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P. G. De Gennes [a b]
[a] Department of Physics, Simon Fraser University, Burnaby 2, B. C., Canada
[b] Physique des solides, Faculté des Sciences, 91 Orsay, France

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Short Range Order Effects in the Isotropic Phase of Nematics and Cholesterics†

P. G. DE GENNES‡

Department of Physics
Simon Fraser University
Burnaby 2, B. C., Canada

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Abstract—We assume that (1) the local state of order in the isotropic phase is a symmetric traceless tensor $Q_{\alpha\beta}$, proportional to the anisotropic part of a tensor property such as the magnetic susceptibility; (2) the free energy may be expanded in powers of $Q_{\alpha\beta}$ and of its gradients. This allows a unified description covering the anomalous magnetic birefringence, the intensity of light scattering, and the properties of the nematic/isotropic interface. For a cholesteric, although the optical rotation is huge in the ordered phase, we predict that it should *not* be anomalous just above the transition point T_c. We also investigate the dynamics of fluctuations of $Q_{\alpha\beta}$, and discuss the flow birefringence, the frequency width of the Rayleigh scattering, and the attenuation of ultrasonic shear waves, in terms of 3 viscosity coefficients.

1. Introduction

The nematic↔isotropic transition is of first order, but weak.(1) In most thermotropic materials, the isotropic phase still shows some remarkable short range order effects above the transition point T_c; we give here a short list of the relevant experiments:

(a) *magnetic birefringence*(2–4): the refractive indices $n_\parallel$ and $n_\perp$ (measured for polarisations respectively parallel and normal to the magnetic field H) differ by an amount

$$n_\parallel - n_\perp = \alpha(T) H^2 \tag{1.1}$$

Near T_c, α may be a hundred times larger than in conventional organic liquids. Plots of $1/\alpha$ versus T are roughly linear and extra-

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‡ Permanent address: Physique des solides, Faculté des Sciences, 91 Orsay, France.

polation suggests that α would diverge at a temperature T^* which is only slightly smaller than T_c ($T_c - T^* \gtrsim 1$ °K).

(b) *intensity of light scattering* I: although smaller than in the nematic phase⁽⁵⁾ I is still significant.⁽⁶⁾ It is essentially independent of the scattering angle θ, and the ratio $I_\perp/I_\parallel$ (for the two conventional polarisation set ups) is $\frac{3}{4}$ as it is for a collection of anisotropic scattering objects with random orientations.⁽⁶⁾ Since I is independent of θ, the size of these objects, or, more accurately, the " coherence length " $\xi(T)$, is smaller than the optical wavelength. Typically we expect $\xi(T_c)$ to be of order 10 times the molecular length (i.e. ~ 200 Å): This is still large enough to allow a macroscopic description of fluctuation and correlation effects. One of the aims of the present paper is to give a detailed definition of these coherence lengths.

(c) *flow birefringence*⁽²⁾: with a flow velocity v, in the x direction, and under a velocity gradient $\partial v/\partial z$, the isotropic phase becomes birefringent, with two optical axes (1) and (2) at 45° from x and z. The difference in refraction indices $n_1 - n_2$ is proportional to the rate of shear

$$n_1 - n_2 = \tau(T)\frac{\partial v}{\partial z} \tag{1.2}$$

τ has the dimension of time, and is much larger than in conventional liquids.

The Zvetkov measurements of τ⁽²⁾ were not very accurate, but, they do show a strong increase of τ when T decreases down to T_c.

(d) *frequency width of the scattered light*: this has been measured with a Fabry–Perot interferometer.⁽³,⁶⁾ The observed line is a single Lorentzian, of half width $(\Gamma/2\pi)$. Γ is small (in the megacycle range) when $T = T_c$, and increases with T. The presence of only one Lorentzian is remarkable, and will be discussed in detail in section 4.

More generally, the aim of the present paper is to give a unified discussion of short range order effect, in terms of a Landau model for the nematic isotropic transition. The principles have been sketched in an earlier short communication.⁽⁷⁾ The first problem is to define an adequate order parameter—here a tensorial object $Q_{\alpha\beta}$, as explained in section 2. Then we assume that the free energy F may be expanded in powers of $Q_{\alpha\beta}$: the symmetry properties of $F(Q)$ then force the transition to be first order. However, just above

T_c, the fluctuations may be large. This is discussed in section 3, together with some static applications, including effects (a) and (b) above, plus the properties of the nematic/isotropic interface. Section 4 discusses the dynamics of fluctuations, using the thermodynamics of irreversible processes as a framework, and including the coupling between molecular rotation and flow. Finally we try to extend these considerations to cholesteric materials: the new feature here is the presence of a term proportional to Q grad Q in the free energy. We discuss the physical implications of this unusual term on the static optical properties in section 5.

2. Definition of an Order Parameter

(a) *microscopic approach*: For a system of rod-like molecules, the natural order parameter, in a nematic phase, is

$$S = \langle \tfrac{1}{2}(3 \cos^2\theta - 1) \rangle \tag{2.1}$$

where θ is the angle between rod axis and nematic axis. For rigid molecules of more general shape, a natural generalisation of (2.1) amounts to use

$$S_{ij}^{\alpha\beta} = \langle \tfrac{1}{2}(3 i_\alpha j_\beta - \delta_{ij}\,\delta_{\alpha\beta}) \rangle \tag{2.2}$$

where i, j, k are three orthonormal vectors linked to the molecule, while α and β are indices referring to the laboratory frame. In a uniaxial nematic of optical axis parallel to z, the only non 0 components of $S_{ij}^{\alpha\beta}$ are the following

$$\left.\begin{aligned} S_{ij}^{zz} &= S_{ij} \\ S_{ij}^{xx} = S_{ij}^{yy} &= -\tfrac{1}{2}S_{ij} \end{aligned}\right\} \tag{2.3}$$

(b) *macroscopic approach*: Many nematic molecules are partly flexible, and different parts of one same molecule would give different S_{ij} tensors. Also, from a thermodynamic point of view, it is preferable to define the amount of order from a macroscopic property, independently of any assumption on the rigidity of the molecules. Consider for instance the anisotropy of the magnetic susceptibility: let us define(8)

$$Q_{\alpha\beta} = \chi_{\alpha\beta} - \tfrac{1}{3}\chi_{\gamma\gamma}\,\delta_{\alpha\beta} \tag{2.4}$$

$Q_{\alpha\beta}$ is a symmetric, traceless tensor: we call it the *tensor order parameter*. It must be emphasized that any other tensor property (i.e. the dielectric constant $\epsilon_{\alpha\beta}$) could have been used to define $Q_{\alpha\beta}$. In the isotropic phase, where $Q_{\alpha\beta}$ is small, any other anisotropic effect is linear in Q. For instance we may write

$$\delta\epsilon_{\alpha\beta} \equiv \epsilon_{\alpha\beta} - \tfrac{1}{3}\epsilon_{\gamma\gamma}\,\delta_{\alpha\beta} = M_{\alpha\beta\gamma\delta}\,Q_{\gamma\delta} \tag{2.5}$$

The only matrix M relating two symmetric traceless tensors ($\delta\epsilon$ and Q) and compatible with rotational invariance is a multiple of the unit matrix. Thus Eq. (1) reduces to

$$\delta\epsilon_{\alpha\beta} = M\,Q_{\alpha\beta} \tag{2.6}$$

For simple rod-like molecules M is simply the ratio of dielectric/magnetic anisotropies in the ordered phase.

We have chosen here to define $Q_{\alpha\beta}$ through the diamagnetic anisotropy for the following reason: theoretical calculations of $\chi_{\alpha\beta}$ are feasible, since magnetic interactions between different molecules are negligible. For instance, with a rigid molecule, let us assume that we know the suspectibility tensor (per molecule) in the molecular frame χ^{ij}. Then $\chi_{\alpha\beta}$ is simply a superposition of individual responses, and if n is the number of molecules/cm^3, we may write

$$Q_{\alpha\beta} = nS^{\alpha\beta}_{ij}\,\chi^{ij}$$

In a uniaxial nematic, the difference between parallel and perpendicular susceptibilities is

$$\chi_{\parallel} - \chi_{\perp} = Q_{zz} - Q_{xx} = \tfrac{3}{2}S_{ij}\,\chi^{ij} \tag{2.7}$$

Equation (2.7) gives, for rigid molecules, the link between the microscopic definition of order (via S) and the macroscopic (via Q). If we had chosen to define Q from the dielectric anisotropy, we could not have produced such explicit formulae—the present theory of dielectric constants in liquids being unable to take into account correctly the electric interactions between different molecules.

(c) *biaxial versus uniaxial nematics*: Our definition of the order parameter covers both uniaxial and biaxial nematic systems: the matrix $Q_{\alpha\beta}$, when diagonalized, may have the form

$$Q_{\alpha\beta} = \begin{bmatrix} \dfrac{-Q+P}{2} & & 0 \\ 0 & \dfrac{-Q-P}{2} & 0 \\ 0 & & Q \end{bmatrix} \tag{2.8}$$

Depending on the form of the free energy F as a function of Q and P, the minimum of F may correspond to $P = 0$ (uniaxial nematic) or $P \neq 0$ (biaxial nematic). The possible existence of biaxial phases has been stressed in particular by Freiser.⁽⁹⁾

3. Free Energy and Static Properties

3.1. LANDAU EXPANSION OF THE FREE ENERGY

Let us assume that the free energy F (per unit volume) may be expanded in powers of $Q_{\alpha\beta}$. Then, retaining only terms which have rotational invariance, we may expect the following structure

$$F = F_0 + \tfrac{1}{2}AQ_{\alpha\beta}Q_{\beta\alpha} + \tfrac{1}{3}BQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + 0(Q^4) - \tfrac{1}{2}Q_{\alpha\beta}H_\alpha H_\beta \qquad (3.1)$$

where F_0 is independent of Q. Because Q is symmetric traceless there is only one invariant of order Q^2 (with the coefficient $A/2$) and one invariant of order Q^3 (there would be two invariants of order Q^4). $A(T)$ is expected to be small near T_c. More precisely we can put

$$A(T) = a(T - T^*)^\gamma \qquad (3.2)$$

where T^* is a temperature slightly below T_c, and γ an unknown exponent.

($\gamma = 1$ in a mean field theory such as the Maier Saupe theory.)

The last term in (3.1) is the anisotropic part of the diamagnetic energy, in a field H. The presence of a cubic term BQ^3 in (3.1) imposes a first order transition, as explained in Fig. 1. If one assumed that an expansion to order Q^4 is acceptable even in the ordered phase, one could derive formulas for the order parameter just below T_c, the latent heat, etc; however, it is not obvious that the terms of order Q^5, etc., are indeed negligible in the ordered phase. For this reason we shall mainly restrict our attention to the isotropic phase ($T > T_c$) where Q is indeed small.

3.2. APPLICATION TO THE MAGNETIC BIREFRINGENCE

In a non 0 external field, the minimum of F (Eq. 3.1) corresponds to a non 0 Q, i.e. to a finite anisotropy in the optical properties. Minimizing F with respect to $Q_{\alpha\beta}$, and keeping in mind the constraint of 0 trace ($Q_{\alpha\alpha} = 0$) one finds (to order H^2) for the thermal average of Q:

$$\langle Q_{\alpha\beta} \rangle = \frac{1}{2A}(H_\alpha H_\beta - \tfrac{1}{3} H^2 \delta_{\alpha\beta}) \qquad (3.3)$$

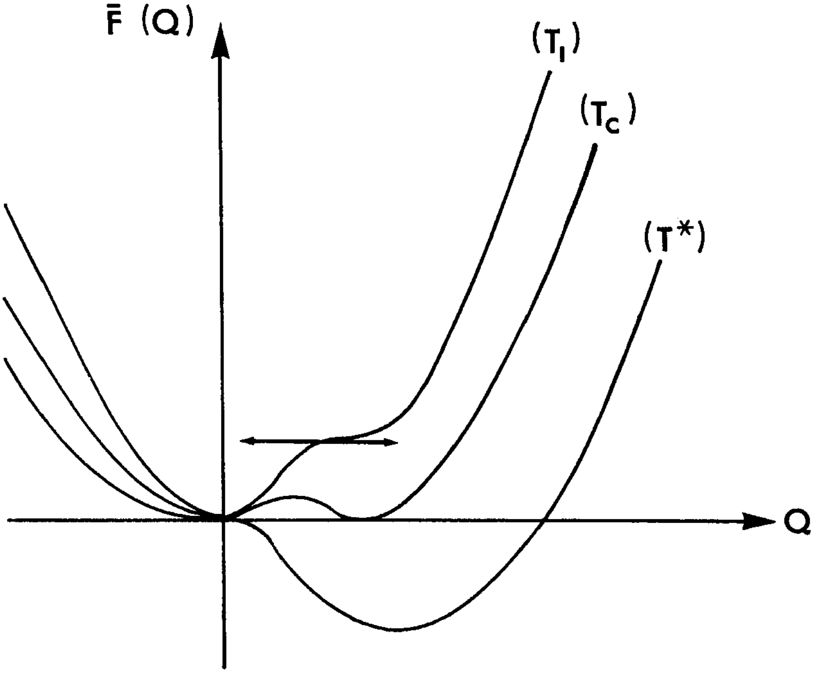


Figure 1. Plot of free energy $\bar{F}$ versus order parameter Q, in zero magnetic field, at various temperatures. T_c is the equilibrium transition point. T^* is the temperature below which the isotropic phase is absolutely unstable. T_1 is the temperature above which the nematic phase is absolutely unstable.

Take for instance H along Z. Then

$$Q_{zz} - Q_{xx} = \frac{H^2}{2A}$$

and from Eq. (2.6), the dielectric anisotropy is

$$\delta\epsilon_{zz} - \delta\epsilon_{xx} = \frac{MH^2}{2A}$$

(where ϵ and M are defined for the frequency of the optical measurement)

Finally the birefringence is obtained by writing $n_\parallel{}^2 = \epsilon_{zz}$, $n_\perp{}^2 = \epsilon_{xx}$

$$n_\parallel - n_\perp = \frac{MH^2}{4A\bar{n}} = \alpha(T)H^2 \tag{3.4}$$

We do not expect any strong variation in M or $\bar{n}$ near T_c, thus

$1/\alpha(T)$ is essentially proportional to $A(T)$. The existing data suggest that $1/\alpha$ is nearly linear in T ($\gamma \cong 1$).

3.3. Definition of Coherence Lengths

Let us now add terms in F which can describe situations where the order parameter varies slowly from point to point. In a nematic fluid, the first terms allowed by symmetry are quadratic in the gradients of Q and have the form

$$F_g = \tfrac{1}{2}L_1 \partial_\alpha Q_{\beta\gamma} \partial_\alpha Q_{\beta\gamma} + \tfrac{1}{2}L_2 \partial_\alpha Q_{\alpha\gamma} \partial_\beta Q_{\beta\gamma} \tag{3.5}$$

where $\partial_\alpha \equiv \partial/\partial x_\alpha$. L_1 and L_2 may be called the elastic constants in the isotropic phase. Their number is smaller than in the ordered phase (where there are three constants$^{(10)}$) because in Eq (3.5) we restrict our attention to terms of order Q^2, i.e. to small Q. To get more information on the meaning of L_1 and L_2 let us consider the case where Q depends only on one co-ordinate, say z. Then

$$F_g = \frac{L_1}{2}[(\partial_z Q_{zz})^2 + (\partial_z Q_{xx})^2 + (\partial_z Q_{yy})^2] + L_1[(\partial_z Q_{xy})^2 + (\partial_z Q_{yz})^2 + (\partial_z Q_{zx})^2] + \frac{L_2}{2}[(\partial_z Q_{zz})^2 + (\partial_z Q_{zx})^2 + (\partial_z Q_{zy})^2] \tag{3.6}$$

From Eq. (3.6) we may derive a number of inequalities which must be satisfied by the elastic constants to ensure stability (i.e., F_g must be positive for all distortions of Q).

Let us start with a situation where Q_{xy} is the only non-vanishing component. Then from Eq. (3.6) we get the stability condition

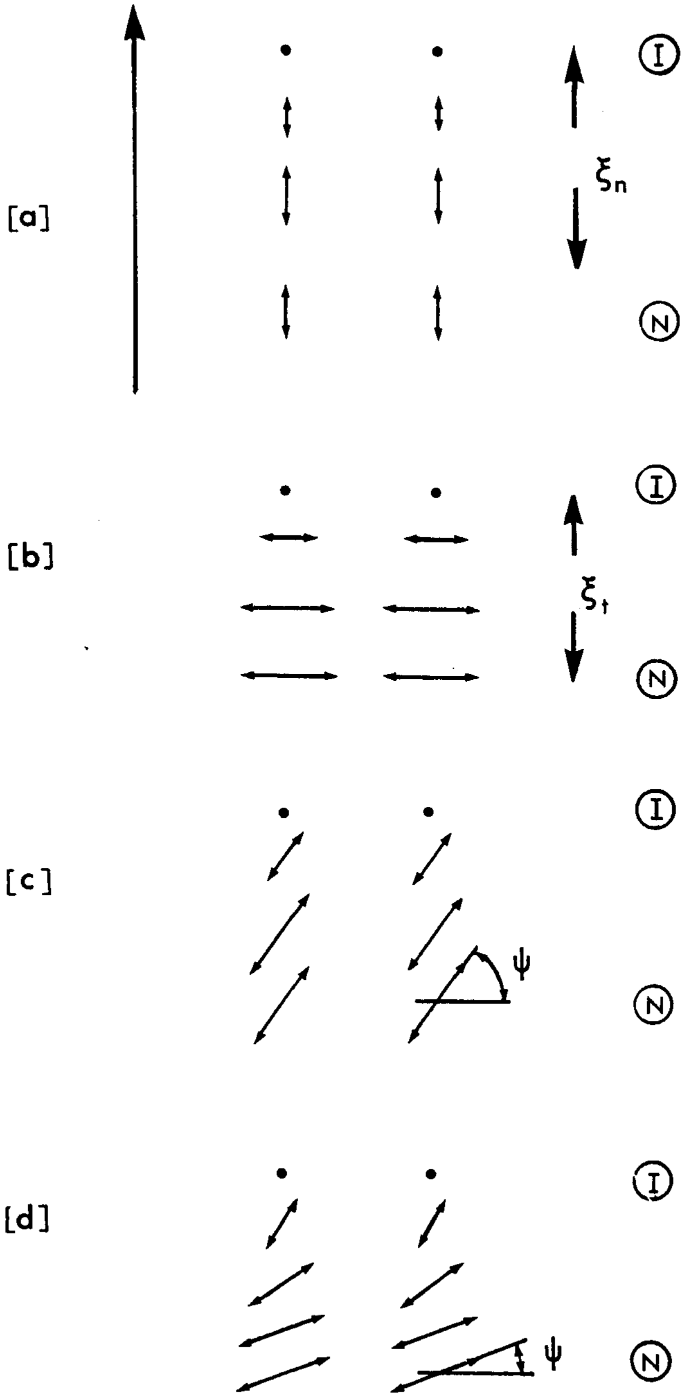
$$L_1 > 0 \tag{3.7}$$

Similarly with Q_{xz} (or Q_{yz}) we obtain

$$L_1 + \tfrac{1}{2}L_2 > 0 \tag{3.8}$$

Considerations involving the diagonal terms Q_{xx}, Q_{yy}, Q_{zz} are more delicate because the sum of these three terms must vanish identically. Let us consider first a case where, at all points, the nematic axis is parallel to $0z$. (Fig. 2a) (at $T = T_c$, this would describe a nematic/isotropic interface with the optical axis normal to the interface). In such a situation we may put

$$Q_{zz} = Q \quad Q_{xx} = Q_{yy} = -\frac{Q}{2} Q_{xy} = Q_{yz} = Q_{zx} = 0$$


[a]
[b]
[c]
[d]
ξ_n
ξ_t
ψ
ψ
Ⓘ
Ⓝ

and we get from Eq. (3.6)

$$F_g = \frac{3L_1 - 2L_2}{4}\left(\frac{\mathrm{d}Q}{\mathrm{d}z}\right)^2 \tag{3.9}$$

Adding the other terms of order Q^2 from Eq. (3.1) we get for the free energy

$$\begin{aligned} F = \bar{F} + F_g &= \tfrac{3}{4}AQ^2 + \frac{3L_1 + 2L_2}{4}\left(\frac{\mathrm{d}Q}{\mathrm{d}z}\right)^2 \\ &= \tfrac{3}{4}A\left[Q^2 + \xi_n^2\left(\frac{\mathrm{d}Q}{\mathrm{d}z}\right)^2\right] \end{aligned} \tag{3.10}$$

$$\xi_n^2(T) = \frac{(L_1 + \frac{2}{3}L_2)}{A(T)} \tag{3.11}$$

where we have defined the " normal coherence length " $\xi_n(T)$. ξ_n^2 must be positive = this implies the inequality

$$L_1 + \tfrac{2}{3}L_2 > 0$$

Now let us go the tangential case of Fig. (2b). Here we assume

$$Q_{xx} = Q \quad Q_{yy} = Q_{zz} = -\frac{Q}{2} \; Q_{xy} = Q_{yz} = Q_{zx} = 0$$

and we obtain for the free energy, to order Q^2

$$F = \tfrac{3}{4}A\left[Q^2 + \xi_t^2(T)\left(\frac{\mathrm{d}Q}{\mathrm{d}z}\right)^2\right] \tag{3.12}$$

where the " tangential coherence length " $\xi_t(T)$ is given by

$$\xi_t^2(T) = (L_1 + \tfrac{1}{6}L_2)\frac{1}{A(T)} \tag{3.13}$$

We also have the stability requirement:

$$L_1 + \tfrac{1}{6}L_2 > 0$$

but, if the conditions (3.7) and (3.11) are satisfied, the other conditions will also be satisfied. The two lengths ξ_n and ξ_t are expected

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Figure 2. Possible structures for the nematic/isotropic interface:
(a) normal case; (b) tangential case; (c) conical case with constant angle in the transition layer; (d) conical case with variable angle.

to be comparable in magnitude (for qualitative discussions we will sometimes replace them by a single length $\xi(T)$). Near T_c the coherence lengths are large (but finite) since $A(T_c)$ is small (but non 0). Qualitatively, neglecting all indices, and neglecting the difference between ξ_n and ξ_t) we may say that the QQ correlation function has the form:

$$\langle Q(0)\, Q(R)\rangle = \frac{\text{const. } k_B T}{L_1 R}\, e^{-R/\xi} \quad (R \gtrsim \xi) \tag{3.14}$$

At first sight we might hope to measure the coherence lengths ξ_n and ξ_t (or suitable admixtures of these two) by a study of the scattered light intensity I. However, the data of Litster and Stinson$^{(6)}$ show that I is essentially independent of the scattering wave vector q. This means then $q\xi \ll 1$ and in this limit we cannot measure ξ.

The magnitude of the scattered intensity is easily derived for $q\xi \ll 1$. Consider for instance the case where the incident light is polarized along x, while the outgoing light is polarized along y. The corresponding intensity $I_\perp$ is proportional to the average square.

$$I_\perp \cong \langle |\delta\epsilon_{zx}|^2\rangle = M^2 \langle Q_{zx}^2\rangle \tag{3.15}$$

To order Q^2 the only terms in the free energy (3.1) involving Q_{zx} are $\frac{1}{2}A(Q_{zx}^2 + Q_{xz}^2) = AQ_{zx}^2$. The gradient terms (3.5) are negligible for $g\xi \ll 1$. Then applying the equipartition theorem gives (per unit volume)

$$A\langle Q_{zx}^2\rangle = \tfrac{1}{2}k_B T$$

$$I_\perp \cong \langle |\delta\epsilon_{zx}|^2\rangle = \frac{M^2 k_B T}{2A}. \tag{3.16a}$$

Similarly, when both polarizations are parallel to X, we get

$$I_\parallel \cong \langle |\delta\epsilon_{zz}|^2\rangle = \tfrac{2}{3}\frac{M^2 k_B T}{A} \tag{3.16b}$$

Thus the intensities are proportional to $1/A$. This has been verified by Stinson and Litster.$^{(6)}$

3.4. THE NEMATIC/ISOTROPIC INTERFACE

In the present paragraph we shall assume that the distortion free energy is correctly described by Eq. (3.5), even when the variations of Q take place in a distance comparable to $\xi(T)$. (This is equivalent to a mean field approximation). We can then apply our earlier Eqs. (3.10) and (3.12) to a discussion of the N/I interface, at $T = T_c$. Here Q goes from a finite value (at $z = -\infty$) to 0 (at $z = +\infty$), the variations taking place in a thickness $\xi(T_c)$ which is large compared with the molecular dimensions a.

Consider first the "normal' case where Q has the structure defined immediately before Eq (3.9). We may write the surface tension γ_r in the form

$$\gamma_n = \int_{-\infty}^{\infty} \mathrm{d}z \left[\bar{F}(Q) + b_n^2 \left(\frac{\mathrm{d}Q}{\mathrm{d}z} \right)^2 \right] \tag{3.17}$$

Here $b_n^2 = (3L_1 + 2L_2)/4$ and $\bar{F}(Q)$ is the free energy (3.1), including now all powers of Q. The origin of free energies is such that $\bar{F}(0) = \bar{F}(Q^*) = 0$ where Q^* is the order parameter in the nematic phase, at $T = T_c$. Writing that the form of $Q(z)$ minimizes γ we get the equation

$$2b_n^2 \frac{\mathrm{d}^2 Q}{\mathrm{d}z^2} = \frac{\partial \bar{F}}{0Q} \tag{3.18}$$

This equation has the first integral

$$b_n^2 \left(\frac{\mathrm{d}Q}{\mathrm{d}z} \right)^2 = \bar{F}(Q) \tag{3.19}$$

where the integration constant must vanish, since both $\mathrm{d}Q/\mathrm{d}z$ and $\bar{F}(Q)$ are zero far from the transition layer. Inserting Eq. (3.19) into (3.17) we get

$$\gamma_n = 2\int_{-\infty}^{\infty} b_n^2 \frac{\mathrm{d}Q}{\mathrm{d}z} \mathrm{d}Q = 2b_n \int_0^{Q^*} [\bar{F}(Q)]^{1/2} \mathrm{d}Q \tag{3.20}$$

Similarly, for the tangential case, we get

$$\left. \begin{aligned} \gamma_t &= 2b_t \int_0^{Q^*} [\bar{F}(Q)]^{1/2} \mathrm{d}Q \\ b_t^2 &= \tfrac{1}{4}(3L_1 + \tfrac{1}{2}L_2) \end{aligned} \right\} \tag{3.21}$$

Comparing (3.20) and (3.21) we see that, if $L_2 > 0$, b_t is smaller than b_n, and $\gamma_t < \gamma_n$ = *the tangential conformation is favoured.* On the other hand, if $L_2 < 0$, the normal conformation is favoured.

A word of caution should be inserted at this point: the actual conformation at the interface may be different from the normal and tangential cases considered above. In macroscopic terms, we may say that the preferred angle between the director and the N/I surface need not be 0, or $\pi/2$: it might be some intermediate angle. To compute the interface tension γ for such cases is difficult. We have only carried out a simple variational calculation, assuming that at all points in the transition layer the medium is uniaxial, with an optical axis which is the same everywhere (making a constant angle ψ with the surface—Fig. 2c). Within this approximation we can show that the minimum of γ occurs either at $\psi = 0$ if $L_2 > 0$) or at $\psi = \pi/2$ if $L_2 < 0$), but not at an intermediate ψ value. But a much more elaborate calculation would be required to elucidate this point completely.

4. Dynamics of Fluctuations

4.1. FLUXES AND FORCES

In the nematic phase we know both from theory[5] and from experiment[11] than an orientational fluctuation of wave vector q relaxes in a purely viscous way (no oscillations) with a time constant τ_g given qualitatively by

$$\frac{1}{\tau_g} \cong \frac{Kg^2}{\eta_{\text{eff}}} \tag{4.1}$$

where K is an average of the Frank elastic constants,[10] and η_{eff} an average viscosity. This result suggests that, above T_c, where the fluid is more disordered, we will also find a strongly dissipative behaviour: such a behaviour may then be analyzed in terms of the thermodynamics of irreversible processes, introducing *fluxes* and *forces*.

(a) *Fluxes*. One group of such fluxes is given by the rate of change in time of $Q_{\alpha\beta}$

$$R_{\alpha\beta} = \frac{\delta Q_{\alpha\beta}}{\delta t} \tag{4.2}$$

The differentiation symbol $\delta/\delta t$ denotes the variation (along one flow line) with respect to the background fluid; in particular, if the fluid is in rotation, the part of the change of Q due to this rotation must be subtracted, as explained in Ref. (7). However, in all what follows, we shall treat v_α and $Q_{\alpha\beta}$ as infinitesimal quantities of first order. Then the difference between $\delta/\delta t$ and the partial derivative $\partial/\partial t$ is of second order and may be neglected:

$$R_{\alpha\beta} \to \frac{\partial Q_{\alpha\beta}}{\delta t} \tag{4.3}$$

Another group of fluxes which is important here is the hydrodynamic shear rate tensor

$$e_{\alpha\beta} = \partial_\alpha v_\beta + \partial_\beta v_\alpha \tag{4.4}$$

We restrict our attention to incompressible flow ($e_{\alpha\alpha} \equiv 0$). As explained in Ref. (5), this appears to be justified because the fluctuations of Q have a frequency spectrum much lower than the sound waves.

(b) *Forces.* The force $\phi_{\alpha\beta}$, conjugate to $Q_{\alpha\beta}$, may be obtained directly from the free energy F (e.g., 3.1, 3.5). We restrict our attention to terms of F which are quadratic on Q, giving linear contributions to ϕ. Furthermore, in most of the applications to be discussed below, the wave vectors q of interest will turn out to be small ($q\xi \ll 1$) and the derivative terms from (3.5) will be negligible; then:

$$\phi_{\alpha\beta} = \frac{-\delta F}{\delta Q_{\alpha\beta}} = -AQ_{\alpha\beta}. \tag{4.5}$$

The force conjugate to $e_{\alpha\beta}$ is $\frac{1}{2}\sigma_{\alpha\beta}$, where $\sigma_{\alpha\beta}$ is the viscous stress tensor.

Finally the entropy source may be written as a bilinear function of fluxes and forces

$$TS = \phi_{\alpha\beta} R_{\alpha\beta} + \tfrac{1}{2}\sigma_{\alpha\beta} e_{\alpha\beta} \tag{4.6}$$

Our choice of fluxes and forces purposely omits certain effects (such as temperature fluctuations) which are not anomalously large and not strongly coupled to the order parameter Q.

4.2. HYDRODYNAMIC EQUATIONS IN THE ISOTROPIC PHASE

We now write down a phenomenological system of linear equations coupling the fluxes and the forces. Since all these quantities are symmetric traceless tensors of rank 2, the most general form for these equations, which is compatible with rotational invariance and the Onsager relations, is⁽¹²⁾:

$$\tfrac{1}{2}\sigma_{\alpha\beta} = \tfrac{1}{2}\eta\, e_{\alpha\beta} + \mu R_{\alpha\beta} \tag{4.7}$$

$$\phi_{\alpha\beta} = \mu\, e_{\alpha\beta} + \gamma R_{\alpha\beta} \tag{4.8}$$

If Q is taken as dimensionless, both R and e have the dimension of frequency. A and σ have the dimension of pressure. The three coefficients η, μ, ν have the dimension of a viscosity.

Imposing that the entropy source (4.6) be positive leads to the inequality

$$2\mu^2 > \nu\eta \tag{4.9}$$

In addition we need the hydrodynamic acceleration equation

$$\rho\frac{dv_\alpha}{dt} \sim \rho\frac{\partial v_\alpha}{\partial t} = \partial_\beta\sigma_{\alpha\beta} - \partial_\beta p \tag{4.10}$$

where ρ is the density and p the scalar pressure, Eqs. (4.5, 8, 9, 10) together with the incompressibility condition ($e_{\alpha\alpha} = 0$) define entirely the problem of small motions.

4.3. Discussion of Experiments

(a) *flow birefringence*: with a flow velocity v along x, and a velocity gradient $e_{xz} = \partial v/\partial z$, we have a steady state ($R_{\alpha\beta} = 0$) corresponding to $\phi_{xz} = \mu\, e_{xz}$ from Eq. (4.8). Inserting Eq. (4.5) for ϕ_{xz} we arrive at

$$Q_{xz} = -\frac{\mu}{A}\frac{\partial v}{\partial z} \tag{4.11}$$

all other components of Q being 0. This implies that two principal axes of the Q tensor (1) and (2) are the bisectors of the x and z axis. The dielectric anisotropy is

$$|\epsilon_1 - \epsilon_2| = M\, Q_{11} - Q_{22}| = MQ_{xy} \tag{4.12}$$

The difference in refracting indices is

$$|n_1 - n_2| = \frac{M}{2n}|Q_{xy}| = \left|\frac{M\mu}{2nA}\right|\frac{\partial v}{\partial z} \tag{4.13}$$

Thus the characteristic time $\tau(T)$ defined in Eq. (1.3) is given by

$$\tau(T) = \frac{M\mu}{2nA(T)} \tag{4.14}$$

In Eq. (4.14) the most important temperature effects come from $A(T)$. The factors M and n are probably temperature insensitive. The friction coefficient μ might vary significantly with T. The data of Zvetkov(3) are not accurate enough to decide on this point.

(b) *inelastic scattering of light—simplified treatment*: For small wave vectors q, it turns out that the characteristic frequencies of the fluctuations of Q are very different from the frequencies associated with v. In such case, the coupling between v and Q is uneffective: in the dynamical Eq. (4.8) for $Q_{\alpha\beta}$ we may neglect the v term. Then we find a simple exponential relaxation for $Q_{\alpha\beta}$, involving one single relaxation rate:

$$\frac{\partial Q_{\alpha\beta}}{\partial t} = -\Gamma Q_{\alpha\beta} \tag{4.15}$$

$$\Gamma(T) = \frac{A(T)}{\nu} \tag{4.16}$$

The consequences of Eq. (4.16) have been investigated by Stinson and Litster.$^{(3)}$ Taking $A(T)$ from the magnetic birefringence, they find that the temperature dependence of Γ can be accounted for if one assumes that ν varies in temperature just as the average viscosity η. Cases where Eq. (4.15) is not applicable (because of the coupling between Q and v) will be discussed in paragraph 4.4.

(c) *shear wave attenuation*: Let us assume that the liquid crystal is driven at an angular frequency ω, with shear waves propagating along z, the flow velocity being along x. The shear stress is from Eq. (4.7)

$$\sigma_{xz} = \eta \frac{\partial v}{\partial z} + 2\mu \frac{\partial Q_{xz}}{\partial t} \tag{4.17}$$

and the equation for the order parameter is:

$$\frac{\partial Q_{xz}}{\partial t} + \Gamma Q_{xz} = -\frac{\mu}{\nu}\frac{\partial v}{\partial x} \tag{4.18}$$

Replacing $\partial/\partial t$ by $i\omega$ and eliminating Q_{xz} between (4.17) and (4.18) we arrive at a simplified form of the acceleration equation

$$i\omega\rho v = \eta(\omega)\frac{\partial^2 v}{\partial x^2} \tag{4.19}$$

where the effective viscosity $\eta(\omega)$ is defined by

$$\eta(\omega) = \eta - \frac{2\mu^2}{\nu}\frac{i\omega}{\Gamma + i\omega} \tag{4.20}$$

Thus $\eta(\omega)$ goes from η (for $\omega \ll \Gamma$) to $\eta - (2\mu^2/\nu)$ (for $\omega \gg \Gamma$) Dispersion anomalies in this frequency range have indeed been observed very recently,(13) but it is not known yet whether the simple form (4.20) accounts for them or not.

The concept of an effective viscosity $\eta(\omega)$ applies only when the penetration depth of the shear waves $(\eta/\rho\omega)^{1/2} = \delta$ is much larger than the coherence length $\xi(T)$. This is indeed correct when $\omega \sim \Gamma$, as can be seen from the following argument:

$$\frac{\xi^2}{\delta^2} = \xi^2 \frac{\rho\Gamma}{\eta} \sim \frac{\rho A L_1}{\eta\gamma A} = \frac{L_1\rho}{\eta\gamma} \tag{4.21}$$

The parameter $L_1\rho/\eta\gamma$ is similar in magnitude and in physical content to the parameter $K\rho/\eta^2$ (K = Frank elastic constant) which is central to the discussion of the fluctuation modes in the ordered phase. As pointed out in Ref. (5) this parameter is of order 10^{-4} or less: thus $\xi/\delta \gtrsim 10^{-2}$ and the concept of an effective viscosity is acceptable.

4.4. Coupled Modes of Birefringence and Flow

We now discuss in more detail the coupled relaxation modes of Q and v, for a Fourier component of given wave vector q. The characteristic frequency associated with v is $\eta q^2/\rho$. The characteristic frequency associated with Q is the Litster width Γ. For small q values, these two frequencies are widely different, and the coupling between v and Q has very little influence on the power spectrum of Q, as measured by light scattering: we made use of this observation in paragraph 3b of this section. Here, we shall focus our attention on the opposite case, where both frequencies are comparable:

$$\Gamma \sim \frac{\eta q^2}{\rho} \tag{4.22}$$

It should be emphasized that (4.22) is compatible with our general assumption $q\xi \ll 1$. In fact, from Eq. (4.16) we see that the condition (4.22) corresponds to

$$q\xi \sim \left(\frac{\eta\nu}{L_1\rho}\right)^{1/2} \sim 10^{-2}$$

Let us put the z axis of our reference frame along q ($\partial/\partial x \to 0$ $\partial/\partial y \to 0$ $\partial/\partial z \to iq$). Because of the incompressibility condition we have only two non 0 components of v (v_x and v_y). v_x is coupled to Q_{xz} by Eqs. (4.7, 4.8). Similarly v_y is coupled to Q_{yz}. All the other components of Q ($Q_{zz}, Q_{xx}, Q_{xy}, \ldots$) are not coupled to the hydrodynamic flow, and relax with a single relaxation rate Γ. From now on, we shall concentrate on Q_{xz} and v_x. With suitable polarizations, the light scattering experiment (performed at wave vector q and frequency shift ω) measures the quantity:

$$S(q\omega) = \int \mathrm{d}t < Q_{xy}(-q, 0)\, Q_{xy}(qt)\, e^{-i\omega t} > \; = \; -\frac{k_\beta T}{\pi\omega} IM[\chi(q\omega)] \tag{4.23}$$

$\chi(q\omega)$ is a response function giving Q_{xy} when the system is submitted to an external perturbation ($H_x H_z$) modulated at wave vector q and frequency ω. Equation (4.23) is a statement of the fluctuation dissipation theorem for χ. Our use of response functions is similar in spirit to Ref. (5). χ may be derived very directly from Eqs. (4.7, 4.8, 4.10), which give, after inclusion of the external pertubation:

$$iq\frac{\mu}{\nu} v_x + (i\omega + \Gamma) Q_{xz} = \Gamma \chi_0 H_x H_z \tag{4.24}$$

$$\left(i\omega + \frac{\eta}{\rho} q^2\right) v_x + \frac{2\mu}{\rho} q\omega\, Q_{xz} = 0 \tag{4.25}$$

Here $\chi_0 = 1/2A$ is the static susceptibility (Eq. 3.3). Solving Eq. (4.24, 4.25) for $Q_{xz} \equiv \chi(q\omega) H_x H_z$ and taking the imaginary part of χ leads to:

$$S(q\omega) = \frac{k_\beta T}{2\pi\nu} \frac{\omega^2 + ab\, q^4}{(\omega^2 - \Gamma a q^2)^2 + \omega^2(\Gamma + bq^2)^2} \tag{4.26}$$

where

$$a = \frac{\eta}{\rho}$$

$$b = \frac{\eta}{\rho} - \frac{2\mu^2}{\nu\rho}$$

Equation (4.26) shows that in general the power spectrum of Q_{xz} is not composed of a single Lorentzian. However, when $aq^2 \ll \Gamma$ we recover a single Lorentzian of width Γ. In the opposite limit ($aq^2 \gg \Gamma$) we also find a single Lorentzian, but with a modified width:

$$\Gamma' = \frac{a}{b}\Gamma \qquad \left(\frac{\Gamma}{a} < q^2 < \xi^{-2}\right) \tag{4.27}$$

The more complicated scattering law described by Eq. (4.26) has not been observed by Litster and Stinson(2,6) but it might be worthwhile to search for it with suitable q values and polarization indices.

5. Extension to Cholesterics

5.1. STRUCTURE OF THE FREE ENERGY

With an optically active material, it is still possible to define an order parameter $Q_{\alpha\beta}$ by Eq. (2.7). The static magnetic susceptibility tensor is always symmetric, and $Q_{\alpha\beta}$ is symmetric traceless. The expansion of the free energy $\bar{F}$ in powers of Q retains the structure (3.1) and Eq. (3.4) for the magnetic birefringence is always valid. Thus, if T^* is only slightly below T_c, cholesterics will show a large magnetic birefringence anomaly, just like nematics.(14)

New features appear when we investigate the terms involving the gradients of Q in the free energy: symmetry allows for a new term

$$F_c = q_0 L_1 \epsilon_{\alpha\beta\gamma} Q_{\alpha\mu} \partial_\gamma Q_{\beta\mu} \tag{5.1}$$

In this formula $\epsilon_{\alpha\beta\gamma}$ is the alternant symbol ($\epsilon_{xyz} = 1$, $\epsilon_{xx\alpha} = 0$, etc.) and is antisymmetric with respect to all pairs of indices. The energy density F_c is a pseudoscalar, and its coefficient must vanish in a nematic. But in a cholesteric F_c must be included: the complete free energy contains (a) the term $\bar{F}$ for a uniform Q; (b) the term F_c (linear in grad Q); (c) the usual term F_g quadratic in the gradients (Eq. 3.5). The coefficient in F_c has been written as $q_0 L_1$ where L_1 is still defined by Eq. (3.5), and q_0 has the dimension of an inverse length. Qualitatively we may say that $2\pi/q_0$ is the helical pitch which the isotropic phase would tend to display for T just above T_c. We shall now explore some consequences of the presence of F_c in the free energy.

5.2. INTENSITY OF LIGHT SCATTERING

Let us now discuss the magnitude of the fluctuations of Q for a Fourier component of given wave vector q. As in section 4, we take our z axis parallel to Q. From Eqs. (3.1, 3.5 and 5.1) we get for the free energy associated with this Fourier component, to order Q^2:

$$\begin{aligned} F(q) = {} & \tfrac{1}{2}(A + L_1 q^2)[\tfrac{3}{2}Q^2 + \tfrac{1}{2}\underline{P}^2 + 2(|Q_{xy}|^2 + |Q_{yz}| + Q_{zx}{}^2|)] \\ & + \tfrac{1}{2}L_2 q^2[Q^2 + |Q_{xz}|^2 + |Q_{zy}|^2] \\ & + 2q_0 L_1[P'' Q'_{xy} - \underline{P'} Q''_{xy} + Q''_{xz} Q'_{yz} - Q'_{xz} Q''_{yz}] \end{aligned} \tag{5.2}$$

In Eq. (5.2) we have used the notation of Eq. (2.8) for the diagonal components of $Q_{\alpha\beta}$. We have also analyzed the Fourier component $Q_{\alpha\beta}(q)$ in its real and imaginary part $Q_{\alpha\beta}(q) = Q'_{\alpha\beta}(q) + iQ''_{\alpha\beta}(q)$. Diagonalizing the quadratic form (5.2) and applying the equipartition theorem we arrive at the following averages:

$$\langle Q_{zz}\rangle \equiv \langle Q^2\rangle = \frac{2k_\beta T}{3(A+L_1 q^2)+2L_2 q^2} \tag{5.3}$$

$$\langle |Q_{xy}|^2\rangle = \tfrac{1}{4}\langle \underline{P}^2\rangle = \frac{k_\beta T(1+\xi_1^2 q^2)}{2A[(1+\xi_1^2 q^2)^2 - 4q_0^2 q^2 \xi_1^4]} \qquad \xi_1^2 = \frac{L_1}{A} \tag{5.4}$$

$$\langle |Q_{xz}|^2\rangle = \langle |Q_{yz}|^2\rangle = \frac{k_\beta T\tilde{A}}{2[\tilde{A}^2 - q_0^2 L_1^2 q^2]} \tag{5.5}$$

$$\tilde{A} = A + (L_1 + \tfrac{1}{2}L_2)\, q^2$$

The fluctuations of Q_{zz}, as defined by Eq. (5.3), are not different from what they are in the nematic state. But all other averages are modified. Let us focus our attention on $I_{xy}(q) = \langle |Q_{xy}|^2\rangle$. Examination of Eq. (5.5) shows the following features

–if $q_0\,\xi_1(T) < \frac{1}{2}$ the maximum of $I_{xy}(q)$ is at $q = 0$

as it is in a nematic

–if $q_0\,\xi_1(T) > \frac{1}{2}$ the maximum of $I_{xy}(q)$ is at *a*

finite q (comparable to q_0): we then have a broad scattering peak which is reminiscent of the Bragg peak in the ordered phase.

However $q_0\,\xi_1$ cannot become much larger than $\frac{1}{2}$: in fact, if $q_0\,\xi_1$ would reach the value 1, the fluctuations $\langle |Q_{ky}|^2\rangle$ would diverge for $q = q_0$. The temperature T^{**}, such that $q_0\,\xi_1(T^{**}) = 1$, is thus the temperature below which the isotropic phase is absolutely unstable. A first order transition from isotropic to cholesteric must occur (because of the Q^3 terms in F) at a temperature $T_c > T^{**}$. Thus $q_0\,\xi(T_c) < 1$.

In many cases we may in fact have $q_0\,\xi(T_c) < \frac{1}{2}$: then $I_{xy}(q)$ has a central peak at all temperatures above T_c, and the tendency to build up a spiral is not strongly apparent in the properties of the isotropic phase.

A similar discussion can be carried out for the components Q_{xz} and Q_{yz}, with qualitatively similar conclusions. It can be shown, however, (using the inequalities of section III on L_1 and L_2) that the fluctuations of Q_{xy} are more singular: if we were able to supercool below T_c, the onset of instability would occur (at $T = T^{**}$) through Q_{xy}, while Q_{xz} is still comparatively small.

5.3. Optical Rotation at Long Wavelengths

Cholesterics in their ordered phase show a huge optical rotation: thus, if the cholesteric → isotropic transition is nearly of second order, we might, at first sight, expect a large optical rotation just above T_c. This is not correct, however, as shown by the following argument.

To derive the optical rotation we essentially look at the forward scattering amplitude for a process where a photon is absorbed at point (1), a virtual photon propagates from (1) to (2), and a final photon is emitted from (2). This gives a second order correction to the non local polarisability tensor, proportional to

$$p_{\alpha\beta}(\mathbf{R}) = \langle Q_{\alpha\gamma}(\mathbf{r}_1)\, T_{\gamma\mu}(\mathbf{R})\, Q_{\mu\beta}(\mathbf{r}_2)\rangle$$
$$\mathbf{R} = \mathbf{r}_1 - \mathbf{r}_2 \qquad (5.6)$$

Here $T_{\gamma\mu}$ represents the virtual photon propagator, and in the long wavelength limit ($\lambda \gg R$) it essentially describes the field of a static dipole:

$$T_{\gamma\mu} = \frac{1}{R^3}\,\delta_{\gamma\mu} - \frac{3}{R^5}\,R_\gamma R_\mu \qquad (5.7)$$

The optical rotation is proportional to Ω/λ^2, where Ω is the integral:

$$\Omega = \int d\mathbf{R}\, p_{xy}(\mathbf{R})\, R_z \qquad (5.8)$$

Ω may be computed in detail from the Eqs. (5.4 and 5.5). Qualitatively, we may estimate Ω as follows: the chiral part of the $\langle QQ\rangle$ correlation function which occurs in (5.6) is of order

$$\langle Q(0)\, Q(\mathbf{R})\rangle_{\text{chiral}} \simeq \frac{k_B T}{L_1 R}\, e^{-R/\xi}\, q_0 R \qquad (5.9)$$

Inserting this in (5.8) we have

$$\Omega \sim q_0 \int 4\pi R^2\, \mathrm{d}R\, \frac{1}{R^2}\, \frac{k_\beta T}{L_1}\, e^{-R/\xi} \sim \text{const}\, \frac{k_\beta T}{L_1}\, q_0\, \xi \qquad (5.10)$$

We have seen that $q_0 \xi \gtrsim 1$. Thus $\Omega \sim k_\beta T/L_1$ is non singular near T_c. It is our hope that this point will soon be checked experimentally.

6. Concluding Remarks

We know that there are spectacular short range effects in the isotropic phase of nematics, and we know how to correlate them in terms of a small number of phenomenological constants. We do not have, however, any measurement of the coherence lengths ξ_n and ξ_t; light scattering involves wavelengths which are too large; studies on the reflectance of the nematic/isotropic interface might be helpful. Qualitatively, since the enhancement factor found in the magnetic birefringence or the flow birefringence reaches values of order 100, we expect the ratio coherence length/molecular length to be of order $\sqrt{100} \sim 10$.

Another attractive direction for experimental work is the study of *metastable phases*. Is it possible to observe a metastable isotropic phase in the small interval $T^* < T < T_c$, and to follow the fluctuations in such a phase? Also, can one measure the temperature T_1 above which the nematic phase is absolutely unstable? Finally, from the nucleation processes of one phase in the other, can one obtain significant information on ξ_n or ξ_t?

All our analysis has been restricted to properties which are quasi-macroscopic (spatial variations slow on the molecular scale). However, certain microscopic properties can be estimated from it: in particular the Pincus calculation of nuclear relaxation rates(15) may be extended to temperatures above T_c, using equations such as (5.26), suitably generalized to cover situations where $q\xi \sim 1$. A qualitative estimate has been described in Ref. (7), but more detailed calculations are clearly required.

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