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The Landau-de Gennes Theory of Liquid Crystal Phase Transitions

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1. Introduction

A physical system in which phase transition(s) can occur is usually characterized by one or more long range order parameters (order parameter for short). For example, in nematic liquid crystals the order parameter is the quantity $S \equiv \langle P_2(\cos\,\theta)\rangle$ as defined in previous chapters;[1-3] in ferromagnets the order parameter is the magnetization in a single domain; and in liquid-gas systems the order parameter is the density difference between the liquid and gas phases. In each of the above cases the state of the system, at any fixed temperature, can be described by an equilibrium value of the order parameter and fluctuations about that value. A phase transition can be accompanied by either a continuous or a discontinuous change in the equilibrium value of the order parameter when the system transforms from one phase to the other. (For simplicity we will consider temperature as the only thermodynamic variable in this paper; the pressure depedence of the various phenomena will be neglected).

From the above discussion it is apparent that an essential element in the theory of phase transitions is the determination, at every temperature, of the equilibrium value and fluctuation amplitude of the order parameter. In principle this can be accomplished if one can calculate the free energy $F[\mathcal{O},T]$ of the system when it is in a state characterized by a value $\mathcal{O}$ of the order parameter and a temperature T. $F[\mathcal{O},T]$ is sometimes called the Landau free energy function to distinguish it from the total free energy of the system. The equilibrium value of the order parameter is that value $\mathcal{O}_{eq}(T)$ which minimizes $F[\mathcal{O},T]$. The relative probability for the system to fluctuate to a state characterized by $\mathcal{O}$ is proportional to $\exp\{-\beta(F[\mathcal{O},T] - F[\mathcal{O}_{eq}(T),T])\}$, where $\beta \equiv 1/k_BT$, k_B being the Boltzmann constant. So far we have neglected spatially nonuniform fluctuations of the system, i.e., fluctuations that produce spatial variation of the order parameter. To include such fluctuations in the theory, one usually first calculates a free energy density at each temperature as a function of the order parameter and its spatial derivatives. The free energy for an arbitrary spatial variation of the order parameter, $\mathcal{O}(\vec{r})$, where $\vec{r}$ denotes spatial position, is then obtained from the free energy density by a volume integration. Thus, in the general case, the theoretical description of a phase transition is equivalent to the determination of the free energy density as a function of the order parameter, its spatial derivatives, and the temperature. However, a rigorous determination of the free energy density function is extremely difficult since it is almost equivalent to the complete solution of the phase transition problem.

In 1937 Landau[4] made an elegant and far-reaching speculation about the functional dependence of the free-energy density on the order parameter and its spatial derivatives near a second-order phase transition point. Briefly, Landau speculated that near a second-order transition the free-energy density function can be expanded as a power series in the order parameter and its spatial derivatives, with temperature dependent coefficients. Landau further argued that, sufficiently close to the transition, only the leading terms of the series are important, so that the expansion of the free-energy density function becomes a simple low-order polynomial. Despite certain shortcomings,[5] Landau's theory of phase transitions has proven to be as good as mean field theory in providing a semi-quantitative description of the specific heat, the order parameter, and the entropy in the vicinity of a second-order phase transition. Moreover, the Landau theory is mathematically simpler than mean field theory, and the inclusion of spatial variations of the order parameter gives it a new dimension not found in mean field theory. Of course, the Landau theory is useful only in a limited temperature range close to the transition point, and it contains more phenomenological parameters than does mean field theory. In these respects it is somewhat less satisfying than mean field theory.

Although originally intended as a theory of second-order phase transitions, the Landau theory can easily be generalized to include first-order phase transitions.[6] de Gennes[7] was the first to successfully apply Landau's theory to the first-order liquid-crystal phase transitions. It is the purpose of the present chapter to develop this Landau–de Gennes theory of liquid-crystal phase transitions and to discuss and illustrate its use. In the following sections, the derivation and discussion of the basic equations will be followed by application of the theory to the calculation of thermodynamic properties and fluctuation phenomena of liquid-crystal phase transitions, and by a description of some of the theory's more novel predictions and their experimental verifications.

2. Derivation of the Fundamental Equations of the Landau–de Gennes Theory

2.1 The Partition Function

We begin by considering a macroscopic system whose equilibrium state is characterized by a spatially invariant, dimensionless, scalar order parameter σ. Any disturbance in the system, such as thermal fluctuations, produces spatial variations of the order parameter. However, for low-energy (long wavelength) fluctuations, the spatial variations occur on a scale much larger than the molecular dimension. Therefore, if we limit our consideration only to the equilibrium state and low-energy fluctuations about the equilibrium state, we can imagine dividing the system into, say, M small, cubic, spatial regions each of volume ΔV. Each of these regions contains a sufficient number of molecules so that long-range order is well defined inside the region, yet is small enough compared to the wavelength of low-energy fluctuations that spatial variation of the order parameter within the region is negligible. The partition function for one such region, say region α, is

$$\mathfrak{z}(\alpha, T) = \sum_i \exp[-\beta E_i(\alpha)], \tag{1}$$

where $E_i(\alpha)$ is the energy of region α (excluding its interaction with the rest of the system) when it is in state i (a state is defined in quantum systems by the eigenstate of the system and in classical systems by a set of numbers giving the spatial positions and momenta of all the particles). In general, the summation extends over all possible states of region α; however, we can make a simplifying approximation since we are only interested in low-energy fluctuations, which produce negligible spatial variation of the order parameter in region α. Thus out of all the possible states i of region α, we only sum over those states p which can be characterized by a single value of the order parameter. The resulting approximation to $\mathfrak{z}(\alpha,T)$ will be denoted by $Z(\alpha,T)$. We now divide the possible values of the order parameter into small intervals of width $\Delta\sigma(\alpha)$ and group together all those states having values of the order parameter in the same interval. By denoting the number of states in the interval centered at $\sigma(\alpha)$ as $N[\sigma(\alpha)]$, it follows that

$$\begin{aligned}\mathfrak{z}(\alpha, T) \simeq Z(\alpha, T) &= \sum_{p} \exp[-\beta E_p(\alpha)] \\ &= \sum_{\sigma(\alpha)} \left\{ \sum_{j=1}^{N[\sigma(\alpha)]} \exp(-\beta E_j[\sigma(\alpha)]) \right\}, \qquad [2]\end{aligned}$$

where $E_j[\sigma(\alpha)]$ is the energy of one of the states having an order parameter value within the interval centered around $\sigma(\alpha)$. Note that $N[\sigma(\alpha)]$ depends on the width of the interval $\Delta\sigma(\alpha)$ and, though region α is small, it still contains a sufficiently large number of molecules that $N[\sigma(\alpha)]$ must be very large in any finite interval $\Delta\sigma(\alpha)$. It is therefore meaningful to define a density of states $\rho[\sigma(\alpha)]$ such that

$$\rho[\sigma(\alpha)] = \lim_{\Delta\sigma(\alpha)\to 0} \frac{N[\sigma(\alpha)]}{\Delta\sigma(\alpha)} . \qquad [3]$$

By reducing $\Delta\sigma(\alpha)$ to a differential, $d\sigma(\alpha)$, and by assuming that the energy of any state p in region α can be expressed as a continuous function, $E[\sigma(\alpha)]$, of the order parameter, Eq. [2] can be accurately replaced by

$$Z(\alpha, T) = \int d\sigma(\alpha)\rho[\sigma(\alpha)] \exp\{-\beta E[\sigma(\alpha)]\}, \qquad [4]$$

where the integral extends over all possible values of the order parameter.

We now define a Landau free energy function $\hat{f}[\sigma(\alpha),T]$ of region α, when it is characterized by the value $\sigma(\alpha)$, as

$$\hat{f}[\sigma(\alpha), T] \equiv E[\sigma(\alpha)] - k_B T \ln \rho[\sigma(\alpha)]. \qquad [5]$$

In terms of $\hat{f}[\sigma(\alpha),T]$, Eq. [4] can be expressed as

$$Z(\alpha, T) = \int d\sigma(\alpha) \exp\{-\beta\hat{f}[\sigma(\alpha), T]\}, \qquad [6]$$

and the total free energy of region α, $F(\alpha,T)$, is given by the usual relation

$$F(\alpha, T) = -k_B T \ln Z(\alpha, T). \qquad [7]$$

Let us now consider the interaction energy between two neighboring regions, say regions α and $\alpha + 1$. When the order parameter characterizing a physical system deviates from spatial uniformity, there is always a restoring force tending to bring the system back into spatial uniformity. It is therefore plausible to treat the interaction between two neighboring regions as being elastic. That is, the interaction energy I between regions α and $\alpha + 1$, when they are characterized by the order parameter values $\sigma(\alpha)$ and $\sigma(\alpha + 1)$, is, to a first approximation, a function of the *difference* between $\sigma(\alpha)$ and $\sigma(\alpha + 1)$. I has the property

$$I[\sigma(\alpha) - \sigma(\alpha + 1), T] = \begin{cases} 0 & \text{for } \sigma(\alpha) = \sigma(\alpha + 1) \\ \text{positive and} & \\ \text{increases with} & \\ |\sigma(\alpha) - \sigma(\alpha + 1)| & \text{for } \sigma(\alpha) \neq \sigma(\alpha + 1), \end{cases} \qquad [8]$$

where $|\ \ |$ denotes the absolute value. The combined Landau free energy of regions α and $\alpha + 1$, when they are characterized by $\sigma(\alpha)$ and $\sigma(\alpha + 1)$, is then given by $\hat{f}[\sigma(\alpha),T] + \hat{f}[\sigma(\alpha + 1),T] + I[\sigma(\alpha) - \sigma(\alpha + 1),T]$. The complete partition function for the two regions, including the interaction, can be written as

$$Z(\alpha, \alpha + 1, T) = \int d\sigma(\alpha) \int d\sigma(\alpha + 1) \exp\{-\beta(\hat{f}[\sigma(\alpha), T] + \hat{f}[\sigma(\alpha + 1), T] + I[\sigma(\alpha) - \sigma(\alpha + 1), T])\}. \qquad [9]$$

It should be noted that if $I = 0$, Eq. [9] gives the expected result $F(\alpha,\alpha + 1,T) = -k_B T \ln Z(\alpha,\alpha + 1,T) = F(\alpha,T) + F(\alpha + 1,T)$ for two noninteracting regions. For the purpose of simplifying the counting, we will define the quantities $\Gamma(\alpha,T)$, $\Gamma(\alpha + 1,T)$ such that

$$\Gamma(\alpha + 1, T) = \Gamma(\alpha, T) = \frac{1}{2} I[\sigma(\alpha) - \sigma(\alpha + 1), T]. \quad [10]$$

In other words, the interaction energy between two neighboring regions is split equally and counted twice: once as belonging to region α and once as belonging to region $\alpha + 1$. Eq. [9] can now be put in the form

$$Z(\alpha, \alpha + 1, T) = \int d\sigma(\alpha) \int d\sigma(\alpha + 1) \exp\{-\beta(\hat{f}[\sigma(\alpha), T] + \hat{f}[\sigma(\alpha + 1), T] + \Gamma(\alpha, T) + \Gamma(\alpha + 1, T))\}. \quad [9a]$$

We can easily generalize Eq. [9a] to obtain the partition function $Z(T)$ of the whole system, where each region interacts elastically with its neighbors:

$$\begin{aligned} Z(T) &= \int d\sigma(1) \int d\sigma(2) \ldots \int d\sigma(M) \exp\left[-\beta \sum_{\alpha=1}^{M} (\hat{f}[\sigma(\alpha), T] + \Gamma(\alpha, T))\right] \\ &= \int D\{\sigma(1), \sigma(2), \ldots \sigma(M)\} \exp\left[-\beta \sum_{\alpha=1}^{M} (\hat{f}[\sigma(\alpha), T] + \Gamma(\alpha, T))\right], \end{aligned} \quad [11]$$

where $\Gamma(\alpha,T)$ is equal to half the interaction energy of region α with its neighbors and is understood to depend on the difference in order parameter values between region α and its neighboring regions. $\{\sigma(1), \sigma(2), \ldots, \sigma(M)\}$ denotes a set of M numbers the value of each of which is bounded by the maximum and minimum values of the order parameter, and the integral over $D\{\sigma(1), \sigma(2), \ldots \sigma(M)\}$ means integration over all possible sets of M numbers with the above constraint. In Fig. 1 we illustrate schematically the equivalence of integration over each $\sigma(\alpha)$ individually and integration over all possible sets $\{\sigma(1), \sigma(2), \ldots, \sigma(M)\}$.

It is convenient at this point to change notation somewhat. We will henceforth label each region by the spatial coordinate $\vec{r}_\alpha$ of its center. Since the volume of each region is ΔV, we can define a free energy density,

$$f[\sigma(\vec{r}_\alpha), T] \equiv \frac{\hat{f}[\sigma(\alpha), T]}{\Delta V}, \quad [12]$$

and an interaction energy density,

$$\gamma(\vec{r}_\alpha, T) \equiv \frac{\Gamma(\alpha, T)}{\Delta V}. \quad [13]$$

Since individual regions are small compared to the entire system, it is the usual practice to regard each region as a spatial "point" in the system. Thus $\sigma(\vec{r}_\alpha) \rightarrow \sigma(\vec{r})$ and $f[\sigma(\vec{r}_\alpha),T] \rightarrow f[\sigma(\vec{r}),T]$, where $\sigma(\vec{r})$ and $f[\sigma(\vec{r}),T]$ are defined at any arbitrary spatial "point" $\vec{r}$. Recall that, to a first approximation, $\Gamma(\alpha,T)$ depends only on differences in the order parameter values between region α and its neighboring regions, so that $\gamma(\vec{r}_\alpha,T)$ can be replaced* by $\gamma[\vec{\nabla}\sigma(\vec{r}),T]$. It therefore follows that

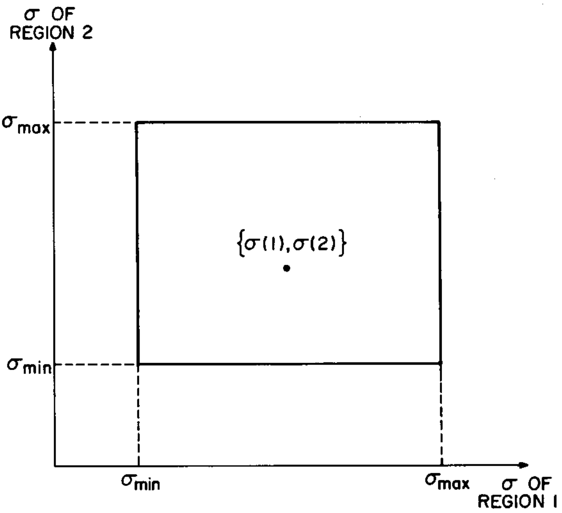

Fig. 1—Schematic illustration of the equivalence of integrating over $d\sigma(1)\ d\sigma(2)$ and summing over all possible sets of numbers $\{\sigma(1),\ \sigma(2)\}$. A set of numbers $\{\sigma(1),\ \sigma(2)\}$ corresponds to a point inside the square as shown; summing over all possible sets assures that the area of the entire square is included. Generalization to any arbitrary number of variables is straightforward.

$$\sum_{\alpha=1}^{M}\{\hat{f}[\sigma(\alpha),T]+\Gamma(\alpha,T)\}=\sum_{\alpha=1}^{M}\{f[\sigma(\vec{r}_\alpha),T]+\gamma(\vec{r}_\alpha,T)\}\Delta V$$

$$\longrightarrow \int_{\substack{\text{volume}\\ \text{of the}\\ \text{sample}}} d^3\vec{r}\,\{f[\sigma(\vec{r}),T]+\gamma[\vec{\nabla}\sigma(\vec{r}),T]\}, \qquad [14]$$

and each set of numbers $\{\sigma(1),\ \sigma(2)\ \ldots\ \sigma\ (M)\}$ is uniquely replaced by

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* Theoretically the interaction term should depend on all orders of spatial derivatives of the order parameter. However, later development will show that one needs only retain the first order spatial derivatives of $\sigma(\vec{r})$ to obtain the Landau expression. Therefore, for simplicity, the function γ will be assumed to depend only on $\nabla\sigma(\vec{r})$.

a spatial function $\sigma(\hat{r})$. Eq. [11] can now be rewritten as

$$Z(T) = \int \boldsymbol{D}\sigma(\vec{r}) \exp\{-\beta \int d^3\vec{r}(f[\sigma(\vec{r}), T] + \gamma[\vec{\nabla}\sigma(\vec{r}), T])\} \quad [15]$$

where we have used Feynman's path integral notation[8] $\boldsymbol{D}\sigma(\hat{r})$ to denote integration over all possible functions $\sigma(\hat{r})$. Eq. [15] is the central result of this subsection. Some of the implications of Eq. [15] are discussed in Appendix A.

2.2 The Landau Expansion

Calculation of the physical properties of a spatially uniform, macroscopic system requires information about $f[\sigma,T]$ only in the immediate vicinity of its minimum at temperature T, due to the sharpness of the peak in the function $\exp\{-\beta V f[\sigma,T]\}$ (See Appendix A). This implies that for a physical system having a second-order phase transiton at $T = T_c$, with $\sigma = 0$ for $T > T_c$ and $\sigma \neq 0$ for $T < T_c$ (such as the ferromagnetic phase transition), many features of the transition can be deduced if $f[\sigma,T]$ is known only in the neighborhood of $\sigma = 0$, $T = T_c$. Landau speculated that the first few derivatives of the function $f[\sigma,T]$ with respect to σ exist, and that they have finite values when evaluated at $\sigma = 0$, $T = T_c$. For a second-order phase transition the value of σ varies continuously and can be arbitrarily small near $T = T_c$; therefore, the Landau assumption enables one to express $f[\sigma,T]$ near $T = T_c$ as[4]

$$f[\sigma, T] = f_0[T] + \lambda(T)\sigma + \frac{1}{2}A(T)\sigma^2 + \frac{1}{3}B(T)\sigma^3 + \frac{1}{4}C(T)\sigma^4 + \ldots . \quad [16]$$

Various properties of the expansion coefficients λ, A, B and C can be obtained from quite general considerations.

For definiteness we will examine the expansion in relation to two physical systems: (1) the CuZn (β-brass) binary alloy and (2) a ferromagnet such as iron. It is well known[9] that CuZn has a second-order, order–disorder transition at $T_c = 742°\mathrm{K}$. The crystal structure at 0°K can be described by two interpenetrating simple cubic lattices each with N_0 sites. Let us suppose that lattice 1 is occupied by Cu atoms and lattice 2 by Zn atoms. As the temperature is raised above

0°K, some Zn atoms will be found on lattice 1 and some Cu atoms on lattice 2 but, so long as the temperature is less than T_c, $N_{Cu}(1)/N_0 > \frac{1}{2}$, where we have denoted the number of copper atoms on lattice 1 by $N_{Cu}(1)$. For temperatures in excess of T_c, complete randomization occurs and $N_{Cu}(1)/N_0 = N_{Zn}(1)/N_0 = \frac{1}{2}$. A suitable order parameter for the system can be defined as

$$\sigma = \frac{N_{\mathrm{Cu}}(1) - N_{\mathrm{Zn}}(1)}{N_0}, \qquad [17]$$

which is zero for $T \geq T_c$ and in the range 0 to 1 for $T < T_c$. It is also obvious that the state characterized by $-\sigma = [N_{Cu}(2) - N_{Zn}(2)]/N_0$ is physically equivalent to the state characterized by $+\sigma$ because the difference between the two can be ascribed to the interchange of labelings for lattices 1 and 2. It follows therefore that the free-energy density for $-\sigma$ must be equal to that for $+\sigma$ and hence $\lambda(T) = B(T) = 0$. In fact, all the terms having odd powers of σ must necessarily have vanishing coefficients. This is a general result not limited to the CuZn system alone. Consider the ferromagnet, iron. In this case the order parameter is given by a vector $\vec{m}$ defined as

$$\vec{m} = \vec{M}/M_0, \qquad [18]$$

where $\vec{M}$ is the magnetization vector and M_0 is the magnitude of the saturation magnetization at 0°K. The equilibrium state is characterized by $\vec{m} = 0$ for temperatures above the Curie point and by $0 < |\vec{m}| \leq 1$ for temperatures below the Curie point. In exact analogy with the case of a scalar order parameter, the free energy density can be expanded in terms of $\vec{m}$. However, since the free energy density is a scalar quantity, the Landau expansion of $f[\vec{m},T]$ about $\vec{m} = 0$ can only contain scalar combinations of $\vec{m}$. It is therefore obvious that $\lambda(T) = 0$. $B(T)$ must also vanish since it is impossible to construct a scalar from three vectors. As before, we see that the coefficients of the odd order terms in the expansion vanish. The above arguments can be similarly applied to other examples of second-order transitions.[10,11] In fact, for a second-order phase transition, one can always define an order parameter such that its equilibrium value is zero for $T \geq T_c$ and nonzero for $T < T_c$ and such that $\lambda(T) = B(T) = 0$ in the Landau expansion of $f[\sigma,T]$.

For a second order phase transition, Eq. [16] thus takes the form

$$f[\sigma, T] \simeq f_0[T] + \frac{1}{2}A(T)\sigma^2 + \frac{1}{4}C(T)\sigma^4 + \ldots . \qquad [19]$$

At this point Landau[4] assumed further that near T_c the coefficient $C(T)$ is a slowly varying function of T compared to $A(T)$ and therefore can be replaced by a constant $C > 0$ in the temperature range of interest. Since the order parameter is zero at equilibrium in the high temperature phase, it is necessary that $\sigma = 0$ be a minimum of $f[\sigma,T]$ for $T > T_c$ and thus $A(T)$ must be positive. However, in the low temperature phase nonzero values of σ must correspond to the minimum in $f[\sigma,T]$. This minimum occurs at $\sigma = \pm[-A(T)/C(T)]^{1/2}$ provided $A(T)$ is negative. Therefore $A(T)$ must be positive for $T > T_c$ and negative for $T < T_c$, which implies that $A(T = T_c)$ must be zero and, in the neighborhood of T_c, $A(T)$ can be approximated by

$$A(T) = a(T - T_c), \qquad [20]$$

where a is a positive constant. We can now rewrite Eq. [19] as

$$f[\sigma, T] \simeq f_0[T] + \frac{1}{2}a(T - T_c)\sigma^2 + \frac{1}{4}C\sigma^4; \quad a, C > 0. \qquad [21]$$

Eq. [21] is illustrated schematically in Fig. 2.

So far we have considered only spatially uniform systems. Generalization of Eq. [21] to include spatial variations of the order parameter involves: (1) replacing σ by $\sigma(\vec{r})$, and (2) including the contribution to the free-energy density due to the interaction term $\gamma[\vec{\nabla}\sigma(\vec{r}),T]$. Following Landau,[4] we expand $\gamma[\vec{\nabla}\sigma(\vec{r}),T]$ in a power series in $\vec{\nabla}\sigma(\vec{r})$ and retain only the leading terms. Again, the expansion can contain only scalar combinations of $\vec{\nabla}\sigma(\vec{r})$ and, since $\gamma[\vec{\nabla}\sigma(\vec{r}),T] = 0$ when $\vec{\nabla}\sigma(\vec{r}) = 0$, we obtain*

$$\gamma[\vec{\nabla}\sigma(\vec{r}), T] \simeq \frac{1}{2}D(T)[\vec{\nabla}\sigma(\vec{r})]^2. \qquad [22]$$

In order that the spatially uniform state be the state of lowest free energy, $D(T)$ must be positive. Furthermore, near the critical temperature, $D(T)$ can be approximated by a constant D. Combining the leading terms in the expansions of $f[\sigma(\vec{r}),T]$ and $\gamma[\vec{\nabla}\sigma(\vec{r}),T]$, we obtain

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* Theoretically, expansion of the interaction term can contain second order scalar combinations such as $\sigma(\vec{r})\vec{\nabla}^2\sigma(\vec{r})$ and $\vec{\nabla}^2\sigma(\vec{r})$. However, $\vec{\nabla}^2\sigma(\vec{r})$ integrated over volume can be converted into a surface integral and can be neglected since the surface contribution is assumed to be small. The volume integral of $\sigma(\vec{r})\vec{\nabla}^2\sigma(\vec{r})$ is equivalent to the integral of $[\vec{\nabla}\sigma(\vec{r})]^2$. Therefore, even in the most general case, the leading term in the expansion is proportional to $[\vec{\nabla}\sigma(\vec{r})]^2$.

$$f[\sigma(\vec{r}), T] + \gamma[\vec{\nabla}\sigma(\vec{r}), T] \simeq \mathfrak{F}_L$$
$$\equiv f_0[T] + \frac{1}{2}a(T - T_c)\sigma^2(\vec{r}) + \frac{1}{4}C\sigma^4(\vec{r}) + \frac{1}{2}D[\vec{\nabla}\sigma(\vec{r})]^2, \quad [23]$$

where $\mathfrak{F}_L$ is usually referred to as the Landau free energy density and a, C, and D are all positive constants.

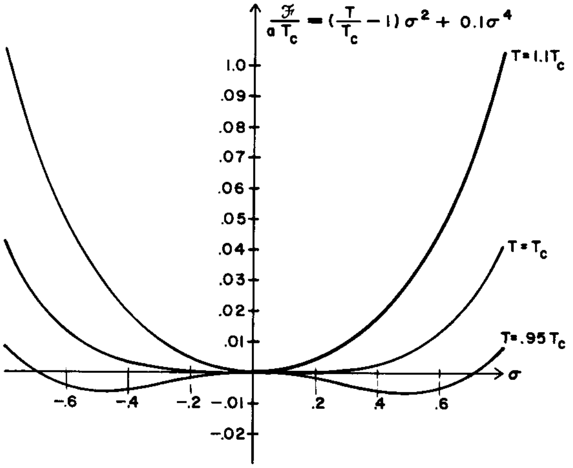

Fig. 2—Illustration of the behavior of Eq. [21]. The Landau free energy density is symmetric about $\sigma = 0$; for $T \geq T_c$ the disordered state ($\sigma = 0$) is the stable state while for $T < T_c$ the ordered state ($\sigma \neq 0$) is the state of lowest free energy.

2.3 Generalization of the Landau Expansion to Liquid Crystals

We must first identify a suitable order parameter for describing liquid crystal phase transitions. In previous chapters, we have seen that for nematic and cholesteric liquid crystals, the molecular ordering at every spatial "point" $\vec{r}$ (where the term "point" has the meaning defined in Section (2.1)) is characterized by a director $\hat{n}(\vec{r})$ pointing along the local axis of uniaxial symmetry, and by a quantity $S(\vec{r})$ giving the local orientational order of the rod-like molecules. $S(\vec{r})$ is defined by

$$S(\vec{r}) = \ll P_2(\cos\theta) \gg_{\vec{r}}, \quad [24]$$

where θ is the angle between the long axis of any molecule in the small region of space associated with "point" $\vec{r}$ and the local director $\hat{n}(\vec{r})$, P_2 is the second Legendre polynomial, and $\ll \gg_{\vec{r}}$ denotes spatial averaging over the configurations of the molecules at "point" $\vec{r}$ ($\ll \gg_{\vec{r}}$ should not be confused with thermal averaging $< >$, which gives the equilibrium value of a quantity. $S(\vec{r})$ should therefore be distinguished from its equilibrium value $<S(\vec{r})>$, which is spatially invariant and temperature-dependent). In Chapter 6 it was shown that in a coordinate system where $\hat{n}(\vec{r})$ coincides with the external z-axis (3-axis), the local order parameter of a nematic or cholesteric liquid crystal is given by*

$$\mathbf{Q}(\vec{r}) = S(\vec{r}) \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \qquad [25]$$

where $\mathbf{Q}(\vec{r})$ denotes that the quantity $Q(\vec{r})$ is a tensor. For arbitrary orientation of $\hat{n}(\vec{r})$ relative to the external coordinate system, the components of $\mathbf{Q}(\vec{r})$ can be expressed as

$$Q_{ij}(\vec{r}) = \frac{1}{2} S(\vec{r})[3n_i(\vec{r})n_j(\vec{r}) - \delta_{ij}], \qquad [26]$$

where $i,j = 1, 2, 3$ denote the components along the three orthogonal axes of the Cartesian coordinate system and $\delta_{ij} = 1$ for $i = j$ and zero otherwise. Comparing the order parameters for a ferromagnet and a liquid crystal, we see that $S(\vec{r})$ corresponds to the magnitude of $\vec{m}$, and the matrix in Eq. [25] corresponds to the unit vector pointing along the direction of magnetization; this matrix can be thought of as a "unit tensor." To see that the order parameter for a liquid crystal cannot be a vector, we observe that $\hat{n}(\vec{r})$ and $-\hat{n}(\vec{r})$ correspond to physically equivalent states and $Q(\vec{r})$ must therefore be proportional to an even order combination of $\hat{n}(\vec{r})$. The two lowest even-order combinations of a unit vector are a scalar and a second rank tensor and, since the liquid-crystal order cannot be completely described by a scalar, we are left with the tensor as our only choice.

Let us now consider the Landau free-energy density expression for liquid crystals. All isotropic-nematic (cholesteric) phase transitions

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* Our definition of $\mathbf{Q}(\vec{r})$ differs from that of de Gennes by a factor of 2.

are first order, and exhibit a discontinuous jump at $T = T_c$ in the equilibrium value of $\mathbf{Q}(\vec{r})$ from $\mathbf{Q}(\vec{r}) = 0$ in the isotropic phase to some finite value in the low temperature phase. Consequently, we expect the Landau expansion about $\mathbf{Q}(\vec{r}) = 0$ to provide a better description of phenomena such as fluctuations in the high-temperature isotropic phase than it does in the low-temperature phase, since the expansion would not be accurate for the values of the order parameter in the low-temperature phase. We will first develop the Landau–de Gennes expansion about the isotropic phase of a nematic liquid crystal and later generalize the expression to include the effects of external fields and the special symmetry of cholesteric liquid crystals. Since the expansion can contain only scalar combinations of $\mathbf{Q}(\vec{r})$ and its spatial derivatives, the term linear in $\mathbf{Q}(\vec{r})$ again vanishes because the scalar $\sum_{i=1}^{3} Q_{ii}(\vec{r})$ (the trace of $\mathbf{Q}(\vec{r})$) is identically zero. The coefficient of the term linear in the spatial derivative of $\mathbf{Q}(\vec{r})$ must also be zero because there is no way of forming a scalar quantity from the derivative. However, unlike the situation described for ferromagnetism and other second order phase transitions, the term cubic in $\mathbf{Q}(\vec{r})$ does not have to vanish because it is possible to construct a scalar from three tensors, and also because $\mathbf{Q}(\vec{r})$ and $-\mathbf{Q}(\vec{r})$ correspond to physically different states, as illustrated in Fig. 3. Thus the free

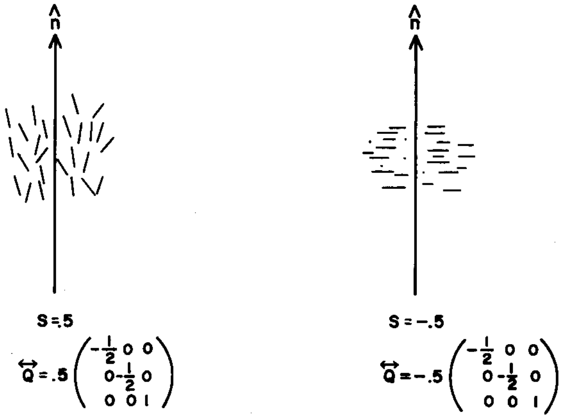

Fig. 3—Schematic illustration of the physical difference in molecular ordering for $S = 0.5$ and $S = -0.5$. The short lines represent projections of the molecular long axes on the plane of the paper. Thus a molecule whose long axis is normal to the paper is represented by a dot.

energy density is no longer required to be symmetric about $\mathbf{Q}(\vec{r}) = 0$. Recalling that the trace of a matrix or of a product of matrices is always a scalar, we may write

$$\begin{aligned}\mathfrak{F}_L = {} & f_0[T] + \frac{1}{2}a(T - T_c^*)Q_{ij}(\vec{r})Q_{ji}(\vec{r}) + \\ & \frac{1}{3}BQ_{ij}(\vec{r})Q_{jk}(\vec{r})Q_{ki}(\vec{r}) + \frac{1}{4}C_1[Q_{ij}(\vec{r})Q_{ji}(\vec{r})]^2 + \\ & \frac{1}{4}C_2Q_{ij}(\vec{r})Q_{jk}(\vec{r})Q_{kl}(\vec{r})Q_{li}(\vec{r}) + \\ & \frac{1}{2}L_1\partial_iQ_{jk}(\vec{r})\partial_iQ_{jk}(\vec{r}) + \frac{1}{2}L_2\partial_iQ_{ij}(\vec{r})\partial_kQ_{kj}(\vec{r}),\end{aligned} \qquad [27]$$

where T_c^* is a temperature slightly below T_c, $a > 0$, B, C_1, C_2, L_1, L_2 are constants; $i, j, k, l = 1,2,3$ denote the components along the three orthogonal axes of the coordinate system; $\partial_i \equiv \partial/\partial x_i$ is the partial derivative with respect to spatial coordinate x_i; and summation over repeated indices is implied. Two points regarding Eq. [27] are worthy of special attention. First, because the order parameter is a tensor, $\mathfrak{F}_L$ contains two fourth-order terms and two spatial derivative terms, in contrast with Eq. [23] where the order parameter is a scalar. Second, a new phenomenological parameter T_c^* has been defined as the temperature at which the curvature of $\mathfrak{F}_L$ at $\mathbf{Q}(\vec{r}) = 0$ changes sign. Since $T_c^* < T_c$, we can find a temperature range, $T_c^* < T < T_c$, in which $\mathbf{Q}(\vec{r}) = 0$ is not the position of the absolute minimum of $\mathfrak{F}_L$ (since otherwise $\mathbf{Q}(\vec{r}) = 0$ would be the equilibrium state for $T < T_c$, which is a contradiction) and yet the curvature of $\mathfrak{F}_L$ at $\mathbf{Q}(\vec{r}) = 0$ is positive. In other words, $\mathbf{Q}(\vec{r}) = 0$ is a relative minimum of $\mathfrak{F}_L$ for $T_c^* < T < T_c$. Since the existence of a relative minimum of $\mathfrak{F}_L$ is a necessary condition for supercooling, it follows that T_c^* can be interpreted physically as that temperature below which supercooling becomes impossible.

Eq. [27] can be put into a more physically interpretable form by substituting Eq. [26] for $Q_{ij}(\vec{r})$ and noting that

$$n_i(\vec{r})\partial_jn_i(\vec{r}) = \frac{1}{2}\partial_j[n_1^2(\vec{r}) + n_2^2(\vec{r}) + n_3^2(\vec{r})] = \frac{1}{2}\partial_j[1] = 0$$

and

$$\begin{aligned}[\hat{n}(\vec{r})\cdot\vec{\nabla}]\hat{n}(\vec{r}) &= \frac{1}{2}\vec{\nabla}[\hat{n}(\vec{r})\cdot\hat{n}(\vec{r})] - \hat{n}(\vec{r}) \times [\vec{\nabla} \times \hat{n}(\vec{r})] \\ &= -\hat{n}(\vec{r}) \times [\vec{\nabla} \times \hat{n}(\vec{r})].\end{aligned}$$

We obtain

$$\begin{aligned}\mathfrak{F}_L = {} & f_0[T] + \frac{3}{4}a(T - T_c^*)S^2(\vec{r}) + \frac{1}{4}BS^3(\vec{r}) + \\ & \frac{9}{16}CS^4(\vec{r}) + \frac{3}{4}L_1[\vec{\nabla}S(\vec{r})]^2 + \frac{9}{4}L_1S^2(\vec{r})(\partial_i n_j(\vec{r}))(\partial_i n_j(\vec{r})) + \\ & \frac{1}{8}L_2[\vec{\nabla}S(\vec{r})]^2 + \frac{3}{8}L_2[\hat{n}(\vec{r})\cdot\vec{\nabla}S(\vec{r})]^2 + \frac{9}{8}L_2S^2(\vec{r})[\vec{\nabla}\cdot\hat{n}(\vec{r})]^2 + \\ & \frac{3}{2}L_2S(\vec{r})[\vec{\nabla}\cdot\hat{n}(\vec{r})][\hat{n}(\vec{r})\cdot\vec{\nabla}S(\vec{r})] + \\ & \frac{3}{4}L_2S(\vec{r})[\hat{n}(\vec{r}) \times (\vec{\nabla} \times \hat{n}(\vec{r}))]\cdot\vec{\nabla}S(\vec{r}) + \\ & \frac{9}{8}L_2S^2(\vec{r})[\hat{n}(\vec{r}) \times (\vec{\nabla} \times \hat{n}(\vec{r}))]^2, \qquad [28]\end{aligned}$$

where $C \equiv C_1 + (C_2/2)$. Eq. [28] can be further reduced by noting that

$$\begin{aligned}(\partial_i n_j(\vec{r}))(\partial_i n_j(\vec{r})) = {} & [\vec{\nabla}\cdot\hat{n}(\vec{r})]^2 + [\hat{n}(\vec{r})\cdot(\vec{\nabla} \times \hat{n}(\vec{r}))]^2 + \\ & [\hat{n}(\vec{r}) \times (\vec{\nabla} \times \hat{n}(\vec{r}))]^2 - \vec{\nabla}\cdot[\hat{n}(\vec{r})(\vec{\nabla}\cdot\hat{n}(\vec{r})) + \hat{n}(\vec{r}) \times \vec{\nabla} \times \hat{n}(\vec{r})], \qquad [29]\end{aligned}$$

where the last term represents the surface contribution to the free-energy density and therefore can be neglected (since the volume integral of $\vec{\nabla}\cdot\vec{V}(\vec{r})$, where $\vec{V}(\vec{r})$ is an arbitrary vector field, can be converted to a surface integral by Gauss's Theorem). Substitution of Eq. [29] into Eq. [28] yields

$$\begin{aligned}\mathfrak{F}_L = {} & f_0[T] + \frac{3}{4}a(T - T_c^*)S^2(\vec{r}) + \frac{1}{4}BS^3(\vec{r}) + \\ & \frac{9}{16}CS^4(\vec{r}) + \frac{3}{4}\left(L_1 + \frac{1}{6}L_2\right)[\vec{\nabla}S(\vec{r})]^2 + \frac{3}{8}L_2[\hat{n}(\vec{r})\cdot\vec{\nabla}S(\vec{r})]^2 + \\ & \frac{9}{4}S^2(\vec{r})\left\{\left(L_1 + \frac{1}{2}L_2\right)[\vec{\nabla}\cdot\hat{n}(\vec{r})]^2 + L_1[\hat{n}(\vec{r})\cdot\vec{\nabla} \times \hat{n}(\vec{r})]^2 + \right. \\ & \left.\left(L_1 + \frac{1}{2}L_2\right)[\hat{n}(\vec{r}) \times \vec{\nabla} \times \hat{n}(\vec{r})]^2\right\} + \frac{3}{2}L_2S(\vec{r})[\vec{\nabla}\cdot\hat{n}(\vec{r})] \times \\ & [\hat{n}(\vec{r})\cdot\vec{\nabla}S(\vec{r})] + \frac{3}{4}L_2S(\vec{r})[\hat{n}(\vec{r}) \times \vec{\nabla} \times \hat{n}(\vec{r})]\cdot\vec{\nabla}S(\vec{r}). \qquad [30]\end{aligned}$$

There are four types of terms in Eq. [30]. The first four terms concern only the value of the orientational order $S(\vec{r})$. The next two terms account for spatial variation of $S(\vec{r})$. Next there is a term concerned with the spatial variation of $\hat{n}(\vec{r})$; we have expressed this term in the familiar form of splay, twist, and bend distortions[12] of the director field $\hat{n}(\vec{r})$. It should be noted that to second order in the Landau expansion there are only two independent elastic constants, L_1 and L_2, whereas in the nematic phase there are known to be three independent elastic constants.[13] The last two terms in Eq. [30] represent the interaction between spatial variations of $S(\vec{r})$ and spatial variations of $\hat{n}(\vec{r})$. Clearly, the mathematics can be quite complicated if $S(\vec{r})$ and $\hat{n}(\vec{r})$ are allowed to vary simultaneously.

Let us now examine the expansion coefficients B, C, L_1, and L_2 in more detail. We will consider first the spatially uniform state which can be described by the first four terms of Eq. [30]. Following Landau, we choose $C > 0$, which requires that $B < 0$ if the equilibrium value of S is to be positive in the low-temperature phase. We illustrate the behavior of $\mathfrak{F}_L$ as a function of S for a spatially uniform system in Fig. 4. Next we consider a state for which $S(\vec{r})$ is constant but $\hat{n}(\vec{r})$ is allowed to vary from point to point. Since the spatially uniform state must be stable against any distortion, it is clear from Eq. [30] that

$$L_1 > 0 \qquad [31]$$

and

$$L_1 + \frac{1}{2}L_2 > 0. \qquad [32]$$

If now we fix $\hat{n}(\vec{r})$ and let $S(\vec{r})$ vary, the same reasoning leads to the inequalities

$$L_1 + \frac{1}{6}L_2 > 0 \text{ for } \hat{n}(\vec{r}) \perp \vec{\nabla}S(\vec{r}) \qquad [33]$$

and

$$L_1 + \frac{2}{3}L_2 > 0 \text{ for } \hat{n}(\vec{r}) \parallel \vec{\nabla}S(\vec{r}). \qquad [34]$$

In order to clarify the physical meaning of L_1 and L_2, imagine a disturbance of the equilibrium state $\mathbf{Q}(\vec{r}) = 0$ of the high temperature phase such that $S(\vec{r} = 0) \neq 0$ along a certain director $\hat{n}$. If $L_1 = L_2 = 0$, we see from Eq. [30] that the disturbance would be a delta function at $\vec{r} = 0$ since the rest of the system, including the immediate region

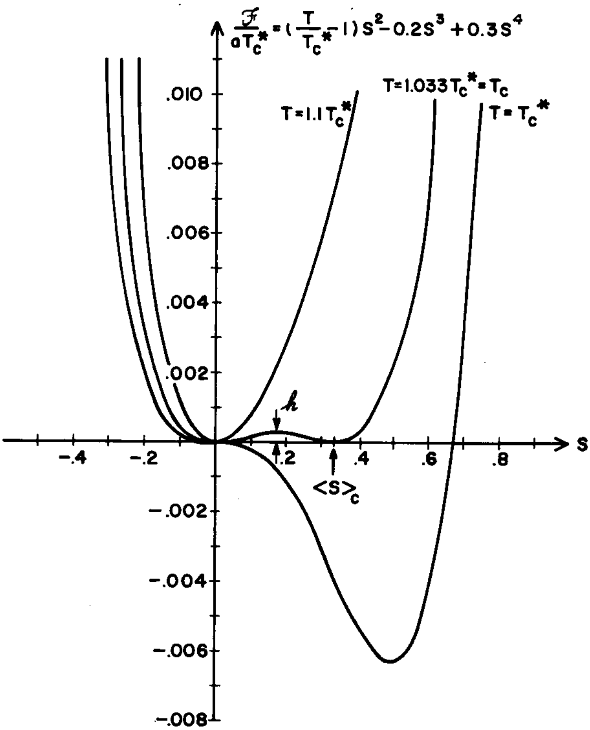

Fig. 4—Illustration of the asymmetry in the Landau free energy density when a non-zero third-order term is included. For $T > T_c$, $S = 0$ is the absolute minimum. As T approaches T_c from above a second minimum appears and for $T = T_c$ the physical states corresponding to the two minima have the same free energy density and are separated by a barrier of height h. For $T_c^* < T < T_c$ the $S \neq 0$ minimum represents the stable state and the $S = 0$ minimum represents the metastable (supercooled) state. For temperatures below T_c^* the metastable state becomes unstable.

surrounding $\vec{r} = 0$, would still prefer to be in its lowest free energy state, $S(\vec{r}) = 0$. However, as soon as $L_1, L_2 \neq 0$, the delta function becomes energetically unfavorable because of the divergence of the spatial derivatives, and any disturbance at $\vec{r} = 0$ must decay in a continuous manner to the equilibrium value $S(\vec{r}) = 0$ over some region of space surrounding $\vec{r} = 0$. The characteristic decay length is determined by the competition between the first four terms of Eq. [30], which tend to minimize the decay length so as to reduce their free-energy contribution, and the spatial derivative terms, which tend to maximize the decay length so as to reduce $|\vec{\nabla}S(\vec{r})|$. The decay of a disturbance of the sort described above ($\hat{n}(\vec{r})$ fixed, $S(\vec{r} = 0) \neq 0$ along $\hat{n}$) is illustrated schematically in Fig. 5. Note that for $L_2 \neq 0$, the decay length of the disturbance parallel to $\hat{n}$ is different from that perpendicular to $\hat{n}$. Specifically, spatial variation of $S(\vec{r})$ in a direction parallel to $\hat{n}$ contributes a free energy density

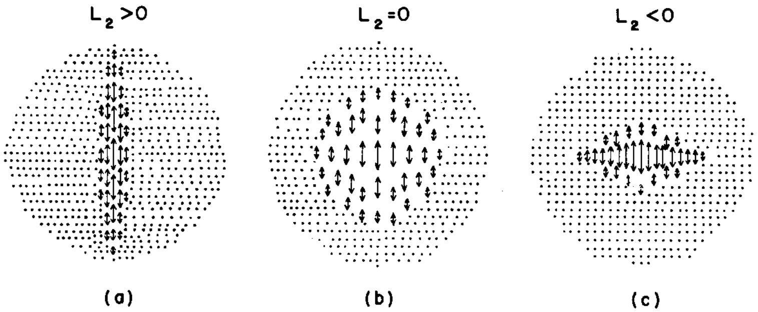

Fig. 5—Illustration of the spatial anistropy in the decay of a disturbance in the local order for different values of L_2. Regions of order are represented by double-headed arrows whose length is proportional to the magnitude of the local order and whose direction is parallel to the local director. The dots represent the surrounding isotropic field. In (a), $L_2 > 0$ and the disturbance (fluctuation) relaxes faster in the direction perpendicular to the director, whereas in (c), $L_2 < 0$ and the relaxation is faster in the direction parallel to the director. In (b), $L_2 = 0$ and the decay pattern is isotropic.

$$\frac{3}{4}\left(L_1 + \frac{2}{3}L_2\right)[\vec{\nabla}S(\vec{r})]^2,$$

whereas spatial variation of $S(\vec{r})$ perpendicular to $\hat{n}$ contributes a free energy density

$$\frac{3}{4}\left(L_1 + \frac{1}{6}L_2\right)[\vec{\nabla}S(\vec{r})]^2.$$

Therefore, if $L_2 > 0$, the elastic constant governing the spatial variation of $S(\vec{r})$ in the direction parallel to $\hat{n}$ is larger than that in the direction perpendicular to $\hat{n}$. Indeed, the elastic constant along a direction which makes an arbitrary angle ψ with $\hat{n}$ is proportional to

$$1 + \frac{1}{6}\frac{L_2}{L_1}(1 + 3\cos^2\psi).$$

The decay pattern of a disturbance for $L_2 > 0$ is shown in Fig. 5a, while that for $L_2 < 0$ is shown in Fig. 5c.

Now, a word about the magnitude of the expansion coefficients a, B, C, L_1, and L_2. Taking the intermolecular interaction energy ($\simeq$ 0.01 eV) as the characteristic energy,[12] the intermolecular separation ($\simeq$ 10 Å) as the characteristic length, and $T_c \simeq 300°\text{K}$ as the characteristic temperature of nematic and cholesteric phases, we can estimate the magnitudes of these coefficients using dimensional analysis. The coefficient a has units of energy/(volume·°K). Combining the characteristic values in the appropriate way leads to $a \simeq 0.005$ J/(cm^3 °K), compared to the measured value[14] of 0.042 J/(cm^3 °K) for MBBA. B and C have units of energy/volume which gives $|B|, |C| \simeq$ 1.6 J/cm^3, in order of magnitude agreement with measured values[14] $\simeq$ 0.5 J/cm^3. Finally, we obtain $|L_1|, |L_2| \simeq 10^{-7}$ dyne which is in reasonable agreement with the experimental value[15] of 10^{-6} dyne.

In the remainder of this section we will generalize Eq. [30] to include the effects of external magnetic and electric fields and also to take account of the finite pitch in the equilibrium state of cholesteric liquid crystals.

Suppose that a static magnetic field $\vec{H}$ is applied to the system. Since nematic and cholesteric liquid crystals are normally diamagnetic, the energy density induced by the magnetic field is given by

$$W_M = -\frac{1}{2}H_i\chi_{ij}(\vec{r})H_j, \tag{35}$$

where χ_{ij} are the components of the susceptibility tensor in units of susceptibility per unit volume. It was shown in Chapter 6 that

$$\boldsymbol{\chi}(\vec{r}) = \frac{2}{3}(\Delta\chi)_{\text{max}}\mathbf{Q}(\vec{r}) + \bar{\chi}\mathbf{I}, \tag{36}$$

where $\mathbf{I}$ is the unit matrix, $(\Delta\chi)_{\text{max}} \equiv N(\zeta_\parallel - \zeta_\perp)$($N$ being the number of molecules per unit volume, and $\zeta_\parallel(\zeta_\perp)$ the susceptibility of a single rod-like molecule parallel (perpendicular) to its long axis), and $\bar{\chi}$ is the susceptibility per unit volume when $\mathbf{Q}(\vec{r}) = 0$. Using Eq. [13]

of Chapter 6, we see that $\bar{\chi} = N\,(2\zeta_\perp + \zeta_\parallel)/3$. Thus, Eq. [35] can be rewritten as

$$W_M = -\frac{1}{3}(\Delta\chi)_{\max}H_iQ_{ij}(\vec{r})H_j - \frac{1}{6}NH^2(2\zeta_\perp + \zeta_\parallel). \qquad [37]$$

Since the last term in Eq. [37] is independent of the order parameter and its gradients, it can be absorbed into the term $f_0[T]$ of $\mathfrak{F}_L$. Therefore, the magnetic field contribution to the free energy density is

$$\begin{aligned}\mathfrak{F}_M &= -\frac{1}{3}(\Delta\chi)_{\max}H_iQ_{ij}(\vec{r})H_j \\ &= -\frac{1}{6}(\Delta\chi)_{\max}S(\vec{r})\{3[\vec{H}\cdot\hat{n}(\vec{r})]^2 - H^2\}.\end{aligned} \qquad [38]$$

Using similar arguments, we obtain the electric field contribution to the free-energy density

$$\mathfrak{F}_E = -\frac{1}{24\pi}(\Delta\epsilon)_{\max}S(\vec{r})\,\{3[\vec{E}\cdot\,\hat{n}(\vec{r})]^2 - E^2\}, \qquad [39]$$

where $(\Delta\epsilon)_{\max}$ is the maximum possible value of $(\epsilon_\parallel - \epsilon_\perp)$, $\epsilon_\parallel(\epsilon_\perp)$ being the dielectric constant parallel (perpendicular) to the local director.

It must be stressed that, unlike our expansion of $\mathfrak{F}_L$, Eq. [30], which is valid only for vanishingly small values of the order parameter, Eqs. [38] and [39] are valid for arbitrary values of the order parameter. In fact, the magnetic and electric energy density expressions of the elastic continuum theory (Eqs. [3] and [4] of Chapter 8) are special cases of Eqs. [38] and [39]. For example, consider the magnetic energy density of the low temperature, anisotropic phase of a system in which only spatial variation of $\hat{n}(\vec{r})$ is important. $S(\vec{r})$ in Eq. [38] can then be replaced by its equilibrium value $<S>$, where $< >$ denotes thermal averaging. The term proportional to $<S>H^2$ can be neglected because of its spatial invariance, and one obtains Eq. [3] of Chapter 8 directly,

$$\mathfrak{F}_M = -\frac{1}{2}\Delta\chi[\vec{H}\cdot\hat{n}(\vec{r})]^2,$$

where $\Delta\chi \equiv (\Delta\chi)_{\max} <S>$.

The expression for the free-energy density can also be generalized to include the special symmetry properties of cholesteric liquid crystals. Cholesteric order is indistinguishable from nematic order on a microscopic scale (see Chapters 1 and 11). However, when we examine the spatial variation of the local order, we find that cholesteric liquid crystals always exhibit helical ordering on a macroscopic scale (compared to molecular dimensions). Moreover, for any given cholesteric liquid crystal, the helical ordering has a definite handedness. In other words, cholesteric liquid crystals are not symmetric under the operation of spatial inversion, since a helix is always either left or right handed and the handedness changes upon inversion. Since the two cholesteric states related by spatial inversion are physically different,[16] the free-energy density is no longer required to be invariant under spatial inversion. This means that the free-energy density can contain pseudoscalar terms as well as the usual scalar terms. de Gennes found that the pseudoscalar term required by cholesteric order is given by[7]

$$\mathfrak{F}_C = \pm 2 q_0 L_1 \epsilon_{ijk} Q_{il}(\vec{r})\, \partial_k Q_{jl}(\vec{r}), \qquad [40]$$

where the + and − signs refer to the two senses of helical pitch; $q_0 \doteq \pi/\lambda_0$ (> 0), λ_0 being the pitch of the cholesteric phase as $T \rightarrow T_c$; and ϵ_{ijk} is the Levi–Cevita antisymmetric tensor of the third rank, which has the property that

$$\epsilon_{ijk} = \begin{cases} 1 & ijk = 123,\ 231,\ 312 \\ -1 & ijk = 213,\ 321,\ 132 \\ 0 & \text{otherwise} \end{cases}$$

Eq. [40] can be reduced to the form

$$\mathfrak{F}_C = \mp \frac{9}{2} q_0 L_1 S^2(\vec{r}) \, \{\hat{n}(\vec{r}) \cdot [\vec{\nabla} \times \hat{n}(\vec{r})]\}, \qquad [41]$$

where the − sign refers to a left-handed helix ($\hat{n}(\vec{r})\cdot[\vec{\nabla} \times \hat{n}(\vec{r})] > 0$) and the + sign refers to a right-handed helix ($\hat{n}(\vec{r})\cdot[\vec{\nabla} \times \hat{n}(\vec{r})] < 0$). Eq. [41] can be combined with the twist term of Eq. [30]

$$(9/4)\, L_1 S^2(\vec{r}) [\hat{n}(\vec{r}) \cdot \vec{\nabla} \times \hat{n}(\vec{r})]^2$$

to yield

$$(9/4)\, L_1 S^2(\vec{r}) [\,|\hat{n}(\vec{r}) \cdot \vec{\nabla} \times \hat{n}(\vec{r})| - q_0]^2 - (9/4)\, L_1 S^2(\vec{r}) q_0{}^2,$$

where | | is the absolute value sign.

The total Landau–de Gennes free-energy density for nematic or cholesteric liquid crystals in an external field is given by

$$\mathfrak{F} = \mathfrak{F}_L + \mathfrak{F}_M + \mathfrak{F}_E + \mathfrak{F}_C = f_0[T] +$$
$$\frac{3}{4}a\left(T - T_c{}^* - \frac{3L_1q_0{}^2}{a}\right)S^2(\vec{r}) + \frac{1}{4}BS^3(\vec{r}) + \frac{9}{16}CS^4(\vec{r}) +$$
$$\frac{3}{4}\left(L_1 + \frac{1}{6}L_2\right)[\vec{\nabla}S(\vec{r})]^2 + \frac{3}{8}L_2[\hat{n}(\vec{r})\cdot\vec{\nabla}S(\vec{r})]^2 +$$
$$\frac{9}{4}S^2(\vec{r})\left\{\left(L_1 + \frac{1}{2}L_2\right)[\vec{\nabla}\cdot\hat{n}(\vec{r})]^2 + L_1[\,|\hat{n}(\vec{r})\cdot\vec{\nabla}\times\hat{n}(\vec{r})\,| - q_0]^2 +\right.$$
$$\left.\left(L_1 + \frac{1}{2}L_2\right)[\hat{n}(\vec{r})\times\vec{\nabla}\times\hat{n}(\vec{r})]^2\right\} +$$
$$\frac{3}{2}L_2S(\vec{r})\left\{[\vec{\nabla}\cdot\hat{n}(\vec{r})][\hat{n}(\vec{r})\cdot\vec{\nabla}S(\vec{r})] + \frac{1}{2}[\hat{n}(\vec{r})\times\vec{\nabla}\times\hat{n}(\vec{r})]\cdot\vec{\nabla}S(\vec{r})\right\} -$$
$$\frac{1}{6}(\Delta\chi)_{\max}S(\vec{r})\{3[\vec{H}\cdot\hat{n}(\vec{r})]^2 - H^2\} -$$
$$\frac{1}{24\pi}(\Delta\epsilon)_{\max}S(\vec{r})\{3[\vec{E}\cdot\hat{n}(\vec{r})]^2 - E^2\}, \qquad [42]$$

where $q_0 = 0$ for nematic liquid crystals. It should be noted that for cholesteric liquid crystals $T_c{}^*$ is replaced by $T_c{}^{**} = T_c{}^* + (3L_1q_0{}^2/a)$ in Eq. [42]; we can interpret $T_c{}^{**}$ as the temperature below which supercooling of cholesterics is impossible. Eq. [42] can also be expressed in terms of $Q_{ij}(\vec{r})$,

$$\mathfrak{F} = f_0[T] + \frac{1}{2}a(T - T_c{}^*)Q_{ij}(\vec{r})Q_{ji}(\vec{r}) +$$
$$\frac{1}{3}BQ_{ij}(\vec{r})Q_{jk}(\vec{r})Q_{ki}(\vec{r}) + \frac{1}{4}C[Q_{ij}(\vec{r})Q_{ji}(\vec{r})]^2 +$$
$$\frac{1}{2}L_1\partial_iQ_{jk}(\vec{r})\partial_iQ_{jk}(\vec{r}) + \frac{1}{2}L_2\partial_iQ_{ij}(\vec{r})\partial_kQ_{kj}(\vec{r}) -$$
$$\frac{1}{3}(\Delta\chi)_{\max}H_iQ_{ij}(\vec{r})H_j - \frac{1}{12\pi}(\Delta\epsilon)_{\max}E_iQ_{ij}(\vec{r})E_j$$
$$\pm\ 2q_0L_1\epsilon_{ijk}Q_{il}(\vec{r})\partial_kQ_{jl}(\vec{r}). \qquad [43]$$

In terms of $\mathfrak{F}$ the partition function for the system is

$$Z(T) = \int \boldsymbol{D}\mathbf{Q}(\vec{r}) \ \exp\{-\beta \textstyle\int d^3\vec{r}\ \mathfrak{F}[\mathbf{Q}(\vec{r}),\ \partial_i\mathbf{Q}(\vec{r}),\ T]\}, \quad [44]$$

where $\boldsymbol{D}\mathbf{Q}(\vec{r})$ denotes integration over all possible tensor fields $\mathbf{Q}(\vec{r})$, and the dependence of $\mathfrak{F}$ on $\mathbf{Q}(\vec{r})$, the spatial derivatives of $\mathbf{Q}(\vec{r})$, and T is explicitly displayed. Eqs. [42] through [44] are the basic equations of the Landau–de Gennes theory of liquid-crystal phase transitions.

3. Thermodynamic Properties of Liquid Crystal Phase Transitions

In this section we use Landau–de Gennes theory to calculate the thermodynamic properties of liquid-crystal phase transitions in terms of the phenomenological parameters a, B, C, and $T_c{}^*$. In particular, we will derive expressions for T_c, the transition temperature; $\langle S\rangle_c$, the equilibrium order parameter value in the low temperature phase at the transition; and Δs, the transition entropy per molecule. We will also calculate the temperature dependence of $\langle S\rangle$ (the equilibrium value of S) for T close to T_c; and h, the height of the free-energy barrier between $\langle S\rangle = 0$ and $\langle S\rangle = \langle S\rangle_c$ at $T = T_c$.

To calculate the thermodynamic properties listed above, it is sufficient to consider a spatially uniform system in which the order parameter value is spatially invariant. This means that the spatial derivative terms in the Landau free-energy density, which are important for the calculation of fluctuation phenomena as shown in the next section, can be neglected for the present purpose. Therefore, from Eq. [42] we get

$$\mathfrak{F}[S,T] = f_0[T] + \frac{3}{4}a(T - T_c{}^*)S^2 + \frac{1}{4}BS^3 + \frac{9}{16}CS^4, \quad [45]$$

where we have set $H = E = q_0 = 0$. The partition function is then given by

$$Z(T) = \int dS \exp\{-\beta V \mathfrak{F}[S,T]\}. \quad [46]$$

From $Z(T)$ one can calculate the free energy density of the system $\mathfrak{F}^0(T)$:

$$\mathfrak{F}^0(T) = \lim_{V\to\infty} \frac{F(T)}{V} = \lim_{V\to\infty} \frac{-k_B T \ln Z(T)}{V}. \quad [47]$$

Thermodynamic properties of the system can be derived directly from $\mathfrak{F}^0(T)$.

In Appendix A it is shown that, if $Z(T)$ is in the form of Eq. [46], then $\mathfrak{F}^0(T)$ is equal to the value of the absolute minimum of the Landau free energy density $\mathfrak{F}$ at temperature T. Moreover, the (temperature-dependent) equilibrium value of the order parameter, $<S>$, is equal to the value of S which minimizes $\mathfrak{F}$ at each T. Therefore, in order to obtain $\mathfrak{F}^0(T)$, we differentiate $\mathfrak{F}$ with respect to S and set the result equal to zero for $S = <S>$:

$$\frac{3}{2}a(T - T_c^*)\langle S\rangle + \frac{3}{4}B\langle S\rangle^2 + \frac{9}{4}C\langle S\rangle^3 = 0. \qquad [48]$$

Eq. [48] has three solutions:

$$\begin{aligned}\langle S\rangle &= 0,\\ \langle S\rangle &= -\frac{1}{6}\frac{B}{C} \pm \sqrt{\frac{1}{324}\frac{B^2}{C^2} + \frac{2}{3}\frac{a}{C}\left(T_c^* + \frac{B^2}{27aC} - T\right)}.\end{aligned} \qquad [49]$$

The above solutions for $<S>$ must be substituted into Eq. [45] to determine which one gives the lowest value of $\mathfrak{F}$. Straightforward calculation yields

$$\mathfrak{F}^0(T) = f_0[T] + \frac{3}{4}a(T - T_c^*)\langle S\rangle^2 + \frac{1}{4}B\langle S\rangle^3 + \frac{9}{16}C\langle S\rangle^4, \qquad [50]$$

where

$$\langle S\rangle = \begin{cases} 0, \text{ for } T \geq T_c^* + \dfrac{B^2}{27aC} \\ -\dfrac{1}{6}\dfrac{B}{C} + \sqrt{\dfrac{1}{324}\dfrac{B^2}{C^2} + \dfrac{2}{3}\dfrac{a}{C}\left(T_c^* + \dfrac{B^2}{27aC} - T\right)}, \\ \qquad \text{for } T \leq T_c^* + \dfrac{B^2}{27aC} \end{cases} \qquad [51]$$

Eq. [51] shows that the system transforms from the high-temperature phase, $<S> = 0$, to the low-temperature phase, $<S> \neq 0$, at a temperature

$$T_c = T_c{}^* + \frac{B^2}{27aC}\,. \tag{52}$$

The order parameter value of the low temperature phase at $T = T_c$, $\langle S\rangle_c$, can be obtained directly from Eq. [51]:

$$\langle S\rangle_c = -\frac{1}{6}\frac{B}{C} + \frac{1}{18}\frac{|B|}{C} = -\frac{2}{9}\frac{B}{C}\,,\quad B < 0. \tag{53}$$

The entropy per molecule, s, can be obtained from $\mathfrak{F}^0(T)$ by differentiation:

$$s = -\frac{1}{N}\left(\frac{\partial\mathfrak{F}^0(T)}{\partial T}\right) = s_0 - \frac{3a}{4N}\langle S\rangle^2, \tag{54}$$

where $s_0 \equiv -(\partial f_0[T]/\partial T)/N$, and the term containing the temperature derivative of $\langle S\rangle$ is zero, because $\partial\mathfrak{F}^0(T)/\partial\langle S\rangle \equiv 0$. Substitution of $\langle S\rangle$, Eq. [51], into Eq. [54] gives the entropy per molecule of the high temperature phase as s_0 and the transition entropy per molecule Δs as

$$\Delta s = -\frac{1}{27}\frac{aB^2}{NC^2}\,. \tag{55}$$

Eqs. [52], [53] and [55] are usually used as the means by which the phenomenological parameters a, B, and C for any particular liquid crystal are determined from the experimental values of $\langle S\rangle_c$, Δs, and $(T_c - T_c{}^*)$. (The value of $T_c{}^*$ can be obtained by light scattering experiments measuring order parameter fluctuations. See Section 5.) In Table 1 we give the values of a, B, C and $(T_c - T_c{}^*)$ for MBBA.

In Fig. 4 we note that at $T = T_c$ there is a free energy barrier between $\langle S\rangle = 0$ and $\langle S\rangle = \langle S\rangle_c$. It is interesting to calculate the height h of this barrier in terms of the phenomenological parameters. The peak of the barrier occurs at $S = S_h$ for which

$$(\partial\mathfrak{F}/\partial S)_{\substack{S=S_h\\T=T_c}} = 0 \quad\text{and}\quad (\partial^2\mathfrak{F}/\partial S^2)_{\substack{S=S_h\\T=T_c}} < 0.$$

Simultaneous solution of these equations requires that $S_h = -B/9C$, which, when substituted into Eq. [45], gives

$$h = \frac{1}{11664}\frac{B^4}{C^3} \,. \qquad [56]$$

The value of h for MBBA is given in Table 1. Eq. [56] illustrates the fact that the order of the phase transition in the Landau–de Gennes theory is determined by the value of B. If B is nonzero, then $h > 0$, and we have a first order phase transition with $\langle S\rangle_c$, Δs nonzero and $T_c > T_c^*$. For $B = 0$, $h = 0$ and the transition is second order with $\langle S\rangle_c = \Delta s = 0$, $T_c = T_c^*$, and $\langle S\rangle \sim (T_c - T)^{1/2}$ for $T < T_c$. For liquid-crystal phase transitions the values of B are nonzero and negative (see Section 2). However, its value is small compared to that for other first-order phase transitions, as evidenced by the relatively small Δs, and that is why liquid-crystal phase transitions are sometimes described as "nearly second order."

Table 1—Values of the Various Phenomenological Parameters for MBBA‡

Parameters	Values	Units
a	0.042	J/cm³ °K
$-B$	0.64	J/cm³
C	0.35	J/cm³
$T_C - T_C^*$	1	°K
L_1	6.1×10^{-7}	dyne
L_2	–	
h	3.35×10^{-4}	J/cm³

‡ Data obtained from refs [14] and [15].

4. Fluctuation Phenomena

In this section we use the Landau–de Gennes theory to discuss thermal fluctuations in the isotropic phase of liquid crystals. For a physical system in thermal equilibrium, the instantaneous value of the order parameter will almost always be equal or close to its mean value (or equivalently, the equilibrium value). However, deviations from the mean value of the order parameter do occur, and the problem is to calculate the magnitude and the statistical distribution of these deviations, or fluctuations. We distinguish between two types of fluctuations: (1) homophase fluctuations, which occur within the range of stability of a single phase and are completely described by the rms deviation of the order parameter from its equilibrium value, and (2) heterophase fluctuations, which occur between two phases and are related to the problems of metastability and supercooling.[17] The qualitative difference between homophase and heterophase fluctuations is apparent in Fig. 4. Near $T = T_c$ there is a free energy barrier of height h (see Section 3), between the minima at $S = 0$ and $S = \langle S \rangle_c$. All fluctuations occurring around $S = 0$, and to the left of the barrier are called homophase fluctuations. Fluctuations that carry the system from one minimum, over the barrier, to the other minimum are called heterophase fluctuations since the two minima correspond to different phases.

4.1 Homophase Fluctuations in the Isotropic Phase

Since homophase fluctuations in the isotropic phase involve only states close to $\mathbf{Q}(\vec{r}) = 0$, we can neglect the cubic and quartic terms in the expansion of $\mathfrak{F}_{\mathrm{L}}$. If we also set $H = E = 0$, Eq. [43] reduces to

$$\begin{aligned}\mathfrak{F} = {} & f_0[T] + \frac{1}{2}a(T - T_c^*)Q_{ij}(\vec{r})Q_{ji}(\vec{r}) + \\ & \frac{1}{2}L_1\partial_i Q_{jk}(\vec{r})\partial_i Q_{jk}(\vec{r}) + \frac{1}{2}L_2\partial_i Q_{ij}(\vec{r})\partial_k Q_{kj}(\vec{r}) \\ & \pm\ 2q_0 L_1 \epsilon_{ijk} Q_{il}(\vec{r})\partial_k Q_{jl}(\vec{r}). \qquad [57]\end{aligned}$$

As shown in Section 2.3, $\mathbf{Q}(\vec{r})$ can be expressed in terms of $S(\vec{r})$ and $\hat{n}(\vec{r})$. If we were to make this substitution in Eq. [57], the resulting expression would contain several interaction terms coupling $S(\vec{r})$, $\hat{n}(\vec{r})$, and their spatial derivatives. Thus, in general, the problem of calculating the fluctuation spectra of $S(\vec{r})$ and $\hat{n}(\vec{r})$ can be quite complicated because of this coupling. In the latter part of this section we will show one way to handle the coupling between $S(\vec{r})$ and $\hat{n}(\vec{r})$, but first we want to consider a simple system that illustrates both the physics of homophase fluctuation phenomena and the mathematics involved in manipulating the formalism developed in previous sections.

Simple Illustrative Example of Homophase Fluctuations

The system we wish to consider is one in which we can neglect the spatial variation of $\hat{n}(\vec{r})$ and treat only the fluctuations of $S(\vec{r})$. Setting all spatial derivatives of $\hat{n}(\vec{r})$ to zero and limiting our discussion for the moment to nematic liquid crystals ($q_0 = 0$), Eq. [57] becomes

$$\mathfrak{F} = f_0[T] + \frac{3}{4}a(T - T_c^*)S^2(\vec{r}) + \frac{3}{4}\left(L_1 + \frac{1}{6}L_2\right)[\vec{\nabla}S(\vec{r})]^2 + \frac{3}{8}L_2[\hat{n}\cdot\vec{\nabla}S(\vec{r})]^2, \qquad [58]$$

where $\hat{n}$ no longer depends upon $\hat{r}$. The problem before us is to calculate the mean square deviation of $S(\hat{r})$ from its equilibrium value $S(\hat{r}) = 0$. As a first step, we note that the partition function for the system is given by

$$Z(T) = \int DS(\vec{r}) \exp[-\beta \textstyle\int_{\substack{\text{volume}\\ \text{of the}\\ \text{sample}}} d^3\vec{r}\ \mathfrak{F}]. \qquad [59]$$

The difficulty in using Eq. [59] for actual calculations lies in the functional integral $\int DS(\hat{r})$ and we therefore digress briefly to consider functional integration.

Functional Integration

It is customary to proceed by Fourier analyzing $S(\hat{r})$ into its Fourier components

$$S(\vec{r}) = \sum_{\vec{q}} S(\vec{q})\, e^{i\vec{q}\cdot\vec{r}}, \qquad [60]$$

where $\hat{q}$ is a particular wavevector, and $S(\hat{q})$ is usually a complex number representing the amplitude of the wave, $\exp(i\hat{q}\cdot\hat{r})$. $S(\hat{q})$ can be obtained from $S(\hat{r})$ by the inverse transformation

$$S(\vec{q}) = \frac{1}{V}\int d^3\vec{r}\ S(\vec{r})\, e^{-i\vec{q}\cdot\vec{r}}. \qquad [61]$$

Since $S(\hat{r})$ is real, Eq. [61] implies that

$$S^*(\vec{q}) = \frac{1}{V}\int d^3\vec{r}\ S(\vec{r})\, e^{i\vec{q}\cdot\vec{r}} = S(-\vec{q}), \qquad [62]$$

where $S^*(\hat{q})$ is the complex conjugate of $S(\hat{q})$. Since there is a one-to-one correspondence between any function $S(\hat{r})$ and its set of Fourier coefficients $\{S(\hat{q})\}$, the functional integral is equivalent to integrating over all possible sets of Fourier coefficients $\{S(\hat{q})\}$. This in turn is equivalent to a multi-dimensional integral in which each Fourier coefficient $S(q)$ is integrated over its possible values, with the constraint $S^*(\vec{q}) = S(-\vec{q})$ which implies that only half the $S(\vec{q})$'s in any set $\{S(q)\}$ can vary independently. We will label the set of all independent $S(\vec{q})$'s by $\{S(\vec{q})\}'$. $\{S(\vec{q})\}'$ can be specified by the condition that if $S(\vec{q})$ is a member of $\{S(\vec{q})\}'$, then $S(-\vec{q})$ is not a member of $\{S(\vec{q})\}'$.

The functional integral can then be written as

$$\int DS(\vec{r}) \equiv J[S(\vec{r});S(\vec{q})]\prod_{\vec{q}}{}' \left\{ \int_0^{2\pi} d\varphi_{S(\vec{q})} \int |S(\vec{q})|\, d|S(\vec{q})| \right\}, \qquad [63]$$

where Π' denotes the product only over those $\vec{q}$'s for which none is the negative of any other, $\varphi_{S(\vec{q})}$ is the phase angle of the complex number $S(\vec{q})$, $|S(\vec{q})| \equiv [S^*(\vec{q})S(\vec{q})]^{1/2}$ is the magnitude of $S(\vec{q})$, and $J[S(\vec{r});\, S(\vec{q})]$ is the Jacobian of the transformation. In order to evaluate the Jacobian we make use of the fact (Section 1) that $\boldsymbol{D}S(\vec{r})$ can be written as $\prod_{\alpha=1}^{M} dS(\vec{r}_\alpha)$, where $S(\vec{r}_\alpha)$ is the value of S in region α. Since each of the M regions has volume ΔV, we have from Eqs. [60] and [61]

$$S(\vec{r}_\alpha) = \sum_{\beta=1}^{M} S(\vec{q}_\beta)\, e^{i\vec{q}_\beta\cdot\vec{r}_\alpha}, \qquad [60a]$$

and

$$S(\vec{q}_\beta) = \frac{\Delta V}{V} \sum_{\alpha=1}^{M} S(\vec{r}_\alpha)\, e^{-i\vec{q}_\beta\cdot\vec{r}_\alpha}. \qquad [61a]$$

It is clear from Eq. [60a] and the definition of a Jacobian that $J[S(\vec{r});\, S(\vec{q})]$ is simply the determinant of the $M \times M$ matrix whose $\alpha\beta$ – element is $\exp(i\vec{q}_\beta\cdot\vec{r}_\alpha)$. It is shown in Appendix B that this determinant is equal to $(V/\Delta V)^{M/2}$. Substituting this factor into Eq. [63] yields

$$\int DS(\vec{r}) \equiv \prod_{\vec{q}}{}' \frac{V}{\Delta V} \left\{ \int_0^{2\pi} d\varphi_{S(\vec{q})} \int |S(\vec{q})|\, d|S(\vec{q})| \right\}, \qquad [63a]$$

where we have used the fact that the product Π' contains $M/2$ factors. We can now proceed with our evaluation of the partition function, Eq. [59], for our idealized example system.

We first integrate Eq. [58] term by term since we will need the volume integral of $\mathfrak{F}$ in evaluating $Z(T)$. The volume integrals of $S^2(\vec{r})$, $[\vec{\nabla}S(\vec{r})]^2$, and $[\hat{n}\cdot\vec{\nabla}S(\vec{r})]^2$ can be expressed in terms of $S(\vec{q})$ and $\vec{q}$ in the form

$$\int_V d^3\vec{r}\,S^2(\vec{r}) = V\sum_{\vec{q}}|S(\vec{q})|^2 = 2V{\sum_{\vec{q}}}'|S(\vec{q})|^2, \qquad [64a]$$

$$\int_V d^3\vec{r}\,[\vec{\nabla}S(\vec{r})]^2 = V\sum_{\vec{q}}q^2|S(\vec{q})|^2 = 2V{\sum_{\vec{q}}}'q^2|S(\vec{q})|^2, \qquad [64b]$$

and

$$\int_V d^3\vec{r}\,[\hat{n}\cdot\vec{\nabla}S(\vec{r})]^2 = V\sum_{\vec{q}}(\hat{n}\cdot\vec{q})^2|S(\vec{q})|^2$$

$$= 2V{\sum_{\vec{q}}}'(\hat{n}\cdot\vec{q})^2|S(\vec{q})|^2, \qquad [64c]$$

where V is the volume of the sample and ${\sum_{\vec{q}}}'$ denotes summing over the $\vec{q}$'s for which none is the negative of any other. In arriving at the above expressions we have used the identity

$$V\delta(\vec{q} + \vec{q}') = \int d^3\vec{r}\,\exp[i(\vec{q} + \vec{q}')\cdot\vec{r}]. \qquad [65]$$

From Eqs. [58], [64a], [64b], and [64c] we obtain

$$\int_V d^3\vec{r}\,\mathfrak{F} = Vf_0[T] +$$

$$2V{\sum_{\vec{q}}}'\left[\frac{3}{4}a(T - T_c{}^*) + \frac{3}{4}\left(L_1 + \frac{1}{6}L_2\right)q^2 + \frac{3}{8}L_2(\hat{n}\cdot\vec{q})^2\right]|S(\vec{q})|^2$$

$$= Vf_0[T] + \frac{3}{2}aV(T - T_c{}^*){\sum_{\vec{q}}}'[1 + \xi^2(T,\psi_{\vec{q}})q^2]|S(\vec{q})|^2 \qquad [66]$$

where

$$\xi(T,\psi_{\vec{q}}) = \frac{\xi_0(\psi_{\vec{q}})(T_c{}^*)^{1/2}}{(T - T_c{}^*)^{1/2}}, \qquad [67]$$

with

$$\xi_0(\psi_{\vec{q}}) = \left[\frac{L_1 + \frac{1}{6}L_2(1 + 3\cos^2\psi_{\vec{q}})}{aT_c{}^*}\right]^{1/2}, \qquad [68]$$

and $\psi_{\vec{q}}$ denotes the angle between $\hat{n}$ and $\vec{q}$. The parameter $\xi(T,\psi_{\vec{q}})$ has units of length and is referred to as a "correlation length" for reasons that will become apparent later. If we substitute typical values[14,15] for L_1, L_2, a, and $T_c{}^*$ in Eq. [68] we find $\xi_0 \approx 10\text{Å}$. For simplicity we will write $\xi(T,\psi_{\vec{q}})$ and $\xi_0(\psi_{\vec{q}})$ as ξ and ξ_0, respectively. Substituting Eq. [66] into Eq. [59], we have for the partition function,

$$Z(T) = \exp\{-\beta V f_0[T]\} \times \int DS(\vec{r}) \prod_{\vec{q}}{}' \exp\left\{-\frac{3}{2}\beta Va(T - T_c{}^*)(1 + \xi^2 q^2)\,|S(\vec{q})|^2\right\}, \qquad [69]$$

which, according to Eq. [63], can be written

$$Z(T) = \exp\{-\beta V f_0[T]\} \prod_{\vec{q}}{}' \left\{\frac{\pi V}{\Delta V} \times \int d|S(\vec{q})|^2 \exp\left[-\frac{3}{2}\beta Va(T - T_c{}^*)(1 + \xi^2 q^2)\,|S(\vec{q})|^2\right]\right\}, \qquad [70]$$

where the angular integral has been explicitly evaluated. If we label the factors in the product in Eq. [70] by $Z(\vec{q},T)$, Eq. [70] reduces to

$$Z(T) = \exp\{-\beta V f_0[T]\} \prod_{\vec{q}}{}' Z(\vec{q}, T). \qquad [71]$$

The total free-energy density of the system is calculated from Eq. [71] in Appendix B. For the moment we note that Eq. [71] can be used to calculate the thermal averages of $S(\vec{q})$ and $|S(\vec{q})|^2$. Since the partition function is the product of wavevector-dependent factors $Z(\vec{q},T)$, the thermal average of any quantity $X[S(\vec{q})]$ associated with wavevector $\vec{q}$ is given by

$$\langle X[S(\vec{q})]\rangle = \frac{\frac{1}{2}\int_0^{2\pi} d\varphi_{S(\vec{q})} \int_0^{\infty} d|S(\vec{q})|^2 X[S(q)] \exp\left\{-\frac{3}{2}\beta Va(T - T_c{}^*)(1 + \xi^2 q^2)\,|S(\vec{q})|^2\right\}}{\pi \int_0^{\infty} d|S(\vec{q})|^2 \exp\left\{-\frac{3}{2}\beta Va(T - T_c{}^*)(1 + \xi^2 q^2)\,|S(\vec{q})|^2\right\}}, \qquad [72]$$

where, in place of the maximum possible value of $|S(\vec{q})|^2$, the upper limit of the $d|S(\hat{q})|^2$ integral has been extended to ∞. This is possible because the factor V in the exponent makes the integrand sharply peaked at $|S(\hat{q})|^2 = 0$, and the error introduced by extending the limit of integration is therefore negligible. We can now calculate the thermal average of $S(\hat{q})$ and $|S(\hat{q})|^2$ using Eq. [72]. Expressing $S(\hat{q})$ in the form $|S(q)| \exp(i\varphi_{S(\hat{q})})$ and substituting it for $X[S(\hat{q})]$ in Eq. [72] we find

$$\langle S(\vec{q})\rangle = 0,$$

and

$$\langle S^2(\vec{q})\rangle = \langle S(\vec{q})S(\vec{q}')\rangle = \langle S(\vec{q})\rangle\langle S(\vec{q}')\rangle = 0, \quad \vec{q} \neq -\vec{q}' \qquad [73]$$

Similar calculation yields

$$\begin{aligned}\langle |S(\vec{q})|^2\rangle &= \frac{2}{3}\,\frac{k_BT}{Va(T - T_c^*)(1 + \xi^2q^2)}\\ &= \frac{2}{3}\,\frac{k_B(T/T_c^*)}{Va\left[\left(\dfrac{T}{T_c^*} - 1\right) + \xi_0^2q^2\right]},\end{aligned} \qquad [74]$$

where the last expression is obtained by the substitution of Eq. [67] for ξ. $<|S(\hat{q})|^2>$ is the square of the amplitude of fluctuation in $S(\hat{r})$ with wavevector $\hat{q}$, and Eq. [74] is simply an expression of the equipartition theorem. It is evident from Eq. [66] that in thermal equilibrium each of the independent modes in the set $\{S(\hat{q})\}'$ contributes a term

$$\frac{3}{2}Va(T - T_c^*)(1 + \xi^2q^2)\langle|S(\vec{q})|^2\rangle$$

to the Landau free energy. Since $S(\hat{q})$ is a complex number with two degrees of freedom (real and imaginary parts), the equipartition theorem requires that

$$\frac{3}{2}Va(T - T_c^*)(1 + \xi^2q^2)\langle|S(\vec{q})|^2\rangle = k_BT, \qquad [75]$$

which is identical to Eq. [74]. The equipartition theorem therefore offers a simple method for calculating the thermal averages of the square of the amplitudes for independent modes.* Three points concerning Eq. [74] warrant further discussion.

First, it appears that all fluctuations vanish in the thermodynamic limit $V \to \infty$. However, this is not the case. Although the fluctuation amplitude for each mode decreases as V increases, the density of modes increases such that the sum of all fluctuation amplitudes remains constant. This is simply demonstrated by calculating the average fluctuation amplitude in real space:

$$\left\langle \frac{1}{V}\int d^3\vec{r}\; S^2(\vec{r}) \right\rangle = \frac{1}{V}\left\langle \int d^3\vec{r}\; S^2(\vec{r})\right\rangle = \sum_{\vec{q}} \langle |S(\vec{q})|^2\rangle,$$

where we have used Eq. [60]. Making the replacement

$$\sum_{\vec{q}} \longrightarrow \frac{V}{(2\pi)^3}\int d^3\vec{q},$$

and substituting Eq. [74] for $\langle|S(\vec{q})|^2\rangle$, we get

$$\left\langle \frac{1}{V}\int d^3\vec{r}\; S^2(\vec{r}) \right\rangle =$$

$$\frac{V}{(2\pi)^3}\int_0^{q_{\max}} 4\pi q^2 dq\, \frac{2}{3}\, \frac{k_B T}{Va(T - T_c{}^*)(1 + \xi^2 q^2)}$$

$$= \frac{k_B T}{3\pi^2 \xi_0{}^3 a T_c{}^*}\left[\xi_0 q_{\max} - \sqrt{\frac{T}{T_c{}^*} - 1}\,\tan^{-1}\left(\frac{\xi_0 q_{\max}}{\sqrt{\frac{T}{T_c{}^*} - 1}}\right)\right], \qquad [76]$$

where $q_{max} \equiv 2\pi$/(smallest length for which the theory is valid) $\simeq$

---

* If, instead of considering only the independent modes, all possible modes were counted, then in thermal equilibrium the contribution of each mode to the Landau free energy would be $(3/4)Va(T - T_c{}^*)(1 + \xi^2 q^2)\langle|S(\vec{q})|^2\rangle$. However, each $S(\vec{q})$ now has only one degree of freedom due to the reality restriction $S^*(\vec{q}) = S(-\vec{q})$ and therefore can only have $\frac{1}{2}k_BT$ of energy. The resulting equation

$$\frac{3}{4}Va(T - T_c{}^*)(1 + \xi^2 q^2)\langle|S(\vec{q})|^2\rangle = \frac{1}{2}k_B T$$

is identical to Eq. [75]. Hence, the same expression for $\langle|S(\vec{q})|^2\rangle$ is obtained independent of how the modes are counted.

$2\pi/(\Delta V)^{1/3}$, ΔV being the volume of an elemental region as defined in Section 2. Eq. [76] expresses the physically reasonable result that the average fluctuation amplitude in real space is independent of V.

The second point we wish to stress concerns the dependence of $<|S(\vec{q})|^2>$ on q and T, shown in Fig. 6. For a given temperature $T > T_c{}^*$, $<|S(\vec{q})|^2>$ decreases with increasing q, and, for fixed q, $<|S(\vec{q})|^2>$ increases as $T \rightarrow T_c{}^*$ from above. We can qualitatively understand this behavior from the following mechanical analogy. Consider the string of coupled pendula shown in Fig. 7. Let the gravitational field play the role of the term $\frac{3}{4}\, a(T - T_c{}^*)S^2(\vec{r})$ in $\mathfrak{F}_L$, and the coupling springs play the role of the terms proportional to the spatial derivatives of $S(\vec{r})$. It is obvious that there are two kinds of os-

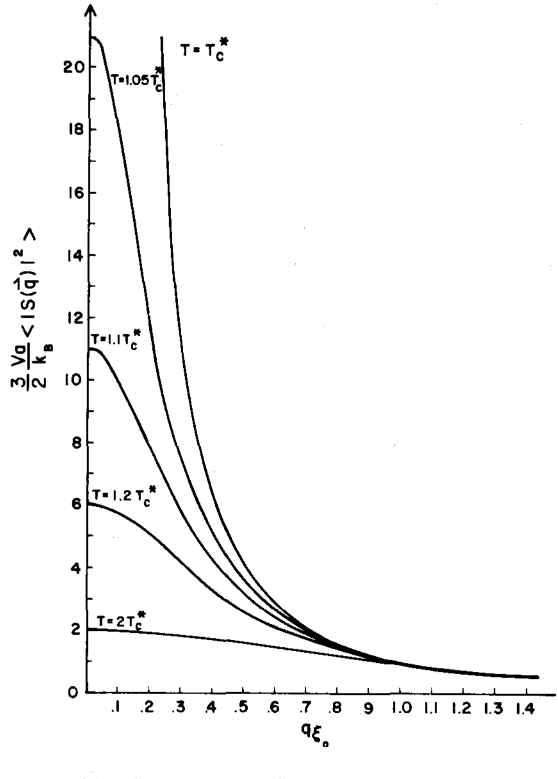

Fig. 6—The square of the fluctuation amplitude plotted as a function of wavevector for different temperatures $T \geq T_c{}^*$. Note that for fixed T the fluctuation amplitude decreases monotonically with increasing q and that for fixed q it increases as T decreases toward $T_c{}^*$.

cillations; one is the oscillation in the gravitational field and the other is the normal mode oscillation of a string of mass points connected by springs. If q denotes the wavenumber associated with the normal

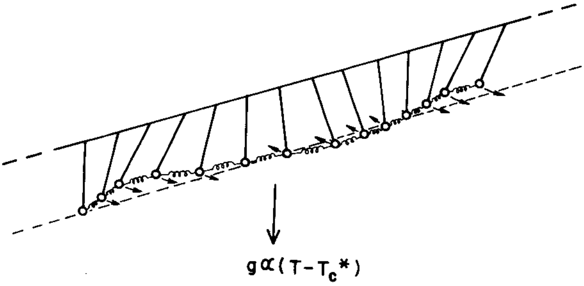

Fig. 7—Mechanical analog illustrating the qualitative features of Fig. 6. The springs play the role of the $[\vec{\nabla} S(\vec{r})]^2$ terms and the gravitational field plays the role of the $(T - T_c^*)S^2(\vec{r})$ term in the Landau free energy density function.

mode oscillation of the elastic linear chain, then for $q = 0$ the springs are not distorted and we have uniform in-phase oscillation of all the pendula in the gravitational field. For $q \neq 0$ each mass point experiences the force from the springs (caused by the relative motion of neighboring mass points) as well as the force due to the gravitational field. The square of the amplitude for the mode with wavevector q is analogous to $|S(\vec{q})|^2$. Suppose now that the system of pendula is in thermal equilibrium at temperature T with each mode having energy $k_BT/2$. For the $q = 0$ mode the entire $k_BT/2$ of energy goes into the oscillation in the gravitational field. However, for a $q \neq 0$ mode part of the $k_BT/2$ of energy is spent in distorting the springs, the remainder going into oscillation in the gravitational field. Thus the amplitude of oscillation for any $q \neq 0$ mode is smaller than that for the $q = 0$ mode. Since the energy stored in the springs increases with q, it follows that, for a fixed temperature, the amplitude of oscillation (and by analogy $<|S(\vec{q})|^2>$) should decrease with increasing q. What happens as $T \rightarrow T_c^*$? This corresponds in our analogy to weakening the gravitational field, with the result that, for a fixed energy input and fixed q, the amplitude of oscillation increases. This increase in fluctuation amplitude as T decreases toward T_c^* is an indication of the growing instability in the high-temperature phase. In fact, at $T = T_c^*$ the fluctuation amplitude $<|S(\vec{q})|^2>$ diverges for $\vec{q} = 0$. T_c^* is thus the temperature below which the isotropic phase is absolutely unstable.

The third point concerns the physical significance of ξ. Consider the correlation function $<S(\vec{r}_1)S(\vec{r}_2)>$. It is obvious that if $L_1 = L_2 = 0$, a disturbance at $\vec{r}_1$ would have no effect on any other spatial point $\vec{r}_2 \neq \vec{r}_1$. The relative phase of fluctuations at two different points would be completely random. Therefore, it is expected that

$$\langle S(\vec{r}_1)S(\vec{r}_2)\rangle = \langle S(\vec{r}_1)\rangle\langle S(\vec{r}_2)\rangle = 0.$$

The interesting case arises when $L_1, L_2 \neq 0$. Then a thermal fluctuation at $\vec{r}_1$can cause a certain amount of in-phase fluctuation at $\vec{r}_2 \neq \vec{r}_1$ and as a result $<S(\vec{r}_1)S(\vec{r}_2)>$ should be nonzero. In general, we can write

$$\langle S(\vec{r}_1)S(\vec{r}_2)\rangle = \sum_{\vec{q}}\sum_{\vec{q}'}\langle S(\vec{q})S(\vec{q}')\rangle \exp\{i(\vec{q}\cdot\vec{r}_1 + \vec{q}'\cdot\vec{r}_2)\}. \quad [77]$$

$<S(\vec{q})S(\vec{q}')>$ can have the following values:

$$\langle S(\vec{q})S(\vec{q}')\rangle = \begin{cases} \langle S(\vec{q})\rangle\langle S(\vec{q}')\rangle = 0, & \vec{q}' \neq -\vec{q} \\ \langle |S(\vec{q})|^2\rangle, & \vec{q}' = -\vec{q} \end{cases} \quad [78]$$

Therefore,

$$\begin{aligned}\langle S(\vec{r}_1)S(\vec{r}_2)\rangle &= \sum_{\vec{q}}\langle |S(\vec{q})|^2\rangle \exp\{i\vec{q}\cdot(\vec{r}_1 - \vec{r}_2)\}\\ &= \sum_{\vec{q}}\frac{2}{3}\,\frac{k_BT}{Va(T - T_c^*)(1 + \xi^2q^2)}\exp\{i\vec{q}\cdot(\vec{r}_1 - \vec{r}_2)\}\\ &\simeq \frac{k_BT}{6\pi^2a(T - T_c^*)}\int_{-1}^{1}d(\cos\theta)\int_0^\infty q^2dq\,\frac{\exp\{iq|\vec{r}_1 - \vec{r}_2|\cos\theta\}}{1 + \xi^2q^2}\\ &= \frac{k_BT}{6\pi\xi_0(aT_c^*)^{1/2}}\,\frac{\exp\{-|\vec{r}_1 - \vec{r}_2|/\xi\}}{|\vec{r}_1 - \vec{r}_2|}.\end{aligned} \quad [79]$$

In converting the sum over all $\vec{q}$ vectors to an integral, we have made the approximation of replacing q_{max}, the upper limit of the integral over dq, by ∞, valid for $q_{max}|\vec{r}_1 - \vec{r}_2| \gg 1$. From Eq. [79] it can easily be checked that if $L_1, L_2 \rightarrow 0$, then $\xi \rightarrow 0$, and $<S(\vec{r}_1)S(\vec{r}_2)> = 0$ for $\vec{r}_1 \neq \vec{r}_2$. For $L_1, L_2 \neq 0$, Eq. [79] states that a thermal disturbance at $\vec{r}_1$ decays exponentially to the equilibrium condition of its surroundings in a characteristic distance ξ. Since ξ is the distance over which fluctuations occur in phase, it is called the "correlation length." ξ diverges as $T \rightarrow T_c{}^*$, and for materials with T_c sufficiently close to $T_c{}^*$ (such as liquid crystals) this behavior of ξ gives rise to various observable phenomena, such as the increase in the light scattering cross section and in the Cotton-Mouton coefficient when T_c is approached (See Sections 5 and 6).

The General Case of Homophase Fluctuations

We will now investigate in more detail what happens when the restriction placed on $\hat{n}(\vec{r})$ in the previous subsection is relaxed. It was pointed out earlier that in such a situation the fluctuations of $S(\vec{r})$ cannot be calculated independently from the fluctuations of $\hat{n}(\vec{r})$, due to interaction terms between them in Eq. [57]. The problem of coupling between different fluctuation modes can be avoided if one considers the thermal fluctuation amplitudes of the tensor order parameter components, $Q_{ij}(\vec{r})$, rather than the fluctuation amplitudes of $S(\vec{r})$ and $\hat{n}(\vec{r})$.

Since $\mathbf{Q}(\vec{r})$ is a symmetric, traceless tensor, only five of its nine components are independent, viz. $Q_{11}(\vec{r}) - Q_{22}(\vec{r})$, $Q_{33}(\vec{r})$, $Q_{12}(\vec{r})$, $Q_{13}(\vec{r})$, and $Q_{23}(\vec{r})$. As before we Fourier analyze each independent component,

$$Q_{ij}(\vec{r}) = \sum_{\vec{q}} Q_{ij}(\vec{q}) \exp\{i\vec{q} \circ \vec{r}\} \qquad [80]$$

with $Q_{ij}(\vec{q})$ defined as

$$Q_{ij}(\vec{q}) = \frac{1}{V}\int d^3\vec{r}\, Q_{ij}(\vec{r}) \exp\{-i\vec{q} \cdot \vec{r}\} = Q_{ij}{}^*(-\vec{q}). \qquad [81]$$

The volume integral of $\mathfrak{F}$, (Eq. [57]), can then be expressed as

$$\int_V \mathfrak{F}\, d^3\vec{r} = Vf_0[T] + V\sum_{\vec{q}} \mathfrak{F}(\vec{q}). \qquad [82]$$

For a wavevector $\vec{q}$ pointing along the 3-axis (z-axis), $\mathfrak{F}(\vec{q})$ has the form

$= [L_1/a(T - T_c^*)]^2$

$$\mathfrak{F}(\vec{q}) = a(T - T_c^*)\Big[\frac{3}{4}(1 + \xi_{\parallel}^2 q^2)\,|Q_{33}(\vec{q})|^2 +$$
$$\frac{1}{4}(1 + \xi_1^2 q^2)\,|Q_{11}(\vec{q}) - q_{22}(\vec{q})|^2 + (1 + \xi_1^2 q^2)\,|Q_{12}(\vec{q})|^2 +$$
$$(1 + \xi_{\perp}^2 q^2)(|Q_{13}(\vec{q})|^2 + |Q_{23}(\vec{q})|^2)\Big] \pm$$
$$2qq_0L_1 i\Big[Q_{12}(\vec{q})(Q_{11}^*(\vec{q}) - Q_{22}^*(\vec{q})) +$$
$$Q_{12}^*(\vec{q})(Q_{22}(\vec{q}) - Q_{11}(\vec{q})) + Q_{23}(\vec{q})Q_{13}^*(\vec{q}) - Q_{13}(\vec{q})Q_{23}^*(\vec{q})\Big], \tag{83}$$

where $\xi_{\parallel}(\xi_{\perp})$ is the value of ξ when $\psi_{\vec{q}}$ is zero ($\pi/2$) and ξ_1 is the value of ξ when $L_2 = 0$. It is clear from Eq. [83] that for $q_0 = 0$, i.e., for nematics, the last term of Eq. [83] vanishes and $Q_{33}(\vec{q})$, $Q_{11}(\vec{q}) - Q_{22}(\vec{q})$, $Q_{12}(\vec{q})$, $Q_{13}(\vec{q})$, $Q_{23}(\vec{q})$ are independent quantities. Since there are no interaction terms containing both $\vec{q}$ and $\vec{q}'$ ($\vec{q} \neq \vec{q}'$) in Eq. [82], we are free to choose the spatial axes for each $\vec{q}$. Thus, Eqs. [82] and [83] represent a general solution, valid for any $\vec{q}$, provided we remember that the 3-axis is parallel to $\vec{q}$. The thermal average of the square of the fluctuation amplitude for each independent mode can be calculated in exactly the same manner as was that for $S(\vec{r})$ in Section 4.1.1. As before, the results can be obtained directly from the equipartition theorem. Therefore, we have, for $q_0 = 0$,[7]

$$\langle|Q_{33}(\vec{q})|^2\rangle = \frac{2}{3}\,\frac{k_BT}{Va(T - T_c^*)(1 + \xi_{\parallel}^2 q^2)}, \tag{84a}$$

$$\langle|Q_{11}(\vec{q}) - Q_{22}(\vec{q})|^2\rangle = \frac{2k_BT}{Va(T - T_c^*)(1 + \xi_1^2 q^2)}, \tag{84b}$$

$$\langle|Q_{12}(\vec{q})|^2\rangle = \frac{k_BT}{2Va(T - T_c^*)(1 + \xi_1^2 q^2)}, \tag{84c}$$

and

$$\langle|Q_{13}(\vec{q})|^2\rangle = \langle|Q_{23}(\vec{q})|^2\rangle = \frac{k_BT}{2Va(T - T_c^*)(1 + \xi_{\perp}^2 q^2)}. \tag{84d}$$

When $q_0 \neq 0$ the situation is quite different, and some of the modes which are independent of each other for $q_0 = 0$ become mixed.

However, if we again take the 3-axis parallel to $\vec{q}$, Eq. [83] can be diagonalized to give

$$\mathfrak{F}(\vec{q}) = a(T - T_c{}^*)\Big[\frac{3}{4}(1 + \xi_\parallel{}^2q^2)\,|Q_{33}(\vec{q})|^2 +$$
$$\frac{1}{4}(1 + \xi_1{}^2q^2)\,\Big|Q_{11}(\vec{q}) - Q_{22}(\vec{q}) \pm \frac{8q_0q\xi_1{}^2i}{(1 + \xi_1{}^2q^2)}\,Q_{12}(\vec{q})\Big|^2 +$$
$$\left(1 + \xi_1{}^2q^2 - \frac{16q_0{}^2q^2\xi_1{}^4}{(1 + \xi_1{}^2q^2)}\right)|Q_{12}(\vec{q})|^2 +$$
$$(1 + \xi_\perp{}^2q^2)\,\Big|Q_{13}(\vec{q}) \pm \frac{2q_0q\xi_1{}^2i}{(1 + \xi_\perp{}^2q^2)}\,Q_{23}(\vec{q})\Big|^2 +$$
$$\left(1 + \xi_\perp{}^2q^2 - \frac{4q_0{}^2q^2\xi_1{}^4}{(1 + \xi_\perp{}^2q^2)}\right)|Q_{23}(\vec{q})|^2\Big]. \qquad [85]$$

It can be seen that the independent modes for cholesterics are different from those for nematics. If we denote the quantity $[Q_{11}(\vec{q}) - Q_{22}(\vec{q}) \pm (8q_0q\,\xi_1{}^2i/(1 + \xi_1{}^2q^2))Q_{12}(\vec{q})]$ by $Q_a(\vec{q})$ and $[Q_{13}(\vec{q}) \pm (2q_0q\,\xi_1{}^2i/(1 + \xi_\perp{}^2q^2))Q_{23}(\vec{q})]$ by $Q_b(\vec{q})$, then the thermal averages of the fluctuation amplitudes of the independent modes are[7]

$$\langle|Q_{33}(\vec{q})|^2\rangle = \frac{2}{3}\,\frac{k_BT}{Va(T - T_c{}^*)(1 + \xi_\parallel{}^2q^2)}, \qquad [86a]$$

$$\langle|Q_a(\vec{q})|^2\rangle = \frac{2k_BT}{Va(T - T_c{}^*)(1 + \xi_1{}^2q^2)}, \qquad [86b]$$

$$\langle|Q_{12}(\vec{q})|^2\rangle = \frac{k_BT(1 + \xi_1{}^2q^2)}{2Va(T - T_c{}^*)[(1 + \xi_1{}^2q^2)^2 - 16q_0{}^2q^2\xi_1{}^4]}, \qquad [86c]$$

$$\langle|Q_b(\vec{q})|^2\rangle = \frac{k_BT}{2Va(T - T_c{}^*)(1 + \xi_\perp{}^2q^2)}, \qquad [86d]$$

and

$$\langle|Q_{23}(\vec{q})|^2\rangle = \frac{k_BT(1 + \xi_\perp{}^2q^2)}{2Va(T - T_c{}^*)[(1 + \xi_\perp{}^2q^2)^2 - 4q_0{}^2q^2\xi_1{}^4]} \qquad [86e]$$

The thermal averages $<|Q_{11}(\vec{q})|^2>$, $<|Q_{22}(\vec{q})|^2>$, and $<|Q_{13}(\vec{q})|^2>$ can also be calculated in terms of the thermal averages of the independent modes given in Eq. [86]. Remembering that $Q_{11}(\vec{q}) + Q_{22}(\vec{q}) + Q_{33}(\vec{q}) = 0$, we obtain

$$\langle |Q_{22}(\vec{q})|^2\rangle = \langle |Q_{11}(\vec{q})|^2\rangle$$

$$= \left\langle \left| \frac{1}{2}\left[Q_a(\vec{q}) \mp \frac{8q_0 q \xi_1{}^2 i}{(1 + \xi_1{}^2 q^2)} Q_{12}(\vec{q}) - Q_{33}(\vec{q}) \right] \right|^2 \right\rangle$$

$$= \frac{1}{4}\left[\langle |Q_a(\vec{q})|^2\rangle + \frac{64 q_0{}^2 q^2 \xi_1{}^4}{(1 + \xi_1{}^2 q^2)^2} \langle |Q_{12}(\vec{q})|^2\rangle + \langle |Q_{33}(\vec{q})|^2\rangle \right]$$

$$= \langle |Q_{12}(\vec{q})|^2\rangle + \frac{1}{4}\langle |Q_{33}(\vec{q})|^2\rangle, \qquad [86f]$$

$$\langle |Q_{23}(\vec{q})|^2\rangle = \langle |Q_{13}(\vec{q})|^2\rangle$$

$$= \left\langle \left| Q_b(\vec{q}) \mp \frac{2q_0 q \xi_1{}^2 i}{(1 + \xi_\perp{}^2 q^2)} Q_{23}(\vec{q}) \right|^2 \right\rangle$$

$$= \langle |Q_b(\vec{q})|^2\rangle + \frac{4 q_0{}^2 q^2 \xi_1{}^4}{(1 + \xi_\perp{}^2 q^2)^2} \langle |Q_{23}(\vec{q})|^2\rangle. \qquad [86g]$$

In deriving Eqs. [86f] and [86g] we have used the fact that the thermal averages of the cross terms between independent modes, such as $<Q_a(\vec{q})Q_{12}{}^*(\vec{q})>$, all vanish.

Due to the fact that the order parameter **Q** is related to macroscopic observable quantities such as the susceptibility tensor **χ** (Eq. [32]) and the dielectric tensor **ε**, fluctuations in the components of **Q** are directly manifested as fluctuations in **ε** and in **χ** and are therefore experimentally measurable. In Section 5 we will show how the fluctuation amplitude, $<|Q_{ij}(\vec{q})|^2>$, can be used to calculate cross section of light scattering by fluctuations in the isotropic phase of liquid crystals. 6

4.2 Heterophase Fluctuations

In this section we will investigate fluctuations that result in the formation of small spatial regions of the low temperature, liquid-crystal phase in the isotropic phase, as the temperature T approaches T_c from above. These so-called "heterophase" fluctuations produce a sudden change in the value of the order parameter, in a local spatial region, from $S = 0$ to a value appropriate to the liquid crystal phase at temperature T. Referring to Fig. 4, such fluctuations carry local regions from the free energy minimum at $S = 0$, over the barrier to the free energy minimum near $S = \langle S \rangle_c$. The small regions of liquid crystal phase so produced are sometimes called "embryos"; their stability and statistical distribution for $T \sim T_c$ are the subject of the following discussion.

Let $\bar{\mathfrak{F}}_i$ denote the value of the Landau free energy density of the spatially uniform isotropic phase and $\bar{\mathfrak{F}}_a$ denote the analogous quantity for the anisotropic, liquid crystal phase. $\bar{\mathfrak{F}}_i$ and $\bar{\mathfrak{F}}_a$ correspond to the values of the two minima in Fig. 4 for T close to T_c, and their difference, $\Delta\bar{\mathfrak{F}} = \bar{\mathfrak{F}}_a - \bar{\mathfrak{F}}_i$, is positive for $T > T_c$, zero for $T = T_c$, and negative for $T < T_c$. For the moment let us set $L_1 = L_2 = 0$ in the Landau free energy expression, which implies perfectly sharp boundaries between the embryos and their surroundings; that is, every point in the system sits in one or the other of the two minima. In this case, the probability of heterophase fluctuations can be easily calculated. If we let P_a denote the probability for a spatial region of volume V_{em} to spontaneously fluctuate from the isotropic phase to the anisotropic phase and P_i be the probability that the same spatial volume would remain in the isotropic phase, then in thermal equilibrium

$$\frac{P_a}{P_i} = \exp[-\beta \Delta \bar{\mathfrak{F}} V_{\mathrm{em}}]. \qquad [90]$$

Eq. [90] is correct, independent of the barrier height h between the two minima of the Landau free energy density, so long as we neglect the energy contributions due to the gradient terms. In this case the barrier height influences only the rate at which the thermal equilibrium distribution is reached, but not the distribution itself. According to Eq. [90] one should expect to observe large heterophase fluctuations near any first order phase transition since $\Delta\bar{\mathfrak{F}} \approx 0$ for T close to T_c. This, of course, is not the case and the reason lies precisely in our neglect of the gradient terms in the Landau free energy density expansion.

If we let $L_1, L_2 \neq 0$, it is clear that formation of an embryo with an infinitely sharp boundary is energetically unfavorable. Therefore, there must necessarily be a boundary layer within which the value of the order parameter varies continuously from that inside the embryo to that of the surrounding isotropic fluid. The tendency of the gradient terms to maximize the spatial extent of the boundary layer is opposed by the accompanying increase in energy associated with values of the order parameter between the two minima, and the boundary layer that obtains represents a compromise between these two forces. In reality, then, we see that the barrier height plays a vital role not only in the rate of approaching the thermal distribution of embryos but also in the final distribution itself. That is, in addition to the free energy $\Delta\bar{\mathfrak{F}}\ V_{em}$, creation of an embryo also requires a certain amount of surface energy μ per unit area.[17] Later in this section we will estimate the magnitude of μ for liquid crystals, but for the present we will calculate the total work Φ required to produce a spherical embryo of radius ρ.

From the above discussion we have

$$\Phi(\rho) = \frac{4}{3}\pi\rho^3\Delta\bar{\mathfrak{F}} + 4\pi\rho^2\mu, \qquad [91]$$

so that the probability for thermally generating an embryo of radius ρ is $\sim \exp[-\beta\Phi(\rho)]$. Fig. 8 shows the behavior of $\Phi(\rho)$ for three different cases: $\Delta\bar{\mathfrak{F}} > 0$, $\Delta\bar{\mathfrak{F}} = 0$, and $\Delta\bar{\mathfrak{F}} < 0$. For $\Delta\bar{\mathfrak{F}} \geq 0$, $T \geq T_c$, $\Phi(\rho)$ is a monotonically increasing function of ρ, and embryos of any radius, once generated, inevitably shrink and disappear. It is also clear that if the value of the surface energy μ is large, then even at $T = T_c$, where $\Delta\bar{\mathfrak{F}} = 0$, the probability for the occurrence of heterophase fluctuations is small. Since the magnitude of the surface energy μ is directly related to the barrier height between the two free energy minima (higher barrier $\longrightarrow$ larger value of μ), it follows that in physical systems where the barrier is high, such as in the liquid-solid phase transitions, fluctuations are usually small and unobservable.

The interesting case arises when $\Delta\bar{\mathfrak{F}} < 0$, i.e., for $T < T_c$. In this case $S = 0$ is a relative minimum, and it is possible to have a supercooled metastable state. In Fig. 8 it is shown that for $\Delta\bar{\mathfrak{F}} < 0$, $\Phi(\rho)$ has a maximum at

$$\rho^* = \frac{2\mu}{|\Delta\bar{\mathfrak{F}}|} = -\frac{2\mu}{\Delta\bar{\mathfrak{F}}} \qquad [92]$$

due to the competition between the volume free energy, which is negative, and the surface energy, which is positive. For embryos of radius $\rho < \rho^*$ the surface energy dominates, and the embryos tend to shrink. However, for those embryos whose radius is greater than ρ^* the volumes free energy dominates, and the embryos tend to grow until the whole sample transforms into the low temperature phase. It follows that if one could avoid producing embryos with radius $\rho \geq \rho^*$, then supercooling of the sample would occur.

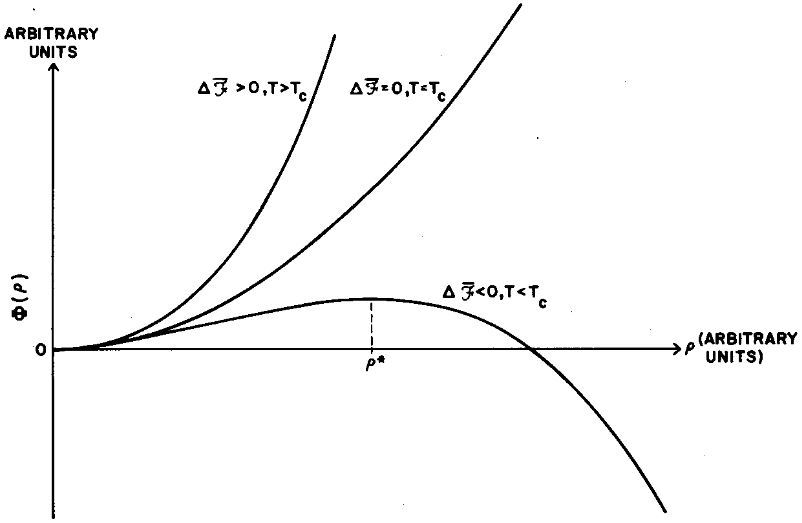

Fig. 8—Plot of the work required to generate an embryo as a function of its radius ρ at different temperatures. For $T \geq T_c$ the work required is an increasing function of ρ so that an embryo of any radius, once generated, must ultimately shrink and disappear. For $T < T_c$, embryos whose radius is greater than a critical radius ρ^* can grow indefinitely until the entire sample has transformed to the ordered phase. Note that if the formation of embryos of radius $\rho > \rho^*$ can be prevented, the sample can be supercooled.

Since the phenomenon of supercooling depends critically on the absence of embryos with radius $\rho > \rho^*$, it is of interest to estimate the relative probability Λ of thermally generating an embryo with radius ρ^* by heterophase fluctuations. We have, for T near T_c,

$$\Lambda \equiv \frac{\text{Probability of generating an embryo with radius } \rho^*}{\text{Probability of the system remaining in isotropic state}}$$

$$\simeq \exp[-\beta\Phi(\rho^*)] = \exp\left[-\frac{1}{3k_BT_c}\,\frac{16\pi\mu^3}{|\Delta\mathfrak{F}|^2}\right]. \quad [93]$$

Since $\Delta\mathfrak{F}$ changes sign at $T = T_c$, we approximate it by the form

$$\Delta\bar{\mathfrak{F}} = \text{const.}\ (T - T_c)$$

for T close to T_c. The constant must be equal to $-N\Delta s$, the transition entropy per unit volume, since, by definition, $-\partial\Delta\bar{\mathfrak{F}}/\partial T|_{T=T_c} = N\Delta s$. Thus,

$$\Delta\bar{\mathfrak{F}} = -N\Delta s(T - T_c),\ \Delta s < 0, \tag{94}$$

which can be substituted into Eq. [93] to give[18]

$$\Lambda \simeq \exp\left[-\frac{16\pi\mu^3}{3k_BT_c^{\,3}\left(\dfrac{T}{T_c} - 1\right)^2 N^2(\Delta s)^2}\right] \tag{95}$$

From Eq. [95] it is evident that if the dimensionless ratio $\mu^3/(k_BT_c^{\,3}N^2(\Delta s)^2)$ is large, Λ is small and supercooling should be easily observable.

We can estimate the value of μ within the framework of Landau–de Gennes theory. For this purpose we will use Eq. [42] with $\vec{H}$, $\vec{E}$, q_0, and L_2 set equal to zero and we will neglect any spatial variation in $\hat{n}(\vec{r})$. Eq. [42] then becomes

$$\mathfrak{F} = f_0[T] + \frac{3}{4}a(T - T_c^*)S^2(\vec{r}) + \frac{1}{4}BS^3(\vec{r}) + \frac{9}{16}CS^4(\vec{r}) + \frac{3}{4}L_1[\vec{\nabla}S(\vec{r})]^2. \tag{96}$$

We will consider a semi-infinite planar sample in which $S(\vec{r})$ varies only as a function of z with boundary values $S(-\infty) = \langle S\rangle_c$ and $S(\infty) = 0$. The origin $z = 0$ is defined arbitrarily by the condition $S(z = 0) = \langle S\rangle_c/2$. From arguments presented previously we expect to find a transition layer in which the value of S varies continuously from $\langle S\rangle_c$ to 0. The free energy per unit area of the transition layer is given by

$$\frac{F\{S(z)\}}{A} = \int_{-\infty}^{\infty} dz\{\mathfrak{F} - f_0[T]\}$$
$$= \int_{-\infty}^{\infty} dz\left\{\frac{3}{4}a(T - T_c^*)S^2(z) + \frac{1}{4}BS^3(z) + \frac{9}{16}CS^4(z) + \frac{3}{4}L_1\left(\frac{dS(z)}{dz}\right)^2\right\} \tag{97}$$

where the dependence of F on $S(z)$ is shown explicitly. The variation of $S(z)$ with z is obtained by minimizing the free energy F. The resulting $S(z)$ must satisfy the Euler-Lagrange equation

$$\frac{d}{dS(z)}\left[\frac{3}{4}a(T - T_c{}^*)S^2(z) + \frac{1}{4}BS^3(z) + \frac{9}{16}CS^4(z)\right] = \frac{3}{2}L_1\frac{d^2S(z)}{dz^2} \qquad [98]$$

Multiplying both sides of Eq. [98] by $dS(z)/dz$ and integrating once with respect to z gives

$$\text{const.} + \frac{3}{4}a(T - T_c{}^*)S^2(z) + \frac{1}{4}BS^3(z) + \frac{9}{16}CS^4(z) = \frac{3}{4}L_1\left(\frac{dS(z)}{dz}\right)^2 . \qquad [99]$$

The constant in Eq. [99] must be zero since $S(\infty) = 0$ and $[dS(z)/dz|_{z=\infty}] = 0$. Therefore, using the fact that $z = 0$ is defined as the point at which $S = \langle S\rangle_c/2$, we have

$$\int_{\langle S\rangle_c/2}^{S(z)} \frac{dS'}{\left[3(T/T_c{}^* - 1)S'^2 + \dfrac{B}{aT_c{}^*}S'^3 + \dfrac{9C}{4aT_c{}^*}S'^4\right]^{1/2}} = -\left(\frac{aT_c{}^*}{3L_1}\right)^{1/2} z$$

or

$$\frac{z}{\xi_1} = G[S(z)] - G[\langle S\rangle_c/2], \qquad [100]$$

should write

$$\ln\left\{\frac{g[S(z)]}{g[\frac{\langle S\rangle}{2}]}\right\}$$

where

$$G(S) = \ln\left\{\frac{-\sqrt{3[(T/T_c{}^*) - 1] + (B/aT_c{}^*)S + (9C/4aT_c{}^*)S^2}}{S} - \frac{\sqrt{3[(T/T_c{}^*) - 1]}}{S} - \frac{(B/aT_c{}^*)}{2\sqrt{3[(T/T_c{}^*) - 1]}}\right\}. \qquad [101]$$

For $T = T_c$, Eq. [100] can be simplified to the form

$$S(z) = \frac{\langle S\rangle_c}{\exp\left(\frac{z}{\xi_1}\right) + 1} \tag{100a}$$

with the aid of Eqs. [52] and [53]. Equations [100], [100a], and [101] give the spatial variation of S as a function of z. Using Eq. [100a] and $\langle S\rangle_c = 0.33$, we obtain $S(z)$ as plotted in Fig. 9 for $T = T_c$. The fact that $S(z)$ decays most rapidly for $S \simeq 0.2$ is understandable because $S = 0.17$ is the position of the barrier peak and therefore such values of S should occupy the smallest portion of the boundary layer in order to minimize the total free energy.

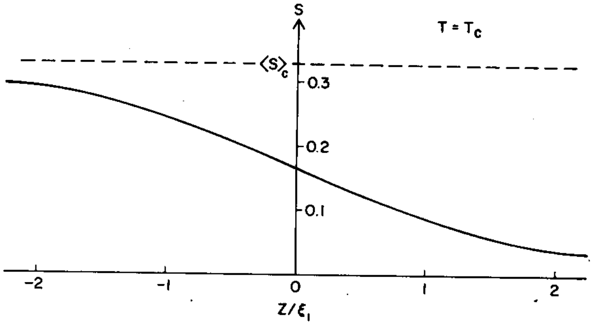

Fig. 9—Variation of the order parameter S as a function of distance in the boundary layer separating the ordered phase, $S = \langle S\rangle_c$, from the disordered phase, $S = 0$, at $T = T_c$.

We can also calculate the surface energy[7] per unit area μ using Eq. [99]. Substituting Eq. [99] into Eq. [97], we get

$$\mu = \int_{-\infty}^{\infty} dz \frac{3}{2} L_1 \left(\frac{dS(z)}{dz}\right)^2 = \frac{3}{2} L_1 \int_{-\infty}^{\infty} dz \frac{dS(z)}{dz} \left(\frac{dS(z)}{dz}\right)$$

$$= \frac{3}{2} L_1 \int_{\langle S\rangle_c}^{0} dS(z) \left(\frac{dS(z)}{dz}\right) . \tag{102}$$

Using Eq. [99] for $dS(z)/dz$ (with the minus sign for $z > 0$), Eq. [102] becomes

$$\mu = \frac{(3L_1 a T_c^*)^{1/2}}{2} \times$$

$$\int_0^{\langle S\rangle_c} dS' S' \left[3\left(\frac{T}{T_c^*} - 1\right) + \frac{B}{aT_c^*} S' + \frac{9C}{4aT_c^*} S'^2 \right]^{1/2} . \qquad [103]$$

Setting $T = T_c$, $L_1 = 6 \times 10^{-7}$ dyne, and using the values of a, B, C, T_c, $<S>_c$, and T_c^* for MBBA, we find $\mu \simeq 0.02$ erg/cm^2. This is in good agreement with the measured value[19] of $\mu \simeq 0.023$ erg/cm^2. Using this value of μ, $\Delta s \simeq 0.16\ k_B$, and $N \simeq 2.3 \times 10^{21}$ cm^{-3}, we obtain the dimensionless ratio $\mu^3/(k_B T_c^{\,3} N^2 (\Delta s)^2) \simeq 0.7 \times 10^{-6}$ for MBBA. Putting this value into Eq. [95] yields the result that Λ is of order e^{-1} ($\Phi(\rho^*) = kT_c$) when $T \simeq T_c - 1$°K, which means that MBBA can at most be supercooled to about 1°K below T_c.[†] Recalling from Section 2.3 that T_c^* was interpreted as that temperature below which supercooling is impossible, we conclude from the above calculation that for MBBA, $T_c^* \simeq T_c - 1$°K. This is in very good agreement with experimental value[14] of $T_c - T_c^* \simeq 1$°K.

5. Observation of Fluctuations Using Light Scattering

Fluctuations in the order parameter are reflected in various physical properties of a liquid crystal material. In this section we will focus on the elastic (Rayleigh) scattering of light by such fluctuations in the isotropic phase of nematic and cholesteric materials near T_c.

We begin by expressing the dielectric constant at an arbitrary point $\vec{r}$ in terms of the order parameter

$$\boldsymbol{\epsilon}(\vec{r}) = \frac{2}{3}(\Delta\epsilon)_{\max}\mathbf{Q}(\vec{r}) + \bar{\epsilon}\mathbf{I}, \qquad [104]$$

where $\bar{\epsilon}$ is the dielectric constant of the isotropic liquid and $\mathbf{I}$ is the unit tensor of the second rank. Since the polarizability $\boldsymbol{\alpha}(\vec{r}) \equiv [\boldsymbol{\epsilon}(\vec{r}) - \mathbf{I}]/4\pi$, we can write

$$\boldsymbol{\alpha}(\vec{r}) = \frac{1}{6\pi}(\Delta\epsilon)_{\max}\mathbf{Q}(\vec{r}) + \frac{\bar{\epsilon} - 1}{4\pi}\mathbf{I}, \qquad [105]$$

which, upon Fourier transformation, becomes

[†] At this temperature the value of ρ^* calculated from Eqs. [92] and [94] is about 80 Å.

$$\alpha(\vec{q}) = \frac{1}{6\pi}(\Delta\epsilon)_{\max}\mathbf{Q}(\vec{q}) + \frac{\bar{\epsilon} - 1}{4\pi}\delta(\vec{q})\mathbf{I}. \qquad [106]$$

Consider an incident light wave (Fig. 10) of the form

$$\vec{E}_{\mathrm{in}} = \hat{e}_{\mathrm{in}}E_0 \exp[i(\vec{k}_{\mathrm{in}} \cdot \vec{r} - \omega t], \qquad [107]$$

with frequency ω and wavevector $|\vec{k}_{in}| = \omega/c$. $\hat{e}_{in}$ in Eq. [107] is a unit polarization vector pointing along the electric field direction of the incident light. This wave will induce a dipole moment per unit volume $\vec{P}(\vec{r})$ in the sample

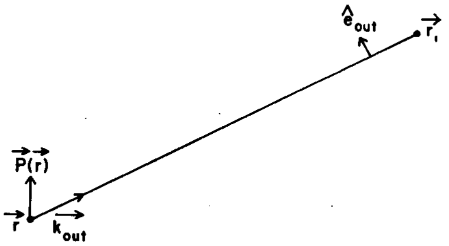

Fig. 10—Graphic illustration of the vector identity, Eq. [110].

$$\vec{P}(\vec{r}) = \alpha(\vec{r}) \cdot \vec{E}_{\mathrm{in}} = \alpha(\vec{r}) \cdot \hat{e}_{\mathrm{in}}E_0 \exp[(\vec{k}_{\mathrm{in}} \cdot \vec{r} - \omega t)]. \qquad [108]$$

At a point $\vec{r}_1$ far from the scattering volume the radiation from a volume $d^3\vec{r}$ around $\vec{r}$ due to the induced oscillating dipole moment $\vec{P}(\vec{r})$ is[20]

$$d\vec{E}_{\mathrm{out}} = -\frac{\omega^2 d^3\vec{r}}{c^2|\vec{r}_1 - \vec{r}|}\,\frac{[(\vec{P}(\vec{r}) \times \vec{k}_{\mathrm{out}}) \times \vec{k}_{\mathrm{out}}]}{|\vec{k}_{\mathrm{out}}|^2}\exp[i\vec{k}_{\mathrm{out}} \cdot (\vec{r}_1 - \vec{r})], \qquad [109]$$

where c is the speed of light and $\vec{k}_{out}$ is a vector of magnitude ω/c pointing in the direction of $(\vec{r}_1 - \vec{r})$. Letting $\hat{e}_{out}$ be the unit vector pointing along the direction of $d\vec{E}_{out}$, we see from Fig. 10 that

$$-\frac{[(\vec{P}(\vec{r}) \times \vec{k}_{\mathrm{out}}) \times \vec{k}_{\mathrm{out}}]}{|\vec{k}_{\mathrm{out}}|^2} = [\hat{e}_{\mathrm{out}} \cdot \vec{P}(\vec{r})]\hat{e}_{\mathrm{out}}. \qquad [110]$$

Substitution of Eqs. [108] and [110] into Eq. [109] yields

$$d\vec{E}_{\text{out}} = \hat{e}_{\text{out}} \frac{\omega^2 E_0}{c^2 R_0} \exp[i(\vec{k}_{\text{out}} \cdot \vec{r}_1 - \omega t)](\hat{e}_{\text{out}} \cdot \alpha(\vec{r}) \cdot \hat{e}_{\text{in}}) \times \exp[i\vec{q} \cdot \vec{r}]d^3\vec{r}, \qquad [111]$$

where $R_0 \equiv |\vec{r}_1 - \vec{r}|$ and $\vec{q} \equiv \vec{k}_{out} - \vec{k}_{in}$. Integrating over the volume of the sample with R_0 treated as a constant ($\vec{r}_1$ is very far from the sample), we obtain an expression for the total scattered electric field at $\vec{r}_1$

$$\vec{E}_{\text{out}} = \hat{e}_{\text{out}} \frac{\omega^2 E_0 V}{c^2 R_0} \exp[i(\vec{k}_{\text{out}} \circ \vec{r}_1 - \omega t)](\hat{e}_{\text{out}} \cdot \alpha(\vec{q}) \cdot \hat{e}_{\text{in}}), \qquad [112]$$

and for the differential Rayleigh scattering cross section $d\sigma_R$

$$d\sigma_R = \frac{|\vec{E}_{\text{out}}|^2}{|E_0|^2} R_0^2 d\Omega = \frac{\omega^4 V^2}{c^4} |\hat{e}_{\text{out}} \cdot \alpha(\vec{q}) \cdot \hat{e}_{\text{in}}|^2 d\Omega, \qquad [113]$$

where $d\Omega$ is the differential solid angle in the direction of $\vec{k}_{out}$. Substituting Eq. [106] into Eq. [113], we find the light scattering power, or Rayleigh ratio, to be

$$R \equiv \frac{1}{V} \frac{d\sigma_R}{d\Omega} = \frac{\omega^4 (\Delta\epsilon)^2_{\text{max}} V}{c^4 (6\pi)^2} |\hat{e}_{\text{out}} \cdot \mathbf{Q}(\vec{q}) \cdot \hat{e}_{\text{in}}|^2, \qquad [114]$$

for $\vec{q} \neq 0$. In the isotropic phase of a nematic or cholesteric liquid crystal the scattering results from thermal fluctuations, and the experimentally measured Rayleigh ratio is therefore given by

$$R = \frac{\omega^4 (\Delta\epsilon)^2_{\text{max}} V}{c^4 (6\pi)^2} \langle |\hat{e}_{\text{out}} \cdot \mathbf{Q}(\vec{q}) \cdot \hat{e}_{\text{in}}|^2 \rangle. \qquad [115]$$

In Fig. 11 we show a scattering geometry in which the wavevector of the incoming light makes an angle υ with that of the outgoing light and $\hat{e}_{out}$ is perpendicular to $\hat{e}_{in}$. If $\hat{e}_1$, $\hat{e}_2$, and $\hat{e}_3$ are unit vectors along the x,y, and z axes, respectively, with $\vec{q} \parallel z$, then

$$\hat{e}_{\text{in}} = \hat{e}_2,$$

and

$$\hat{e}_{\text{out}} = \cos\frac{\upsilon}{2}\,\hat{e}_3 - \sin\frac{\upsilon}{2}\,\hat{e}_1. \qquad [116]$$

It follows that

$$\langle|\hat{e}_{\text{out}}\cdot\mathbf{Q}(\vec{q})\cdot\hat{e}_{\text{in}}|^2\rangle = \left\langle\left|\cos\frac{\upsilon}{2}Q_{32}(\vec{q}) - \sin\frac{\upsilon}{2}Q_{12}(\vec{q})\right|^2\right\rangle. \qquad [117]$$

Since $Q_{23}(\vec{q})$ and $Q_{12}(\vec{q})$ are independent, the cross terms in Eq. [117] average to zero, leaving

$$\langle|\hat{e}_{\text{out}}\cdot\mathbf{Q}(\vec{q})\cdot\hat{e}_{\text{in}}|^2\rangle = \cos^2\frac{\upsilon}{2}\langle|Q_{32}(\vec{q})|^2\rangle + \sin^2\frac{\upsilon}{2}\langle|Q_{12}(\vec{q})|^2\rangle. \qquad [118]$$

Substituting Eq. [118] into Eq. [115] and using the results of Eq. [86] we have, finally, that the Rayleigh ratio for the scattering geometry of Fig. 11 is

$$R = \frac{\omega^4(\Delta\epsilon)^2_{\max}k_BT}{c^4(6\pi)^2a(T - T_c{}^*)}\left[\cos^2\frac{\upsilon}{2}\,\frac{(1 + \xi_\perp{}^2q^2)}{[(1 + \xi_\perp{}^2q^2)^2 - 4q_0{}^2\xi_1{}^4q^2]} + \sin^2\frac{\upsilon}{2}\,\frac{(1 + \xi_1{}^2q^2)}{[(1 + \xi_1{}^2q^2)^2 - 16q_0{}^2\xi_1{}^4q^2]}\right], \qquad [119]$$

where $|\vec{q}| = (2\omega/c)\sin\upsilon/2$.

For nematic materials $q_0 = 0$ and Eq. [119] shows that the scattering intensity decreases with increasing q. For cholesteric materials, on the other hand, $q_0 \neq 0$ and the second term of Eq. [119] can be peaked for a value of q such that

$$q = \frac{(4q_0\xi_1 - 1)^{1/2}}{\xi_1} > 0, \qquad [120]$$

provided $q_0\xi_1 > 1/4$. Physically this means that if the correlation length ξ_1 is of order $\lambda_0/10$ then fluctuations in cholesteric order will produce incomplete helices with ~1/10 of a pitch, which couple strongly to the incident and scattered light waves when the transfer wavevector $\vec{q}$ satisfies Eq. [120]. As $T \rightarrow T_c^*$ from above, ξ_1 increases and the peak in the second term of Eq. [119] diverges at $q_0\xi_1 = \frac{1}{2}$ which corresponds to the temperature $T = T_c^* + 4q_0^2L_1/a$ (Recall that $\xi_1 = [L_1/a(T - T_c^*)]^{1/2}$).

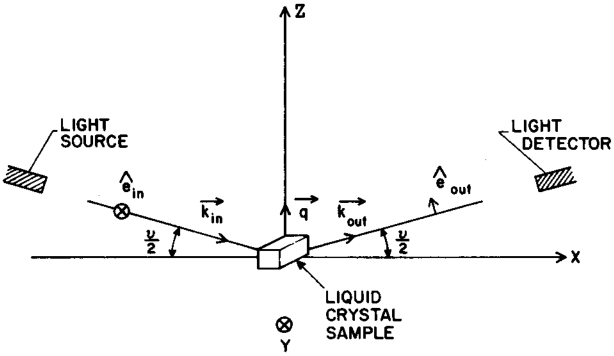

Fig. 11—Illustration of the geometry used in the light scattering experiment discussed in Section 5. Note that $\vec{q}$ is chosen to be along the *z*-direction to conform with the convention used in the text.

The Rayleigh ratio has been measured in the isotropic phase of both nematic[14,21] and cholesteric[22] liquid crystals. Agreement between these measurements and the predictions of the Landau–de Gennes theory is excellent in both cases.

6. Magnetic Birefringence and the Paranematic Susceptibility

Consider the effect of applying a static or slowly varying magnetic field to a sample of nematic liquid crystal in its isotropic phase. Assuming that $\hat{n} \parallel \vec{H}$, we can write the magnetic contribution to the free energy density as (see Eq. [38])

$$\mathfrak{F}_M = -\frac{1}{3}(\Delta\chi)_{\max} S(\vec{r}) H^2. \qquad [121]$$

The equilibrium state in the presence of the magnetic field will have finite order since $\mathfrak{F}_M$ is negative; the average value of this order $\bar{S}(H)$ can be calculated straightforwardly. We have

$$\bar{S}(H) \equiv \left\langle \frac{1}{V} \int_V d^3\vec{r}\, S(\vec{r}) \right\rangle_H \equiv \langle S(\vec{q} = 0) \rangle_H =$$

$$\frac{\int DS(\vec{r}) \left[\frac{1}{V} \int d^3\vec{r} S(\vec{r}) \right] \exp \left\{ -\beta \int d^3\vec{r} \left(\mathfrak{F}_L - \frac{(\Delta\chi)_{\max}}{3} S(\vec{r}) H^2 \right) \right\}}{\int DS(\vec{r}) \exp \left\{ -\beta \int d^3\vec{r} \left(\mathfrak{F}_L - \frac{(\Delta\chi)_{\max}}{3} S(\vec{r}) H^2 \right) \right\}}, \qquad [122]$$

where $\langle\ \rangle_H$ denotes the thermal average with the magnetic field H present.

$\bar{S}(H)$ depends on H quadratically and, furthermore, since $\bar{S}(H)$ is expected to be small and $\bar{S}(H = 0) = 0$, we can make the following expansion

$$\bar{S}(H) = \eta H^2 + \ldots$$

where

$$\eta = \left. \frac{\partial \bar{S}(H)}{\partial (H^2)} \right|_{H^2=0}$$

is the paranematic susceptibility. Substituting for $\bar{S}(H)$ from Eq. [122] and evaluating the resulting expression in the limit $H^2 \to 0$, we find

$$\eta = \frac{1}{k_B T} \frac{(\Delta\chi)_{\max}}{3} V \left\{ \langle |S(\vec{q} = 0)|^2 \rangle_{H^2=0} - \langle S(\vec{q} = 0) \rangle^2_{H^2=0} \right\}$$

$$= \frac{(\Delta\chi)_{\max} V}{3 k_B T} \langle |S(\vec{q} = 0)|^2 \rangle, \qquad [123]$$

In the approximation $B = C = 0$, we can substitute Eq. [74] into Eq. [123] and get

$$\eta = \frac{2(\Delta\chi)_{\max}}{9a(T - T_c^*)} \qquad [124]$$

Taking $(\Delta\chi)_{\max} \simeq 10^{-6}$ cgs units, $a \simeq 4.2 \times 10^5$ erg/°K cm^3, $T = T_c$, and $T_c - T_c^* = 1$°K, we find $\eta \simeq 5 \times 10^{-13}$ cm^3/erg. For a field $H \simeq$ 10 KOe this results in an equilibrium order $\bar{S}(10 \text{ KOe}) \simeq 5 \times 10^{-5}$.

The paranematic susceptibility is directly related to the phenomenon of magnetic birefringence. Any anisotropic property is proportional to the induced order. Specifically we can write

$$\Delta\epsilon \equiv \epsilon_{\parallel} - \epsilon_{\perp} = M_0\langle S(q = 0)\rangle_H \equiv M_0\bar{S}(H) \qquad [125]$$

where M_o is a constant and $\epsilon_{\parallel}(\epsilon_{\perp})$ is the long wavelength ($q = 0$) dielectric constant parallel (perpendicular) to $\hat{H}$. However, $\Delta\epsilon = (\epsilon_{\parallel}^{1/2} - \epsilon_{\perp}^{1/2})(\epsilon_{\parallel}^{1/2} + \epsilon_{\perp}^{1/2}) \simeq 2n\Delta n$, n being the refractive index, and using our previous result for $\bar{S}(H)$, Eq. [125] becomes

$$n\Delta n = \frac{M_0(\Delta\chi)_{\max}}{9a(T - T_c^*)}\ H^2. \qquad [126]$$

Rearranging Eq. [126] gives

$$\begin{aligned}\frac{\Delta n}{H^2} &= \frac{M_0(\Delta\chi)_{\max}}{9an(T - T_c^*)} \\ &= \frac{M_0\eta}{2n}\end{aligned} \qquad [127]$$

The quantity $\Delta n/H^2$ is called the Cotton-Mouton coefficient which is seen to diverge at $T = T_c^*$ and to fall off as $(T - T_c^*)^{-1}$ above T_c^*. Measurements of magnetic birefringence have been made for MBBA,[14] and the inverse Cotton-Mouton coefficient was plotted as a function of temperature. The experimental behavior is in complete agreement with Eq. [127]. Analysis of the data yields $T_c^* \simeq T_c - 1°\text{K}$.

Acknowledgment

We express our appreciation to Dr. R. Cohen for helpful discussions and to Dr. P. J. Wojtowicz for assistance in some numerical calculations and careful reading of the manuscript.

Appendix A

In this appendix we illustrate some implications of Eq. [15]. Consider a hypothetical system in which the function $\gamma[\vec{\nabla}\sigma(\vec{r}),T]$ is given by

$$\exp\{-\beta\gamma[\vec{\nabla}\sigma(\vec{r}),T]\} = \delta[\vec{\nabla}\sigma(\vec{r})]. \qquad [128]$$

The interaction energy defined by Eq. [128] reflects a rigid coupling between neighboring spatial regions. Substituting Eq. [128] into Eq. [15], we see that the only form of $\sigma(\vec{r})$ that can contribute to the integral is $\sigma(\vec{r})$ = constant, since any spatial variation of $\sigma(\vec{r})$ would make the integrand vanish due to the particular form of $\gamma[\vec{\nabla}\sigma(\vec{r}),T]$. The delta function thus simplifies the functional integral $\int \boldsymbol{D}\sigma(\vec{r})$, which can be written as $\int d\sigma(1) \ldots \int d\sigma(M)$, (see Section 1) to a one-dimensional integral $\int d\sigma$. Eq. [15] therefore becomes

$$Z(T) = \int d\sigma \exp\{-\beta V f[\sigma, T]\}. \qquad [129]$$

At any particular temperature, $f[\sigma,T]$ has a minimum. If $\sigma_0(T)$ is the value of σ which minimizes $f[\sigma,T]$ at temperature T, then the integrand in Eq. [129] has a peak at $\sigma = \sigma_0(T)$. In the spirit of Landau's approach, let us approximate $Z(T)$, Eq. [129], by using a Taylor series approximation for $f[\sigma,T]$ around its minimum:

$$f[\sigma, T] \simeq f_0[T] + \frac{1}{2}A(T)[\sigma - \sigma_0(T)]^2, \quad A(T) > 0 \qquad [130]$$

where $f_0[T] \equiv f[\sigma_0(T),T]$. Then

$$Z(T) \simeq \exp\{-\beta V f_0[T]\}\int d\sigma \exp\{-\beta V A(T)[\sigma - \sigma_0(T)]^2/2\}. \qquad [131]$$

Note that the integrand in Eq. [131] is a Gaussian centered at $\sigma_0(T)$ with half width $[\beta VA(T)]^{-1/2}$. As $V \to \infty$, the width of the peak approaches zero and the approximation, Eq. [131], becomes exact. It also follows that in the limit $V \to \infty$ the thermal distribution function, $\exp\{-\beta Vf[\sigma,T]\}/Z(T)$, approaches a delta function peaked at $\sigma_0(T)$. This observation is the basis of the well-known result that in the thermodynamic limit the thermal average of σ, denoted by $<\sigma>$, is equal to the value of $\sigma_0(T)$ that minimizes the Landau free energy function $f[\sigma,T]$, that is, the equilibrium value.

For a sufficiently large volume V the integral in Eq. [131] can be evaluated to give

$$Z(T) \simeq \left(\frac{2\pi}{\beta V A(T)}\right)^{1/2} \exp\{-\beta V f_0[T]\}. \qquad [132]$$

From Eq. [132] the free energy density in the thermodynamic limit $V \to \infty$ is evaluated to be

$$\lim_{V\to\infty} \frac{F(T)}{V} = f_0[T] + \lim_{V\to\infty} \frac{k_B T}{2V}\left[\ln \frac{2\pi}{\beta V A(T)}\right] = f_0[T]. \qquad [133]$$

Eq. [133] states the result that in a spatially uniform system, where the partition function can be expressed by Eq. [129], the free energy density at temperature T is equal to the value of the minimum of the Landau free energy density function $f[\sigma,T]$ at that temperature.

The magnitude of the fluctuations in this hypothetical system can also be evaluated. If the thermal average of the quantity σ is defined by

$$\langle \sigma^{\nu} \rangle = \frac{1}{Z(T)} \int d\sigma\, \sigma^{\nu} \exp\{-\beta V f[\sigma, T]\}, \qquad [134]$$

then the root mean square fluctuation of the order parameter is

$$[\langle(\sigma - \langle\sigma\rangle)^2\rangle]^{1/2} = [\langle\sigma^2\rangle - \langle\sigma\rangle^2]^{1/2}. \qquad [135]$$

Carrying out the calculation with the approximation of Eq. [130] and V large, we obtain

$$[\langle\sigma^2\rangle - \langle\sigma\rangle^2]^{1/2} = [\pi/\beta V A(T)]^{1/4}, \qquad [136]$$

which vanishes in the limit of $V \to \infty$ unless, of course, $A(T) \to 0$. This result, which is the same as the corresponding result of the mean field theory, is purely an artifact of having required the whole system to fluctuate in phase by the specific choice of $\gamma[\vec{\nabla}\sigma(\vec{r}),T]$ in Eq. [128].

To see the effect of specifying a different $\gamma[\vec{\nabla}\sigma(\vec{r}),T]$, let us set

$$\gamma[\vec{\nabla}\sigma(\vec{r}), T] = 0 \qquad [137]$$

and calculate the free energy density. In this case Eq. [15] becomes

$$\begin{aligned} Z(T) &= \int D\sigma(\vec{r}) \exp\{-\beta(\textstyle\int d^3\vec{r} f[\sigma(\vec{r}), T])\} \\ &= \int d\sigma(1) \ldots \int d\sigma(M) \exp\left\{-\beta \Delta V \sum_{\alpha=1}^{M} f[\sigma(\alpha), T]\right\} \\ &= \left[\int d\sigma \exp\{-\beta \Delta V f[\sigma, T]\}\right]^M, \end{aligned} \qquad [138]$$

where ΔV is the elementary volume as defined before, $M = V/\Delta V$, and V is the volume of the whole system. Using the same approximation for $f[\sigma,T]$ as that given by Eq. [130], we get

$$Z(T) \simeq \left(\frac{2\pi}{\beta\Delta VA(T)}\right)^{\frac{M}{2}} \exp\{-\beta Vf_0[T]\}. \qquad [139]$$

The free energy density is then

$$\lim_{V\to\infty} \frac{F(T)}{V} = f_0[T] + \lim_{V\to\infty} \frac{k_BTM}{2V}\left[\ln \frac{2\pi}{\beta\Delta VA(T)}\right]. \qquad [140]$$

As $V \to \infty$, we have $M \to \infty$ such that $V/M = \Delta V =$ constant. Therefore,

$$\lim_{V\to\infty} \frac{F(T)}{V} = f_0[T] + \frac{k_BT}{2\,\Delta V}\left[\ln \frac{2\pi k_BT}{\Delta VA(T)}\right]. \qquad [141]$$

Eq. [141] differs from Eq. [133] by an additional term which can be attributed to spatial fluctuations of the order parameter. In contrast to the previous case where the whole system fluctuates in phase, fluctuations in a system where $\gamma[\vec{\nabla}\sigma(\vec{r}),T] = 0$ are completely uncorrelated from one spatial region to the next.

In real systems, coupling between a small part of the sample with the rest is neither zero nor rigid but can be described as elastic. This implies that for physical systems the order parameter fluctuations at two different spatial points are partially correlated, the degree of correlation being a decreasing function of the separation between the two points. These expectations are made explicit by calculations in Section 4.

Appendix B

In this appendix we wish to obtain the Jacobian factor for Eq. [63] and thence to evaluate the free energy density given by Eq. [70].

From Eq. [60a] it is clear that the Jacobian is given by $\|\exp(i\vec{q}_\beta\cdot\vec{r}_\alpha)\|$, the determinant of the $M \times M$ matrix with elements $\exp(i\vec{q}_\beta\cdot\vec{r}_\alpha)$ in column α and row β. The inverse for the matrix for which the $\alpha\beta$ – element is $[\exp(i\vec{q}_\beta\cdot\vec{r}_\alpha)]$ can be obtained from Eqs. [60a] and [61a];

$$S(\vec{r}_\alpha) = \sum_\beta S(\vec{q}_\beta) \exp\{i\vec{q}_\beta \cdot r_\alpha\}$$

$$= \frac{\Delta V}{V}\sum_\beta \sum_\gamma \exp\{-i\vec{q}_\beta \circ \vec{r}_\gamma\} \exp\{-i\vec{q}_\beta \cdot \vec{r}_\alpha\} S(\vec{r}_\gamma) \qquad [142]$$

which implies

$$\frac{\Delta V}{V}\sum_\beta \exp\{-i\vec{q}_\beta \cdot \vec{r}_\gamma\} \exp\{i\vec{q}_\beta \cdot \vec{r}_\alpha\} = \delta_{\gamma\alpha} = \begin{cases} 1 & \gamma = \alpha \\ 0 & \gamma \neq \alpha \end{cases} \qquad [143]$$

Therefore, the inverse matrix has element

$$\frac{\Delta V}{V} e^{-i\vec{q}_\beta \cdot \vec{r}_\alpha}$$

in row α and column β. From matrix algebra and Eq. [143] we get

$$\|\delta_{\alpha\gamma}\| = 1 = \|\exp(i\vec{q}_\beta \cdot \vec{r}_\alpha)\| \cdot \|\frac{\Delta V}{V} \exp(-i\vec{q}_\beta \cdot \vec{r}_\alpha)\|$$

$$= \|\exp(i\vec{q}_\beta \cdot \vec{r}_\alpha)\| \cdot \|\frac{\Delta V}{V}\| \cdot \|\exp(i\vec{q}_\beta \cdot \vec{r}_\alpha)\|^*$$

$$= \left(\frac{\Delta V}{V}\right)^M \|\exp(i\vec{q}_\beta \cdot \vec{r}_\alpha)\| \cdot \|\exp(i\vec{q}_\beta \cdot \vec{r}_\alpha)\|^* . \qquad [144]$$

Therefore, apart from a phase factor, which we set equal to zero, the Jacobian is given by $(V/\Delta V)^{M/2}$.

From Eq. [70] the integral is easily evaluated to give

$$Z(\vec{q}, T) = \frac{2\pi}{3} \frac{k_B T}{\Delta V a(T - T_c^*)(1 + \xi^2 q^2)}, \qquad [145]$$

where the upper limit of integration for $d|S(\vec{q})|^2$ is set equal to ∞. The total free energy of the system is given by

$$F(T) = -k_B T \ln Z(T) = V f_0[T] -$$

$$k_B T \sum_{\vec{q}}{}' \ln\left[\frac{2\pi}{3} \frac{k_B T}{\Delta V a(T - T_c^*)(1 + \xi^2 q^2)}\right] = V f_0[T] -$$

$$\frac{k_B T}{2} \frac{V}{(2\pi)^3} \int_0^{q_{\max}} 4\pi q^2 dq \ln\left[\frac{2\pi}{3} \frac{k_B T}{\Delta V a(T - T_c^*)(1 + \xi^2 q^2)}\right] \qquad [146]$$

where the summation over the independent set of $\vec{q}$ vectors is extended to every $\vec{q}$ with the final sum multiplied by ½. The integral can be evaluated to give a free-energy density expression

$$\frac{F(T)}{V} = f_0[T] - \frac{k_B T q^3_{\max}}{12\pi^2} \left\{ \ln \left[\frac{1}{12\pi^2} \frac{k_B T q^3_{\max}}{a(T - T_c{}^*)(1 + \xi^2 q^2_{\max})} \right] + \frac{2}{3} - \frac{2}{\xi^2 q^2_{\max}} + \frac{2 \tan^{-1} \xi q_{\max}}{\xi^3 q^3_{\max}} \right\} \qquad [147]$$

where we have set $\Delta V \equiv (2\pi)^3/q^3{}_{max}$. Eq. [147] can be easily reduced to the two limits, Eqs. [133] and [141], discussed in Appendix A. On the one hand, the rigid coupling limit can be obtained by reducing the degrees of freedom of the system from M independently varying components to a single independently varying component. This can be accomplished by letting $q_{max} \rightarrow 0$ in Eq. [147], which is equivalent to requiring $\Delta V \rightarrow V$ and $M \rightarrow 1$. The zero coupling limit, on the other hand, can simply be obtained by letting $\xi \rightarrow 0$ in Eq. [147].

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