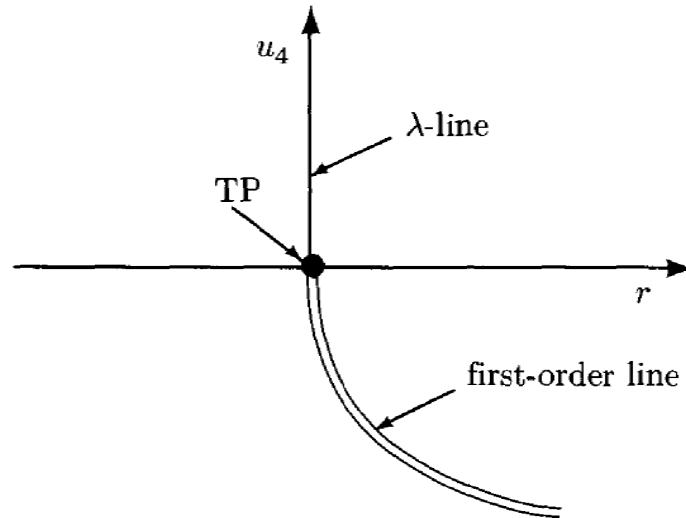


Fig. 4.6.2. Phase diagram for the free energy of Eq. (4.6.1). The line $r = 0$, $u_4 > 0$ is a second-order lambda line, shown as a single line in the figure. The line $r = \frac{1}{2}|u_4|^2/u_6$ is a line of first-order transition, shown as a double line in the figure. The point TP, $r = 0$, $u_4 = 0$, is a tricritical point.

transition since the specific heat curve resembles the Greek letter λ .) It meets the line of first-order transitions for $u_4 < 0$ at a *tricritical point*, $(r, u_4) = (0, 0)$.

The value of the order parameter, the latent heat along the first-order line, and the limit of metastability on heating can be calculated as in the previous section:

$$\phi_c = \pm[|u_4|/(2u_6)]^{1/2}, \quad (4.6.3)$$

$$q = -T_c s = \frac{1}{4}|u_4|/u_6, \quad (4.6.4)$$

$$r^{**} = a(T^{**} - T^*) = 2|u_4|^2/(3u_6).$$

Notice that both ϕ_c and q go to zero at the tricritical point where there is no longer a first-order transition. Note also that along the first-order line there is coexistence of three phases: the disordered phase with $\phi = 0$ and two ordered phases with $\phi = \pm|\phi_c|$. When $u_4 = 0$, there is a second-order transition but with an order parameter critical exponent β of $1/4$ rather than $1/2$:

$$\phi = \pm[-r/6u_6]^{1/4}. \quad (4.6.5)$$

Similarly, when an external ordering field h is applied at the tricritical point,

$$\phi = (h/6u_6)^{1/5}, \quad (4.6.6)$$

implying that the exponent δ is 5 rather than 3. The other critical exponents, γ and ν , for the tricritical point are the same in mean-field theory for $u_4 = 0$ and for $u_4 > 0$.

Fig. 4.6.2 depicts the phase diagram in the vicinity of a tricritical point in the most natural variables for the model free energy of Eq. (4.6.1). In real systems, all of the potentials are functions of the experimentally controllable parameters such as temperature, pressure, chemical potential, concentration of species, or external