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Fluctuations and light scattering in liquid crystals

A Yu Val'kov, V P Romanov, A N Shalaginov

Contents

Abstract. The review is devoted to theoretical and experimental problems in the study of liquid crystals by light scattering methods. Nematic, cholesteric, and smectic liquid crystals in the isotropic and ordered phases are considered. The possible types of fluctuations are discussed for each phase. In the isotropic phase, special attention is devoted to pretransition phenomena. The influence on light scattering by unusual properties of liquid crystals such as the marked anisotropy, gyrotropy, and the presence of a regular periodic structure is examined in detail. The characteristic features of Green's function of Maxwell's equations for such media are discussed. The influence of the finite size and of the surface effects in the liquid crystal on the fluctuations and light scattering is considered. The problem of taking into account multiple scattering is discussed. The theoretical results are illustrated by the available experimental data.

A Yu Val'kov St Petersburg Institute of Trade and Economics,
194018 St Petersburg. Fax 7(812)247-81-54,
E-mail apver@onti.phys.lgu.spb.su
V P Romanov Faculty of Physics, St Petersburg State University,
198904 Petrodvorets, St Petersburg
Fax 7(812)427-72-40. E-mail: apver@onti.phys.lgu.spb.su
A N Shalaginov Marine Technical University, 198262 St Petersburg
Fax 7(812)113-81-09. E-mail: arcadi@onti.phys.lgu.spb.su

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1. Introduction

After the invention of lasers, the light scattering method became one of the most effective procedures of the investigation of condensed systems. It has been thoroughly developed both experimentally and theoretically and is used successfully in the study of a wide variety of physical systems [1 – 3]. Since the medium is then subjected to a minimal external influence, this method is particularly promising for systems with a high susceptibility, for example a liquid near second-order phase transition points, liquid crystals, etc. However, when light scattering methods were applied to complex objects such as liquid crystals, a whole series of problems arose which had not been previously analysed in detail. These are related primarily to the necessity to consider the fluctuations of the tensor order parameter and sometimes of two and more interacting order parameters [4, 5]. Large scale fluctuations are usually analysed for variables of the scalar type, for example the density or concentration near the critical points [6] or for a vector n-component order parameter [7, 8]. For liquid crystals, the fluctuations of the order parameter are frequently anomalously large and the intensity of scattering by them can exceed the scattering intensity in the usual organic liquids by several orders of magnitude [9 – 11]. Another problem is associated with the unusual optical properties of liquid crystals. The large optical anisotropy, the presence of a regular periodic structure, the characteristic size of which may be of the order of magnitude of the light wavelength, and the anomalously large optical activity may be regarded as such properties [9–14]. Finally, surface effects play a significant role for liquid crystals in small volumes [15]. All these features lead to major complications in the solutions of light scattering problems and to difficulties in the analysis of experimental data.

From the general statistical point of view, the order in liquid crystals is described by the distribution function of molecules with respect to angles and by the microscopic function of the density of molecules. If one is interested solely in the Rayleigh light scattering, then, in describing the order in main types of liquid crystals, one can restrict the treatment to a parameter representing a second rank tensor $R_{\alpha\beta}(\boldsymbol{r},t)$. The tensor $R_{\alpha\beta}$ can be constructed on the basis of any physical quantity with the same tensor dimensions (for example, the magnetic susceptibility, the relative permittivity, etc.) [9, 16].

It is convenient to consider separately the orientation order parameter

$$S_{\alpha\beta}(\boldsymbol{r},\,t)=R_{\alpha\beta}(\boldsymbol{r},\,t)-\tfrac{1}{3}\delta_{\alpha\beta}R_{\gamma\gamma}(\boldsymbol{r},\,t)$$

which is a traceless tensor, and a scalar parameter

$$\rho(\boldsymbol{r},\,t)=\tfrac{1}{3}R_{\gamma\gamma}(\boldsymbol{r},\,t),$$

characterising the microscopic density.

Since we are interested in the problem of light scattering, we shall select henceforth the traceless component of the relative permittivity $\varepsilon_{\alpha\beta}(\boldsymbol{r},t)$ at an optical frequency ω_0 as $S_{\alpha\beta}(\boldsymbol{r},t)$, neglecting the time and spatial dispersions of the tensor ε. In the absence of intrinsic absorption, the tensor $S_{\alpha\beta}(\boldsymbol{r},t)$ can then be regarded as real and symmetrical.

The equilibrium values of $\langle S_{\alpha\beta}(\boldsymbol{r})\rangle=S^{\,0}_{\alpha\beta}(\boldsymbol{r})$ and $\langle\rho(\boldsymbol{r})\rangle=\rho_0(\boldsymbol{r})$, where the $\langle\ldots\rangle$ denotes statistical averaging, are related directly to the type of phase of the liquid crystal. The symmetrical tensor $S^{\,0}_{\alpha\beta}(\boldsymbol{r})$ can be diagonalised in the local coordinate system $\boldsymbol{e}^0_1(\boldsymbol{r}),\boldsymbol{e}^0_2(\boldsymbol{r}),\boldsymbol{e}^0_3(\boldsymbol{r})$:

$$S^{\,0}_{\alpha\beta}(\boldsymbol{r})=\sum_{j=1}^{3}s^0_j(\boldsymbol{r})e^0_{j\alpha}(\boldsymbol{r})e^0_{j\beta}(\boldsymbol{r})\,,\tag{1.1}$$

where s^0_1, s^0_2 and s^0_3 are the eigenvalues of the tensor $S^{\,0}_{\alpha\beta}:s^0_1+s^0_2+s^0_3=0$.

In the isotropic phase (I-phase), $s^0_1=s^0_2=s^0_3$.

The case of a nonzero s^0_j corresponds to the ordered phase of the liquid crystal. If two of the three eigenvalues s^0_1,s^0_2,s^0_3 are identical, then such a phase is locally uniaxial. Otherwise it is locally biaxial. If the system is spatially homogeneous, i.e. $\rho_0(\boldsymbol{r})$, $s^0_j(\boldsymbol{r})$, and $\boldsymbol{e}^0_j(\boldsymbol{r})$ are independent of the point $\boldsymbol{r}$, then it constitutes a uniaxial (N-phase) or a biaxial (N$_2$-phase) nematic liquid crystal (NLC).

In cholesteric liquid crystals (CLC), the $\boldsymbol{e}^0_j(\boldsymbol{r})$ axes rotate helicoidally: $\boldsymbol{e}^0_1(\boldsymbol{r})=[\cos(\boldsymbol{p}_0\cdot\boldsymbol{r}),\sin(\boldsymbol{p}_0\cdot\boldsymbol{r}),0]$, $\boldsymbol{e}^0_2(\boldsymbol{r})=[-\sin(\boldsymbol{p}_0\cdot\boldsymbol{r}),\ \cos(\boldsymbol{p}_0\cdot\boldsymbol{r}),0]$, and $\boldsymbol{e}^0_3(\boldsymbol{r})=\boldsymbol{p}_0/p_0=(0,0,1)$, while the values of $s^0_j(\boldsymbol{r})$ and $\rho_0(\boldsymbol{r})$ are constant. The quantity $2\pi/p_0$ represents the pitch of the cholestric helix. Cholesteric liquid crystals are usually locally uniaxial: $s^0_1=s^0_2$.

In smectic liquid crystals (SLC), the density $\rho_0(\boldsymbol{r})$ is one-dimensionally periodic in space. In the simplest version,

$$\rho_0(\boldsymbol{r})=\rho_{00}+\psi_0\cos(\boldsymbol{q}_0\cdot\boldsymbol{r}-u_0)\,,\tag{1.2}$$

where $2\pi/q_0$ is the period of the smectic layers of the order of magnitude of the molecular size, $\boldsymbol{e}_0=\boldsymbol{q}_0/q_0$ is the direction of the normal to the layers, and u_0 represents the initial phase. If $s^0_1(\boldsymbol{r})=s^0_2(\boldsymbol{r})=\text{const}\neq0$, $\boldsymbol{e}^0_j(\boldsymbol{r})=\text{const}$, and $\boldsymbol{e}^0_3=\boldsymbol{e}_0$, then such a phase corresponds to the smectic A phase (S$_\text{A}$-phase). If $s^0_j(\boldsymbol{r})=\text{const}$ and $\boldsymbol{e}^0_j(\boldsymbol{r})=\text{const}$ but none of the $\boldsymbol{e}^0_j$ $(j=1,2,3)$ axes coincides with $\boldsymbol{e}_0$, then the corresponding phase is a smectic C phase (S$_\text{C}$-phase).

Even more complex liquid crystal phases — smectic B, C*, F, and H phases, discotic phases, etc. exist [4, 5, 9, 10], but we shall not consider them here. For uniaxial liquid crystals, such as smectic A liquid crystals, and also for the vast majority of nematic and cholestric liquid crystals, the equilibrium value of the tensor order parameter $S^{\,0}_{\alpha\beta}$ can be conveniently written in the form

$$S^0_{\alpha\beta}=S_0(n^0_\alpha n^0_\beta-\tfrac{1}{3}\delta_{\alpha\beta})\,;\tag{1.3}$$

where $S_0=-3s^0_2=-3s^0_3$ and $\boldsymbol{n}^0=\boldsymbol{e}^0_1$. The scalar S_0 has the significance of the average degree of order of the long axes of the molecule along the director vector $\boldsymbol{n}^0$ [9].

The fluctuations of the order parameter

$$\varphi_{\alpha\beta}(\boldsymbol{r},\,t)=S_{\alpha\beta}(\boldsymbol{r},\,t)-S^0_{\alpha\beta}(\boldsymbol{r}),$$

$$\delta\rho(\boldsymbol{r},\,t)=\rho(\boldsymbol{r},\,t)-\rho_0(\boldsymbol{r})\tag{1.4}$$

generate in the medium fluctuation inhomogeneities of the relative permittivity $\delta\varepsilon_{\alpha\beta}$, which scatter light.

The principal contribution to the light scattering in liquid crystals comes from the orientation fluctuations $\varphi_{\alpha\beta}(\boldsymbol{r},t)$. This is associated with the fact that the fluctuations $\delta\rho$ in cases where $\rho_0(\boldsymbol{r})=\text{const}$ (nematic and cholesteric liquid crystals) have the same order of magnitude in liquid crystals as in the usual liquids. On the other hand, in smectic liquid crystals, where $\rho_0(\boldsymbol{r})$ is periodic, there are appreciable fluctuations $\delta\rho$ but their characteristic scale $q_0^{-1}\ll\lambda$ (the light wavelength) and they are hardly manifested in the usual light scattering. We shall therefore henceforth consider only the scattering by orientation fluctuations $\varphi_{\alpha\beta}$ unless otherwise stipulated. The tensor $\varphi_{\alpha\beta}$ has in the general case five independent fluctuation modes $\xi_1,\ldots,\xi_5$.

The space time pair correlation function

$$G_{\alpha\beta\gamma\rho}(\boldsymbol{r}_1,\,\boldsymbol{r}_2;\,t_1-t_2)=\langle\varphi_{\alpha\beta}(\boldsymbol{r}_1,\,t_1)\varphi_{\gamma\rho}(\boldsymbol{r}_2,\,t_2)\rangle\tag{1.5}$$

is used in the statistical description of the fluctuation $\delta\varepsilon_{\alpha\beta}=\varphi_{\alpha\beta}$. In particular, the intensity of single light scattering is expressed in terms of this function [1–3]:

$$I(\boldsymbol{e}^{(\text{i})},\,\boldsymbol{e}^{(\text{s})})=\int_{-\infty}^{\infty}\frac{\text{d}\omega}{2\pi}\,I(\boldsymbol{e}^{(\text{i})},\,\boldsymbol{e}^{(\text{s})},\,\omega)\,,\tag{1.6}$$

where the spectral intensity of the scattering at the point $\boldsymbol{r}$ is

$$\begin{aligned}I(\boldsymbol{e}^{(\text{i})},\,\boldsymbol{e}^{(\text{s})},\,\omega)=Y_0\int_{V_\text{s}}&\text{d}\boldsymbol{r}_1\text{d}\boldsymbol{r}_2\,e^{(\text{s})}_\alpha e^{(\text{s})}_\beta T_{\alpha\gamma}(\boldsymbol{r},\,\boldsymbol{r}_1;\,\omega+\omega_0)\\&\times T^{\,*}_{\beta\delta}(\boldsymbol{r},\,\boldsymbol{r}_2;\,\omega+\omega_0)G_{\gamma\mu\delta\nu}(\boldsymbol{r}_1,\,\boldsymbol{r}_2;\,\omega)\\&\times E^{\,(\text{i})}_{\,0}(\boldsymbol{r}_1)E^{\,(\text{i})*}_{\,0}(\boldsymbol{r}_2)e^{(\text{i})}_\mu e^{(\text{i})}_\nu\,,\end{aligned}\tag{1.7}$$

Y_0 is a constant linked to the definition of the intensity, and V_s is the scattering volume. This formula refers to the case of a harmonic incident wave.

$$\boldsymbol{E}^{(\text{i})}_0(\boldsymbol{r},\,t)=\boldsymbol{E}^{(\text{i})}_0(\boldsymbol{r})\text{e}^{-\text{i}\omega_0 t}=\boldsymbol{e}^{(\text{i})}E^{\,(\text{i})}_{\,0}(\boldsymbol{r})\text{e}^{-\text{i}\omega_0 t}\,,\tag{1.8}$$

where $T_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}';\omega)$ is Green's function of Maxwell's equations at the point $\boldsymbol{r}$ in the ω-representation, $\boldsymbol{e}^{(\text{i})}$ and $\boldsymbol{e}^{(\text{s})}$ are the polarisation vectors of the incident and scattered light, and $\widehat{G}(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega)$ is the frequency Fourier transform of the correlation functions (1.5).

Formula (1.6) defines the integral intensity of the scattered light. In the description of a real experiment on light scattering, it is usually sufficient to use for Green's function $\widehat{T}(\boldsymbol{r},\boldsymbol{r}';\,\omega+\omega_0)$ its asymptotic form in the remote region $|\boldsymbol{r}-\boldsymbol{r}'| \gg \lambda$. Bearing in mind that the characteristic hydrodynamic frequencies ω of the correlation function $\widehat{G}(\boldsymbol{r},\boldsymbol{r}';\,\omega)$ are much smaller than the optical frequencies ω_0, the frequency shift may be neglected in Green's functions $\widehat{T}$ in Eqn (1.7), i.e. $\widehat{T}(\boldsymbol{r},\boldsymbol{r}';\,\omega+\omega_0)$ may be replaced by $\widehat{T}(\boldsymbol{r},\boldsymbol{r}';\,\omega_0)$. The integral intensity defined by Eqn (1.6) is then defined by the spatial correlation function

$$G_{\alpha\beta\gamma\rho}(\boldsymbol{r}_1,\,\boldsymbol{r}_2) = \langle \varphi_{\alpha\beta}(\boldsymbol{r}_1,\,t)\varphi_{\gamma\rho}(\boldsymbol{r}_2,\,t)\rangle = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, G_{\alpha\beta\gamma\rho}(\boldsymbol{r}_1,\,\boldsymbol{r}_2;\,\omega)\,. \tag{1.9}$$

In this case the argument t of the function $\widehat{\varphi}(\boldsymbol{r},t)$ can be omitted bearing in mind that the corresponding correlators are simultaneous.

For the calculation of the correlation function $\widehat{G}(\boldsymbol{r},\boldsymbol{r}')$, it is essential to know the contribution of the fluctuations $\widehat{\varphi}(\boldsymbol{r})$ to the thermodynamic potential of the liquid crystal Φ. The deviations of $S_{\alpha\beta}(\boldsymbol{r})$ from the state of equilibrium $(S^{\,0}_{\alpha\beta})$ require an expenditure of energy. The magnitude of this distortion energy actually determines the probability of the given fluctuation [18].

From the standpoint of the general principles of the continuum theory of liquid crystals [4, 9, 10, 17], the quantity Φ is a functional of the invariants of the parameters $S_{\alpha\beta}(\boldsymbol{r})$ and $\rho(\boldsymbol{r})$ and their gradients. If one is interested solely in fairly smooth distortions of the orientational structure of the liquid crystal, then one need retain in Φ only gradient terms of an order in ∇ not higher than the second. In nematics and cholesterics, where $\rho_0(\boldsymbol{r}) = \text{const}$, the interaction of the fluctuations in ρ and $S_{\alpha\beta}$ is insignificant and the contribution $\delta\rho$ to the thermodynamic potential may be disregarded. The expansion of the thermodynamic potential includes in this case invariants of the type

$$S_{\alpha\beta},\ldots,\,S_{\gamma\delta}\,, \tag{1.10}$$

$$S_{\alpha\beta},\ldots,\,S_{\gamma\delta}\nabla_{\rho}S_{\mu\nu}\,\nabla_{\xi}S_{\tau\sigma}\,, \tag{1.11}$$

$$e_{\mu\nu\rho}S_{\alpha\beta},\ldots,\,S_{\gamma\delta}\nabla_{\xi}S_{\tau\sigma}\,, \tag{1.12}$$

contracted over all pairs of indices; here $e_{\mu\nu\rho}$ is a fully antisymmetric third rank unit vector. It follows from symmetry considerations that the invariants (1.12) in ∇ can exist only for chiral liquid crystals (cholesteric, smectic C*, etc. liquid crystals) [9, 18]. We may also note that invariants of the type $\mathrm{Sp}(\widehat{S}^{\,n})$ are expressed, for any n, in terms of two independent invariants $\mathrm{Sp}(\widehat{S}^{\,2})$ if $\mathrm{Sp}(\widehat{S}^{\,3})$ as a consequence of the recurrence relation

$$\mathrm{Sp}\,\widehat{S}^{\,n+1} = \tfrac{1}{2}\,\mathrm{Sp}\,\widehat{S}^{\,2}\,\mathrm{Sp}\,S^{\,n-1} + \tfrac{1}{3}\,\mathrm{Sp}\,\widehat{S}^{\,3}\,\mathrm{Sp}\,\widehat{S}^{\,n-2}\,. \tag{1.13}$$

This approach constitutes in fact an extension of the Oseen–Frank continuum theory [9, 10] to the case where liquid crystals are described not in terms of the director vector $\boldsymbol{n}(\boldsymbol{r})$ but in terms of the tensor order parameter.

In smectic liquid crystals, it is essential to take into account both the orientation order parameter $S_{\alpha\beta}(\boldsymbol{r})$ and the structural parameter $\rho_0(\boldsymbol{r})$. Since $\rho_0(\boldsymbol{r})$ is not a smooth function of the coordinates, it is necessary, strictly speaking, to take into account arbitrarily high orders of the spatial derivatives of $\rho_0(\boldsymbol{r})$. However, in order to obtain the principal characteristics of smectic liquid crystals, it is sufficient to take into account the spatial derivatives of $\rho_0(\boldsymbol{r})$ up to the fourth order inclusive [19]. In particular, Eqn (1.2) is then obtained from the condition for a minimum in the corresponding potential. An alternative approach [20], in which Eqn (1.2) is postulated and the smooth complex amplitude $\psi(\boldsymbol{r})$,

$$\psi(\boldsymbol{r}) = |\psi(\boldsymbol{r})|\,e^{-iq_0 u(\boldsymbol{r})}\,, \tag{1.14}$$

is adopted as the order parameter, is more common. The quantity $u(\boldsymbol{r})$ has the significance of the projection onto $\boldsymbol{q}_0$ of the vector $\boldsymbol{u}(\boldsymbol{r})$ of the displacements of the smectic layers, while $|\psi(\boldsymbol{r})|$ is the amplitude of the density wave. $|\psi_0(\boldsymbol{r})| = \psi_0$ corresponds to the equilibrium value of the parameter $\psi_0(\boldsymbol{r})$ and $u(\boldsymbol{r}) = u_0$ in Eqn (1.2).

The present review is devoted to the problem of the study of fluctuations and light scattering in liquid crystals. Theoretical and experimental results are described in parallel. The theoretical consideration is fairly detailed. The final expressions are quoted, so far as possible, in a form permitting direct comparison with experiment. The principal types of liquid crystals — nematic, cholesteric, and smectic — are considered. Both the ordered and isotropic phases of the liquid crystals are discussed. A brief resumé is presented at the end of each section and the possible prospects for further research are discussed.

2. The isotropic phase of nematics

2.1 Fluctuations and light scattering intensity

The properties of liquid crystals in the isotropic phase do not differ from those of the usual organic liquids with anisotropic molecules. However, the nature of the behaviour associated with the correlations in the orientations of the molecules and in particular with the fluctuations of the tensor order parameter $\varphi_{\alpha\beta}(\boldsymbol{r})$ are in the present instance completely different. In the vicinity of the point corresponding to transition to the ordered phase, the amplitude of the fluctuations increases sharply and the fluctuation kinetics exhibit a critical retardation. The characteristic features of the behaviour of a liquid crystal in the region of the phase transition can be obtained with the aid of the model proposed by de Gennes [9, 16, 17, 21]. The Landau expansion of the thermodynamic potential is used as a basis [18]:

$$\Phi(\widehat{S}\,) = \Phi(0) + \tfrac{1}{2}A_0\,\mathrm{Sp}\,\widehat{S}^{\,2} - \tfrac{1}{3}B_0\,\mathrm{Sp}\,\widehat{S}^{\,3} + \tfrac{1}{4}C_0(\mathrm{Sp}\,\widehat{S}^{\,2})^2\,,$$

where $\Phi(0)$ is the contribution to the potential not associated with the orientation and B_0 and C_0 are positive constants. In Landau's theory, $A_0 = A'_0\tau$, $A'_0 > 0$, $\tau = (T - T^*)/T^*$, and T^* is the temperature at which the isotropic phase loses its stability. In the isotropic phase, the average value of $\widehat{S}$ is zero. A characteristic feature of the above expansion is the presence of a third order term in $\widehat{S}$. The cubic term is introduced because states with $+\widehat{S}$ and $-\widehat{S}$ are physically completely different: $S_0 > 0$ describes the preferred orientation along $\boldsymbol{n}^0$, while $S_0 < 0$ describes the preferred orientation in the plane perpendicular to $\boldsymbol{n}^0$ [9].

This model predicts a first-order phase transition at a temperature $T_c = T^*[1 + (B_0^2/27A'_0C_0)]$, the difference $T_c - T^*$ is usually approximately 1 K, while the heat of transition $Q = A'_0B_0^2/27C_0^2$ is very low (~ 1 J cm^{-3}) [9, 22].

The phase transition is a weak first-order phase transition over a wide range in which free transition phenomena, characteristic of second-order transitions, are observed [22]. A detailed description of the behaviour of the liquid crystal in the region of the phase transition requires the introduction of an effective Hamiltonian [7, 18]. When account is taken of up to sixth-order terms in $\widehat{S}$, it assumes the following form:

$$\begin{aligned}H_{\mathrm{eff}} = \int \mathrm{d}\mathbf{r}\,\big[&\tfrac{1}{2} A\,\mathrm{Sp}\,\widehat{S}^2 + \tfrac{1}{2} L_1(\nabla_\alpha S_{\beta\gamma})^2 + \tfrac{1}{2} L_2(\nabla_\alpha S_{\alpha\beta})^2\\ &- \tfrac{1}{3} B\,\mathrm{Sp}\,\widehat{S}^3 + \tfrac{1}{4} C\,(\mathrm{Sp}\,\widehat{S}^2)^2 + \tfrac{1}{5} E\,\mathrm{Sp}\,\widehat{S}^2\,\mathrm{Sp}\,\widehat{S}^3\\ &+ \tfrac{1}{6} D_1(\mathrm{Sp}\,\widehat{S}^2)^3 + \tfrac{1}{6} D_2(\mathrm{Sp}\,\widehat{S}^3)^2\big]\,, \end{aligned} \qquad (2.1)$$

where $A = A'\tau$, A', L_1, L_2, B, C, D_1, and D_2 are constants, $L_1 > 0$, and $L_1 + (2/3)L_2 > 0$ [4, 17]. Usually $A' > 0$ and $B > 0$.

We shall use below the Fourier spatial-time transformations defined by the relations

$$F(\mathbf{r}, t) = \frac{1}{V}\sum_{\mathbf{q}}\int_{-\infty}^{\infty}\frac{\mathrm{d}\omega}{2\pi}\,F_{\mathbf{q}}(\omega)\exp\left[\mathrm{i}(\mathbf{q}\cdot\mathbf{r} - \omega t)\right],$$

$$F_{\mathbf{q}}(\omega) = \int_V \mathrm{d}\mathbf{r}\int_{-\infty}^{\infty}\mathrm{d}t\,F(\mathbf{r}, t)\exp[-\mathrm{i}(\mathbf{q}\cdot\mathbf{r} - \omega t)]\,, \qquad (2.2)$$

in a finite system with a volume V, in which the substitutions $V^{-1}\sum_{\mathbf{q}} \to (2\pi)^{-3}\int \mathrm{d}\mathbf{q}$ and $F_{\mathbf{q}} \to F(\mathbf{q})$ are carried out in the case of an unbounded system.

We introduce the coordinate system $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{p}\}$, where $\mathbf{p} = \mathbf{q}/q$ is a unit vector along $\mathbf{q}$, $\mathbf{e}_1$ and $\mathbf{e}_2$ are unit vectors orthogonal to the vector $\mathbf{q}$, and $\mathbf{e}_1 = \mathbf{e}_2 \times \mathbf{p}$ to make the treatment concrete. In this coordinate system, the tensor $\varphi_{\alpha\beta,\mathbf{q}}$ can be conveniently parametrised in the form [23, 24]

$$\begin{aligned}\varphi_{\alpha\beta,\mathbf{q}} = {}&\xi_{1,\mathbf{q}}(p_\alpha e_{1\beta} + p_\beta e_{1\alpha}) + \xi_{2,\mathbf{q}}(p_\alpha e_{2\beta} + p_\beta e_{2\alpha})\\ &+ \xi_{3,\mathbf{q}}(e_{1\alpha}e_{2\beta} + e_{1\beta}e_{2\alpha}) + \xi_{4,\mathbf{q}}(e_{1\alpha}e_{1\beta} - e_{2\alpha}e_{2\beta})\\ &+ \xi_{5,\mathbf{q}}\sqrt{3}(n^0_\alpha n^0_\beta - \tfrac{1}{3}\delta_{\alpha\beta})\,. \end{aligned} \qquad (2.3)$$

Consider the fluctuations of the modes ξ_j ($j = 1-5$) in the Gaussian approximation. On substituting $\widehat{S} = \widehat{\varphi}$ from Eqn (2.3) in Eqn (2.1), we have

$$\begin{aligned}H^{(1)}_{\mathrm{eff}} = \frac{1}{V}\sum_{\mathbf{q}}\{&[A + (L_1 + \tfrac{1}{2}L_2)q^2](|\xi_{1,\mathbf{q}}|^2 + |\xi_{2,\mathbf{q}}|^2)\\ &+ (A + L_1 q^2)(|\xi_{3,\mathbf{q}}|^2 + |\xi_{4,\mathbf{q}}|^2)\\ &+ [A + (L_1 + \tfrac{2}{3}L_2)q^2]|\xi_{5,\mathbf{q}}|^2\}\,. \end{aligned} \qquad (2.4)$$

Evidently the parametrisation $\varphi_{\alpha\beta,\mathbf{q}}$ introduced is convenient because the fluctuations of the modes $\xi_{1,\mathbf{q}}, \ldots, \xi_{5,\mathbf{q}}$ are independent. The mean squares of the fluctuation modes can be easily found from Eqn (2.4):

$$\langle|\xi_{j,\mathbf{q}}|^2\rangle = \tfrac{1}{2}k_{\mathrm{B}}TV(A + L_{(j)}q^2)^{-1}\,, \quad j = 1-5\,, \qquad (2.5)$$

where

$$L_{(1)} = L_{(2)} = L^{(3)}\,, \quad L_{(3)} = L_{(4)} = L^{(1)}\,, \quad L_{(5)} = L^{(2)}\,,$$

$$L^{(1)} = L_1 + \tfrac{2}{3}L_2\,, \quad L^{(2)} = L_1 + \tfrac{1}{2}L_2\,, \quad L^{(3)} = L_1\,,$$

and k_{B} is the Boltzmann constant.

It is seen from Eqn (2.5) that the fluctuations of all five modes ξ_j behave in a critical manner at $T - T_{\mathrm{c}}$ but their growth is limited by the interruption due to the first-order phase transition at a temperature $T_{\mathrm{c}} \neq T^*$. It is interesting to note that, in contrast to the scalar order parameter, here we have not one but three correlation lengths $r_{\mathrm{c}j} = (L^{(j)}/A)^{1/2}$ ($j = 1-3$), which depend on two parameters, L_1 and L_2, and they are linked to one another by the relation $4r^2_{\mathrm{c}2} = r^2_{\mathrm{c}3} + 3r^2_{\mathrm{c}1}$.

The correlator defined by Eqn (1.9) in an unbounded spatially homogeneous medium depends solely on the difference between the arguments $\widehat{G}(\mathbf{r}_1, \mathbf{r}_2) = \widehat{G}(\mathbf{r}_1 - \mathbf{r}_2)$. From Eqns (2.3) and (2.5), we find in the $\mathbf{q}$ representation [23, 25]

$$G_{\alpha\beta\gamma\rho}(\mathbf{q}) = k_{\mathrm{B}}T\sum_{j=1}^{3}B^{(j)}_{\alpha\beta\gamma\rho}(\mathbf{p})(A + L^{(j)}q^2)^{-1}\,, \qquad (2.6)$$

where

$$\begin{aligned}B^{(3)}_{\alpha\beta\gamma\rho}(\mathbf{p}) = {}&\tfrac{1}{2}(\delta_{\alpha\gamma}p_\beta p_\rho + \delta_{\alpha\rho}p_\beta p_\gamma + \delta_{\beta\rho}p_\alpha p_\gamma + \delta_{\beta\gamma}p_\alpha p_\rho\\ &- 4p_\alpha p_\beta p_\gamma p_\rho)\,,\end{aligned}$$

$$B^{(2)}_{\alpha\beta\gamma\rho}(\mathbf{p}) = \tfrac{3}{2}(p_\alpha p_\beta - \tfrac{1}{3}\delta_{\alpha\beta})(p_\gamma p_\rho - \tfrac{1}{3}\delta_{\gamma\rho})\,,$$

$$\widehat{B}^{(1)}(\mathbf{p}) = \widehat{I} - \widehat{B}^{(2)}(\mathbf{p}) - \widehat{B}^{(3)}(\mathbf{p})\,,$$

and the tensor

$$I_{\alpha\beta\gamma\rho} = \tfrac{1}{2}(\delta_{\alpha\gamma}\delta_{\beta\rho} + \delta_{\alpha\rho}\delta_{\beta\gamma}) - \tfrac{1}{3}\delta_{\alpha\beta}\delta_{\gamma\rho}\,, \qquad (2.7)$$

plays the role of a unit tensor for the given symmetry.

We shall now consider the intensity of the light scattered by these fluctuations. In terms of the Born' approximation, it can be written in the form [1–3]

$$I(\mathbf{e}^{(\mathrm{i})}, \mathbf{e}^{(\mathrm{s})}) = Z^{(\mathrm{i})}_0\mathrm{e}^{-\sigma L_{\mathrm{tr}}}\,e^{(\mathrm{i})}_\alpha e^{(\mathrm{i})}_\beta G_{\alpha\nu\beta\mu}(\mathbf{q}_{\mathrm{sc}})e^{(\mathrm{s})}_\nu e^{(\mathrm{s})}_\mu\,, \qquad (2.8)$$

where $Z^{(\mathrm{i})}_0 = I^{(\mathrm{i})}_0 V_{\mathrm{s}}(\omega_0^2/4\pi c^2 R)^2$, $I^{(\mathrm{i})}_0$ is the intensity (the modulus of the Boynting vector) of incident light, c is the velocity of light in a vacuum, $\mathbf{R}/R$ is the direction towards the observation point, R is the distance from this point to the scattering volume V_{s}, $V_{\mathrm{s}}^{1/3} \ll R$, L_{tr} is the path traversed by light in the medium, σ the extinction coefficient (linked to the energy lost in the scattering process), $\mathbf{e}^{(\mathrm{i})}$ and $\mathbf{e}^{(\mathrm{s})}$ are the polarisation vectors, $\mathbf{k}^{(\mathrm{i})}$ and $\mathbf{k}^{(\mathrm{s})}$ are the wave vectors for the incident and scattered waves respectively, and $\mathbf{q}_{\mathrm{sc}} = \mathbf{k}^{(\mathrm{s})} - \mathbf{k}^{(\mathrm{i})}$ is the scattering vector.

The scattering intensity for arbitrary polarisations $\mathbf{e}^{(\mathrm{i})}$ and $\mathbf{e}^{(\mathrm{s})}$ can be found from Eqns (2.6) and (2.8):

$$I(\mathbf{e}^{(\mathrm{i})}, \mathbf{e}^{(\mathrm{s})}) = \varLambda\sum_{j=1}^{3}\frac{\nu^{(j)}(\mathbf{e}^{(\mathrm{i})}, \mathbf{e}^{(\mathrm{s})})}{1 + (q_{\mathrm{sc}}r_{\mathrm{c}j})^2}\,, \qquad (2.9)$$

where

$$\varLambda = I^{(\mathrm{i})}_0 V_{\mathrm{s}}R_{\mathrm{sc}}R^{-2}\mathrm{e}^{-\sigma L_{\mathrm{tr}}}\,,$$

$$\nu^{(1)}(\mathbf{e}^{(\mathrm{i})}, \mathbf{e}^{(\mathrm{s})}) = \tfrac{1}{2} + \tfrac{1}{6}x^2_{\mathrm{is}} - \nu^{(2)}(\mathbf{e}^{(\mathrm{i})}, \mathbf{e}^{(\mathrm{s})}) - \nu^{(3)}(\mathbf{e}^{(\mathrm{i})}, \mathbf{e}^{(\mathrm{s})})\,,$$

$$\nu^{(2)}(\mathbf{e}^{(\mathrm{i})}, \mathbf{e}^{(\mathrm{s})}) = \tfrac{3}{2}(x_{\mathrm{pi}}x_{\mathrm{ps}} - \tfrac{1}{3}x_{\mathrm{is}})^2\,,$$

$$\nu^{(3)}(\mathbf{e}^{(\mathrm{i})}, \mathbf{e}^{(\mathrm{s})}) = \tfrac{1}{2}x^2_{\mathrm{pi}} + \tfrac{1}{2}x^2_{\mathrm{ps}} + x_{\mathrm{is}}x_{\mathrm{pi}}x_{\mathrm{ps}} - 2x^2_{\mathrm{pi}}x^2_{\mathrm{ps}}\,; \qquad (2.10)$$

here $x_{\mathrm{is}} = \mathbf{e}^{(\mathrm{i})}\cdot\mathbf{e}^{(\mathrm{s})}$, $x_{\mathrm{pi}} = \mathbf{p}\cdot\mathbf{e}^{(\mathrm{i})}$, $x_{\mathrm{ps}} = \mathbf{p}\cdot\mathbf{e}^{(\mathrm{s})}$, and $\mathbf{p} = \mathbf{q}_{\mathrm{sc}}/q_{\mathrm{sc}}$. The quantity R_{sc} is the scattering constant defined as follows [26]:

$$R_{\mathrm{sc}} = \frac{\pi^2}{5\lambda^4}\,G_{\alpha\beta\alpha\beta}(\mathbf{q} = 0) = \left(\frac{\omega_0^2}{4\pi c^2}\right)^2\frac{k_{\mathrm{B}}T}{A}\,. \qquad (2.11)$$

In terms of the mean field approximation, $\varLambda \sim \tau^{-\gamma}$, $\gamma = 1$, while all the correlation radii $r_{\mathrm{c}j} \sim \tau^{-\nu}$ and $\nu = 0.5$. When account is taken of Eqns (2.9) and (2.10), formula (2.8) makes it possible, in particular, to formulate expressions for the scattering intensities corresponding to all the polarisations usually employed in the experiment:

$$I_{\mathrm{V}}^{\mathrm{V}}=\frac{A}{2}\left[\frac{1}{1+(q_{\mathrm{sc}}r_{\mathrm{c1}})^2}+\frac{1}{3}\,\frac{1}{1+(q_{\mathrm{sc}}r_{\mathrm{c2}})^2}\right],$$

$$I_{\mathrm{H}}^{\mathrm{V}}=\frac{A}{2}\left[\frac{\cos^2(\theta_{\mathrm{sc}}/2)}{1+(q_{\mathrm{sc}}r_{\mathrm{c1}})^2}+\frac{\sin^2(\theta_{\mathrm{sc}}/2)}{1+(q_{\mathrm{sc}}r_{\mathrm{c2}})^2}\right],$$

$$I_{\mathrm{H}}^{\mathrm{H}}=\frac{A}{2}\left[\frac{\cos^4(\theta_{\mathrm{sc}}/2)}{1+(q_{\mathrm{sc}}r_{\mathrm{c1}})^2}+\frac{1}{3}\,\frac{\sin^4(\theta_{\mathrm{sc}}/2)}{1+(q_{\mathrm{sc}}r_{\mathrm{c2}})^2}\right], \qquad (2.12)$$

where θ_{sc} is the scattering angle, $q_{\mathrm{sc}}=2k_0\sin(\theta_{\mathrm{sc}}/2)$ and $k_0=|\boldsymbol{k}^{(\mathrm{i})}|=|\boldsymbol{k}^{(\mathrm{s})}|$ are the wavenumbers in the medium. It is seen from these formulae that by studying the light scattering indicatrixes for different components, it is possible, in principle, to determine all three correlation radii $r_{\mathrm{c}j}$.

Hitherto there have been no experimental independent determinations of all three correlation radii $r_{\mathrm{c}j}$. This is associated with the fact that, owing to the interruption by the first-order phase transition, it is impossible, in principal, to carry out measurements at $\tau \ll 10^{-3}$. Hence the asymmetry arising in the light scattering indicatrix is very small [27, 28]. The fact that this asymmetry is nonzero has been noted by Chu et al. [29]. The first fairly reliable data have been obtained by Stinson and Litster [30]. Very careful measurements have been made by Gulary and Chu [31] for MBBA. They measured the light scattering intensity to within 0.1% for two fixed angles $\theta_{\mathrm{sc}}=21.4°$ and $158.6°$. The components of the scattered light $I_{\mathrm{V}}^{\mathrm{V}}$ and $I_{\mathrm{H}}^{\mathrm{V}}$ were measured. It follows from Eqn (2.12) that the first order of the asymmetry of the scattering indicatrix in these components is defined by the expressions $q_{\mathrm{sc}}^2(3r_{\mathrm{c1}}^2+r_{\mathrm{c2}}^2)/4$ and $q_{\mathrm{sc}}^2[r_{\mathrm{c1}}^2\cos^2(\theta_{\mathrm{sc}}/2)+r_{\mathrm{c2}}^2\sin^2(\theta_{\mathrm{sc}}/2)]$ respectively. Gulary and Chu [31] did not observe a difference between these quantities. This justifies the use of the single correlation radius $r_{\mathrm{c}j}=r_{\mathrm{c}}$ approximation for the description of the SLC isotropic phase, which corresponds to the condition $L_2=0$ in Eqn (2.1). It follows from Eqn (2.2) that in this case the scattering depolarisation coefficient $I_{\mathrm{H}}^{\mathrm{V}}/I_{\mathrm{V}}^{\mathrm{V}}=3/4$, which has been confirmed experimentally [26–31]. The maximum angular asymmetry, measured by Gulary and Chu [31], was 1%, which corresponds to $r_{\mathrm{c}}\approx 120$ Å. The temperature dependence of $r_{\mathrm{c}}=r_0\tau^{-\nu}$ with $\nu=0.5$ has been confirmed [30, 31]. Gulary and Chu [31] and Stinson and Litster [30] found that the parameter $r_0=5.5\pm0.2$ Å and 6.8 ± 1.0 Å respectively.

The extinction coefficient σ, characterising the decrement in the decay of normal waves propagated in the medium, is determined by the imaginary components of the effective relative permittivity [32]. For the calculation of the extinction coefficient in terms of the lowest order in fluctuations, it is usually sufficient to integrate the total relative scattering intensity per unit volume over all the directions $\boldsymbol{k}^{(\mathrm{s})}$ [32, 33]. When $k_0r_{\mathrm{c}j}\ll 1$ (it was found in the above investigations [30, 31] that $k_0r_{\mathrm{c}j}\leqslant 0.1$), we have

$$\sigma=\frac{40\pi}{9}R_{\mathrm{sc}}\,. \qquad (2.13)$$

An expression for σ corresponding to arbitrary $k_0r_{\mathrm{c}j}$ has been published [26].

2.2 Pretransitional phenomena in the isotropic phase

The $I\rightarrow N$ phase transition is a first-order transition, but it is accompanied, as in second-order transitions, by an increase in the intensity of the scattered light [26–31], an increase in the magnetic birefringence [27], an anomalous behaviour of the heat capacity [34, 35], and a critical retardation of fluctuations [27, 36–38]. This is associated with the fact that the phase transition entails a small jump in the specific volume [39] and an insignificant heat of transition [40–42] (see also Anisimov [22]) and should be accompanied by an increase in the fluctuation order parameter in the vicinity of T_{c}.

In the early studies of Stinson and Litster [27, 36], it was already shown that the reciprocal of the light scattering intensity $I^{-1}(T)$ in a MBBA nematic, with the experimental accuracy specified *a priori*, varies linearly with temperature over a fairly wide range of the latter ($T-T_{\mathrm{c}}\approx 20$ K) (Fig. 1), which corresponds to the critical susceptibility index $\gamma=1.0$. Subsequently this conclusion was confirmed in experiments both on light scattering [28–31] and on birefringence (the Cotton–Mouton effect) [43]—in the latter case for five different nematic liquid crystals. The correlation radius index ν proved to be 0.5 [30, 31]. The most natural explanation of these facts is that in the given instance there is a region where the Landau theory applies [9, 16]. However, the hypothesis of the possible tricritical nature of the $I\leftrightarrow N$ phase transition has also been put forward [35, 44].

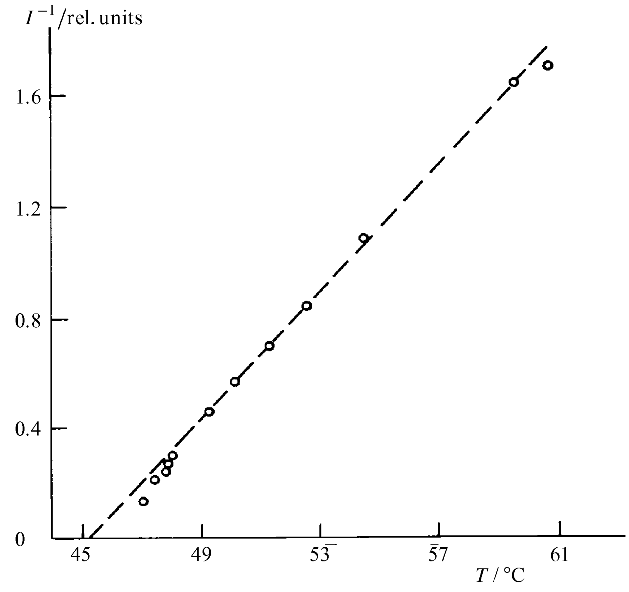

Figure 1. Temperature variation of the reciprocal of the scattering intensity in MBBA at a scattering angle $\theta=21.4°$ [31].

Nevertheless, as can be seen from Fig. 1, 2–2.5 K beyond the point corresponding to the transition to the ordered phase T_{c} a deviation from the $I^{-1}(T)$ linear relation is observed and the light scattering intensity begins to increase faster with temperature. Thus in the study of Gulary and Chu [31] the inclusion of the experimental points in the immediate vicinity of T_{c} in the interpretation of the results altered the index γ from 1.0 to 0.85 ± 0.05. This phenomenon is of special interest because deviations from universal laws over a wide temperature range are not observed in the majority of physical systems [6–8].

The simplest cause of the observed anomaly in the behaviour of the scattering intensity as a function of temperature may be of purely 'apparatus' origin — an increase in the contribution of multiple scattering in the immediate vicinity of T_c. The characteristic features of the behaviour of the susceptibility in the vicinity of T_c have been analysed in detail in a BMOAB liquid crystal by light scattering methods [26]. The measurements were performed for two polarisations I_V^V and I_H^V at a fixed scattering angle of 90°. The error of all the measurements was $\sim 0.7\%$. Their results are presented in Fig. 2. The $I^{-1}(T)$ relation is represented by a straight line. A deviation from linearity is observed only 1.5–2.5 K beyond the transition point T_c, reaching 30–40% in the immediate vicinity of T_c. The degree of depolarisation over the entire range of the measurements was close to 3/4. Calculation of the contribution by double scattering to the total intensity, carried out [26] by the method of Adzhemyan et al. [46], showed that even in the immediate vicinity of T_c its contribution was $\sim 3\%$. This means that the observed deviations from universal laws cannot be accounted for by multiple scattering. The nonuniversality of the temperature variation of the susceptibility of an isotropic nematic liquid crystal near T_c has been confirmed also in experiments on magnetic birefringence [47].

Together with the increase in the scattered light intensity, an anomalous rise in the heat capacity C_p is also observed in the vicinity of the transition point T_c [22]. The reason for this is the increase in fluctuations at $T \to T_c$. Since formulae (2.11) and (2.12) can in fact be regarded as representing the lowest (Gaussian) fluctuation contribution to the scattered intensity, it is of interest to consider the analogous Gaussian fluctuation contribution also to the heat capacity C_p. The corresponding formula for nematics can be obtained directly from the known scalar fluctuation contribution [8, 18], provided that one takes into account the number of fluctuations modes ξ_j ($j = 1-5$) and the difference between their correlation radii r_{cj}:

$$C_p = C_p^{\mathrm{reg}} + \frac{k_B}{16\pi}(2r_{01}^{-3} + r_{02}^{-3} + 2r_{03}^{-3})\tau^{-1/2}, \tag{2.14}$$

where C_p^{reg} is the regular component of the heat capacity, usually fitted by the linear function $X + YT$, $r_{0j}^2 = L^{(j)}/A'$ ($j = 1-3$). Interpretation of the experimental heat capacity data for BMOAB and MBBA [34, 48] by Adzhemyan et al. [26] showed that here the situation is the same as for the light scattering intensity. In the temperature range $4 \leqslant T - T_c \leqslant 20$ K, Eqn (2.14) describes the results to within $\sim 0.05\%$, which is close to the experimental accuracy. When points with $T_c - T < 4$ K are included in the treatment, the agreement with experiment is sharply impaired. This is illustrated in Fig. 3. The effective parameter $r_{0,\mathrm{eff}} = [(2r_{01}^{-3} + r_{02}^{-3} + 2r_{03}^{-3})/5-^{1/3} \approx 5.2$ Å, obtained for MBBA in the range $4\,\mathrm{K} \leqslant T - T_c$, agrees well with the independent value $r_0 = 5.5 \pm 0.2$ Å found [31] for the same liquid crystal by optical methods on the assumption of the equality $r_{0j} = r_0$ ($j = 1-3$). The latter confirms, in particular, that the single correlation length approximation can be used also for the heat capacity.

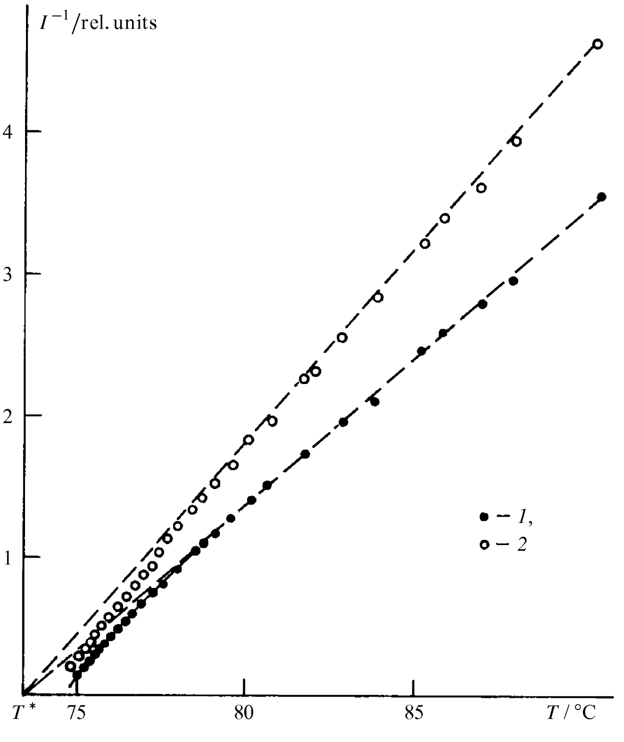

Figure 2. Temperature variation of the reciprocal of the scattering intensity in BMOAB: (1) the I_V^V components; (2) the I_H^V component; dashed lines — linear fits to remote points; the continuous line passing through experimental points for the I_V^V component was fitted by Eqn (1.15) taking into account terms as far as τ^{-2} [26].

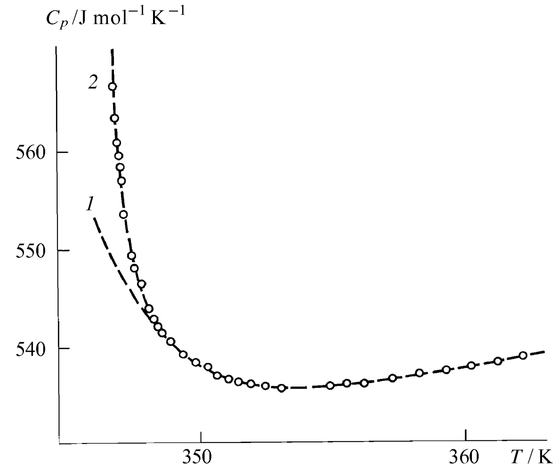

Figure 3. Temperature variation of the heat capacity C_p in the isotropic phase of BMOAB [34, 48]: dashed line 1 — Eqn (1.14) fitted to the remote points; dashed line 2 — a formula of type (1.17) fitted taking into account terms as far as $\tilde{\tau}^{-7/2}$ [26, 54].

These results show that there is a large range of temperatures for the isotropic phase of nematic liquid crystals, where the behaviour of the system (at least its susceptibility and heat capacity) is described within the framework of the mean field approximation, but appreciable deviations from this approximation are observed in the vicinity of T_c.

Various explanations for these characteristics of the behaviour of a nematic liquid crystal have been proposed. One of them is that the nonuniversality of the behaviour indicates a transition to the fluctuation region, where the interaction of the order parameter fluctuations becomes significant [21, 26, 49]. Other hypotheses are based on the necessity to take into account the interaction of $\varphi_{\alpha\beta}$ with other order parameters, for example the smectic order parameters [50, 51].

The attempts to describe the behaviour of the system in the immediate vicinity of T_c by the renormalisation group methods [52, 53] lead to results inconsistent with experiment [22]. This apparently means that the first-order phase transition takes place before the attainment of the region of intense fluctuations. In such a situation, it is natural to employ the perturbation theory in terms of non-Gaussian terms [Eqn (2.1)] for the calculation of the characteristics of nematics near T_c.

The temperature dependences of the susceptibility the $\chi(\tau) = 1/A'\widetilde{\tau}$ [21, 26, 49, 54], the correlation radius $r_c = r_0\widetilde{\tau}^{-1/2}$ [21, 54], and the heat capacity [26, 54] were calculated on the basis of this approach:

$$\widetilde{\tau} = \tau[1 + y_D - y_C\,\tau^{-1/2} - (\tfrac{1}{7}y_C^2 - y_{BE})\tau^{-1}\ln\tau^{-1}$$
$$-y_B\,\tau^{-3/2} + \ldots], \tag{2.15}$$

for the susceptibility,

$$\widetilde{r}_0^{\,2} = r_0^2[1 + (\tfrac{1}{189}\,y_C^2 + \tfrac{1}{4}\,y_{BE})\tau^{-1} + \tfrac{1}{12}\,y_B\,\tau^{-3/2} + \ldots] \tag{2.16}$$

for the correlation radius, and

$$C_p = C_p^{\rm reg} + \frac{5k_{\rm B}}{16\pi r_0^3}\,\tau^{-1/2}\left[1 + \frac{1}{2}\,y_D\right.$$
$$\left. + \frac{1}{2}\left(\frac{1}{7}\,y_C^2 - y_{BE}\right)\tau^{-1}\ln\tau^{-1} + \frac{2}{3}\,y_B\,\tau^{-3/2} + \ldots\right], \tag{2.17}$$

for the heat capacity, where

$$y_C = 7M_0\frac{C}{A'}, \quad y_B = \frac{7}{12}\,M_0\frac{B^2}{A'^2},$$
$$y_{BE} = \frac{77}{33}\,M_0^2\frac{BE}{A'^2}, \quad y_D = \frac{7}{2}\,\frac{M_0^2}{A'}(D_1 + 18D_2),$$
$$M_0 = \frac{k_{\rm B}T}{4\pi A' r_0^3}. \tag{2.18}$$

The calculations were performed in terms of the one-loop [21, 49] and three-loop [26, 54] approximations. We may note that, owing to the differences in the procedure used to eliminate divergences, the results of studies described in Refs 21 and 49 and in 26 and 54 differ somewhat. In the former [21, 49], the divergences in the diagrams were eliminated by introducing a limiting cut-off momentum q_m, which became an additional model parameter. In the second group of studies [26, 54], the parts of the diagrams diverging at $q_m \to \infty$ were included in the renormalised model constants [Eqn (2.1)], while in the finite parts of the diagrams the limiting transition $q_m \to \infty$ was carried out. Eqns (2.15)–(2.17) are consistent with the second set of results [26, 54]. The region of the applicability of Eqns (2.15)–(2.17) as asymptotic expansions is determined by the decrease in the corresponding terms. The inequalities

$$y_C\,\tau^{-1/2} \ll 1, \; y_B\,\tau^{-3/2} \ll 1, \; y_{BE}\,\tau^{-1}\ln\tau^{-1} \ll 1, \; y_D \ll 1\,,$$

are in this instance an analogue of the Ginzburg criterion [6–8, 18]. The convergence of the series (2.15)–(2.17) can be significantly accelerated, weakening thereby the requirements of the Ginzburg criterion by changing from τ and r_0 in Eqns (2.16)–(2.18) and in the correction terms (2.15)–(2.17) to a description in terms of the quantities $\widetilde{\tau}$ and $\widetilde{r}_0$ [54].

The experimental data were interpreted in terms of formulae of the type (2.15)–(2.17) [21, 26, 54]. Gramsbergen et al. [21] interpreted data for the intensity of the scattered light in 8CB liquid crystals using the known parameters of the latter in the nematic phase. By varying T^* and the limiting wavenumber q_m, they were able [21] to describe the behaviour of the scattering intensity as a function of temperature over the entire experimental range of the latter (admittedly the natural values of q_m were not then always obtained). Adzhemyan et al. [26] subjected the heat capacity and scattering intensity (more precisely R_{sc}) data for the BMOAB liquid crystal to a joint treatment. The parameters of the Landau–de Gennes model [Eqn (2.1)] were determined. It was found that the coefficient C of $\widehat{S}^4$ is negative for the given liquid crystal, which made it necessary to take into account in Eqn (2.1) higher-order terms in $\widehat{S}$. The parameters obtained [26] agree with the experimental latent heat of transition $Q = 1.17\ {\rm J\,cm^{-3}}$ in BMOAB [42] when fluctuation corrections are applied to this quantity [54]. The parameter r_0 for BMOAB proved to be 6.0 ± 0.5 Å and $A' = 39 \pm 2\ {\rm J\,cm^{-3}}$. The agreement between the theory and experiment is illustrated in Figs 2 and 3. We obtained similar results also for MBBA. Here it was also found that $C < 0$ and $r_0 \approx 5.7$ Å, which agrees with direct measurements [31]; $A' \approx 33\ {\rm J\,cm^{-3}}$. The (2.1) model together with the parameters obtained describe satisfactorily also experimental data [55, 56] for the temperature dependence of the scalar order parameter $S(T)$, which determines the degree of order in the nematic phases of BMOAB and MBBA. Here one should note that the experimental index β of the order parameter is close to 0.25 [44, 57], which Kyes [44] used as a basis for the hypothesis that the I $\to$ N transition is tricritical. On the other hand, when the sixth-order term in $\widehat{S}$ is taken into account, the (2.1) model yields the index $\beta = 0.25$ but this time in terms of the mean field approximation.

In order to account for the deviation from the mean field behaviour of a nematic liquid crystal in the isotropic phase, it has been suggested [50, 51] that account be taken of the interaction of the nematic order parameter $S_{\alpha\beta}$ with the smectic parameter ψ. For example, when account is taken of the expression for the thermodynamic potential with the smectic invariants $|\psi|^2$, $|\nabla\psi|^2$, and $|\nabla^2\psi|^2$, the interaction terms $\nabla_\alpha\psi\,\nabla\psi^*\,S_{\alpha\beta}$ and $\nabla_\alpha\psi\,\nabla_\beta\psi^*\,S_{\alpha\gamma}S_{\gamma\beta}$, and the invariants defined by Eqns (1.10) and (1.11), the temperature dependence of the susceptibility in terms of the one-loop approximation assumes the form

$$\widetilde{\tau} = \tau + a_1(\tau + \tau_{\rm SN})^{-1/2} - a_2(\tau + \tau_{\rm SN})^{-3/2}\,, \tag{2.19}$$

where $a_{1,2}$ are constants, $a_2 > 0$, the parameter $\tau_{\rm SN} = (T^* - T_{\rm S}^*)/T^*$ has the significance of the relative width of the nematic phase, and $T_{\rm S}^*$ is the temperature of the divergence of the smectic fluctuations in the absence of the interaction of $\widehat{S}$ and ψ [50].

A somewhat different model of the interaction of nematic and smectic fluctuations was proposed in another study [51]. Instead of the scalar order parameters ψ, a second rank tensor was employed [51]. The fluctuation corrections to the susceptibility, to the correlation radius, and to the heat capacity were calculated in terms of the one-loop approximation:

$$
\begin{aligned}
&\tilde{\tau} = \tau + a_1(\tilde{\tau}+\tau_{\mathrm{SN}})^{-1/2} - a_2(\tilde{\tau}+\tau_{\mathrm{SN}})^{-3/2} , \\
&\tilde{r}_0^2 = r_0^2[1 + \tfrac{3}{4}a_2(\tilde{\tau}+\tau_{\mathrm{SN}})^{-5/2}] , \\
&C_p = C_p^{\mathrm{reg}} + \frac{5k_{\mathrm{B}}}{16\pi\tilde{r}_0^3}\left(\frac{\partial\tilde{\tau}}{\partial\tau}\right)^2 \tilde{\tau}^{-1/2} . \qquad (2.20)
\end{aligned}
$$

The expression for $\tilde{\tau}$ in Eqn (2.20) differs from Eqn (2.19) by the replacement $\tau \to \tilde{\tau}$ in the correction terms, i.e. it actually represents an equation for $\tilde{\tau}$ and effectively takes into account higher-order terms in the perturbation theory than Eqn (2.19).

The temperature variation of the scattering intensity in the homologous series of $\overline{n}\mathrm{O}\overline{4}$ ($n = 1-8$) liquid crystals, in which the width of the nematic phase varies from ~40 K ($n = 2$) to ~2.5 K ($n = 7$), has been measured [50]. A correlation was observed between the deviation of $I^{-1}(T)$ from linearity and the width of the nematic phase τ_{SN}: the smaller the width of the nematic phase, the greater the nonlinearity of $I^{-1}T$ (Fig. 4). Quantitative treatment of the experimental data for the 7O4 liquid crystal demonstrated a satisfactory agreement with Eqn (2.19). Joint treatment of the scattering intensity [58] and heat capacity [41] data for the 8CB liquid crystal, carried out [51] in terms of Eqns (2.20) with variable parameters T^*, a_1, a_2, τ_{SN}, and r_0, also demonstrated agreement with experiment.

Experiments [59] involving the measurement of the temperature variation of the light scattering intensity in a mixture of two liquid crystals, $\overline{6}\mathrm{O}\overline{6}\mathrm{NO}_2$ and $\overline{6}\mathrm{O}\overline{10}$, with a variable concentration x are of interest in this connection. When x was varied from 1.00 to 0.60 in this system, the width of the N-phase changed from 7 K to zero, which made it possible to vary continuously the parameter τ_{SN} from 0.006 to -0.02, passing through zero in the vicinity of the N $-$ S$_{\mathrm{A}}$ $-$ I triple point. A satisfactory agreement between the experimental data and the first formula in Eqn (2.20) was obtained.

On the other hand, a study [21] of the light scattering intensity [21] for the nCB homologous series of liquid crystals ($n = 5-12$) with the width of the nematic phase varied from ~11 K ($n = 5$) to ~1.7 K ($n = 9$) did not reveal an explicit correlation between the deviation of $I^{-1}(T)$ from linearity and the width of the N-phase τ_{SN} despite the fact that the deviations of $I^{-1}(T)$ from linearity were considerable.

2.3 Kinetics of the fluctuations of the order parameter

In describing the kinetics of the fluctuations in the isotropic phase of a liquid crystal, we shall choose, as before, the fluctuating component of the relative permittivity tensor $\delta\varepsilon_{\alpha\beta}$ as the order parameter.

De Gennes proposed a system of phenomenological equations describing the kinetics of the fluctuations [9]:

$$
\begin{aligned}
&A'\tau\delta\varepsilon_{\alpha\beta} = 2\mu\dot{u}_{\alpha\beta} + \nu\delta\dot{\varepsilon}_{\alpha\beta} , \\
&\sigma_{\alpha\beta} = 2\eta\dot{u}_{\alpha\beta} + 2\mu\delta\dot{\varepsilon}_{\alpha\beta} , \\
&\rho\ddot{u}_\alpha = \frac{\partial\sigma_{\alpha\beta}}{\partial r_\beta} ; \qquad (2.21)
\end{aligned}
$$

where η is the shear viscosity at zero frequency, ν and μ are phenomenological coefficients having the dimensions of viscosity, $u_{\alpha\beta} = (1/2)(\partial u_\alpha/\partial r_\beta + \partial u_\beta/\partial r_\alpha)$ is the deforma-

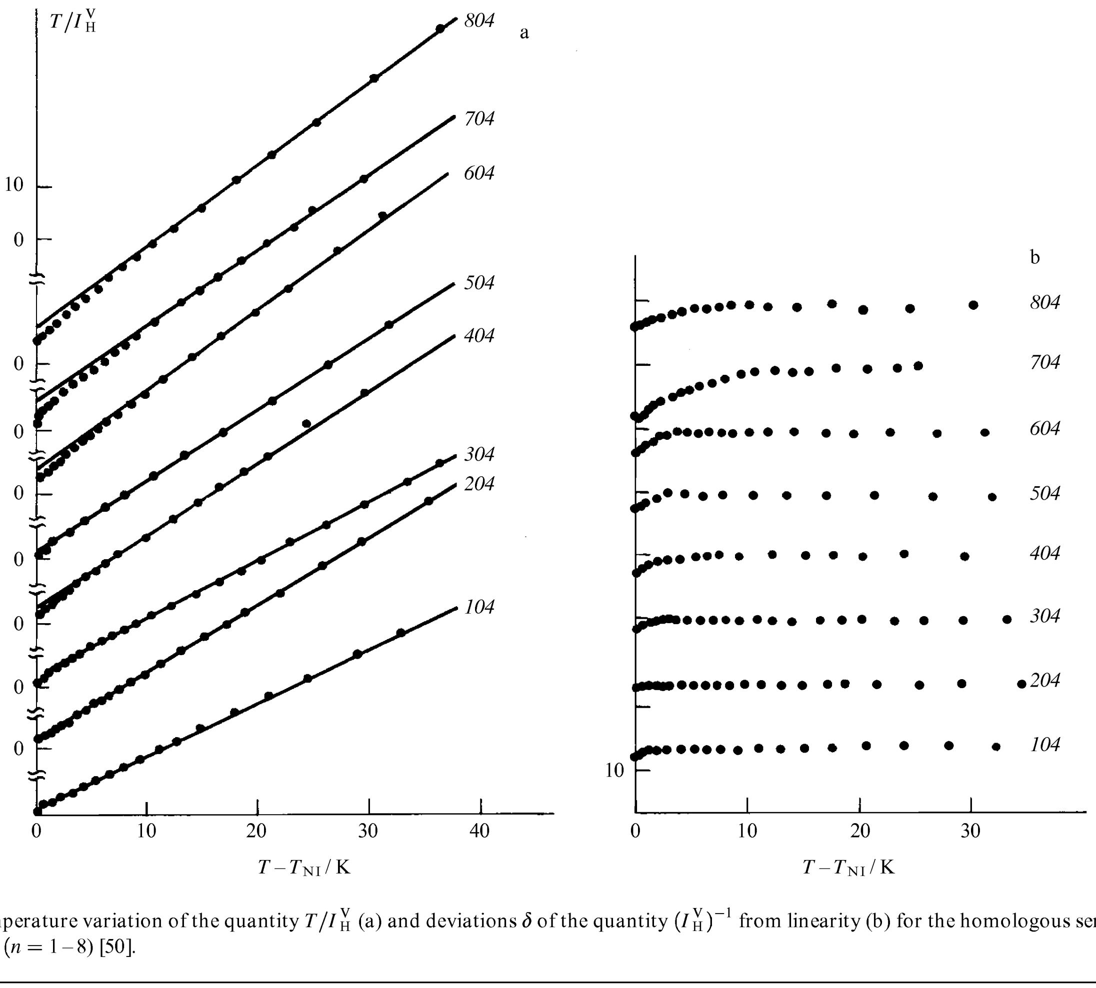

Figure 4. Temperature variation of the quantity $T/I_{\mathrm{H}}^{\mathrm{V}}$ (a) and deviations δ of the quantity $(I_{\mathrm{H}}^{\mathrm{V}})^{-1}$ from linearity (b) for the homologous series of liquid crystals $\overline{n}\mathrm{O}\overline{4}$ ($n = 1-8$) [50].

tions tensor, $\boldsymbol{u}$ is the displacement tensor, and $\sigma_{\alpha\beta}$ is the stresses tensor. Eqns (2.21) describe purely transverse motions and do not include volume terms. The quantity $\tau_r = \nu/A'\tau$ has the significance of the relaxation time of the variable $\delta\varepsilon_{\alpha\beta}$, while $2\mu^2/\nu$ represents the orientation contribution to the shear viscosity.

Experimental study of the kinetics of the order parameter in liquid crystals on the basis of the depolarised light scattering spectra, of the kind carried out for ordinary organic liquids, is extremely difficult owing to the range of frequencies in which the relaxation times τ_r are located: in the region 20–30 K beyond T_c, these frequencies are of the order of magnitude of several tens of megahertz [37] and they can be investigated with the aid of single pass Fabry–Perot etalons in which the distance between the mirrors is up to 10 cm.
A single-frequency laser must be used as the light source. As T_c is approached, the frequency $\nu_r = 1/2\pi\tau_r$ diminishes to several megahertz and in the immediate vicinity of T_c it can be of the order of magnitude or less than 1 MHz. In this case, the resolving power of the usual etalons is insufficient and it is necessary to employ spectroscopic instruments with a greater resolution, for example confocal Fabry–Perot interferometers with a base of several tens of centimetres [27, 36]. Additional difficulties in such experiments are associated with the instability of the emission from the lasers, which in the case of single-frequency ionic lasers is 5–10 MHz s^{-1}. On the other hand, this frequency range is rather large for optical mixing spectroscopy owing to the limitations imposed by the time resolution of the electronic hardware used in the standard correlators [60].

Apparently owing to experimental complexities, the amount of data on the kinetics of the order parameter in nematic liquid crystals, obtained from light scattering spectra, is much smaller than in the numerous studies on the edge of the Rayleigh line in the usual liquids. The studies by Stinson and Litster [27, 36] in MBBA were performed in the immediate vicinity of T_c. It was shown that the spectra of the I_V^V and I_H^V components are identical and that the distribution of intensities in them is described by the Lorentz line. It was found that experimental data satisfy the empirical relation $\nu_r = (T^0 - 40.58)^{1.33}$ MHz. After the inclusion of the temperature variation of the shear viscosity, the variation of ν_r can be fitted satisfactorily by a linear function of $T - T_c$. Gierke and Flygare [37] investigated in detail the spectrum of the depolarised scattering in MBBA and in its solutions in carbon tetrachloride with the aid of a confocal interferometer with a 2 GHz dispersion region. For pure MBBA, the measurements were performed in the region not closer than 27 K to T_c, where $\nu_r = 25 \pm 2$ MHz.

A complete quantitative comparison between de Gennes' theory and experiment is an important experimental task. This permits the determination of the nature of the relaxation of the shear viscosity η and the study of the behaviour of the parameters μ and ν. Together with light scattering spectra, in this case it is necessary to employ also other experimental data. This is associated with the fact that in liquid crystals in the vicinity of the I → N transition there is no fine structure and the distribution of intensities in the spectrum is close to the dispersion distribution because $1/\tau_r \ll \eta q_{sc}^2/\rho$.

The Maxwell effect contains additional information. In an experiment on birefringence in a flow, optical anisotropy arises owing to the rate of deformation gradient, so that the first of Eqns (2.21) assumes the form

$$-A'\tau\delta\varepsilon_{\alpha\beta} = 2\mu\dot{u}_{\alpha\beta}\,. \tag{2.22}$$

If the flow is directed along the x axis and the velocity gradient is directed along the z axis, then the optical anisotropy is given by

$$\delta n = -\frac{\mu}{A'\tau\bar{n}}\frac{\partial u_x}{\partial z}\,, \tag{2.23}$$

where $\delta n = \varepsilon_a/2\bar{n}$ ($\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp$, $\varepsilon_\parallel$ and $\varepsilon_\perp$ being the lengths of the principal axes of the relative permittivity tensor $\hat{\varepsilon}$) and $\bar{n}$ the average refractive index.

The scattered light spectrum is given by the following formula at the limit $qr_{cj} \ll 1$:

$$I_H^V(\omega) \sim \frac{1}{\pi}\left\{\frac{\tau_r^{-1}}{\omega^2 + \tau_r^{-2}}\sin^2\frac{\theta_{sc}}{2}\right.$$
$$\left. +\tau_r^{-1}\frac{\omega^2 + \left(q_{sc}^2\eta/\rho\right)^2(1 - R_r)}{(q_{sc}^2\eta/\rho\tau_r - \omega^2)^2 + \omega^2[\tau_r^{-1} + (1 - R_r)q_{sc}^2\eta/\rho]^2}\cos^2\frac{\theta_{sc}}{2}\right\}, \tag{2.24}$$

where $R_r = 2\mu^2/\nu\eta$ is the relative contribution of orientations to the shear viscosity.

The most complete analysis of the spectrum of the depolarised scattering in MBBA has been carried out by Alms et al. [61]. The measurements were performed using a laser with a wavelength $\lambda = 5145$ Å and a power of 1 W at a fixed scattering angle of 90°. The scattered radiation was recorded with a Fabry–Perot interferometer having a dispersion range of 7.4 GHz. The measurements were performed in the temperature range 150–230 °C. The

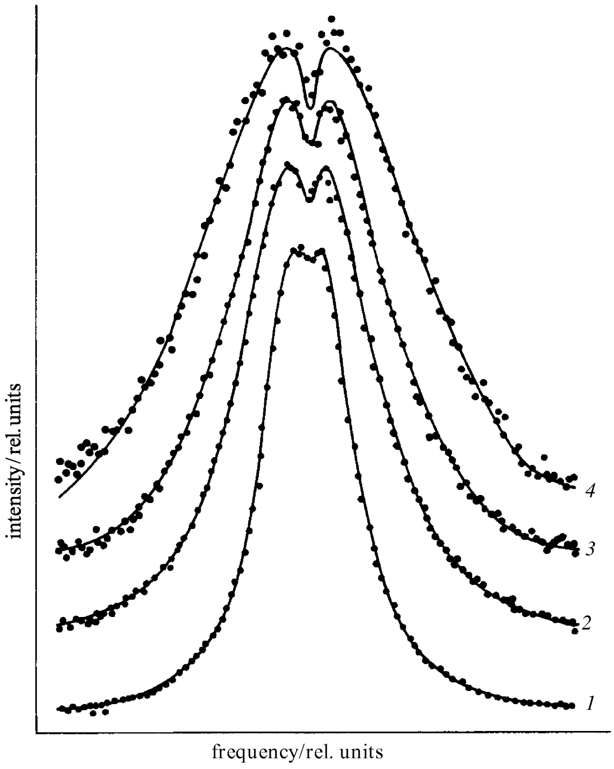

Figure 5. Spectrum of the I_H^V component in the isotropic phase of MBBA in terms of arbitrary scales at different temperatures: (*1*) $T = 150$ °C; (*2*) $T = 180$ °C; (*3*) $T = 210$ °C; (*4*) $T = 230$ °C. The continuous lines have been fitted by Eqn (1.24) using τ_r, $q_{sc}^2\eta/\rho$, and R_r as the adjustable parameters [61].

temperature was maintained with an accuracy to within ±0.5 °C. Fig. 5 presents the spectrum of the $I_{\mathrm{H}}^{\mathrm{V}}$ components for four temperatures. Evidently, all the spectra exhibit a fine structure. The distortions introduced by the apparatus function of the etalon were excluded with the aid of the deconvolution procedure described by Alms et al. [62]. The quantities R_{r}, $q_{\mathrm{sc}}^2\eta/\rho$, and τ_{r} were determined from the spectra obtained. Within the limits of experimental accuracy, $R_{\mathrm{r}} = 0.36 \pm 0.02$ does not vary in the measured experimental range. On the basis of this experimental fact, it was postulated that R_{r} remains unaltered up to the transition temperature T_{c}, which was 45 °C for the given MBBA specimen.

The ratio ν_{r}/A' was determined from the temperature variation τ_{r}. For this purpose, the data [37, 61] on the half width of the contour of the $I_{\mathrm{H}}^{\mathrm{V}}$ component were extrapolated to the I → N transition point. An empirical expression was used for A', which yields $A' = 75.4\,\mathrm{J\,cm^{-3}}$ in the vicinity of the transition point, exceeding by a factor greater than 2 the experimental value $A' = 32.6\,\mathrm{J\,cm^{-3}}$ obtained from measurements of the integral scattered light intensity.

This led to the calculation of the parameters ν and μ for several temperatures near the I → N transition point. Since it had been postulated earlier that R_{r} is independent of temperature, the relaxing component of the viscosity $\Delta\eta = 2\mu^2/\nu$ remained constant as the transition point T_{c} was approached and was of the order of 6 cP.

When Zubkov et al. [63] formulated their experiments designed to investigate the kinetics of the fluctuations of the order parameter, their main task was to perform experiments in the immediate vicinity of T_{c}. This makes it possible to avoid hypotheses of different kinds concerning the temperature dependence of the parameters of the phenomenological theory.

Since there is no fine structure in the $I_{\mathrm{H}}^{\mathrm{V}}$ component of the scattered light near T_{c}, data on the Maxwell constant M were resorted to. The measurements were performed for two liquid crystals — MBBA and BMOAB. The behaviour of the relaxa-tion time as a function of temperature was investigated on apparatus in which the spectroscopic instrument was a three-pass Fabry – Perot interferometer. The temperature range in which the measurements were performed was limited by the instability of the laser radiation as regards frequency. In MBBA, the point closest to T_{c} at which measurements were made was at a distance of $T - T_{\mathrm{c}} = 7\,\mathrm{K}$, while in BMOAB the above temperature difference diminished to $T - T_{\mathrm{c}} = 5\,\mathrm{K}$. The measured relaxation times were fitted by the expression

$$\tau_{\mathrm{r}} = J_0 (T - T^*)^{-1} \mathrm{e}^{T/T_{\mathrm{r}}} ,$$

where $J_0 = 4.99 \times 10^{-12}\,\mathrm{sK}$ and $T_{\mathrm{r}} = 3750\,\mathrm{K}$ in MBBA and $J_0 = 4.06 \times 10^{-13}\,\mathrm{sK}$ and $T_{\mathrm{r}} = 4700\,\mathrm{K}$ in BMOAB.

As in the case of the Maxwell constant, in fitting the temperature variation of τ_{r} it was assumed that T^* does not differ greatly from the value obtained from the integral light scattering intensity.

Using experimental data for τ_{r} and M, the coefficients μ and ν were calculated. It was found that, as assumed by Alms et al. [61], the quantity $\Delta\eta$ depends only slightly on temperature, whereas the characteristic frequency of this contribution varies almost critically. The calculated value of $\Delta\eta$ is approximately 3.5 cP for MBBA, i.e. is smaller by a factor of 2 than in the study of Alms et al. [61].

Finally, it is important to emphasise that $\Delta\eta = 2\mu^2/\nu$ is of course independent of the choice of the order parameter, although the coefficients μ and ν are wholly determined by this choice.

Formally a nematic liquid crystal in the isotropic phase is an ordinary organic liquid. Light is scattered in such systems both by scalar density fluctuations and by tensor anisotropy fluctuations. However, as a result of the similarity to the ordered liquid crystal phase, tensor fluctuations, which almost wholly determine the light scattering by the system, predominate under these conditions. The integral scattering intensity in the isotropic phase of nematic liquid crystals has been investigated in very great detail and there is in this instance a satisfactory agreement between theory and experiment. The spectral composition of the scattered light has been thoroughly investigated only in the region remote from the phase transition point. In the immediate vicinity of T_{c}, the number of reliable results is small owing to the experimental difficulties described in Section 2.3. Improvement of the correlation spectroscopic technique gives rise to the hope for a considerable progress in this field in the immediate future.

As regards the critical behaviour of fluctuations in the I-phase, here are at present at least two alternative approaches whereby the experimental $\chi(T)$ and $C_p(T)$ relations in the isotropic phase of nematic liquid crystals can be described satisfactorily — the model of the interaction of nematic fluctuations and the model of the interaction of nematic and smectic fluctuations. Apparently the first and second mechanisms operate in nematic liquid crystals with broad and narrow nematic phases respectively. It is fairly difficult to separate these two effects because the temperature variations defined by Eqns (2.15) – (2.17) and by Eqns (2.19) and (2.20) are similar. Evidently, in order to throw light on the situation it is necessary to include in the joint treatment a greater number of various independent experiments, for example additional data on $R_{\mathrm{c}}(T)$ in the I-phase and T_{c}, Q, $C_p(T)$, $\chi(T)$, and $r_{\mathrm{c}}(T)$ in the N-phase. In the N-phase, it is essential to take into account the corresponding fluctuation corrections.

3. The ordered phase of nematics

3.1 Fluctuations of the order parameter in the ordered phase of nematics

In the study of fluctuations in the ordered phase of a nematic, the treatment is usually restricted to the consideration of the fluctuations of the director $\delta\boldsymbol{n} = \boldsymbol{n} - \boldsymbol{n}^0$ [9, 10]. The Oseen – Frank continuum theory, operating with the directors' field $\boldsymbol{n} = \boldsymbol{n}(\boldsymbol{r})$, is used to describe the distorted state of nematics. The corresponding potential Φ (the Frank energy) assumes the form

$$\Phi = \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\big[K_{11}(\operatorname{div}\boldsymbol{n})^2 + K_{22}(\boldsymbol{n}\cdot\operatorname{curl}\boldsymbol{n})^2 + K_{33}|\boldsymbol{n}\times\operatorname{curl}\boldsymbol{n}|^2 - \chi_{\mathrm{a}}(\boldsymbol{n}\cdot\boldsymbol{H})^2\big] , \tag{3.1}$$

where K_{jj} $(j = 1-3)$ are the Frank moduli, χ_{a} is the anisotropy of the magnetic susceptibility, and $\boldsymbol{H}$ is the magnetic field strength. For low values of δn, the fluctuations may be assumed to be transverse relative to the director: $\delta\boldsymbol{n} \approx \delta\boldsymbol{n}_{\perp}$. For $\chi_{\mathrm{a}} > 0$, when $\boldsymbol{n}^0 \| \boldsymbol{H}$, the mean square of their Fourier components is [9]

$$\langle|\delta n_{j,\boldsymbol{q}}|^2\rangle = Vk_{\mathrm{B}}T(q_\perp^2K_{jj}+q_\parallel^2K_{33}+\chi_{\mathrm{a}}H^2)^{-1}\,, \tag{3.2}$$

where

$$\delta\boldsymbol{n}_{\perp,\boldsymbol{q}} = \delta n_{1,\boldsymbol{q}}\,\boldsymbol{e}_1(\boldsymbol{q}_\perp)+\delta n_{2,\boldsymbol{q}}\,\boldsymbol{e}_2(\boldsymbol{q}_\perp)\,,$$

$$\boldsymbol{e}_1(\boldsymbol{q}_\perp)=\boldsymbol{q}_\perp/q_\perp,\quad \boldsymbol{e}_2(\boldsymbol{q}_\perp)=\boldsymbol{n}^0\times\boldsymbol{e}_1(\boldsymbol{q}_\perp),\quad j=1,\,2\,. \tag{3.3}$$

Here $\boldsymbol{q}_{||}$ and $\boldsymbol{q}_\perp$ are components of the wave vector $\boldsymbol{q}$ along and across $\boldsymbol{n}^0$.

These fluctuations are anomalously large and in the absence of an external field with $\boldsymbol{q}\to\boldsymbol{0}$, the Fourier components $\delta\boldsymbol{n}_{j,\boldsymbol{q}}$ increase without limit. However, the integrals with respect to $\mathrm{d}^3\boldsymbol{q}$, which determine the mean square of the fluctuations in the $\boldsymbol{r}$-space, remain finite [18]. Typical values of the nematic parameters are $\chi_{\mathrm{a}}\sim10^{-7}$ and $K_{jj}\sim10^{-6}$ dyn for $H\leqslant10^3$ Oe [9]. Therefore, for the characteristic optical values of the wave vector $q\sim k_0=\omega/c\sim10^5\ \mathrm{cm}^{-1}$, we have a small parameter $\Delta=\chi_{\mathrm{a}}H^2/k_0^2K_{jj}<10^{-5}$ and the 'field' term $\chi_{\mathrm{a}}H^2$ in Eqn (3.2) may be neglected.

The order parameter $S_{\alpha\beta}(\boldsymbol{r})$, which is described at each point $\boldsymbol{r}$ by Eqn (1.3) with $S_0=\mathrm{const}$ and the director $\boldsymbol{n}=\boldsymbol{n}(\boldsymbol{r})$, corresponds to the Oseen–Frank theory. This implies the conservation of uniaxiality and of the degree of order S_0 in the system subjected to fluctuations. If, apart from fluctuations of the director, one is also interested in local changes in S_0 and in the appearance of local biaxiality, then the distorted state of the nematic must be described in terms of the tensor order parameter $S_{\alpha\beta}(\boldsymbol{r})$ [24, 25]. In the uniaxial phase with the equilibrium director $\boldsymbol{n}^0$, it is convenient to use the parametrisation proposed by Pokrovskii and Kats [24] for fluctuations of the tensor order parameter $\varphi_{\alpha\beta}(\boldsymbol{r})$:

$$\varphi_{\alpha\beta}(\boldsymbol{r})=\varphi_{\alpha\beta}^{\perp(1)}(\boldsymbol{r})+\varphi_{\alpha\beta}^{\perp(2)}(\boldsymbol{r})+\varphi_{\alpha\beta}^{\|}(\boldsymbol{r})\,, \tag{3.4}$$

where

$$\varphi_{\alpha\beta}^{\perp(1)}(\boldsymbol{r})=\xi_1(\boldsymbol{r})(n_\alpha^0e_{1\beta}+n_\beta^0e_{1\alpha})+\xi_2(\boldsymbol{r})(n_\alpha^0e_{2\beta}+n_\beta^0e_{2\alpha}),$$

$$\varphi_{\alpha\beta}^{\perp(2)}(\boldsymbol{r})=\xi_3(\boldsymbol{r})(e_{1\alpha}e_{2\beta}+e_{1\beta}e_{2\alpha})+\xi_4(\boldsymbol{r})(e_{1\alpha}e_{1\beta}-e_{2\beta}e_{2\alpha}),$$

$$\varphi_{\alpha\beta}^{\|}(\boldsymbol{r})=\sqrt{3}\xi_5(\boldsymbol{r})(n_\alpha^0n_\beta^0-\tfrac{1}{3}\delta_{\alpha\beta})\ . \tag{3.5}$$

Here $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, and $\boldsymbol{n}^0$ are a set of three orthogonal unit vectors. The tensors $\varphi_{\alpha\beta}^{\perp(1)}$, $\varphi_{\alpha\beta}^{\perp(2)}$, and $\varphi_{\alpha\beta}^{||}$ are defined invariantly in Eqn (3.2) in the sense that for any other choice of auxiliary axes $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ corresponding to a fixed $\boldsymbol{n}^0$, each of these tensors is conserved and only the pairs of variables $\xi_{1,2}$ and $\xi_{3,4}$ are altered. In terms of the terminology of Pokrovskii and Kats [24], the modes $\xi_{1,2}$ are referred to as transverse uniaxial, $\xi_{3,4}$ are transverse biaxial, and ξ_5 is longitudinal. The quantities ξ_1/S_0 and ξ_2/S_0 have the significance of projections of the vector of the fluctuations of the director δn onto the axes $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$:

$$\delta n_\perp(\boldsymbol{r})=\frac{\xi_1(\boldsymbol{r})\boldsymbol{e}_1+\xi_2(\boldsymbol{r})\boldsymbol{e}_2}{S_0}\,. \tag{3.6}$$

It is usually understood that the fluctuations occur spontaneously — as a result of the random thermal movement of the molecules of the system. Such are, for example, the density or anisotropy fluctuations in the isotropic medium and all the types of fluctuations ξ_j $(j=1-5)$ introduced in the ordered and isotropic phases may also have the same origin. However, in the ordered phase the specific symmetri-cal properties of the nematic liquid crystal — the degeneracy of its continuous symmetry group — lead to the possibility of yet another mechanism for the generation of the fluctuations $\xi_{3,4,5}$ as a result of the large scale fluctuations of the director [23, 24]. In order to demonstrate this, we shall consider the change in the tensor $S_{\alpha\beta}$ following an arbitrary finite, but not infinitesimal, rotation of the director $\boldsymbol{n}^0$:

$$\boldsymbol{n}=\boldsymbol{n}^0+\delta\boldsymbol{n}=\boldsymbol{n}^0(1+\delta n_\|)+\frac{\xi_1}{S_0}\boldsymbol{e}_1+\frac{\xi_2}{S_0}\boldsymbol{e}_2\,, \tag{3.6a}$$

where $\delta n_{||}=\boldsymbol{n}^0\cdot\boldsymbol{\delta n}$. Taking into account the retention of the length $\boldsymbol{n}^2=(\boldsymbol{n}^0)^2=1$ ('the principle of the conservation of the modulus' [7]),

$$2\delta n_\|+\delta n_\|^2+(\xi_1^2+\xi_2^2)S_0^{-1}=0\,, \tag{3.7}$$

we find that the fluctuation of the order parameter in this rotation is

$$\begin{aligned}\tilde\varphi_{\alpha\beta}(\boldsymbol{r})&=S_0]n_\alpha(\boldsymbol{r})n_\beta(\boldsymbol{r})-\tfrac{1}{3}\delta_{\alpha\beta}]-S_{\alpha\beta}^0=\varphi_{\alpha\beta}^{\perp(1)}(\boldsymbol{r})(1+\delta n_\|)\\&\quad+\tilde\xi_3(\boldsymbol{r})(e_{1\alpha}e_{2\beta}+e_{1\beta}e_{2\alpha})+\tilde\xi_4(\boldsymbol{r})(e_{1\alpha}e_{1\beta}-e_{2\beta}e_{2\alpha})\\&\quad+\sqrt{3}\,\tilde\xi_5(\boldsymbol{r})(n_\alpha^0n_\beta^0-\tfrac{1}{3}\delta_{\alpha\beta})\,,\end{aligned} \tag{3.8}$$

where

$$\begin{aligned}\tilde\xi_3(\boldsymbol{r})&=\frac{\xi_1(\boldsymbol{r})\xi_2(\boldsymbol{r})}{S_0}\,,\\ \tilde\xi_4(\boldsymbol{r})&=\frac{\xi_1^2(\boldsymbol{r})-\xi_2^2(\boldsymbol{r})}{2S_0}\,,\\ \tilde\xi_5(\boldsymbol{r})&=-\sqrt{3}\,\frac{\xi_1^2(\boldsymbol{r})+\xi_2^2(\boldsymbol{r})}{2S_0}\,.\end{aligned} \tag{3.9}$$

Thus, according to the second-order terms in $\xi_{1,2}$, the fluctuations of the director generate longitudinal ($\tilde\xi_5$) and biaxial ($\tilde\xi_{3,4}$) fluctuations. The appearance of nonclassical longitudinal fluctuations $\tilde\xi_5$ of this nature is associated with the fact that the local deviations of the director lead to a decrease in the average degree of order in the system along $\boldsymbol{n}^0$. The appearance of nonclassical biaxial fluctuations $\tilde\xi_{3,4}$ can be easily understood in relation to the uniaxial ellipsoid: when this axis deviates from $\boldsymbol{n}^0$, the cross-section in the plane orthogonal to $\boldsymbol{n}^0$ becomes noncircular.

In order to calculate the correlation function of the spontaneous fluctuations ξ_j, it is essential to have the corresponding expression for the fluctuation contribution to the thermodynamic potential of the nematic liquid crystal $\delta\boldsymbol{\Phi}$. By virtue of the symmetry of the nematic liquid crystal relative to the reflection of all the coordinate axes, $\boldsymbol{r}\to-\boldsymbol{r}$, only invariants of the types defined by Eqns (1.10) and (1.11) contribute to $\boldsymbol{\Phi}$.

The density of the homogeneous component of the potential $\boldsymbol{\Phi}_0$, determined by invariants of type (1.10), can be conveniently regarded, by virtue of Eqn (1.13), as a function $\boldsymbol{\Phi}(x,y)$ of two independent invariants of the order parameter $S_{\alpha\beta}:x=\mathrm{Sp}\,\widehat{S}^2,\ \ y=\mathrm{Sp}\,\widehat{S}^3,\ \ x^3\leqslant6y^2$ [24]. Taking into account the interaction with the external field H, we have in terms of the lowest order in $\widehat{S}$

$$\boldsymbol{\Phi}_0=\boldsymbol{\Phi}(x,\,y)-(\chi_{\mathrm{a}}S_{\alpha\beta}H_\alpha H_\beta/2S_0)\,. \tag{3.10}$$

For the case $\chi_{\mathrm{a}}>0$, when $\boldsymbol{n}^0||\boldsymbol{H}$, the equilibrium condition

$$2S_0\frac{\partial\boldsymbol{\Phi}_0}{\partial x}+S_0^2\frac{\partial\boldsymbol{\Phi}_0}{\partial y}=\frac{1}{2S_0}\chi_{\mathrm{a}}H^2\,, \tag{3.11}$$

which is a consequence of the uniaxiality of the nematic liquid crystal, leads to

$$\delta\boldsymbol{\Phi}_0^{(\mathrm{N})}=\tfrac{1}{2}[A_{\mathrm{H}}(\xi_1^2+\xi_2^2)+\tilde A_\perp(\xi_3^2+\xi_4^2)+\tilde A_\|\xi_5^2]\,, \tag{3.12}$$

where

$$A_{\mathrm{H}} = \chi_{\mathrm{a}} H^{2} S_0^{-2}, \quad \widetilde{A}_{\perp} = A_{\perp} - 2A_{\mathrm{H}},$$

$$\widetilde{A}_{\parallel} = A_{\parallel} + 2A_{\mathrm{H}}, \quad A_{\perp} = 12 \frac{\partial \Phi_0}{\partial x},$$

$$A_{\parallel} = 3 \frac{\partial^2 \Phi_0}{\partial S^2} = 4 \left(-\frac{\partial \Phi_0}{\partial x} + \frac{4}{3} S_0^2 \frac{\partial^2 \Phi_0}{\partial x^2} + \frac{4}{3} S_0^3 \frac{\partial^2 \Phi_0}{\partial x \, \partial y} + \frac{1}{3} S_0^3 \frac{\partial^2 \Phi_0}{\partial y^2} \right). \tag{3.13}$$

All the derivatives in Eqn (3.12) are calculated subject to the condition $x^3 = 6y^2$ [23, 24]. The conditions for the stability of the ordered phase are specified by the inequalities $\widetilde{A}_{\perp} > 0$ and $\widetilde{A}_{\parallel} > 0$.

Analysis similar to that specified by Eqns (3.10)–(3.13) shows that, in the case where $\chi_{\mathrm{a}} < 0$, that state of the nematic with $\boldsymbol{n}^0 \perp \boldsymbol{H}$, minimising the Frank energy specified by Eqn (3.1), is unstable in relation to the biaxial fluctuations $\xi_{3,4}$. As a result, a weak biaxiality proportional to $\chi_{\mathrm{a}} H^2$ should arise in the nematic for $\chi_{\mathrm{a}} < 0$.

The inhomogeneous part of Φ can be constructed from invariants of type (1.11) having generated all possible contractions of two tensors $\nabla_{\alpha} \varphi_{\beta\gamma}$ and an even number of vectors $\boldsymbol{n}^0$. There are 11 such invariants. As a result we have the following expression, in the Gaussian approximation, for the fluctuation contribution to the thermodynamic potential of the nematic by the modes $\xi_{1,\boldsymbol{q}}, \ldots, \xi_{5,\boldsymbol{q}}$ with the given wave vector $\boldsymbol{q}$ [23]:

$$\delta \Phi^{(\mathrm{N})} = \frac{1}{2V} \left[\mathcal{K}_1 \xi_1^2 + \mathcal{K}_2 \xi_2^2 + \mathcal{C}_{\perp} (\xi_3^2 + \xi_4^2) + \mathcal{C}_{\parallel} \xi_5^2 + 2\mathcal{D} (\xi_1 \xi_4 + \xi_2 \xi_3) + 2\mathcal{H} \xi_1 \xi_5 + 2\mathcal{F} \xi_4 \xi_5 \right], \tag{3.14}$$

where

$$\mathcal{K}_j = S_0^{-2} (q_{\perp}^2 K_{jj} + q_{\parallel}^2 K_{33} + \chi_{\mathrm{a}} H^2), \quad j = 1, 2,$$

$$\mathcal{C}_{\perp} = \widetilde{A}_{\perp} + q^2 (b_{\perp} + c_{\perp} \cos^2 \psi),$$

$$\mathcal{C}_{\parallel} = \widetilde{A}_{\parallel} + q^2 (b_{\parallel} + c_{\parallel} \cos^2 \psi),$$

$$\mathcal{D} = q^2 d \sin 2\psi, \quad \mathcal{H} = q^2 h \sin 2\psi, \quad \mathcal{F} = q^2 f \sin^2 \psi; \tag{3.15}$$

here $b_{\perp,\parallel}$, $c_{\perp,\parallel}$, d, f, and h are independent coefficients and ψ is the angle between $\boldsymbol{q}$ and $\boldsymbol{n}^0$. Eqn (3.14) refers to the selection of the auxiliary axes e_1 and e_2 in Eqn (3.5) in conformity with Eqn (3.3). Designations of the type $\xi_j^2 = \xi_{j,\boldsymbol{q}} \xi_{j,\boldsymbol{q}}^*$, $2\xi_j \xi_i = \xi_{j,\boldsymbol{q}} \xi_{i,\boldsymbol{q}}^* \xi_{j,\boldsymbol{q}}^* + \xi_{i,\boldsymbol{q}}$, where the asterisk denotes complex conjugation, are implied in Eqn (3.14).

In the case of not very strong fields H, only the coefficients $\widetilde{A}_{\perp,\parallel}$ can exhibit a pronounced temperature dependence in Eqn (3.14). For the weak first-order transition I → N, only the ξ_5 mode exhibits a critical behaviour among the ξ_j modes. The second-order transition $\mathrm{N} \to \mathrm{N}_2$ is characterised by a critical behaviour of the ξ_3 and ξ_4 modes, while both $\xi_{3,4}$ and ξ_5 exhibit a critical behaviour in the transition in the region of the $\mathrm{I}-\mathrm{N}-\mathrm{N}_2$ tricritical point. It is of interest to note that, as a consequence of Eqn (3.13), $\widetilde{A}_{\perp}$ can become zero for fairly strong fields H, and hence a transition to a biaxial phase with a critical behaviour of the $\xi_{3,4}$ modes should be observed.

In the usual Landau–de Gennes model [Eqn (2.1)] with $E = D_1 = D_2 = 0$, $C > 0$, and $H = 0$, there is a first-order I → N transition. $T_{\mathrm{c}} = T^*[1 + (B^2/27A'C)]$ for this transition, while the temperature corresponding to the loss of stability by the N-phase is $T^{**} = T^*[1 + (B^2/24A'C)]$. The coefficients $A_{\perp}$ and $A_{\parallel}$ then assume the following form in the vicinity of T^{**}:

$$A_{\parallel}(T) = \frac{2}{3} B \left(\frac{3A'}{2C} \right)^{1/2} \left(\frac{T^{**} - T}{T^{**}} \right)^{1/2} + 4A' \frac{T^{**} - T}{T^{**}},$$

$$A_{\perp}(T^{**}) = B^2/2C > 0. \tag{3.16}$$

Attention may be drawn to the identity $T_{\mathrm{c}} - T^* = 8(T^{**} - T_{\mathrm{c}})$, i.e. this model predicts that T^{**} is much closer to T_{c} than T^* and the observation of critical phenomena on the side of the nematic phase might be of interest. The quantity

$$\delta \Phi(\xi_1, \xi_2) = \frac{1}{2V} \left(\mathcal{K}_1 |\xi_{1,\boldsymbol{q}}|^2 + \mathcal{K}_2 |\xi_{2,\boldsymbol{q}}|^2 \right) \tag{3.17}$$

in Eqn (3.14) is the fluctuation analogue of the Frank energy defined by Eqn (3.1).

We may note that this method for the derivation of the elastic distortion energy makes possible certain conclusions of a general nature concerning the behaviour of the Frank moduli K_{jj} as functions of S_0, which follow from the general symmetrical considerations. In particular,

$$K_{11} = k_1 S_0^2 + k_2 S_0^3 + \ldots,$$

$$K_{22} = k_3 S_0^2 + k_4 S_0^3 + \ldots,$$

$$K_{33} = k_1 S_0^2 + k_5 S_0^3 + \ldots. \tag{3.18}$$

where $k_1, \ldots, k_5$ are constants, i.e. $K_{11} - K_{33} \sim S_0^3 + \ldots$.

If it is assumed that the terms containing q^2 in Eqn (3.15) are small compared with the constants $\widetilde{A}_{\perp}$ and $\widetilde{A}_{\parallel}$, then, to within second-order terms in $\boldsymbol{q}$, the following expressions follow from Eqn (3.14) for the quadratic correlators of the fluctuations $\xi_{1,\boldsymbol{q}}, \ldots, \xi_{5,\boldsymbol{q}}$:

$$\langle \xi_j^2 \rangle_{\boldsymbol{q}} = k_{\mathrm{B}} T S_0^2 (q_{\perp}^2 K_{jj} + q_{\parallel}^2 K_{33} + \chi_{\mathrm{a}} H^2)^{-1}, \quad j = 1, 2,$$

$$\langle \xi_3^2 \rangle_{\boldsymbol{q}} = k_{\mathrm{B}} T \left\{ \widetilde{A}_{\perp} + q^2 [b_{\perp} + c_{\perp} \cos^2 \psi - q^2 d^2 \sin^2 (2\psi) \mathcal{K}_2^{-1}] \right\}^{-1},$$

$$\langle \xi_4^2 \rangle_{\boldsymbol{q}} = k_{\mathrm{B}} T \left\{ \widetilde{A}_{\perp} + q^2 [b_{\perp} + c_{\perp} \cos^2 \psi - q^2 d^2 \sin^2 (2\psi) \mathcal{K}_1^{-1}] \right\}^{-1},$$

$$\langle \xi_5^2 \rangle_{\boldsymbol{q}} = k_{\mathrm{B}} T \left\{ \widetilde{A}_{\parallel} + q^2 [b_{\parallel} + c_{\parallel} \cos^2 \psi - q^2 d^2 \sin^2 (2\psi) \mathcal{K}_1^{-1}] \right\}^{-1}. \tag{3.19}$$

Attention should be drawn to the fact that the fluctuations $\langle \xi_1^2 \rangle$ and $\langle \xi_2^2 \rangle$ expressed in terms of this approximation agree with the familiar results of de Gennes [Eqn (3.2)] [9].

The correlators of the nonclassical quantities $\langle \widetilde{\xi}_3^2 \rangle_{\boldsymbol{q}}$, $\langle \widetilde{\xi}_4^2 \rangle_{\boldsymbol{q}}$, $\langle \widetilde{\xi}_5^2 \rangle_{\boldsymbol{q}}$, and $\langle \widetilde{\xi}_4 \widetilde{\xi}_5 \rangle_{\boldsymbol{q}}$ have singularities $\sim q^{-1}$ for $H = 0$. In particular,

$$\langle \widetilde{\xi}_4^2 \rangle_{\boldsymbol{q}} = \frac{1}{3} \langle \widetilde{\xi}_5^2 \rangle_{\boldsymbol{q}} = \frac{(k_{\mathrm{B}} T)^2 S_0}{16 q K_{33}^{1/2}} \left[K_{11}^{-1} K_1^{-1/2}(\psi) + K_{22}^{-1} K_2^{-1/2}(\psi) \right],$$

$$\langle \widetilde{\xi}_4 \widetilde{\xi}_5^* \rangle_{\boldsymbol{q}} = \sqrt{3} \frac{(k_{\mathrm{B}} T)^2 S_0}{16 q K_{33}^{1/2}} \left[K_{22}^{-1} K_2^{-1/2}(\psi) - K_{11}^{-1} K_1^{-1/2}(\psi) \right], \tag{3.20}$$

where $K_j(\psi) = K_{jj}\cos^2\psi + K_{33}\sin^2\psi$. The correlation function $G_{\alpha\beta\gamma\rho}(\boldsymbol{q})$ in the N-phase can be easily found from Eqns (3.19) and (3.20). In particular, when account is taken of the fluctuations of the director, we have

$$G_{\alpha\beta\gamma\rho}(\boldsymbol{q}) = \sum_{j=1}^{2}\langle\xi_j^2\rangle_{\boldsymbol{q}}(e_{j\alpha}n_\beta^0 + e_{j\beta}n_\alpha^0)(e_{j\gamma}n_\rho^0 + e_{j\rho}n_\gamma^0). \quad (3.21)$$

The complete expression for $G_{\alpha\beta\gamma\rho}$ taking into account all the modes ξ_j and $\widetilde{\xi}_j$ has already been published [23].

3.2 Fluctuations in biaxial nematics

Apart from the isotropic and uniaxial nematic phases, there is also a biaxial phase in nematic liquid crystals. It was observed experimentally in lyotropic nematic liquid crystals [64]. Theoretical studies on this phase and the corresponding phase transitions have been carried out also in terms of lattice models [65, 66], the Maier–Saupe mean field theory [67], and the Landau theory [52, 66]. An analogue of the Frank energy has been formulated [68] for the N_2-phase and in other studies [69] its hydrodynamics were established. The fluctuations in this phase have been considered within the framework of the Landau theory [70] and from a general symmetrical standpoint [71].

The corresponding analogue of Eqn (1.3) for the equilibrium value of the order parameter $\widehat{S}^0$ assumes the following form in this case [9, 52]:

$$S_{\alpha\beta}^0 = S_1 n_\alpha^0 n_\beta^0 + S_2 m_\alpha^0 m_\beta^0 - \tfrac{1}{3}(S_1 + S_2)\delta_{\alpha\beta}\,; \quad (3.22)$$

where $\boldsymbol{n}^0$ and $\boldsymbol{m}^0$ are mutually orthogonal unit vectors $S_1 \neq 0$, $S_2 \pm 0$, and $S_1 \neq S_2$. Eqn (3.22) corresponds to the choice $\boldsymbol{n}^0 = \boldsymbol{e}_1^0$, $\boldsymbol{m}^0 = \boldsymbol{e}_2^0$, $S_1 = 2s_1^0 + s_2^0$, and $S_2 = s_1^0 + 2s_2^0$ in Eqn (1.1). In the biaxial phase, described by the order parameter defined by Eqn (3.22), the fluctuation tensor $\varphi_{\alpha\beta}$ can be conveniently expressed in the form (3.4), using the parametrisation

$$\begin{aligned}\varphi_{\alpha\beta}^{\perp(1)}(\boldsymbol{r}) &= \xi_1(\boldsymbol{r})(m_\alpha^0 e_\beta^0 + m_\beta^0 e_\alpha^0) + \xi_2(\boldsymbol{r})(n_\alpha^0 e_\beta^0 + n_\beta^0 e_\alpha^0)\\ &\quad + \xi_3(\boldsymbol{r})(n_\alpha^0 m_\beta^0 + n_\beta^0 m_\alpha^0)\,,\\ \varphi_{\alpha\beta}^{\perp(2)}(\boldsymbol{r}) &= \xi_4(\boldsymbol{r})\big[(2S_2 - S_1)n_\alpha^0 n_\beta^0 + (S_2 - 2S_1)m_\alpha^0 m_\beta^0\\ &\quad + (S_1 - S_2)\delta_{\alpha\beta}\big],\\ \varphi_{\alpha\beta}^{\parallel}(\boldsymbol{r}) &= \xi_5(\boldsymbol{r})S_{\alpha\beta}^0\,,\end{aligned} \quad (3.23)$$

where $\boldsymbol{e}^0 = \boldsymbol{m}^0 \times \boldsymbol{n}^0$ is a unit vector orthogonal to $\boldsymbol{n}^0$ and $\boldsymbol{m}^0$.

We may note that an infinitesimal rotation of the tensor $S_{\alpha\beta}^0$ corresponds to the fluctuations $\varphi_{\alpha\beta}^{\perp(1)}$. In this sense, they can be regarded as fluctuations of the directors $\boldsymbol{n}^0$ and $\boldsymbol{m}^0$. Here it must be emphasised, however, that the quantities $\boldsymbol{n}^0$ and $\boldsymbol{m}^0$ are not independent, since they are linked by the orthogonality condition $\boldsymbol{n}^0 \cdot \boldsymbol{m}^0 = 0$. As in a uniaxial nematic, these are the most intense fluctuations in the limit $\boldsymbol{q} \to \boldsymbol{0}$ because uniform rotations of the nematic liquid crystal as a whole do not require an energy expenditure.

As for the uniaxial phase, fluctuations of this type (ξ_1, ξ_2, and ξ_3) contribute in terms of second-order terms to the remaining modes ξ_4 and ξ_5 by virtue of the principle of the conservation of the modulus:

$$\begin{aligned}\widetilde{\xi}_4 &= \left(\xi_1^2\frac{S_1 + S_2}{S_2 - S_1} + \xi_2^2\frac{S_1 - 2S_2}{S_1} + \xi_3^2\frac{2S_1 - S_2}{S_2}\right)\\ &\quad \times\big[2(S_1^2 - S_1 S_2 + S_2^2)\big]^{-1},\\ \widetilde{\xi}_5 &= -3(\xi_1^2 + \xi_2^2 + \xi_3^2)/2(S_1^2 - S_1 S_2 + S_2^2)\,.\end{aligned} \quad (3.24)$$

In considering the density of the uniform component of the energy of the distortion of a biaxial nematic liquid crystal $\varPhi_0(x, y)$ ($x = \mathrm{Sp}\,\widehat{S}^2$, $y = \mathrm{Sp}\,\widehat{S}^3$), one must take into account the fact that the equilibrium conditions have in this case the following form (for $H = 0$):

$$\frac{\partial\varPhi_0}{\partial x} = 0, \quad \frac{\partial\varPhi_0}{\partial y} = 0\,. \quad (3.25)$$

To within terms of the order of $\widehat{\varphi}^2$, we have

$$\delta\varPhi_0^{(\mathrm{N}_2)} = A_{44}\xi_4^2 + 2A_{45}\xi_4\xi_5 + A_{55}\xi_5^2\,, \quad (3.26)$$

where A_{44}, A_{45}, and A_{55} are constants, $A_{44} > 0$, and $D = A_{44}A_{55} - A_{45}^2 > 0$.

The nonuniform component of the fluctuation contribution to the energy of the distortion of a biaxial nematic can be derived by setting up all possible invariants comprising the vectors $\boldsymbol{m}^0$ and $\boldsymbol{n}^0$ and two tensors $\nabla_\alpha\varphi_{\beta\gamma}$. The number of such invariants is 37. Certain invariants are then interdependent by virtue of the orthogonality condition $\boldsymbol{m}^0 \cdot \boldsymbol{n}^0 = 0$. As a result, the complete expression for the distortion energy $\delta\varPhi^{(\mathrm{N}_2)}$ contains 27 phenomenological coefficients when account is taken of all the modes $\xi_1, \ldots, \xi_5$.

The contribution to the thermodynamic potential of a biaxial nematic liquid crystal associated with the principal Goldstone modes $\xi_{1,\boldsymbol{q}}$, $\xi_{2,\boldsymbol{q}}$, and $\xi_{3,\boldsymbol{q}}$ contains 12 elastic moduli (cf Trebin [68]):

$$\delta\varPhi^{(\mathrm{N}_2)}(\xi_1, \xi_2, \xi_3) = \frac{1}{2V}\sum_{i,j=1}^{3}\mathcal{K}_{ij}\,\xi_i\,\xi_j\,, \quad (3.27)$$

where

$$\begin{aligned}\mathcal{K}_{ii} &= q^2(K_{ii}^{(1)}\cos^2\psi_1 + K_{ii}^{(2)}\cos^2\psi_2 + K_{ii}^{(3)}\cos^2\psi_3),\\ \mathcal{K}_{ij} &= 2q^2 K_{ij}\cos\psi_i\,\cos\psi_j, \quad i \neq j\,.\end{aligned} \quad (3.28)$$

Here ψ_i ($i = 1-3$) are the angles formed by the wave vector $\boldsymbol{q}$ with the axes $\boldsymbol{n}^0$, $\boldsymbol{m}^0$, and $\boldsymbol{e}^0$ respectively. The fluctuations of the modes ξ_1, ξ_2, and ξ_3 are of the Goldstone type:

$$\langle\xi_i^2\rangle_{\boldsymbol{q}} \sim q^{-2} \quad \text{and} \quad \langle\xi_i\xi_j\rangle_{\boldsymbol{q}} \sim q^{-2}\ (i, j = 1-3)\,. \quad (3.29)$$

Correlators of weaker classical fluctuations of type ξ_4 and ξ_5 permit going to the limit $\boldsymbol{q} \to \boldsymbol{0}$ and are given by

$$\langle\xi_4^2\rangle = \frac{k_{\mathrm{B}}TA_{44}}{D}\,, \quad \langle\xi_5^2\rangle = \frac{k_{\mathrm{B}}TA_{55}}{D}\,,$$

$$\langle\xi_4\xi_5^*\rangle = \frac{k_{\mathrm{B}}TA_{45}}{D} \quad (3.30)$$

when $\boldsymbol{q} = 0$. The mode ξ_4 behaves critically in the transition to the N-phase and all the correlators $\langle\xi_4^2\rangle$, $\langle\xi_5^2\rangle$, and $\langle\xi_4\xi_5\rangle$ diverge at $\boldsymbol{q} \to 0$ in the region of the N_2–N–I tricritical point.

The correlators of the nonclassical fluctuations $\widetilde{\xi}_4$ and $\widetilde{\xi}_5$ have a singularity $\sim q^{-1}$, as in a uniaxial phase.

3.3 Light scattering in the ordered phase of a uniaxial nematic

One of the main problems in the theoretical description of light scattering in the ordered phase of a nematic is associated with the fact that, in terms of its optical properties, this phase is an anisotropic crystal. In uniaxial nematics, to which we shall confine ourselves in this section, the equilibrium relative permittivity tensor assumes the form

$$\varepsilon^0_{\alpha\beta} = \varepsilon_\perp \delta_{\alpha\beta} + \varepsilon_{\mathrm{a}} n^0_\alpha n^0_\beta \,, \tag{3.31}$$

where $\varepsilon_{\mathrm{a}} = \varepsilon_{\|} - \varepsilon_\perp$; $\varepsilon_{\|}$ and $\varepsilon_\perp$ are the relative permittivities along and across $\boldsymbol{n}^0$ respectively. Since the optical anisotropy of the majority of nematics is not small (it reaches 0.3 and more [14] at an optical frequency $\varepsilon_{\mathrm{a}}/\varepsilon_\perp$), it follows that, in any theory of the propagation and scattering of light in nematics claiming to allow a quantitative comparison with experiment, it is essential to take into account the anisotropy.

Lax and Nelson constructed a logical general theory of light scattering in anisotropic media [72–74]. Its principal results reduce to the following. Green's function for an electromagnetic field in a uniaxial medium has the following form in terms of the $\boldsymbol{q}$, ω representation [72]:

$$T_{\alpha\beta}(\boldsymbol{k}, \omega) = \sum_{j=1}^{3} \frac{k^2_{(j)}}{k^2 - k^2_{(j)} - \mathrm{i}0} \, \frac{e^{(j)}_\alpha e^{(j)}_\beta}{\left(\boldsymbol{e}^{(j)}, \hat{\varepsilon}^0 \boldsymbol{e}^{(j)}\right)} \,, \tag{3.32}$$

where $\boldsymbol{e}^{(j)}$ are the vectors of the polarisations of the normal waves in the medium [$\boldsymbol{e}^{(1)}$ is an ordinary wave (0), $\boldsymbol{e}^{(2)}$ is an extraordinary wave (e), and $\boldsymbol{e}^{(3)}$ is a longitudinal wave] and $k_{(j)}$ are their wavenumbers ($j = 1-3$):

$$k_{(1)} = \varepsilon_\perp^{1/2} \frac{\omega}{c} \,, \quad k_{(2)} = \left[\frac{\varepsilon_\perp \varepsilon_\|}{\varepsilon_\perp + \varepsilon_{\mathrm{a}} (\boldsymbol{n}^0 \cdot \boldsymbol{s})^2} \right]^{1/2} \,, \quad k_{(3)} = \infty \,, \tag{3.33}$$

where $\boldsymbol{s} = \boldsymbol{k}/k$; $\boldsymbol{e}^{(1)}$, $\boldsymbol{e}^{(2)}$, and $\boldsymbol{e}^{(3)}$ are unit vectors determined by the following conditions: $\boldsymbol{e}^{(1)} \perp \boldsymbol{n}^0$, $\boldsymbol{e}^{(1)} \perp \boldsymbol{s}$; $\boldsymbol{e}^{(2)} \perp (\hat{\varepsilon}^0)^{-1} \boldsymbol{s}$ with $\boldsymbol{e}^{(2)}$ located in the plane of the vectors $\boldsymbol{s}$ and $\boldsymbol{n}^0$; $\boldsymbol{e}^{(3)} = \boldsymbol{s}$.

The asymptotic form of Green's function (3.32) in terms of the $\boldsymbol{r}$, ω representation has the following form for large distances R [73]:

$$T_{\alpha\beta}(\boldsymbol{R}, \omega) = \frac{\omega^2}{4\pi c^2 R} \sum_{j=1}^{3} n^2_{(j)} \frac{e^{(j)}_\alpha e^{(j)}_\beta}{\left(\boldsymbol{e}^{(j)}, \hat{\varepsilon}^0 \boldsymbol{e}^{(j)}\right)} f_{(j)} \mathrm{e}^{i \boldsymbol{k}^{(j)}_{\mathrm{st}} \cdot \boldsymbol{R}} \,, \tag{3.34}$$

where

$$\boldsymbol{k}^{(1)}_{\mathrm{st}} = \varepsilon_\perp^{1/2} \frac{\omega}{c} \frac{\boldsymbol{R}}{R} \,,$$

$$\boldsymbol{k}^{(2)}_{\mathrm{st}} = \left[\frac{\varepsilon_\perp \varepsilon_\|}{\left(R, (\hat{\varepsilon}^0)^{-1} R\right)} \right]^{1/2} \frac{\omega}{c} (\hat{\varepsilon}^0)^{-1} \boldsymbol{R} \,,$$

$$n^2_{(1)} = \varepsilon_\perp \,, \quad n^2_{(1)} = \varepsilon_\| \varepsilon_\perp / (\boldsymbol{s}, \hat{\varepsilon}^0 \boldsymbol{s}) \,,$$

$$f_{(1)} \equiv 1 \,, \quad f_{(2)} = \left\{ \frac{(\boldsymbol{s}, \hat{\varepsilon}^0 \boldsymbol{s}) [\boldsymbol{s}, (\hat{\varepsilon}^0)^2 \boldsymbol{s}]}{\varepsilon_\| \varepsilon_\perp^2} \right\}^{1/2} ; \tag{3.35}$$

Here $\boldsymbol{s} = \boldsymbol{k}_{(j)}/k_{(j)}$ and $\boldsymbol{k}_{(j)} = \boldsymbol{k}^{(j)}_{\mathrm{st}}$ for all the quantities. (Cf also Motulevich's earlier results [1, 75]).

Eqn (3.34) makes it possible to find an expression for the intensity of single light scattering in a uniaxial anisotropic medium [73]:

$$I(\boldsymbol{e}^{(i)}, \boldsymbol{e}^{(s)}) = Z^{(i)}_0 \frac{n_{(s)} f^2_{(s)}}{n_{(i)} \cos \delta^{(i)} \cos^3 \delta^{(s)}} \times e^{(s)}_\nu e^{(s)}_\mu G_{\nu\rho\mu\eta}(\boldsymbol{q}_{\mathrm{sc}}) e^{(i)}_\rho e^{(i)}_\eta \,. \tag{3.36}$$

Here the notation is the same as in Eqn (2.8); $\boldsymbol{k}^{(s)} = \boldsymbol{k}^{(s)}_{\mathrm{st}}$,

$$\cos \delta^{(j)} = \left(\boldsymbol{e}^{(j)}, \hat{\varepsilon}^0 \boldsymbol{e}^{(j)}\right)^{1/2} / n_{(j)} \,, \tag{3.37}$$

$\delta^{(j)}$ is the angle between the electric field vector $\boldsymbol{e}^{(j)}$ and the electric induction vector $\hat{\varepsilon}^0 \boldsymbol{e}^{(j)}$ (for an ordinary ray $\delta^{(1)} = 0$). In the derivation of Eqn (3.36), use was also made of the formula

$$|\boldsymbol{S}^{(j)}| = (c/4\pi) |\boldsymbol{E}^{(j)}|^2 n_{(j)} \cos \delta^{(j)} \tag{3.38}$$

for the modulus of the Poynting vector in an anisotropic medium, where $\boldsymbol{E}^{(j)}$ is the amplitude of a jth type wave.

Eqn (3.36) refers to the case where the incident and scattered rays are propagated within the medium. The effects associated with allowance for the influence of the refraction of the incident and scattered rays at the boundary of the specimen have already been examined [73, 74].

As already stated above, the main contribution to the scattering in nematic liquid crystals comes from the Goldstone modes ξ_1 and ξ_2. Scattering by these modes is particularly pronounced for low values of q_{sc}, i.e. close to the forward direction. Since in terms of lowest-order terms in S_0 it follows from Eqn (3.18) that $K_{jj} \sim S_0^2$, the quantities $\langle \xi^2_{1,2} \rangle_{\boldsymbol{q}}$ depend only weakly on S_0 at $H \to 0$ according to Eqn (3.19). Therefore, the quantity $k_{\mathrm{B}} T/I$ should be virtually independent of temperature throughout the region of the existence of the N-phase up to the phase transition point T_{c}.

If one is interested in comparatively weak biaxial and longitudinal fluctuations ξ_j and $\tilde{\xi}_j$ ($j = 3-5$), then, in order to isolate them against the background of intense fluctuations of the director, it is desirable to have experimental geometries in which the contribution of the modes $\xi_{1,2}$ to the scattering is minimal. It is found that experimental geometries exist in which single scattering by the modes $\xi_{1,2}$ is altogether absent. This question has been considered in a number of studies [9, 17, 23–25, 76]. Taking into account the optical anisotropy, all such geometries have been found [76]:

$$\begin{aligned}
&(1)\ \boldsymbol{n}^0 \cdot \boldsymbol{e}^{(i)} = \boldsymbol{n}^0 \cdot \boldsymbol{e}^{(s)} = 0 \,, \\
&(2)\ \boldsymbol{n}^0 \parallel \boldsymbol{e}^{(i)} \parallel \boldsymbol{e}^{(s)} \perp \boldsymbol{k}^{(s)}, \boldsymbol{k}^{(i)} \,, \\
&(3)\ \boldsymbol{n}^0 \parallel \boldsymbol{q}_{\mathrm{sc}} = \boldsymbol{k}^{(s)} - \boldsymbol{k}^{(i)} \,, \\
&(4)\ \boldsymbol{n}^0 \parallel \boldsymbol{k}^{(s)} + \boldsymbol{k}^{(i)} \,.
\end{aligned} \tag{3.39}$$

In geometries (3) and (4), the polarisation vectors $\boldsymbol{e}^{(i)}$ and $\boldsymbol{e}^{(s)}$ should lie in the scattering plane $\boldsymbol{k}^{(s)}, \boldsymbol{k}^{(i)}$. Geometry (1) refers to scattering of the (0) → (0) type, while geometries (2)–(4) refer to the (e) → (e) type. The scattering intensities in these geometries, containing only the contributions by the $\xi_{3,4,5}$ modes, have been calculated [76]. It is interesting to note that, according to geometry (1), when an ordinary ray is incident on an ordered nematic liquid crystal the intensity of its scattering by the fluctuations of the director is zero, i.e. the entire singly scattered light (scattered at any angles) has the polarisation of the extraordinary wave.

The first experiments on light scattering in the ordered phase of a uniaxial nematic were carried out fairly long ago [77]. It was found that the characteristics of the polarisation and angular intensity distributions and their behaviour as a function of temperature found [77] for the PAA and PAF liquid crystals can be satisfactorily accounted for by the theory of light scattering by the director fluctuations $\xi_{1,2}$ described above [9, 12, 78]. This was confirmed also in subsequent experiments on MBBA [79].

Measurement of the angular dependence of the scattering constitutes at the present time a widely used and convenient method for the determination of the ratio of the Frank moduli. For example, in the geometry where $\boldsymbol{k}^{(s)}, \boldsymbol{k}^{(i)} \perp \boldsymbol{n}^0$ ($i = 1$, $s = 2$), we have from Eqn (3.36) at $H = 0$

$$I(\boldsymbol{e}^{(i)}, \boldsymbol{e}^{(s)}) = Z_0^{(i)} \frac{k_{\mathrm{B}} T \varepsilon_{\mathrm{a}}^2 \varepsilon_{\|}}{\varepsilon_{\perp} q_{\mathrm{sc}}^2} \times \left[\frac{\cos^2(\theta_{\mathrm{sc}}/2)}{K_{11}} + \frac{\sin^2(\theta_{\mathrm{sc}}/2)}{K_{22}} \right]; \qquad (3.40)$$

where $q_{\mathrm{sc}}^2 = (\omega/c)^2 [\varepsilon_{\|} + \varepsilon_{\perp} - 2(\varepsilon_{\|}\varepsilon_{\perp})^{1/2} \cos\theta_{\mathrm{sc}}]$. It is significant that in this geometry $\delta^{(2)} = 0$ and $n_{(2)} = \varepsilon_{\|}^{1/2}(\omega/c)$, i.e. the anisotropy is hardly manifested in the angular factors with the exception of the refraction at the boundary of the specimen. Eqn (3.40) makes it possible to find the ratio K_{11}/K_{22} [10, 77, 80]. A fairly complete analysis of the problem of the determination of K_{ii}/K_{jj} has been carried out [187].

The light scattering method has been applied [81] to the determination of two ratios of the Frank moduli: K_{23}/K_{22} and K_{33}/K_{11}. The measurements were performed in a polymeric nematic with a very low optical anisotropy $\varepsilon_{\mathrm{a}} \approx 0.001$. This made it possible to neglect multiple scattering and to use the formulae for scattering in an isotropic medium. The source of light was a 100 mW argon laser ($\lambda = 5145$ Å) and the thickness of the specimen was $L = 40$ μm. For each scattering angle ($2.5° < \theta_{\mathrm{sc}} < 65°$), two scattering geometries were considered — one geometry described by Eqn (3.40) and another with $i = 1$, $s = 2$, and $\boldsymbol{q} \| \boldsymbol{n}^0$. In the latter case, $I(\boldsymbol{e}^{(i)}, \boldsymbol{e}^{(s)}) \sim \cos^2(\theta_{\mathrm{sc}}/2) K_{33} q_{\mathrm{sc}}^2$. Fig. 6 illustrates the angular dependence of the ratio of the intensities J in these geometries as a function of $\tan(\theta_{\mathrm{sc}}/2)$. The theoretical curve is a parabola: $J = (K_{33}/K_{22}) \tan^2(\theta_{\mathrm{sc}}/2) + K_{33}/K_{11}$. Interpreta-tion of the data in Fig. 6 yielded $K_{33}/K_{22} = 13.0 \pm 0.4$ and $K_{33}/K_{11} = 1.17 \pm 0.03$ for the given nematic.

In spectroscopic measurements of light scattering, one can obtain information about the Leslie coefficients in addition to the ratio of the Frank moduli. The formula for the spectral intensity of the scattering by director fluctuations in terms of the hydrodynamic approximation is given by Eqns (3.36), (3.21), (3.19), and (3.2), where, for the correlators $\langle |\xi_j|^2 \rangle = S_0^2 \langle |\delta n_j|^2 \rangle$ ($j = 1, 2$), account should be taken of additional cofactors which are proportional to $\tau_j/(\omega^2 + \tau_j^2)$ in spectroscopic measurements and to $\exp(-t/\tau_j)$ in measurements by the methods of correlation spectroscopy; here we have [82]

$$\tau_1^{-1} = [q^2 K_{(1)}(\psi) + \chi_{\mathrm{a}} H^2] \times \left\{ \frac{1}{\gamma_1} + \frac{1}{2} \frac{[1 + \lambda_1 \cos(2\psi)]^2}{2\nu_3 \cos^2(2\psi) + (\nu_1 + \nu_2) \sin^2(2\psi)} \right\},$$

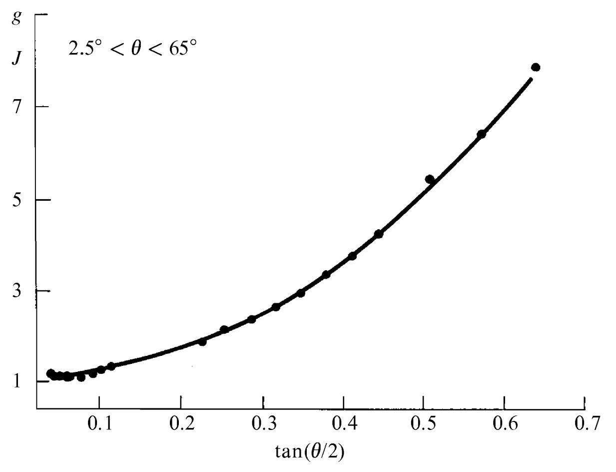

Figure 6. Angular dependence of the scattering intensity ratio J, one intensity being described by Eqn (2.40) and the other corresponding to the case with $i = 1$ and $s = 2$ and $\boldsymbol{q} \| \boldsymbol{n}_0$ for a polymeric liquid crystal [81]. Circles — experimental data; the continuous line was fitted by the theoretical relation $J = K_{33}/K_{11} + (K_{33}/K_{22}) \tan^2(\theta/2)$.

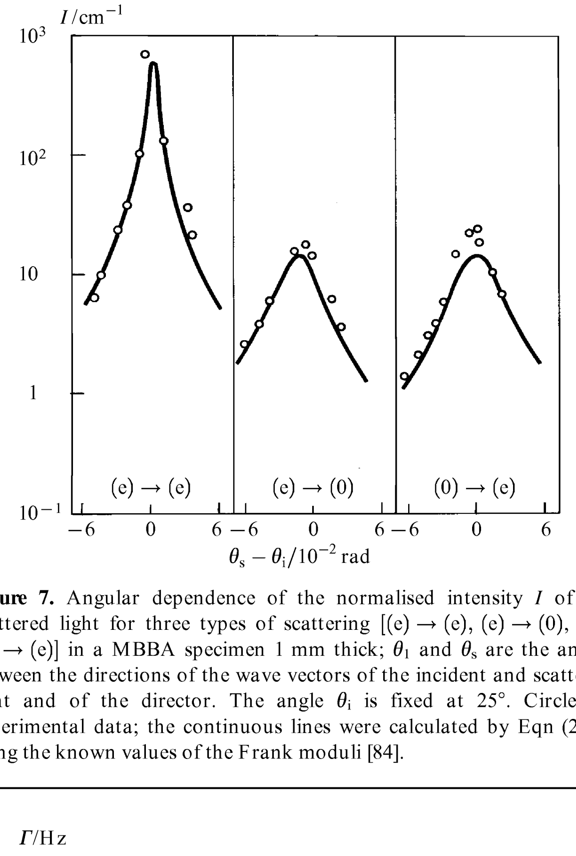

Figure 7. Angular dependence of the normalised intensity I of the scattered light for three types of scattering [(e) → (e), (e) → (0), and (0) → (e)] in a MBBA specimen 1 mm thick; θ_{i} and θ_{s} are the angles between the directions of the wave vectors of the incident and scattered light and of the director. The angle θ_{i} is fixed at 25°. Circles — experimental data; the continuous lines were calculated by Eqn (2.36) using the known values of the Frank moduli [84].

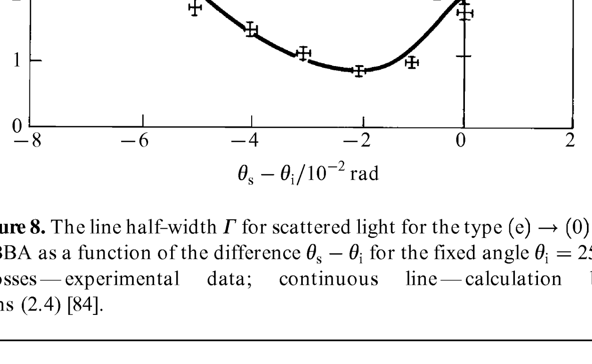

Figure 8. The line half-width Γ for scattered light for the type (e) → (0) in MBBA as a function of the difference $\theta_{\mathrm{s}} - \theta_{\mathrm{i}}$ for the fixed angle $\theta_{\mathrm{i}} = 25°$. Crosses — experimental data; continuous line — calculation by Eqns (2.4) [84].

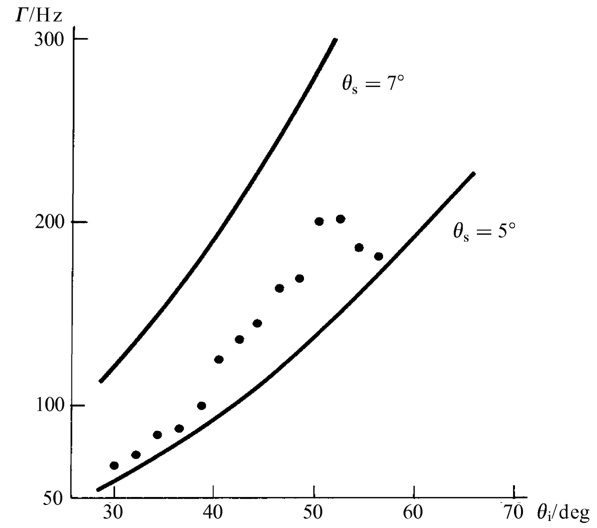

Figure 9. Dependence of the half-width Γ for scattered light in oriented MBBA on the angle θ_i between the direction of incident light and the director for a fixed scattering angle θ_s between $\boldsymbol{k}^s$ and $\boldsymbol{n}$ of the order of 7°. Continuous lines — calculation for the angles $\theta_s = 5°$ and 7° [85].

$$\tau_2^{-1} = [q^2 K_{(2)}(\psi) + \chi_a H^2] \times \left\{ \frac{1}{\gamma_1} + \frac{(1+\lambda_1)^2}{4[\nu_2 \tan^2(2\psi) + \nu_3]} \right\}, \qquad (3.41)$$

where λ_1, γ_1, ν_1, ν_2, and ν_3 are kinetic coefficients. The corresponding spectrum of nonclassical fluctuations $\tilde{\xi}_j$ has a non-Lorentzian form. The quantity $\langle \tilde{\xi}_5^2 \rangle_{q,\omega}$ has been calculated by Kamenskii and Kats [83].

Fig. 7 illustrates the experimental angular dependence of the integral intensity of the scattered light in MBBA for three types of polarisations of the incident and scattered light [(0) → (e), (e) → (0), (e) → (e)] [84]. Curves calculated using the known values of the Frank moduli are also presented. Fig. 8 illustrates the angular dependence of the effective frequencies $\omega_{\text{eff}} = 1/\tau_{\text{eff}}$ obtained by the methods of correlation spectroscopy. As in Fig. 7, the continuous line represents the values calculated using the experimental kinetic coefficients and the Frank moduli. Both figures show a satisfactory agreement between the theory and experiment, which confirms the possibility of determining the parameters for liquid crystals from light scattering data.

A method has been proposed [85] for the determination of the viscoelastic constants of nematics from measurements of the spectral line width (LW) of the light scattered by the fluctuations of the director as a function of the angle $\theta_{(i)}$ between $\boldsymbol{n}^0$ and $\boldsymbol{k}^{(i)}$. The scattering angle $\theta_{\text{sc}} \approx 7°$ was constant in the above study [85] and only the orientation of the cell was varied, while the receiver and the emitter were stationary. The geometries of the (0) → (e), (e) → (0), and (e) → (e) scattering were considered. Fig. 9 illustrates the dependence of the half-width Γ on the angle $\theta_{(i)}$. The continuous line corresponds to the theoretical calculation for the scattering angles $\theta_{\text{sc}} = 7°$ and 5°.

Measurements of the dependence of the relaxation times τ_1 and τ_2 on q_{sc}^2 have made it possible to determine [81] the ratios of the viscosity coefficients in a polymeric nematic. The absolute values of the Leslie coefficients were determined by resorting to the quantity K_{33} determined on the basis of the Fréedericksz transition.

Measurements have been made [86] of the absolute light scattering intensities corresponding to different polarisations and all three Frank moduli have been determined for MBBA. The results are $K_{11} = (5.7 \pm 0.3) \times 10^{-7}$, $K_{22} = (4.0 \pm 0.2) \times 10^{-7}$, and $K_{33} = (7.3 \pm 0.5) \times 10^{-7}$ dyn.

Light scattering methods are used to determine the Frank moduli also by indirect measurements. Thus a novel method has been proposed [87] for the determination of the critical magnetic field strength H_c in the Fréedericksz effect, from

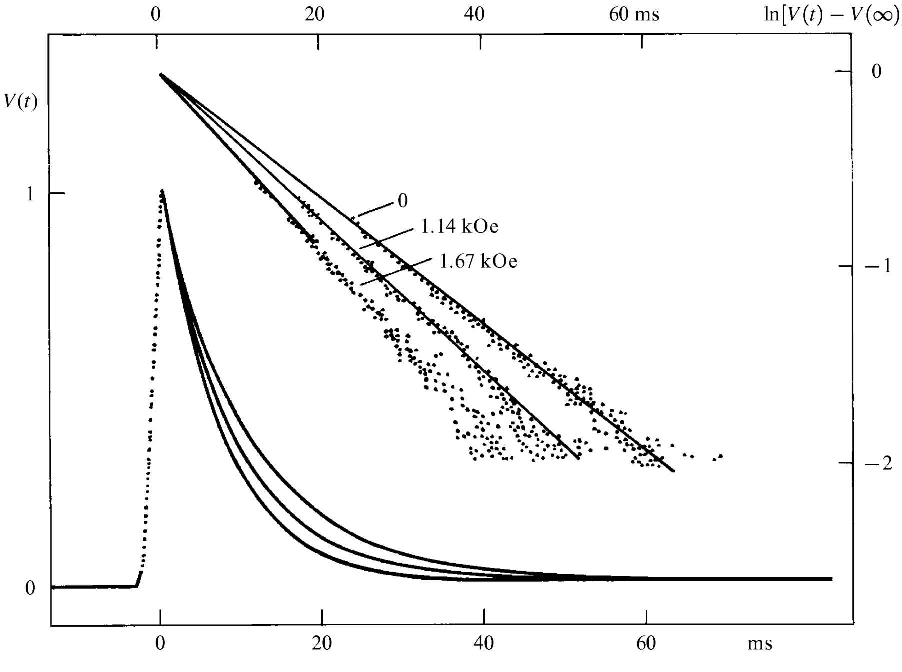

Figure 10. Decay of the time correlation function $V(t)$ in the 5CB liquid crystal at 29.9 °C for different applied field strengths. The logarithmic scale illustrates the purely exponential nature of the decay process [87].

which it is possible to find the Frank modulus $K_{22} = \chi_a(H_c L/\pi)^2$, L being the thickness of the specimen. The idea of the method is as follows. A cell with an oriented nematic was charged with a small admixture of extraneous particles. The rate of diffusion of these particles was measured by light scattering methods. For a zero magnetic field strength, the diffusion across the director was measured. In an external field, where the Freédericksz transition occurred and the director at the centre of the cell began to undergo a pole reorientation, the parallel component of the diffusion coefficient began to influence the diffusion relaxation time, the diffusion process was accelerated and the relaxation time diminished. Fig. 10 presents the variation of the rate for different field strengths H. Fig. 11 illustrates the threshold nature of the variation of the relaxation time as a function of H. The above measurements [87] were performed on a 5CB liquid crystal containing 0.1% of an admixture. The results of the measurement of K_{22} agree with the results of other workers within the limits of experimental accuracy (to within about 10%). A similar idea for the determination of the critical field strength H_c by a light scattering method was applied by Galatola [183]. However, the determination was based not on the spectrum but on the distortion of the symmetry of the angular distribution of the intensity.

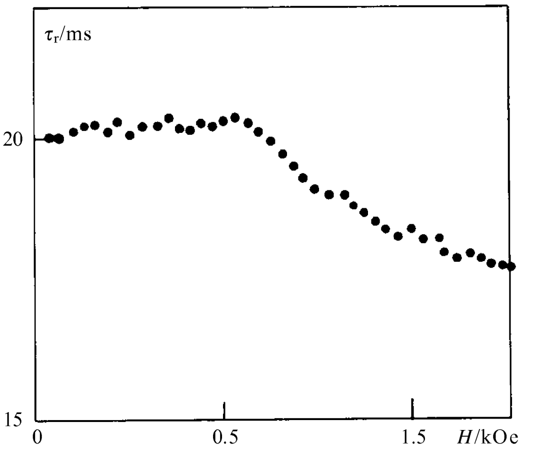

Figure 11. Dependence of the relaxation time τ_r in the 5CB liquid crystal on the applied magnetic field H at 31.7 °C [87].

Apart from the integral and spectral intensities, the statistics of photocounts during scattering by the fluctuations of the director has been investigated in nematics [88]. For the usual Gaussian fluctuations involving very short measurement times, the photocount distribution function should be exponential. The experiment carried out on 5CB, MBBA, and DIBAB liquid crystals showed that the distribution function has a Gaussian–Lorentzian form (Fig. 12). According to the authors, the deviations from the Gaussian behaviour can be explained by the nonlinear interaction of the modes $\xi_{j,q}$ ($j = 1, 2$) with different wave vectors $\boldsymbol{q}$.

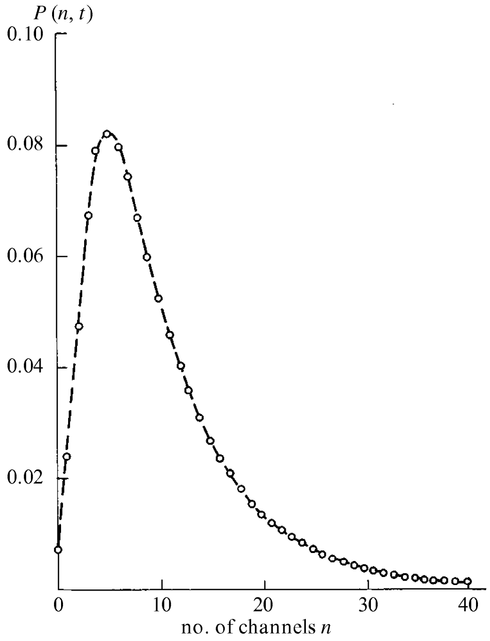

Figure 12. Distribution function $P(n,t)$ for photocounts expressed in terms of the numbers of channels n detected during a period $t = 10^{-3}$ s for light scattered by a homeotropically oriented specimen of a DIBAB nematic liquid crystal at $T = 0.989T_c$ [88].

The light scattering in biaxial nematics has been considered in terms of the optical isotropy approximation [70]. A detailed study taking into account the optical anisotropy has not been carried out hitherto so far as we are aware. From the purely optical point of view, the study of light scattering in these systems is of interest, in particular, in connection with the familiar phenomena of the external and internal conical refraction in biaxial crystals [33, 89].

3.4 Fluctuations of the director and light scattering in a bounded nematic

The previous discussion concerned the case of an unbounded nematic, so that only bulk phase contributions to the energy were taken into account. On the other hand, real experiments are carried out in small cells where the surface energy may play a significant role. The presence of boundaries alters the nature of the fluctuations of the director. One of the methods for the measurement of the energy of the anchoring of the director to the support is based on this effect [90].

Suppose that the liquid crystal is enclosed in a cell with a thickness L between plane-parallel plates and that the origin of coordinates is located at the centre of the cell, the z axis being directed along the normal to the plates. We shall assume that the interaction of the director with the support is taken into account in terms of the Rapini potential [15, 91]. The surface contribution to the thermodynamic potential then assumes the form

$$\Phi_{\rm surf} = -W\,\frac{1}{2}\int \mathrm{d}^2\boldsymbol{r}_\perp [n_z^2(\boldsymbol{r}_\perp,\, L/2) + n_z^2(\boldsymbol{r}_\perp,\, -L/2)] \qquad (3.42)$$

for the homeotropic orientation $(z \| \boldsymbol{n}^0)$ and

$$\Phi_{\rm surf} = \frac{1}{2}\int \mathrm{d}^2\boldsymbol{r}_\perp [W_y n_y^2(\boldsymbol{r}_\perp,\, L/2) + W_y n_y^2(\boldsymbol{r}_\perp,\, -L/2) + W_z n_z^2(\boldsymbol{r}_\perp,\, L/2) + W_z n_z^2(\boldsymbol{r}_\perp,\, -L/2)] \qquad (3.43)$$

for the planar orientation $(z \perp \boldsymbol{n}^0)$; here W, W_y, and W_z are the surface densities of the anchoring energy and $\boldsymbol{x}$ is the light orientation axis. The total thermodynamic potential, linked to the director field, is

$$\Phi = \Phi_{\text{bulk}} + \Phi_{\text{surf}}\,, \tag{3.44}$$

where the bulk phase energy Φ_{bulk} is the Frank energy defined by Eqn (3.1).

As an example, we shall consider the fluctuations of the director in a homeotropically oriented cell. The standard computational method involves the expansion of the fluctuations in terms of intrinsic modes. The solution is formulated as an infinite series, the determination of each member of the series involving the solution of a transcendental equation [90, 92, 93]. A method permitting a solution in a closed form has been proposed [94].

We shall now proceed to the two-dimensional Fourier spectrum $\delta n(\boldsymbol{q}_\perp, z)$ with $\boldsymbol{q}_\perp \perp z$. The contribution of the fluctuations with the given $\boldsymbol{q}_\perp$ to $\delta\Phi$ [Eqn (3.44)] is

$$\delta\Phi = \frac{1}{2}\sum_{j=1}^{2}\left\{\int_{-L/2}^{L/2} \mathrm{d}z\,\left[K_{jj}q_\perp^2|\delta n_j(z)|^2 + K_{33}|\partial_z\delta n_j(z)|^2\right] + W\left[|\delta n_j(L/2)|^2 + |\delta n_j(-L/2)|^2\right]\right\}. \tag{3.45}$$

Here the modes δn_j ($j = 1, 2$) are defined by Eqn (3.3) and the argument $\boldsymbol{q}_\perp$ in the function $\delta\boldsymbol{n}(\boldsymbol{q}_\perp, z)$ has been omitted.

In an unbounded medium, the procedure used to find the correlation function is as follows. Differentiation by parts in the formula for $\delta\Phi$ and neglect of the terms outside the integral expression lead to an expression of the type $\delta\Phi = (\delta n, \widehat{A}\delta n)/2$, where $\widehat{A}$ is a self-adjoint differential operator, while the scalar product implies integration with respect to continuous variable and summation over the indices. The correlation function is then obtained in the form $\widehat{G} = k_{\mathrm{B}}T\widehat{A}^{-1}$. A characteristic feature of bounded media is that $\delta\Phi$ contains terms outside the integral expression, which must be taken into account in the inversion of the operator $\widehat{A}$. In this case, the task may be reduced to the selection of boundary conditions for the functions $\delta\boldsymbol{n}(\boldsymbol{q}_\perp, z)$ such that, firstly, $\delta\Phi$ has a quadratic form and, secondly, the corresponding operator $\widehat{A}$ is self-adjoint over the subspace dense in terms of L^2.

In this case, the boundary conditions are

$$W\,\delta\boldsymbol{n} \pm K_{33}\partial_z\delta\boldsymbol{n} = 0, \quad z = \pm L/2\,. \tag{3.46}$$

Then

$$\delta\Phi = \frac{1}{2}\sum_{j=1}^{2}\int_{-L/2}^{L/2}\mathrm{d}z\,\delta n_j^*(\boldsymbol{q}_\perp, z)\widehat{A}_j\delta n_j(\boldsymbol{q}_\perp, z)\,, \tag{3.47}$$

where

$$\widehat{A}_j = K_{jj}q_\perp^2 - K_{33}\partial_z^2\,. \tag{3.48}$$

Thus the boundary conditions (3.46) make it possible to eliminate the terms outside the integral in the expression for $\delta\Phi$. Since the operators $\widehat{A}_j$ are symmetrical and the adjoint operators $\widehat{A}_j^*$ have been defined for the same class of functions, it follows that the $\widehat{A}_j$ are self-adjoint [95]. Thus the correlation functions of the director fluctuations in the $\boldsymbol{q}_\perp, z$ representation, i.e. $G_j(\boldsymbol{q}_\perp; z, z') = \langle\delta n_j(z)\delta n_j(z')\rangle_{\boldsymbol{q}_\perp}$, must satisfy the equations

$$\widehat{A}_j\widehat{G}_j = k_{\mathrm{B}}T\,\delta(z - z')\,, \tag{3.49}$$

i.e. it is necessary to invert the operators $\widehat{A}_j$ taking into account the boundary conditions (3.46). For $z \neq z'$, the differential equations (3.49) are homogeneous and can be readily solved. By joining the solutions for the regions $z > z'$ and $z < z'$ taking into account the boundary conditions (3.46), we obtain

$$G_j(\boldsymbol{q}_\perp; z, z') = \frac{k_{\mathrm{B}}T}{2K_{33}\varDelta_{1j}\beta_j}\left\{(\beta_j^2 - w^2)\cosh[\beta_j(z + z')] + \varDelta_{2j}\cosh[\beta_j(z - z')] - \varDelta_{1j}\sinh(\beta_j|z - z'|)\right\}; \tag{3.50}$$

where $\varDelta_{1j} = (\beta_j^2 + w^2)\sinh(\beta_j L) + 2\beta_j w\cosh(\beta_j L)$, $\varDelta_{2j} = (\beta_j^2 + w^2)\cosh(\beta_j L) + 2\beta_j w\sinh(\beta_j L)$, $\beta_j = \boldsymbol{q}_\perp^2(K_{jj}/K_{33})^{1/2}$ ($j = 1, 2$), and $w = W/K_{33}$ is the inverse length characterising the anchoring of the nematic crystal to the substrate [15].

The series expansions of the correlation function in the intrinsic modes of the fluctuations taken from Refs 90, 92, and 93 can be obtained, provided that Eqn (3.50) is expanded as a meromorphic function of $\boldsymbol{q}_\perp$ into simple fractions.

The correlation functions of the director fluctuations for a planar cell can be calculated in a similar although technically actually a more complex way [94].

It is of interest to compare the correlation functions $G_j^L(\boldsymbol{q}_\perp; z, z')$ in a bounded cell having a thickness L [Eqn (3.50)] with the corresponding inverse Fourier transform $G_j^H(\boldsymbol{q}; z - z')$ of the quantity defined by Eqn (3.2) in an unbounded specimen subjected to an external field H. In terms of the notation of Eqn (3.50), we have

$$G_j^H(\boldsymbol{q}_\perp; z - z') = \frac{k_{\mathrm{B}}T}{K_{33}(\beta_j^2 + w_H^2)^{1/2}} \times \exp\left[-(\beta_j^2 + w_H^2)^{1/2}|z - z'|\right], \tag{3.51}$$

where $w_H = H(\chi_{\mathrm{a}}/K_{33})^{1/2}$ is the inverse magnetic coherence length. The director fluctuations in an unbounded specimen for $H = 0$ are of the Goldstone type: $G_j(\boldsymbol{q}) \sim q^{-2} \to \infty$ for $q \to 0$. When $H \neq 0$,

$$G_j^H(\boldsymbol{q} = 0) = \int_{-\infty}^{\infty}\mathrm{d}z'\,G_j^H(\boldsymbol{q}_\perp = 0;\, z - z') = \frac{k_{\mathrm{B}}T}{K_{33}}\frac{1}{w_H^2}. \tag{3.52}$$

For the correlation function (3.50) in a bounded cell, the analogous integral has the following form after the removal of the indeterminacy at $\boldsymbol{q}_\perp \to 0$:

$$\int_{-L/2}^{L/2}\mathrm{d}z'\,G_j^L(\boldsymbol{q}_\perp = 0;\, z, z') = \frac{k_{\mathrm{B}}T}{K_{33}}\frac{1}{2w}\left[L + w\left(\frac{L^2}{4} - z^2\right)\right]. \tag{3.53}$$

For $L \to \infty$ and $w_H \to 0$, both equations, (3.52) and (3.53), diverge quadratically, which reflects the Goldstone nature of the director fluctuations for $L = \infty$ and $H = 0$. However, it is significant that, for a finite L, the quantity defined by Eqn (3.53) diverges (albeit linearly) if $w \to 0$. Thus not only in a bounded medium but also in thin nematic liquid crystal films the director fluctuations are singular in the absence of anchoring to the support.

Since the definition of the vectors $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ in Eqn (3.23) is based solely on the transverse component of $\boldsymbol{q}_\perp$ of the wave vector $\boldsymbol{q}$, the correlation function $G_{\gamma\nu\lambda\nu}(\boldsymbol{q}; z', z'')$ of the relative permittivity fluctuations in the $\boldsymbol{q}_\perp, z$ representation is again defined by Eqn (3.22), in which it is only necessary to replace $\langle\xi_j^2\rangle_q$ by $S_0^2 G_j(\boldsymbol{q}_\perp; z', z'')$ (where $S_0 = \varepsilon_{\mathrm{a}}$). The intensity of light singly scattered by director fluctuations in a planar cell is then given by

$$I(\boldsymbol{e}^{(i)}, \boldsymbol{e}^{(s)}) \sim \frac{1}{L}\int_{-L/2}^{L/2} \mathrm{d}z' \int_{L/2}^{L/2} \mathrm{d}z'' \exp[-\mathrm{i}q_{\mathrm{sc}}^{\|}(z'-z'')]$$

$$\times e_{\gamma}^{(s)} e_{\lambda}^{(s)} G_{\gamma\mu\lambda\nu}(\boldsymbol{q}_{\mathrm{sc}}^{\perp}; z', z'') e_{\mu}^{(i)} e_{\nu}^{(i)}, \qquad (3.54)$$

where $\boldsymbol{q}_{\mathrm{sc}}^{\|}$ and $\boldsymbol{q}_{\mathrm{sc}}^{\perp}$ are the longitudinal and transverse, relative to the z axis, components of the scattering vector $\boldsymbol{q}_{\mathrm{sc}}$. The integrals in Eqn (3.54) are evaluated analytically [94].

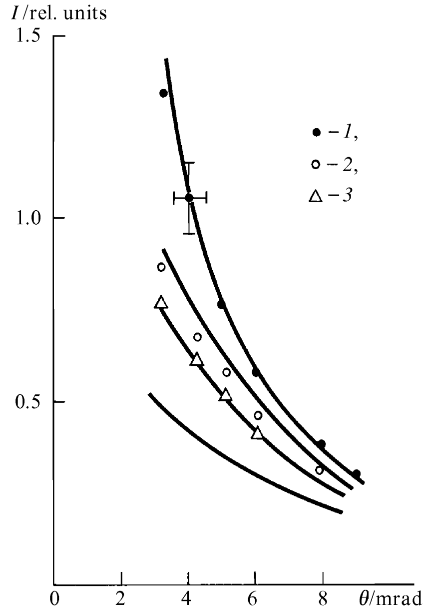

Figure 13. Angular dependence of the intensity of the (e) → (e) scattering in MBBA specimens 20 – 100 μm thick and oriented planarly on several surfaces: (*1*) poly(vinyl alcohol) coating; (*2*) rubbed glass; (*3*) PAC varnish coating; continuous lines — calculation using the anchoring energies (from above downwards) $W_y = 5 \times 10^{-5}$, 10^{-4}, 2×10^{-4}, and 5×10^{-4} erg cm^{-2}. The polarisation vector of the incident radiation makes an angle of 20° with the director [90].

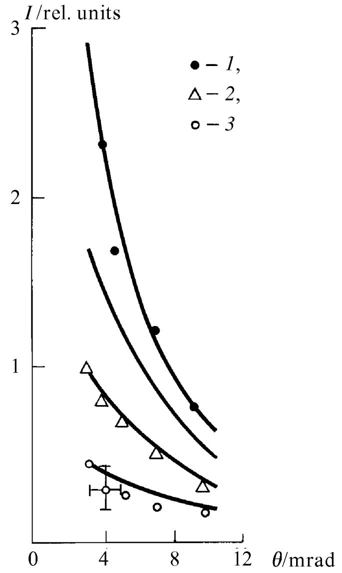

Figure 14. Angular dependence of the intensity of the (e) → (e) scattering in MBBA specimens planarly oriented by PAC varnish for different thicknesses of the cell: (*1*) $L = 80$ μm; (*2*) $L = 50$ μm; (*3*) $L = 35$ μm. Continuous lines — calculation for $W_y = 5 \times 10^{-4}$ erg cm^{-2}: (*1*) $L = 80$ μm; (*2*) $L = 50$ μm; (*3*) $L = 35$ μm; (*4*) $L = 65$ μm. The polarisation vector of the incident light makes an angle of 20° with the director [90].

The results of measurements of the intensity of the scattering of the extraordinary ray in an unusual cell with a planarly oriented nematic liquid crystal have been published [90]. The radiation from helium-neon ($\lambda = 6328$ Å) and argon ($\lambda = 5145$ Å) lasers was used. The polarisation vector of the incident radiation made an angle of 20° with the director. The anchoring energy was determined for MBBA in glass cells having a thickness $L = 20 - 100$ μm with oriented coatings of poly(vinyl alcohol) [PVAL (Translator)] and PAC [poly-acrylic? (Translator)] varnish or with supports rubbed in one direction. Figs 13 and 14 present the angular dependences of the scattered light intensities for different anchoring energies and thicknesses of the specimens [90]. Evidently the angular distribution is sensitive both to the thickness of the specimen and to the anchoring energy, the latter eliminating the divergence of the intensity in forward scattering. The anchoring energies were found by comparing the theory with the experimental results: $W \approx (2 \pm 0.05) \times 10^{-4}$ erg cm^{-2} for glass rubbed in one direction, $W \approx (5 \pm 2) \times 10^{-4}$ erg cm^{-2} for the PAC varnish, and $W \approx (1 \pm 0.2) \times 10^{-4}$ erg cm^{-2} for PVAL.

Fig. 15 illustrates the dependence of the intensity of the (e) → (e) scattering calculated by Eqn (3.54) for a homeotropically oriented nematic liquid crystal cell in the case of normal incidence. It is of interest to note that, in contrast to the inclined incidence, here there is a dip corresponding to the zero angle, its width being greater the greater the anchoring energy.

3.5 The effective relative permittivity and the extinction coefficient

As a result of the presence of fluctuations, the effective relative permittivity of the medium $\varepsilon_{\alpha\beta}^{\mathrm{eff}}$ becomes nonlocal [32]. In terms of the lowest-order terms, the nonlocal component of $\varepsilon_{\alpha\beta}^{\mathrm{eff}}$ is given by

$$\varepsilon_{\alpha\beta}^{\mathrm{eff}}(\boldsymbol{k}, \omega) - \varepsilon_{\alpha\beta}^{0} = \int \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3} G_{\alpha\nu\beta\mu}(\boldsymbol{k} - \boldsymbol{q}, \omega) T_{\nu\mu}(\boldsymbol{q}, \omega)\,. \qquad (3.55)$$

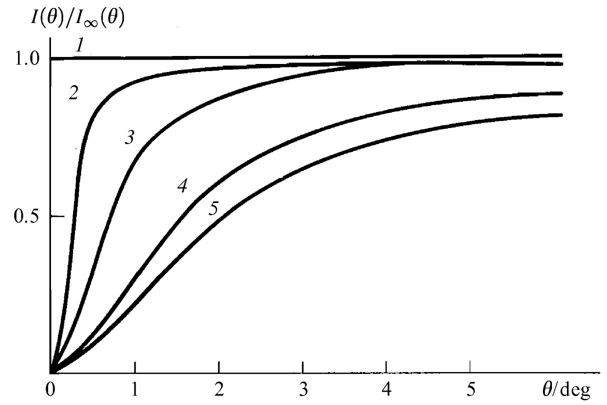

Figure 15. Angular dependence of the intensity of the light scattered by a homeotropically oriented liquid crystal cell referred to the intensity in an unbounded medium $I_{\infty}(\theta)$ for different values of $\alpha = W/Kk$: (*1*) $\alpha = 0$; (*2*) $\alpha = 0.001$; (*3*) $\alpha = 0.01$; (*4*) $\alpha = 0.01$; (*5*) $\alpha = 1$; $kL = 100$ [94].

Corrections to the real ($\widehat{\varepsilon}'$) and imaginary ($\widehat{\varepsilon}''$) components of $\widehat{\varepsilon}^{\rm eff}$ may be found from Eqns (3.55) and (3.32) and Sokhotskii's formula $(x-{\rm i}0)^{-1}=P(1/x)+{\rm i}\delta(x)$, where P is the symbol denoting the principal value of the integral. The imaginary component then reduces to a double integral and determines the extinction coefficients $\sigma_{(i)}=(\omega/{\rm c})n_{(i)}^{-1}\cos^{-2}\delta^{(i)}e_{\alpha}^{(i)}\varepsilon''_{\alpha\beta}(\boldsymbol{k}^{(i)},\omega)e_{\beta}^{(i)}(i=1,2)$ for the ordinary and extraordinary waves [76]:

$$\sigma_{(i)}=\left(\frac{\omega^2}{4\pi c^2}\right)^2\frac{e_{\alpha}^{(i)}e_{\beta}^{(i)}}{n_{(i)}\cos^2\delta^{(i)}}$$

$$\times\sum_{s=1}^{2}\int{\rm d}\Omega_{\boldsymbol{k}^{(s)}}\frac{n_{(s)}e_{\mu}^{(s)}e_{\nu}^{(s)}}{\cos^2\delta^{(s)}}G_{\alpha\mu\beta\nu}(\boldsymbol{k}^{(s)}-\boldsymbol{k}^{(i)})\,, \qquad (3.56)$$

where ${\rm d}\Omega_{\boldsymbol{k}^{(s)}}$ denotes integration over all the directions $\boldsymbol{k}^{(s)}$.

Eqn (3.56) represents the anisotropic version of the optical theorem [32] the attenuation of the mean field in a randomly inhomogeneous medium without intrinsic absorption is due to the loss of light in scattering:

$$\sigma_{(i)}=\Sigma_{(i)}\cos^{-1}\delta^{(i)}\,, \qquad (3.57)$$

where $\Sigma_{(i)}$ is the overall scattering cross-section — the integral of the relative scattering intensity per unit volume with respect to all the angles [Eqn (3.36)]. The corresponding formula for $\Sigma_{(i)}$ has been obtained by Langevin and Bouchiat [96].

Since the main contribution to the scattering and hence to the extinction in nematics is associated with the director fluctuations $\xi_{1,2}$, calculation of $\sigma_{(i)}$ can be restricted to fluctuations of only one type (estimates have shown that the contribution of the $\xi_{3,4,5}$ modes to $\sigma_{(i)}$ is 2–3 orders of magnitude less than the contribution of the $\xi_{1,2}$ modes [76]).

We now introduce the designation $\sigma_{(i,s)}$ for the contribution to $\sigma_{(i)}$ due to the scattering of a (s)th type wave: $\sigma_{(i)}=\sigma_{(i,1)}+\sigma_{(i,2)}$. It follows immediately from Eqn (3.57) and geometry 1 in Eqn (3.39) that $\sigma_{(1,1)}\equiv 0$ and $\sigma_{(1)}=\sigma_{(1,2)}$.

The exact analytical calculation of the double integral (3.56) with the correlation function (3.22), (3.2) is fairly cumbersome. Numerical calculations of $\Sigma_{(i)}$ have been carried out [84]. The problem may be significantly simplified by employing the fact that the parameter $\Delta=\chi_{\rm a}H^2/k_0^2K_{jj}<10^{-5}$ (see Section 3.1) is small. In particular, in the limit $\Delta\to 0$ we have

$$\sigma_{(1)}(\theta)=\sigma_0\int_{-1}^{1}{\rm d}u\frac{1-u^2}{(1+a_0u^2)^{3/2}}$$

$$\times[(1-u^2)I_{12}(t_1,\,t_2)+I_2(t_2)]\,, \qquad (3.58)$$

$$\sigma_{(2,1)}(\theta)=\frac{\sigma_0 n_{(2)}^3(\theta)\sin^2\theta}{\varepsilon_{\parallel}^{3/2}}$$

$$\times\int_{-1}^{1}{\rm d}u\left[v_0^2(1-u_0^2)I_{12}(t_1,\,t_2)+I_2(t_2)\right]\,, \qquad (3.59)$$

where

$$\sigma_0=\frac{\omega^2}{8\pi c^2}\frac{k_{\rm B}T}{K_{33}}\frac{\varepsilon_{\rm a}^2}{(\varepsilon_{\perp}\varepsilon_{\parallel})^{1/2}}\,,$$

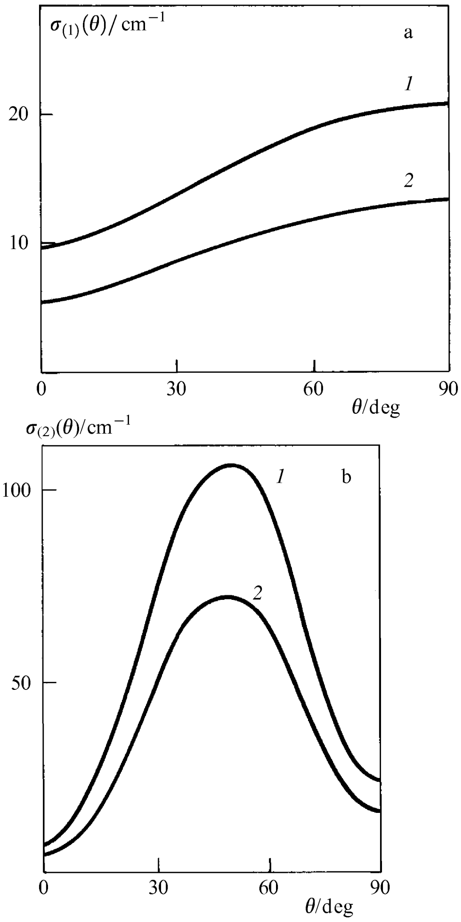

Figure 16. Angular dependence of the extinction coefficients of the ordinary ray $\sigma_{(1)}(\theta)$ (a) and the extraordinary ray $\sigma_{(2)}(\theta)$ (b) calculated by Eqns (2.58) and (2.61) for the PAA (curves *1*) and MBBA (curves *2*) in liquid crystals [76].

$$I_2(t)=(P_1^2+2tP_1P_2+t^2P_3^2)^{-1/2}\,,$$

$$I_{12}(t_1,\,t_2)=I_1(t_2)-I_1(t_1)\,,$$

$$I_1(t)=tP_1^{-1}[P_1+tP_2+I_2^{-1}(t)]^{-1}\,,$$

$$P_1=(v_1\cos\theta-u)^2,\quad P_2=v_0\sin^2\theta+1-u^2\,,$$

$$P_3=v_1\sin^2\theta+u^2-1,\quad v_1=\left[(1+a_0u^2)/(1+a_0)\right]^{1/2},$$

$$v_0=n_2(\theta)/\varepsilon_{\perp}^{1/2},\quad a_0=\varepsilon_{\rm a}/\varepsilon_{\perp},\quad t_j=K_{jj}/K_{33}\,, \qquad (3.60)$$

θ is the angle between $\boldsymbol{k}^{(i)}$ and $\boldsymbol{n}^0$, $v=v_1$ in Eqn (3.58), $v=v_0$ in Eqn (3.59). Assuming that $k_{\rm B}T\sim 4\times 10^{-14}$ erg, $K_{jj}\sim 10^{-6}$ dyn, $\omega/c\sim 10^5\ {\rm cm}^{-1}$, $\varepsilon_{\rm a}\sim 1$, and $\varepsilon_{\perp,\parallel}\sim 3$, we find that $\sigma_0\approx 5\ {\rm cm}^{-1}$ and, bearing in mind that the integral multipliers in Eqns (3.58) and (3.59) are of the order of magnitude of 2.5 and 0–5 in the first and second integrals, we find respectively $\sigma_{(1)}\sim 10$–$20\ {\rm cm}^{-1}$ and $\sigma_{(2,1)}\sim 0$–$20\ {\rm cm}^{-1}$. Fig. 16a presents the angular dependence of $\sigma_{(1)}(\theta)$ calculated by Eqn (3.58).

However, the contribution of $\sigma_{(2,2)}$ cannot be calculated in this way — the corresponding integral for $\theta\neq 0$ and 90° diverges logarithmically at $\Delta\to 0$. The reason for the divergence is the Goldstone nature of the correlator of the director fluctuations at $H\neq 0:\langle\delta n_j^2\rangle_q\sim q^{-2}$, which leads to an anomalously pronounced scattering at low angles θ_{sc} when $\boldsymbol{q}_{\mathrm{sc}} = \boldsymbol{k}^{(s)} - \boldsymbol{k}^{(i)} \to \boldsymbol{0}$. There is no divergence in the quantities $\sigma_{(2,1)}$ and $\sigma_{(1)} = \sigma_{(1,2)}$ since generally speaking $|\boldsymbol{k}^{(1)}| \neq |\boldsymbol{k}^{(2)}|$ in an anisotropic medium and the scattering vector $\boldsymbol{q}_{\mathrm{sc}}$ does not become zero. For $\theta = 0°$ or $90°$, the quantity $\lim_{\Delta \to 0} \sigma_{(2,2)}$ is finite because it follows from Eqn (3.39) that under these conditions the (e) → (e) type forward scattering intensity becomes zero due to the presence of the angular multipliers.

A method has been proposed [96] for the determination of the absolute values of all three Frank moduli from measurements of the extinction coefficient in the three experimental geometries in which the limiting transition $\lim_{\Delta \to 0} \sigma_{(i)}$ is permissible: $\boldsymbol{k}^{(i)} \| \boldsymbol{n}^0 [\sigma_{(1)}(0°)]$; $\boldsymbol{k}^{(i)} \perp \boldsymbol{n}^0$, $\boldsymbol{e}^{(i)} \perp \boldsymbol{n}^0 [\sigma_{(1)}(90°)]$; $\boldsymbol{k}^{(i)} \perp \boldsymbol{n}^0$, $\boldsymbol{e}^{(i)} \| \boldsymbol{n}^0 [\sigma_{(2)}(0)]$. The measurements were performed in MBBA specimens with thicknesses $L = 1, 1.5$, and 2 mm oriented by a magnetic field with a strength H ranging from 10^3 to 3×10^3 G. The values of the Frank moduli obtained agreed well with the results of measurements by other methods. This procedure for the determination of the Frank moduli is convenient and is widely used nowadays. In particular, K_{jj} ($j = 1-3$) have been determined [97] for the 8CB monomer in the temperature range $-10\,\mathrm{K} \leqslant T - T_{\mathrm{c}} \leqslant 0$ K and for the lyotropic polymer PBLG at a fixed temperature and two concentrations.

The author [97] notes an appreciable influence of the size of the specimen employed on $\sigma_{(i)}$. Thus, when the thickness of the cell L was varied from 2 to 0.2 mm in 8CB, the quantity $\sigma_{(1)}(0)$ varied from 2.35 to 3.05 cm^{-1}, while $\sigma_{(2)}(0)$ varied from 2.86 to 3.85 cm^{-1} (Fig. 17). The values of K_{jj} found proved to be systematically larger than those derived from data for the Fréedericksz transition, which has been explained [97] by the influence of the orienting magnetic field.

In the calculation of $\sigma_{(2)}(\theta)$ in the range $0 < \theta < 90°$, account must be taken of the finite nature of the small parameter Δ. The asymptotic expansion of $\sigma_{(2)}$ in terms of the parameter $L_H/\lambda \sim \Delta^{-1/2}$, where $L_H = 2\pi(K_{33}/\chi_{\mathrm{a}} H^2)^{1/2}$ is the magnetic coherence length, is of the form [76]

$$\sigma_{(2)}(\theta) = \sigma_0 U(\theta) \frac{t_1(F_1 + F_2)}{F_1(t_1 F_1 + t_1 F_2)} \ln \frac{L_H}{2\lambda} + \sigma^{\mathrm{const}}_{(2,2)}(\theta) + \sigma_{(2,1)}(\theta) + \mathrm{O}(\Delta^{1/2}) , \qquad (3.61)$$

where

$$U(\theta) = (\varepsilon_{\perp}\varepsilon_{\|})^{3/2} \sin^2 2\theta / (\varepsilon_{\perp} \cos^2\theta + \varepsilon_{\|} \sin^2\theta)^2 ,$$

$$F_j = (t_j^2 \varepsilon_{\|}^2 \cos^2\theta + t_j \varepsilon_{\perp}^2 \sin^2\theta)^{1/2} , \qquad (3.62)$$

($j = 1, 2$), and $\sigma^{\mathrm{const}}_{(2,2)}(\theta)$ is the contribution to $\sigma_{(2,2)}$ in terms of zero order in Δ. The quantity $\sigma^{\mathrm{const}}_{(2,2)}$ is of the order of magnitude of $\sigma_{(2,1)}$ and $\sigma_{(1)}$ and its angular variation is smooth over the entire range $0 < \theta < 90°$. For typical nematics with $\varepsilon_{(\mathrm{a})} \sim 1$, $K_{jj} \sim 10^6$ dyn, $H \sim 10^2$ Oe, and $\chi_{\mathrm{a}} \sim 10^{-7}$, we have $L_H/\lambda \sim 3 \times 10^3$ and $\sigma_{(2)} \sim 60\,\mathrm{cm}^{-1}$. Evidently $\sigma_{(2)}(\theta)$ depends greatly on the angle θ and is several times greater than the extinction coefficient for the ordinary ray. Fig. 16b presents plots of the angular dependence $\sigma_{(2)}(\theta)$ calculated by Eqns (3.61) and (3.59) [76]. A fit linear in θ was used for $\sigma^{\mathrm{const}}_{(2,2)}(\theta)$ between $\sigma_{(2,2)}(0) = \sigma_{(1,2)}(0)$ and $\sigma_{(2,2)}(90°)$, which permits the limiting transition $\Delta \to 0$. Plots similar to that in Fig. 16 have been obtained [84] on the basis of numerical calculation of the double integral (3.56).

If the nematic liquid crystal is considered in the absence of an external field, then the problem of the divergence of $\sigma_{(2,2)}$ remains. We may note that the logarithmic 'infrared' divergence of the extinction coefficient for correlators of the Goldstone type for light scattering at the second-order phase transition point, where the correlation radius of the fluctuations r_{c} is infinite, was noted a very long time ago [98, 99]. [Under these conditions, $\sigma \sim \ln(r_{\mathrm{c}}/k_0)$.] According to Placzek [98] and Rocard [99], the divergence can be eliminated if account is taken of the finite size of the scattering system L. On the one hand, the correlation radius is in this case actually limited by the size of the specimen: $r_{\mathrm{c}} \leqslant L$ [98]. On the other hand, the divergence of σ is eliminated after the introduction of $L < \infty$ if account is taken of the diffraction effects in scattering at low angles $\theta \sim \lambda/L$ [99]: in the calculation of the extinction coefficient

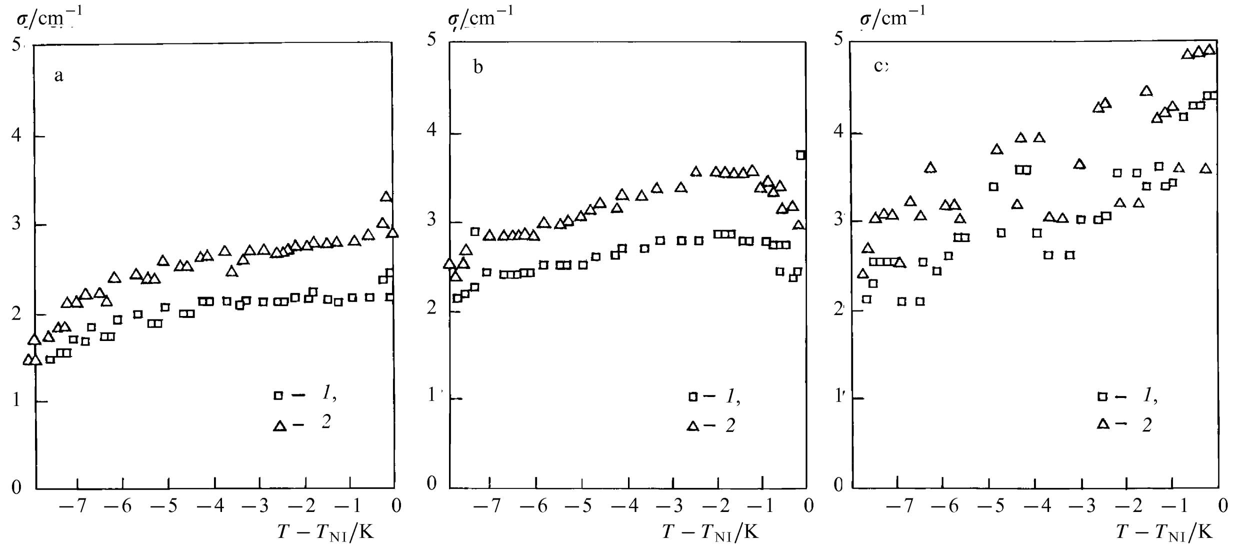

Figure 17. Temperature variation of the extinction coefficient $\sigma_{(1)}(0)$ (*1*) and $\sigma_{(2)}(\theta)$ (*2*) for the 8CB liquid crystal ($T_{\mathrm{NI}} = 314.5$ K) and different thicknesses of the specimen: (a) $L = 0.2$ cm; (b) $L = 0.1$ cm; (c) $L = 0.04$ cm [97].

by Eqn (3.57), the integral with respect to $\mathrm{d}\Omega_{k^{(s)}}$ must be truncated at scattering angles θ_{sc} of the order of magnitude of the angle of diffraction $\theta_{\mathrm{dif}} \approx \lambda/L$ by the specimen as a whole. (See the first edition of the book by Landau and Lifshitz [33] and also Fabelinskii [1].) In the first case, the truncating parameter L is the transverse dimension and in the second it is the longitudinal dimension of the specimen relative to the direction of propagation of the incident wave.

It is remarkable that, in the course of the development of the theory of critical phenomena, it was discovered that the total scattering cross-section at the second-order phase transition point is nevertheless finite also for $L \to \infty$ because, instead of the Goldstone spectrum $G(\boldsymbol{q}) \sim q^{-2}$, there is at this point a weaker singularity $G(\boldsymbol{q}) \sim q^{-2+\eta}$, where η is the Fisher exponent [6–8]. However, for nematics, the reasoning employing the finite size of the system L is entirely applicable [33]. In terms of the main orders in the parameter λ/L, both approaches [98, 99] yield the same result, namely Eqn (3.61), where it is sufficient to replace L_H by L.

These results are sufficient for the description of extinction in real optical experiments. However, the fundamental question of the behaviour of the extinction coefficients $\sigma_{(2)}$ in an unbounded nematic in the absence of an external field remains obscure. This question proved to be related to the problem of confinement in the field theory and has been analysed in a series of studies [100–103], initially for the case of scalar waves and the correlation function $G(\boldsymbol{q}) \sim q^{-2}$ [100–102], and then for electromagnetic waves and the real correlator (3.21) [103]. It was found that the divergence of the extinction coefficient $\sigma_{(2)}$ for $H = 0$ and $L = \infty$ is due to the fact that the true asymptotic behaviour of the mean field in such systems involves a superexponential attenuation:

$$\langle \boldsymbol{E}^{(j)}(\boldsymbol{r})\rangle = \boldsymbol{e}^{(j)} E_0^{(j)} \exp[\mathrm{i}\boldsymbol{k}^{(j)}\cdot\boldsymbol{r}] \exp[-\boldsymbol{k}''\cdot\boldsymbol{r}\,\ln(\boldsymbol{k}^{(j)}\cdot\boldsymbol{r}) + \zeta]\,, \tag{3.63}$$

where ζ is a constant of the order of unity. The physical significance of the appearance of the unusual superexponential attenuation in such systems is that, in anomalously intense forward scattering, yet another mechanism — the superposition of waves with randomly displaced phases scattered almost in the forward direction — arises apart from the usual mechanism of the attenuation of the mean field as a result of the sideways escape of the scattered radiation [which leads to the exponential Bouguer law $\langle \boldsymbol{E}^{(j)}(\boldsymbol{r})\rangle \sim \exp(-\boldsymbol{k}''\cdot\boldsymbol{r})$] [102]. For a correct calculation of the field parameter in directions close to $\theta_{\mathrm{sc}} = 0$ in such systems, it is essential to use methods taking into account in the diagram series for the mean field all the diagrams and not only those least connected, as is usually done in methods based on the Dyson resummation [32]. It has been shown [101] that the simplest method of this kind is the eikonal method. The eikonal approximation makes it possible to derive correctly the principal logarithmic term of the asymptotic expression (3.63). However, the constant ζ is then found to diverge in the limit $q \to \infty$ ('ultraviolet divergence'). In order to eliminate the divergence, it is necessary to achieve a certain improvement of the eikonal approximation, for example one must use the method for the separation of the degrees of freedom of the fluctuating field into 'fast' and 'slow', applying different types of perturbation theory to them [104, 105], which has been used by Adzhemyan [101], or an alternative method [102] which does not require the separation of the modes.

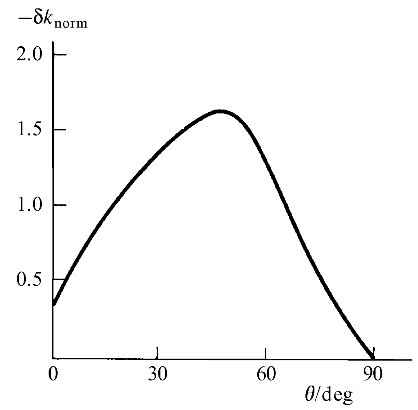

Figure 18. Dependence of the term added to the real component of the wave vector $\delta k = (\omega/c)\mathrm{Re}\,\delta\varepsilon^{\mathrm{eff}}/2\varepsilon_{\perp}^{-1/2}$ on the angle θ between k_0 and the director. The quantity δk (cm^{-1}) is obtained by multiplying δk_{norm} by $k_{\mathrm{B}}T/\lambda^2 K$, where K is the effective value of the Frank modulus [106].

The fluctuation contribution to the real part of the effective relative permittivity, which is determined by the integral in the sense of the principal quantity in Eqn (3.56), renormalises the real part of the wavenumber $k^{(i)}$. We may note that the correct calculation of this contribution usually requires the elimination of the ultraviolet divergence of the integral. This small contribution, which is usually neglected, leads in the case of a uniaxial nematic to an interesting qualitative effect — the wavenumber of the ordinary wave $k^{(1)}$ begins to depend, albeit only weakly, on the direction of its propagation [106]. Fig. 18 illustrates the calculated [106] angular dependence of the correction to $k^{(1)}$ for the 5CB liquid crystal.

3.6 Multiple light scattering in nematics

The appreciable, compared with $\sigma_{(1)}$, extinction coefficient of the extraordinary ray $\sigma_{(2)}$ can, at first sight, lead to the conclusion that the extraordinary ray decays much faster than the ordinary one. Thus the cause of such a large extinction coefficient $\sigma_{(2)}$ is random phase shifts of the extraordinary waves scattered almost in the forward direction; virtually the entire light is concentrated in the region $\theta_{\mathrm{sc}} = 0$ and has the same polarisation of the extraordinary ray. Thus the extraordinary coherent laser ray in an ordered nematic is transformed as a result of multiple forward rescattering into a diffuse beam with a relatively small expansion without a significant change in the total intensity and polarisation. The 'extinction coefficient' of this diffuse beam is of the same order of magnitude as $\sigma_{(1)}$ owing to scattering at large angles. This effect has been confirmed experimentally (Fig. 19) [107]. Direct determination of $\sigma_{(2)}$ from the attenuation of the transmitted ray therefore presents considerable difficulties. The method for the determination of $\sigma_{(2)}$ based on the measurement of the degree of coherence of the wave transmitted through the specimen can apparently prove effective here.

It is seen from the effect described that theoretical study of the angular dependence of the multiple scattering in an ordered nematic (in the first place for the extraordinary ray is of considerable interest. For $H \to 0$ in the region $\theta_{\mathrm{sc}} \approx 0$, it is then necessary to take into account all the scattering multiplicities. Examination of the analogous scalar problem by the eikonal method [102, 108], by the Glauber method [109], and on the basis of the radiation transfer equation (RTE)

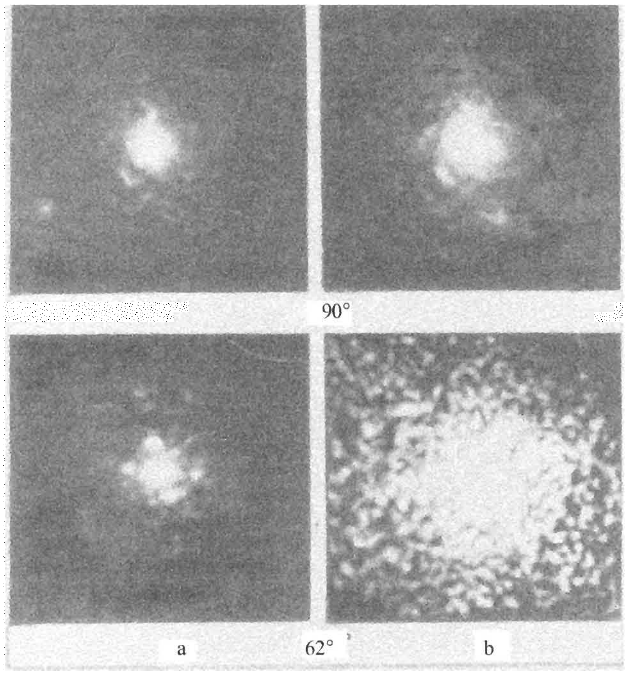

Figure 19. Image of the ray which has passed through a cell with a planarly oriented H-106 liquid crystal 2 mm thick for two angles of incidence θ [107] of the ordinary (a) and extraordinary (b) rays.

is the low angle approximation [110], showed that the multiple scattering indicatrix $I_{\text{mult}}(\theta)$ in the region of small angles $\theta = \theta_{\text{sc}}$ differs significantly from the single scattering indicatrix $\sim \theta^{-2}$. Thus, according to the literature [102, 108–110], the singularity in $I_{\text{mult}}(\theta)$ at $\theta \to 0$ has the form

$$I_{\text{mult}}(\theta) \sim \theta^{-(2-z/z_0)}\,, \tag{3.64}$$

where z is the path traversed by light in the medium and z_0 is the length parameter of the order of $\sigma_{(1)}^{-1}$. The result [Eqn (3.64)] has been recently extended [111] to the case of real nematics, where it is necessary to take into account the vector nature of the electromagnetic field $\boldsymbol{E}$ and the tensor nature of the correlation function $G_{\alpha\beta\gamma\rho}$. The nature of the singularity defined by Eqn (3.64) in the multiple scattering indicatrix at $z/z_0 < 2$ is retained in this case also. The point is that the anomalously intense forward scattering is associated solely with the extraordinary wave and that, when scattering at low angles is considered, the presence of the ordinary wave may be neglected, i.e. one can proceed in fact from the vector to the scalar problem.

On the other hand, if the problem of multiple scattering in an ordered nematic liquid crystal in the presence of an external field H is considered, whereupon the correlation radius of the fluctuations becomes finite, then strictly speaking the ordinary ray cannot be neglected. The principal problem consists in this instance in the fact that a direct extension of the eikonal approximation does not exist for such a bimodal problem because the so-called linear interaction of the modes arises [112]: waves with one type of polarisation enter the medium but, after repeated rescattering by tensor fluctuations, waves with both types of polarisation are present at the exit from the medium.

There exists another approach to the description of the angular distribution of the scattered radiation which is closely related to the eikonal approximation in the unimodal problem [32], but, in contrast to the latter, it permits a direct extension to the multimodal case. This approach is based on the use of a system of radiation transfer equations for the description of the simultaneous process involving the propagation of the extraordinary and ordinary rays. For the radiation transfer equation to apply, it is necessary that the inequality $\sigma_{(i)} r_{\text{c}} \ll 1$ should hold [32, 113]. If account was taken of the fact that, in experiments with nematic liquid crystal specimens having a thickness of the order of 1 cm a magnetic field is used to orient the single crystal [96, 97, 107], then the extinction coefficient can be calculated by Eqn (3.61) and the magnetic coherence length L_H can be used as r_{c}. Estimates have shown that, for typical nematics in a field $H \sim 10^3$ G, these inequalities do hold. The radiation transfer equation for a scalar field in the stationary case has the following form [32, 113]:

$$\big[(\boldsymbol{m}, \nabla) + \sigma\big] a(\boldsymbol{r}, \boldsymbol{m}) = \int \mathrm{d}\Omega_{\boldsymbol{m}'} F(\boldsymbol{m}, \boldsymbol{m}') a(\boldsymbol{r}, \boldsymbol{m}') + b(\boldsymbol{r}, \boldsymbol{m})\,; \tag{3.65}$$

where $\boldsymbol{m}$ is a unit vector, σ the extinction coefficient, F the scattering indicatrix, $a(\boldsymbol{r}, \boldsymbol{m})$ the intensity at the point $\boldsymbol{r}$ of the waves propagated in the direction specified by $\boldsymbol{m}$, and b the radiation source. The coherence function characterising the radiation [32] has in the case of an electromagnetic field four independent components by virtue of the transverse nature of the waves [114]. Instead of these, four Stokes parameters are usually employed [115]. One then obtains, instead of Eqn (3.65), a system of four equations. In an anisotropic medium, where there are two types of waves with their own polarisations and wave vectors, the number of independent components of the coherence function reduces to two [116]:

$$\begin{aligned}&\big[(\boldsymbol{s}^{(i)}, \nabla) + \sigma_{(i)}\big] a_{(i)}(\boldsymbol{r}, \boldsymbol{m}) \\ &\quad = \sum_{j=1}^{2} \int \mathrm{d}\Omega_{\boldsymbol{m}'} F_{(ij)}(\boldsymbol{m}, \boldsymbol{m}') a_{(j)}(\boldsymbol{r}, \boldsymbol{m}') + b_{(i)}(\boldsymbol{r}, \boldsymbol{m})\,,\end{aligned} \tag{3.66}$$

$(i = 1, 2)$; here $\boldsymbol{s}^{(i)}$ is the direction of the group velocity of a wave of type (i) [identical? (Translator)] with the direction of the wave vector $\boldsymbol{m}$, $F_{(ij)}(\boldsymbol{m}, \boldsymbol{m}')$ is the indicatrix of the scattering of a type (j) wave to give a type (i) wave, and $b_{(i)}$ is the source of emission of type (i) waves. We may draw attention to the fact that, in contrast to an isotropic medium, in Eqns (3.66) account is taken of the difference between the directions of the group velocity and the wave vector. If a wave of type (j) having an intensity $I_0^{(j)}$ is propagated in the medium in the direction of $\boldsymbol{m}_0$, then scattering by random inhomogeneities results in the conversion of its energy into the energy of incoherent radiation. If the incoherent component is considered as $a_{(i)}(\boldsymbol{r}, \boldsymbol{m})$, then the source is given by the quantity

$$b_{(i)}(\boldsymbol{r}, \boldsymbol{m}) = I_0^{(j)} F_{(ij)}(\boldsymbol{m}, \boldsymbol{m}_0) \exp[-\sigma_{(j)} \boldsymbol{m}_0 \cdot \boldsymbol{r}]\,. \tag{3.67}$$

For known values of $a_{(j)}(\boldsymbol{r}, \boldsymbol{m})$, it is easy to find the experimental average Poynting vector and the electromagnetic energy density [116].

Eqns (3.66) have a simple physical significance. The variation of the energy of type (i) waves along the ray [the term $(\boldsymbol{s}, \nabla) a_{(i)}(\boldsymbol{r}, \boldsymbol{m})$] takes place, firstly, as a result of losses on scattering in other directions and in the form of other types of waves [the term $\sigma_{(i)} a_{(i)}(\boldsymbol{r}, \boldsymbol{m})$] and, secondly, as a result of the scattering of type (j) waves with the wave vectors $k_{(j)}\boldsymbol{m}'$ in the form of type (i) waves with the wave vector $k_{(i)}\boldsymbol{m}$ (the integral term) and also as a result of emission from the source $b_{(i)}$.

A characteristic feature of this system for a nematic liquid crystal is that the indicatrixes $F_{(ij)}$ for different types of waves (i and j) are significantly different. The indicatrix F_{22} has a sharp peak at $\boldsymbol{m} \approx \boldsymbol{m}'$, since the extraordinary ray is scattered mainly in the forward direction with a polarisation $\boldsymbol{e}^{(2)}$. The indicatrixes $F_{(12)}$ and $F_{(21)}$ do not have such a maximum for forward scattering because the wavenumbers $k_{(1)}$ and $k_{(2)}$ are different. The quantity $F_{(11)}$ is identically equal to zero, since the scattering of the ordinary ray by the fluctuations of the director to give another ordinary ray does not occur. Eqns (3.66) allow a description of the joint propagation of the ordinary and extraordinary waves in nematics taking into account multiple scattering. However, in the general case integration of Eqns (3.66) is possible only by numerical methods because the extinction coefficients depend on the direction $\boldsymbol{m}$, while the indicatrixes $F_{(ij)}$ are functions of $\boldsymbol{m}$ and $\boldsymbol{m}'$ and not only of the angle between them.

The problem simplifies significantly when the extraordinary ray is incident on the specimen, whereupon the source $b_{(2)}(\boldsymbol{r},\boldsymbol{m})$ has a sharp maximum in the direction of propagation $\boldsymbol{m}_0$ of the incident ray. Then in the region of low scattering angles $F_{(22)} \gg F_{(21)}$ and the term in the equation for $a_{(2)}(\boldsymbol{r},\boldsymbol{m})$, taking into account the scattering of the ordinary wave to give the extraordinary wave, may be neglected. A closed equation is obtained for $a_{(2)}(\boldsymbol{r},\boldsymbol{m})$, which can be considered in terms of the low angle approximation [32, 113] i.e. with the replacement $(\boldsymbol{s},\nabla) \to (\boldsymbol{m}_0,\nabla)$.

The angular distribution of the intensities of the extraordinary waves for different depths of penetration z, obtained [116] on the basis of the low angle approximation, is presented in Fig. 20. Evidently, for z less than several extinction lengths, the angular intensity distribution is approximately the same as for single scattering. For higher values of z, appreciable broadening of the ray begins. This is associated with the fact that the indicatrix for the scattering of the extraordinary ray to give another extraordinary ray is very greatly extended in the forward direction, so that its variation in the region of low angles is appreciable only after several scattering steps. For large values of z, the low angle approximation becomes inapplicable. In this case, it is essential to employ the complete system of transfer equations.

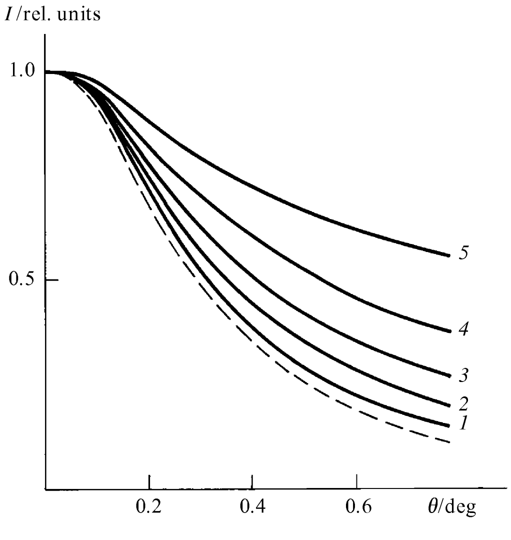

Figure 20. Angular distribution of the intensity of scattered light with polarisation of the extraordinary ray for different lengths of the traversed path $l = \sigma_{(2)}z$, where $\sigma_{(2)}$ is the extinction coefficient of the extraordinary ray calculated by Eqn (2.61) in the presence of an external field: (*1*) $l = 2$; (*2*) $l = 4$; (*3*) $l = 6$; (*4*) $l = 8$; (*5*) $l = 10$ (dashed line — single scattering intensity) [116].

From the standpoint of fluctuations and light scattering, the ordered nematic phase is a very interesting and fairly complex object. A complete description of the fluctuations is complicated by the multicomponent nature of the order parameter. A correct description of the scattering requires in its turn allowance for the anisotropy. The most interesting feature of the ordered phase is the presence of singular modes of the director fluctuations leading to an anomalously intense light scattering in the vicinity of the forward direction. On the one hand, this leads to the diffuse regime in the propagation of the extraordinary ray in nematics and also to a very unusual superexponential decay of the mean field. On the other hand, the usually weak effect of the finiteness of the system and its interaction with the bounding surfaces become significant under these conditions.

The problem of the study of the critical behaviour of the system in the transition to the isotropic phase should be regarded in the first place as one of the future fundamental problems concerning the ordered nematic phase. In this connection, there are experimental data on the temperature variation of the heat capacity, the order parameter, and the Frank moduli but a detailed combined treatment of experimental data taking into account fluctuation corrections, of the kind carried out for the isotropic phase, has not yet been performed.

Information about the critical behaviour of the system can be obtained also from light scattering data, provided that one isolates the contribution of longitudinal fluctuations from the total intensity. An attempt to carry out these fairly difficult measurements has been undertaken [162]. The measurement of the angular dependence of the extinction coefficient of the ordinary ray is of interest. This will make it possible to determine the Frank moduli by optical methods with a higher accuracy than the determination based on the Fréedericksz transition or from measurements of three values of the extinction coefficient in the method of Langevin and Bouchiat [96].

Experiments on the multiple scattering of the extraordinary ray in nematic liquid crystals and the study of the kinetics of the fluctuations of the director on the basis of low angle multiple scattering data have also been of interest. In thin nematic liquid crystal specimens, it is necessary to investigate the influence of the surface Frank moduli (of the K_{24} and K_{13} type) on the fluctuations and to take into account the boundaries of the system in the scattering problem.

For biaxial nematics, the theory is still far from perfect: the study of the angular dependence of the scattering taking into account the anisotropy and the calculation of the extinction coefficient are required. We may note that Green's function for the electromagnetic field in a biaxial medium with allowance for external and internal conical refraction phenomena, which is essential for the description of the scattering, has been recently obtained [163]. The correlation function for the fluctuations of singular modes in a bounded cell has not been calculated either. In this connection, we may draw attention to the effect recently predicted theoretically — the phase transition of a uniaxial nematic to the biaxial state under the influence of the bounding surface [179, 180].

It has been found that the interaction with the substrate under special conditions can lead to fully biaxial ordering in the surface layer of a nematic liquid crystal. Such quasi-two-dimensional ordering is found to be stable for a fairly strong interaction with the substrate, whereupon the bounding surface tends to orient the molecules along the layer also at temperatures $T_c < T < T_s$, where T_c is the phase transition temperature in an unbounded nematic and T_s is the tempera-ture of the transition to the biaxial state. For anchoring energies greater than a certain critical value, this is a second-order phase transition. Pretransitional phenomena may be investigated by the light scattering method. The correspond-ing experiments have not apparently been carried out, but the problem has been considered theoretically in detail in a study [180] where both the integral and spectral characteristics of the scattering of light were calculated within the framework of a two-dimensional model.

4. The isotropic phase of cholesteric liquid crystals (CLC)

The so-called chiral liquid crystals occupy a special place in the optics of liquid crystals. They include cholesteric liquid crystals, chiral smectic liquid crystals, as well as the blue phases of liquid crystals. The high-temperature cholesteric phase is structurally simplest. The properties of this medium have a number of characteristic features associated with the chirality of the molecules. The normal waves are circularly polarised and the wave vectors corresponding to the right and left circular polarisations are different. As a result of this, a linearly polarised wave is subjected to the rotation of the plane of polarisation. In the pretransitional region, the magnitude of this rotation exceeds by a factor of hundreds the intrinsic molecular rotation [117, 118]. There is also a possibility of the temperature-induced inversion of the sign of the optical activity [119]. The right- and left-polarised waves have different extinction coefficients, i.e. circular dichroism is observed [120]. The relative permittivity tensor for the medium has a nonzero antisymmetric component, which like the symmetrical component, may fluctuate and lead to antisymmetric light scattering [121].

4.1 Fluctuations of the order parameter

The absence of inversion in the symmetry point group of the cholesteric liquid crystal leads to the existence of an additional invariant (the Lifshitz invariant) in the expansion of the thermodynamic potential [Eqn (2.1)] in powers of the order parameter [9, 18]. In the Gaussian approximation, the expansion has the form [16]

$$\Phi = \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\big[AS_{\alpha\beta}S_{\alpha\beta} + L_1(\nabla_\alpha S_{\beta\gamma})^2 + L_2(\nabla_\alpha S_{\alpha\gamma})^2 + 2de_{\alpha\beta\gamma}S_{\alpha\beta}\nabla_\gamma S_{\beta\gamma}\big]\,, \tag{4.1}$$

where d is a pseudoscalar and the remaining notation is the same as in Eqn (2.1). In order to determine the correlation function, it is convenient to carry out the Fourier transformation and to express the order parameter by a linear combination of five traceless tensors $\pi_{\alpha\beta}^{(j)}(\boldsymbol{p})$ ($j = 0, \pm1, \pm2$) [122]:

$$S_{\alpha\beta,q} = \sum_{j=-2}^{2} \xi_q^{(j)}\pi_{\alpha\beta}^{(j)}(\boldsymbol{p})\,, \tag{4.2}$$

where $\boldsymbol{p} = \boldsymbol{q}/q$. The tensors $\pi_{\alpha\beta}^{(j)}(\boldsymbol{p})$ are defined by the equations

$$\pi_{\alpha\beta}^{(0)}(\boldsymbol{p}) = \sqrt{\frac{3}{2}}\left(p_\alpha p_\beta - \frac{1}{3}\delta_{\alpha\beta}\right),$$

$$\pi_{\alpha\beta}^{(2)}(\boldsymbol{p}) = m_\alpha(\boldsymbol{p})m_\beta(\boldsymbol{p})\,,$$

$$\pi_{\alpha\beta}^{(1)}(\boldsymbol{p}) = \frac{\mathrm{i}}{\sqrt{2}}\big[m_\alpha(\boldsymbol{p})p_\beta + m_\beta(\boldsymbol{p})p_\alpha\big]\,,$$

$$\pi_{\alpha\beta}^{(-j)}(\boldsymbol{p}) = (-1)^j\pi_{\alpha\beta}^{(j)}(-\boldsymbol{p})\,, \tag{4.3}$$

where $\boldsymbol{m}(\boldsymbol{p}) = (\boldsymbol{e}_1 + \mathrm{i}\boldsymbol{e}_2)/\sqrt{2}$ is a complex vector and $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ are unit vectors which form a right-handed triad with $\boldsymbol{p} : \boldsymbol{e}_1 \times \boldsymbol{e}_2 = \boldsymbol{p}$.

In terms of the basis comprising the tensor $\pi_{\alpha\beta}^{(j)}(\boldsymbol{p})$, the thermodynamic potential (4.1) has the form

$$\Phi = \frac{1}{2V}\sum_{l=-2}^{2}\sum_{q}\lambda^{(l)}(q)|\xi_q^{(l)}|^2\,, \tag{4.4}$$

where

$$\lambda^{(l)}(q) = \lambda_l + \Delta_l(q - q_l)^2\,, \quad \lambda_l = A - \frac{l^2d^2}{4\Delta_l}\,,$$

$$\Delta_l = L_1 + \frac{1}{6}L_2(4 - l^2)\,, \quad q_l = \frac{ld}{2\Delta_l}\,. \tag{4.5}$$

With the aid of Eqn (4.4), it is easy to find, in terms of the Gaussian approximation, the mean square fluctuations of the mode $\xi^{(l)}$ and the correlation function for the fluctuations of the order parameter:

$$\langle\xi^{(l)}\xi^{(l)}\rangle_q = \frac{k_\mathrm{B}T}{\lambda^{(l)}(q)}\,, \tag{4.6}$$

$$G_{\alpha\beta\gamma\delta}(\boldsymbol{q}) = \sum_{l=-2}^{2}\frac{k_\mathrm{B}T}{\lambda^{(l)}(q)}\pi_{\alpha\beta}^{(l)}(\boldsymbol{p})\pi_{\gamma\delta}^{(l)*}(\boldsymbol{p})\,. \tag{4.7}$$

The stability condition consists in the fact that the quantities $\lambda^{(l)}(\boldsymbol{q})$ must be positive for all wave vectors $\boldsymbol{q}$, i.e. $\lambda_l > 0$ and $\Delta_l > 0$. If $\lambda_l = 0$, then $\lambda^{(l)}(q_l) = 0$ and arbitrarily large fluctuations, with a wave vector $\boldsymbol{q}$ ($|\boldsymbol{q}| = q_l$), of the mode assigned the number l are possible. The temperature T_l^* at which this occurs is the temperature of the absolute instability of the l mode. In the model defined by Eqn (4.1), we have

$$T_l^* = T^* + \frac{l^2d^2}{4A'\Delta_l}\,. \tag{4.8}$$

It follows from the identity $4\Delta_2^{-1} - \Delta_1^{-1} = 3\Delta_0(\Delta_1\Delta_2)^{-1}$ and the stability conditions $\Delta_l > 0$ that the inequalities $T_0^* = T^* < T_1^* = T_{-1}^* < T_2^* = T_{-2}^*$ hold. However, the temperature T_2^* is not attained because the break due to a first-order phase transition occurs at a temperature $T_c > T_2^*$. Since the modes with $l = \pm2$ have the highest temperature of absolute instability, effects associated primarily with the fluctuations of precisely these modes are manifested in the vicinity of the phase transition point.

4.2 The effective relative permittivity

In the propagation of light in a cholesteric liquid crystal, the influence of fluctuations leads, firstly, to the attenuation of light as a result of scattering by inhomogeneities, secondly, to the appearance of fluctuation-induced rotation of the plane of polarisation, and, thirdly, to the manifestation of circular dichroism associated with the fact that the right- and left-polarised waves have different extinction coefficients. All these effects can be described with the aid of the effective relative permittivity $\varepsilon_{\alpha\beta}(\boldsymbol{q},\omega)$. In an isotropic gyrotropic medium, it can be expressed in the form [33, 123]

$$\varepsilon_{\alpha\beta}(\boldsymbol{q},\,\omega) = \varepsilon_{\perp}(\boldsymbol{q},\,\omega)(\delta_{\alpha\beta} - p_\alpha p_\beta) + \varepsilon_{\parallel}(\boldsymbol{q},\,\omega)p_\alpha p_\beta$$

$$+2\mathrm{i}\nu(\boldsymbol{q},\,\omega)q e_{\alpha\beta\gamma}p_\gamma\,, \tag{4.9}$$

where $\varepsilon_{\perp}$, $\varepsilon_{\parallel}$, and ν are even functions of $\boldsymbol{q}$ by virtue of the Onsager symmetry principle [18], ν being a pseudoscalar. As a result of the presence of the last term in Eqn (4.9), the eigenwaves in such a medium have a circular polarisation. Indeed, the equation for planar waves assumes the form

$$\left[(\delta_{\alpha\beta} - p_\alpha p_\beta)\left(q^2 - \frac{\omega^2}{c^2}\,\varepsilon_{\perp}(\boldsymbol{q},\,\omega)\right) - \frac{\omega^2}{c^2}\,\varepsilon_{\parallel}(\boldsymbol{q},\,\omega)p_\alpha p_\beta\right.$$

$$\left.-2q\nu(\boldsymbol{q},\,\omega)\,\frac{\omega^2}{c^2}\,\mathrm{i}e_{\alpha\beta\gamma}p_\gamma\right]E_\beta(\boldsymbol{q},\,\omega) = 0\,. \tag{4.10}$$

The operator on the left-hand side of this equation has the eigenvectors $\boldsymbol{p}$, $\boldsymbol{m}$, and $\boldsymbol{m}^*$. The condition that the eigenvalues are zero determines the corresponding dispersion equations for normal waves:

$$\frac{\omega^2}{c^2}\varepsilon_{\parallel}(\boldsymbol{q},\,\omega) = 0 \tag{4.11}$$

for a longitudinal wave with a polarisation vector $\boldsymbol{p}$ and

$$q^2_{(\pm1)} \mp 2q_{(\pm1)}\nu(q_{(\pm1)},\,\omega)\frac{\omega}{c} - \varepsilon_{\perp}(q_{(\pm1)},\,\omega)\frac{\omega^2}{c^2} = 0 \tag{4.12}$$

for a wave with circular polarisations $\boldsymbol{m}$ and $\boldsymbol{m}^*$, $\boldsymbol{q}_{(1)}$ corresponding to the right polarisation and $\boldsymbol{q}_{(-1)}$ to the left polarisation.

In the absence of spatial dispersion, when $\varepsilon_{\parallel} = \varepsilon_{\perp} = \varepsilon^0 = \text{const}$ and $\nu = 0$, Eqn (4.12) has the solutions $q_{(\pm1)} = \pm k$, where $k = (\varepsilon^0)^{1/2}\omega/c$. The effects associated with spatial dispersion are usually small ($\varepsilon^0 \gg \nu k$) [123], so that one can put $\varepsilon_{\perp}(\boldsymbol{q}_{(\pm1)},\omega) = \varepsilon_{\perp}(k,\omega)$ and $\nu(\boldsymbol{q}_{(\pm1)},\omega) = \nu(k,\omega)$ in Eqn (4.12). In terms of this approximation, the wavenumbers are defined by the expressions [33]

$$q_{(\pm1)} = \frac{\omega}{c}\left\{[\varepsilon_{\perp}(k,\,\omega)]^{1/2} \mp \frac{\omega}{c}\,\nu(k,\,\omega)\right\}. \tag{4.13}$$

The quantities $\varepsilon_{\perp}(k,\omega)$ and $\nu(k,\omega)$ are complex in the general case. The real component $\nu(k,\omega)$ determines the difference between the wavenumbers of the right- and left-polarised waves and is responsible for the rotation of the plane of polarisation (optical activity). The angle of rotation per unit wavelength is $(\omega/c)^2\,\mathrm{Re}\,\nu(k,\omega)$. The quantities $\mathrm{Im}\,\varepsilon(k,\omega)$ and $\mathrm{Im}\,\nu(k,\omega)$ are associated with the attenuation of the waves because they determine the imaginary component of the wave vector:

$$\mathrm{Im}\,q_{(\pm1)} = \frac{\omega}{c}\left\{\frac{\mathrm{Im}\,\varepsilon_{\perp}(k,\,\omega)}{2[\mathrm{Re}\,\varepsilon_{\perp}(k,\,\omega)]^{1/2}} \mp \frac{\omega}{c}\,\mathrm{Im}\,\nu(k,\,\omega)\right\}. \tag{4.14}$$

If there is no energy absorption in the system, then the attenuation of the wave is fully associated with the scattering by random inhomogeneities. In this case, we obtain $\sigma_{(\pm1)} = 2\,\mathrm{Im}\,q_{(\pm1)}$ for the extinction coefficients of the right-polarised wave ($\sigma_{(1)}$) and the left-polarised wave ($\sigma_{(-1)}$). When $\mathrm{Im}\,\nu \neq 0$, the extinction coefficients $\sigma_{(\pm1)}$ are different and circular dichroism is manifested in the medium.

The antisymmetric component of the effective relative permittivity tensor is defined by the following expression according to Eqn (3.55):

$$\varepsilon_{\alpha\gamma}(\boldsymbol{q},\,\omega) - \varepsilon_{\gamma\alpha}(q,\,\omega) = \frac{\omega^2}{c^2}\int\frac{\mathrm{d}\boldsymbol{\kappa}}{(2\pi)^3}\,T_{\beta\gamma}(\boldsymbol{\kappa}+\boldsymbol{q})$$

$$\times\left[G_{\alpha\beta\gamma\delta}(\boldsymbol{\kappa}) - G_{\alpha\beta\gamma\delta}(-\boldsymbol{\kappa})\right]. \tag{4.15}$$

On substituting the correlation function G [Eqn (4.7)] in Eqn (4.15), we obtain $\nu(k,\omega) = \nu_1(k,\omega) + \nu_2(k,\omega)$, where

$$\nu_j(\boldsymbol{q},\,\omega) = \frac{\omega^2}{(2\pi)^3 q^2 c^2}\,e_{\alpha\gamma\mu}q_\mu\int\mathrm{d}\boldsymbol{\kappa}\,\frac{\kappa}{(\boldsymbol{q}+\boldsymbol{\kappa})^2 - k^2 - \mathrm{i}0}$$

$$\left[\delta_{\alpha\beta} - \frac{(\boldsymbol{\kappa}+\boldsymbol{q})_\beta(\boldsymbol{\kappa}+\boldsymbol{q})_\delta}{k^2}\right]\frac{\varDelta_j q_j}{\lambda^{(j)}(q)\lambda^{(-j)}(q)}$$

$$\times\mathrm{Im}\left[\pi^{(j)}_{\alpha\beta}(\boldsymbol{\eta})\pi^{(j)}_{\delta\gamma}(\boldsymbol{\eta})\right], \tag{4.16}$$

($j = 1,2$); here $\boldsymbol{\eta} = \boldsymbol{\kappa}/\kappa$, $\varDelta_j$, $\lambda^{(j)}$, and q_j are defined by Eqns (4.5) and (4.13). The term ν_1 in Eqn (4.16) represents the sum of the contributions of the modes designated by numbers 1 and -1, while the term ν_2 represents the sum due to the modes designated by 2 and -2. The zero mode does not contribute to the antisymmetric component of the relative permittivity tensor. After evaluating the integrals in Eqn (4.16) for $q = k$, we obtain [119, 124]

$$\mathrm{Re}\,\nu_1(k,\,\omega) = \frac{q_1}{24\varepsilon^0\pi\varDelta_1\widetilde{\lambda}_1^{1/2}}\,,\quad \mathrm{Im}\,\nu_1 = 0\,, \tag{4.17}$$

$$\mathrm{Re}\,\nu_2(k,\,\omega) = \frac{q_1}{64\varepsilon^0\pi\varDelta_2\widetilde{\lambda}_2^{1/2}}\,\mathrm{Re}\left\{(q_2 + \mathrm{i}\widetilde{\lambda}_2^{1/2})\right.$$

$$\left.\times\left[\frac{2}{3} + 2(\alpha^2+1) - (\alpha^3+\alpha)\ln(\alpha-1)\right]\right\}, \tag{4.18}$$

where $\widetilde{\lambda}_j = \lambda_j/\varDelta_j$, $\alpha = (q_2 + \mathrm{i}\widetilde{\lambda}_2)/2k$, and

$$\mathrm{Im}\,\nu_2(k,\,\omega) = -\frac{q_2}{32\pi\varDelta_2 k}\int_0^1\mathrm{d}\xi(\xi^5+\xi^3)$$

$$\times\left\{\left[\frac{\widetilde{\lambda}_2}{4k^2} + \left(\xi - \frac{q_2}{2k}\right)^2\right]\left[\frac{\widetilde{\lambda}_2}{4k^2} + \left(\xi + \frac{q_2}{2k}\right)^2\right]\right\}^{-1}. \tag{4.19}$$

The integral in Eqn (4.19) can be expressed in terms of elementary functions [124]. If the system is fairly close to the phase transition point ($\widetilde{\lambda}_2 \ll q_2^2$), one can put $\alpha = q_2/2k$ and Eqn (4.18) assumes the following form:

$$\mathrm{Re}\,\nu_2 = \frac{q_2}{48\pi\varepsilon^0\varDelta_2\widetilde{\lambda}_2^{1/2}}\left[\frac{3}{2}\left(\alpha^2 + \frac{4}{3}\right) - \frac{3}{4}(\alpha^3+\alpha)\ln\left|\frac{\alpha+1}{\alpha-1}\right|\right].$$

The sign of the contribution of the modes with $l = \pm2$ to the optical activity depends on α. For fairly large values of α, the signs of the contributions of the modes with $l = \pm2$ and

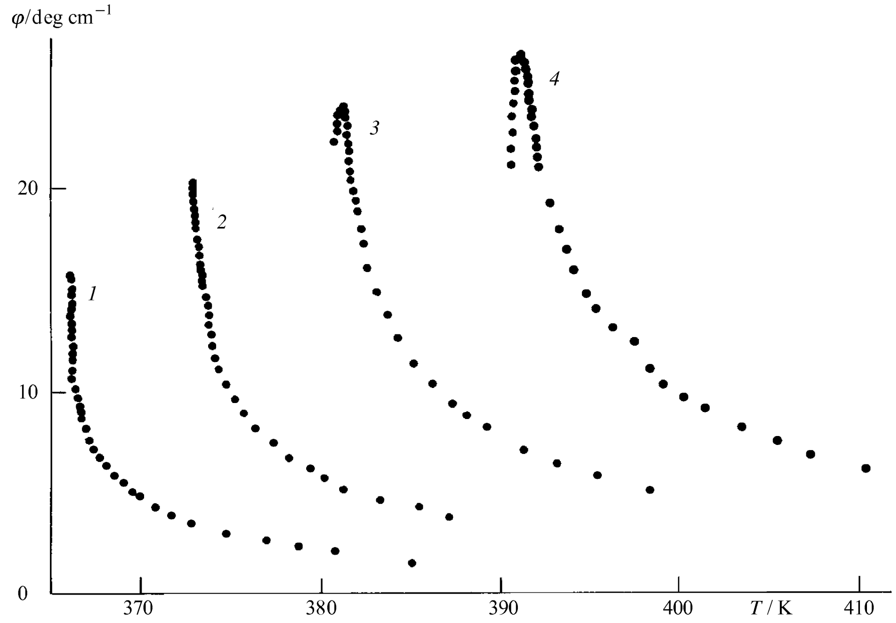

Figure21. Temperature dependence of the angle of rotation φ per unit length for CE2 solutions; concentration (wt%): (*1*) 40; (*2*) 60; (*3*) 80; (*4*) 100 [125].

$l = \pm 1$ are different, the contribution $\mathrm{Re}\, v_1$ predominating in the region remote from the phase transition temperature. As can be seen from Eqns (4.17) and (4.18), at temperature close to the phase transition point we have $\mathrm{Re}\, v_j \sim (T - T_j^*)^{-1/2}$, and, since $T_2^* > T_1^*$, the contribution $\mathrm{Re}\, v_2$ becomes decisive. The nonmonotonic temperature variation of the optical activity, caused by the competition between the contributions $\mathrm{Re}\, v_1$ and $\mathrm{Re}\, v_2$, has been predicted [119]. The optical activity of a solution of the highly chiral 4″-(2-methylbutylphenyl)-4′-(2-methylbutyl)biphenyl-4-carboxylate (CE2) cholesteric liquid crystal in a nonchiral liquid crystal has been measured in the region of the phase transition [125]. By varying the concentration, it was possible to regulate the chirality of the solution and for pure CE2 the quantity q_2 in Eqn (4.5) was 100 nm, whereas the value for a 40% solution (by weight) was 250 nm. The temperature dependence of the optical activity was investigated. The difference between the temperatures at different points in the specimen did not exceed 0.03 K. The accuracy of the measurement of the angle of rotation of the plane of polarisation was to within ±0.01°. The He–Ne laser ($\lambda = 633$ nm) was chosen as the source of light. Fig. 21 presents the variation of the angle of rotation per unit length as a function of temperature at different concentrations. Least squares treatment of the results yielded the following values for pure CE2: $A' = 0.92 \times 10^6$ erg cm^{-3} K, $L_1 = 6.2 \times 10^{-7}$ erg cm^{-3}, molecular rotation $\varphi = -4.8$ deg cm^{-1}, $T_1^* = 389.28$ K, and $T_2^* = 390.17$ K.

In contrast to the optical activity, only the modes with $l = \pm 2$ contribute to the circular dichroism. A qualitative conclusion concerning the temperature variation of the circular dichroism can be reached on the basis of Eqn (4.19). The integrand expression has poles at the points $\xi = (\pm q_2 \pm \mathrm{i}\lambda_2^{1/2})$. If $q_2/2k < 1$, then a singularity arises at $\lambda_2 \to 0$ (near the phase transition point) along the integration path. $\mathrm{Im}\, v_2$ then increases as $\lambda_2^{-1/2}$, i.e. $\mathrm{Im}\, v_2 \sim (T - T_2^*)^{-1/2}$. On the other hand, if $q_2/2k > 1$, i.e. half the wavelength is greater than the pitch of the helix formed in the transition, then there is no such singularity. In the region remote from the phase transition point, $\mathrm{Im}\, v$ decreases as $(T - T^*)^{-2}$. Thus the temperature variation of the circular dichroism in the pretransitional region is nonuniversal and depends significantly on the parameters of the medium. For example, the $(T - T^*)^{-1/2}$ regime cannot be observed owing to the break due to the first-order transition.

The pretransitional behaviour of the circular dichroism in cholesteryl nonanoate has been studied experimentally [120]. It was shown that, in the region $|T - T_c| < 1.5$ K, this relation is described satisfactorily by the formula $\Delta D = A_1(T)/\lambda^a$, where the exponent $a = 5.4 \pm 0.2$ and $A_1(T) = A_{10}/(T - T^*)$. The

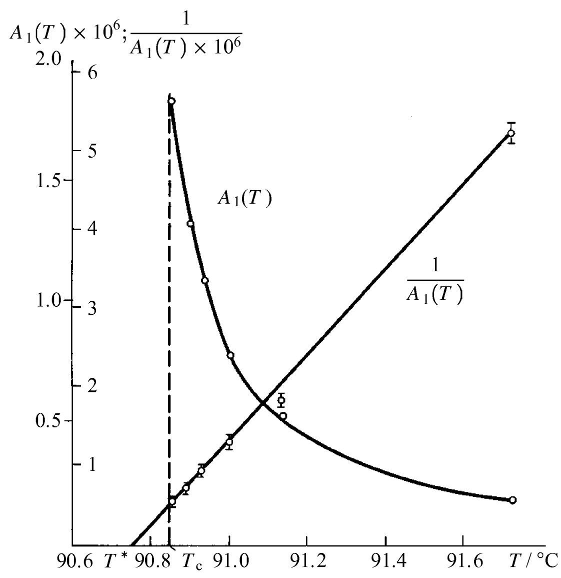

Figure 22. Temperature variation of the circular dichroism in cholesteryl nonanoate in the region preceding transition to the blue phase [120].

$A_1(T)$ and $A_1^{-1}(T)$ relations are illustrated in Fig. 22 and correspond to the temperature $T^* = 90.76 \pm 0.01$ and $T_c = 90.85 \pm 0.01$ °C. These results do not conflict with theoretical predictions because the power exponent in the temperature variation of the dichroism varies from $-1/2$ to -2 and a relation of the $(T - T^*)^{-1}$ type is possible over a narrow temperature range.

The symmetrical part of the relative permittivity tensor also yields the imaginary component, which determines the extinction coefficient. As can be seen from Eqn (4.14), it is sufficient to calculate $\varepsilon_\perp(k, \omega)$ in order to determine the extinction coefficient. According to Eqns (3.55) and (4.1), we have

$$\varepsilon_\perp(\boldsymbol{q}, \omega) = \frac{\omega^2}{4c^2}\left(\delta_{\alpha\gamma} - \frac{q_\alpha q_\gamma}{q^2}\right)$$
$$\times \int \frac{\mathrm{d}\boldsymbol{\kappa}}{(2\pi)^3} T_{\beta\delta}(\boldsymbol{q} + \boldsymbol{\kappa})[G_{\alpha\beta\gamma\delta}(\boldsymbol{\kappa}) + G_{\alpha\beta\gamma\delta}(-\boldsymbol{\kappa})]\,. \qquad (4.20)$$

Having put $|\boldsymbol{q}| = k$ in Eqn (4.20), it is possible to obtain with the aid of Sokhotskii's formula the final expression for the imaginary component $\varepsilon_\perp(k, \omega)$. We may note that, in the region remote from the phase transition point, where $\lambda^{(j)} \sim 1/A$, we have $\operatorname{Im} \varepsilon_\perp(k, \omega) \sim |T - T^*|^{-1}$. If the wavelength is less than twice the pitch of the helix formed $(q_2/2k < 1)$, then, for $T = T_2^*$, there is a singularity in the integral defined by Eqn (4.20). In this case, $\operatorname{Im} \varepsilon_\perp(k, \omega) \sim (T - T_2^*)^{-1/2}$.

Thus in the vicinity of the phase transition point, the circular dichroism, the optical activity, and the extinction coefficient increase as $(T - T_2^*)^{-1/2}$, provided that the wavelength of light is less than twice the pitch of the helix. The optical activity in the pretransitional region may change sign for highly chiral cholesteric liquid crystals.

4.3 The scattering intensity

In calculating the scattering intensity in gyrotropic media, account must be taken of the fact that Green's function in Eqn (1.7) must be calculated taking into account the gyrotropy. Furthermore, apart from the relative permittivity fluctuations, there is also a possibility of gyrotropy fluctuations in such a medium.

In media with natural gyrotropy, the electromagnetic induction vector $\boldsymbol{D}(\boldsymbol{r})$ depends not only on the field strength $\boldsymbol{E}(\boldsymbol{r})$ at a given point but also on its spatial derivatives. In an isotropic homogeneous nonmagnetic medium with gyrotropy, the material equation assumes the form [33, 123]

$$D_\alpha(\boldsymbol{r}) = (\varepsilon_0 \delta_{\alpha\beta} + 2\nu_0 e_{\alpha\beta\gamma} \nabla_\gamma) E_\gamma(\boldsymbol{r})\,, \qquad (4.21)$$

where ε^0 and ν_0 are constants and the coefficient 2 of ν_0 has been introduced for convenience. Green's function for the electromagnetic field $\widehat{T}$ in a medium with the material equation (4.21) has been obtained [126]. In particular, in terms of the $\boldsymbol{r}$, ω representation in the remote zone approximation, we have

$$T_{\alpha\beta}(\boldsymbol{r}, \omega) = \frac{1}{4\pi r(\omega/c)[\varepsilon^0 + \nu_0(\omega/c)^2]^{1/2}}$$
$$\times \sum_j \mathrm{e}^{\mathrm{i}\boldsymbol{q}_{(j)} \cdot \boldsymbol{r}} q_{(j)} m_\alpha^{(j)} m_\beta^{(j)*}\,, \qquad (4.22)$$

where $q_{(j)}$ are defined by Eqn (4.13) for $\nu(k, \omega) = \nu_0$ $(j = \pm 1)$. Eqn (4.22) represents the sum of two diverging spherical waves with circular polarisations $\boldsymbol{m}^{(j)}$ and the wavenumbers $q_{(j)}$. The term with $j = -1$ corresponds to the left-polarised wave and that with $j = 1$ corresponds to the right-polarised wave. It is convenient to describe the scattering in terms of these waves.

In the calculation of the scattering intensity, one should take into account the fact that the presence in the medium of spatial dispersion and in particular of gyrotropy leads to an additional contribution to the expression for the Poynting vector [33, 123]:

$$S_\alpha = \frac{c^2}{8\pi\omega} \operatorname{Re}[\boldsymbol{E} \times \boldsymbol{H}^*]_\alpha - \frac{\omega}{16\pi} \frac{\partial \varepsilon_{\beta\mu}(\boldsymbol{k}, \omega)}{\partial k_\alpha} E_\beta^* E_\mu\,,$$

where in our case we have according to Eqn (4.21)

$$\varepsilon_{\alpha\beta}(\boldsymbol{k}, \omega) = \varepsilon^0 \delta_{\alpha\beta} + 2\mathrm{i}\nu_0 e_{\alpha\beta\mu} k_\mu\,.$$

The material equation assumes the following form when account is taken of the relative permittivity and gyrotropy fluctuations [121, 123, 127]:

$$D_\alpha(\boldsymbol{r}) = \left[\varepsilon_{\alpha\beta}(\boldsymbol{r}) + \nabla_\rho \gamma_{\alpha\beta\rho}(\boldsymbol{r})\right] E_\beta(\boldsymbol{r}) + 2\gamma_{\alpha\beta\rho}(\boldsymbol{r}) \nabla_\rho E_\beta(\boldsymbol{r})\,, \qquad (4.23)$$

where $\gamma_{\alpha\beta\rho}$ is a tensor antisymmetric with respect to α and β and

$$\varepsilon_{\alpha\beta} = \varepsilon_0 \delta_{\alpha\beta} + \delta\varepsilon_{\alpha\beta}\,,$$

$$\gamma_{\alpha\beta\rho} = \nu_0 e_{\alpha\beta\rho} + e_{\alpha\beta\mu} \kappa_{\mu\rho}\,.$$

The tensor $\kappa_{\alpha\beta}$ determines the gyrotropy fluctuations. The presence in Eqn (4.23) of a second term containing spatial derivatives $\gamma_{\alpha\beta\rho}$ is associated with allowance for the Onsager symmetry principle [121, 128, 129].

We obtain in this case the following expression for the scattering intensity [121]:

$$I(\alpha, \beta) = I_0^{(i)} C_{(i)} (-\mathrm{i}\beta e_{\gamma\chi\lambda} s_\lambda + \delta_{\gamma\chi} - s_\gamma s_\chi)$$
$$\times (-\mathrm{i}\alpha e_{\nu\mu\sigma} i_\sigma + \delta_{\nu\mu} - i_\nu i_\mu)$$
$$\times \left[\langle \delta\varepsilon_{\mu\gamma} \delta\varepsilon_{\nu\chi} \rangle_q + \mathrm{i} h_\rho \left(\langle \delta\gamma_{\mu\rho\gamma} \delta\varepsilon_{\nu\chi} \rangle_q - \langle \delta\gamma_{\nu\rho\chi} \delta\varepsilon_{\mu\gamma} \rangle_q\right)\right.$$
$$\left. + h_\rho h_\zeta \langle \delta\gamma_{\mu\rho\gamma} \delta\gamma_{\nu\zeta\chi} \rangle_q \right]\,, \qquad (4.24)$$

where

$$C_{(i)} = \frac{\omega^2 V_s k_{(i)}^2}{(8\pi c R)^2 [\varepsilon^0 + (\omega^2 \nu_0^2 / c^2)]}\,,$$

$\boldsymbol{h} = \boldsymbol{h}^{(i)} + \boldsymbol{k}^{(s)}$, the unit vectors $\boldsymbol{i}$ and $\boldsymbol{s}$ are the directions of propagation of the incident and scattered waves, and α and β are numbers characterising the circular polarisations of the incident and scattered waves $(\alpha, \beta = \pm 1)$, $\boldsymbol{q} = \boldsymbol{q}_{\mathrm{sc}} = \boldsymbol{k}^{(s)} - \boldsymbol{k}^{(i)}$, and the remaining notation is the same as in Eqn (2.8). We may note that, regardless of the polarisation of the incident light, waves having both polarisations are formed on scattering. Both the fluctuations of the symmetrical component of the relative permittivity $\delta\widehat{\varepsilon}$ and the fluctuations of the gyrotropy $\widehat{\kappa}$ (antisymmetric scattering [33]) contribute to the scattering intensity.

In the isotropic phase of cholesteric liquid crystals, the fluctuations of the order parameter $\varphi_{\alpha\beta}$ are most pronounced. In the linear approximation, one can assume that $\kappa_{\alpha\beta} = g\varphi_{\alpha\beta}$, where g is a constant. Under these conditions, the first term in the square bracket in Eqn (4.24), which is not associated with the gyrotropy fluctuations, makes the main contribution to the scattering. The contributions of the remaining two terms are of the order of magnitude of r_{m}/λ and $(r_{\mathrm{m}}/\lambda)^2$ respectively, where r_{m} is a dimension of the order of magnitude of the molecular dimension [33, 123]. However, allowance for the gyrotropy fluctuations can lead in certain cases to qualitative changes in the scattering pattern, for example to a difference between the intensities $I(+1,-1)$ and $I(-1,+1)$ [121]. The contribution to the scattering intensity associated with the relative permittivity fluctuations [the first expression on the right hand side in Eqn (4.24)] has the form

$$I(\alpha,\beta) = I_0 C_{(i)} \sum_{l=-2}^{2} f^{(l)} \langle \xi^{(l)} \xi^{(l)*} \rangle_q \,, \tag{4.25}$$

where

$$\begin{aligned} f^{(0)} &= \tfrac{1}{6}\left[(1+\cos^2\psi)(1-\alpha\beta+\cos^2\psi)+1\right], \\ f^{(1)} &= \tfrac{1}{2}(1-\alpha\beta)\cos^2\psi\,, \\ f^{(2)} &= \tfrac{1}{4}\left\{4\alpha\beta\sin^2\psi + \left[2(\alpha+\beta)\sin\psi + 1 + \sin^2\psi\right]\right. \\ &\quad \left.\times\left[1+\sin^2\psi\right]\right\}, \end{aligned} \tag{4.26}$$

$f^{(-l)}(\alpha,\beta) = f^{(l)}(-\alpha,-\beta)$ $(l = 1, 2)$ and $\psi = \theta_{\mathrm{sc}}/2$ (θ_{sc} is the scattering angle). The complete expression for $I(\alpha,\beta)$, taking into account both the $\delta\varepsilon$ and $\delta\gamma$ fluctuations, has been published [121]. In the vicinity of the point of transition to the ordered phase, the $\xi^{(2)}$ or $\xi^{(-2)}$ mode is manifested most intensely in the scattering depending on whether a right-handed or left-handed helix is formed after the transition. The contributions of these modes depend on the polarisation of the incident and scattered light. For example, for a right-handed cholesteric liquid crystal the contribution to the intensity by the $\xi^{(2)}$ mode, when the incident and scattered waves are right-polarised, greatly exceeds the scattering intensity for other polarisations at almost all scattering angles. The scattering under these conditions is predominantly in the backward direction [121]. This effect is similar to the reflection of waves in an ordered cholesteric when the direction of the polarisation of the wave is the same as the direction of the helix in the cholesteric.

There have been comparatively few experimental studies on light scattering in the isotropic phase of a cholesteric. Measurements have been carried out under the conditions of both circular [130] and linear [131] polarisations. The first measurements with circular polarisations were carried out in a study [132] where right as well as left circular polarisations of the exciting light were used. The measurements were made for the angles θ_{sc} ranging from 30° to 130°. The interpretation of the above experimental data [132] involved certain difficulties because all five modes contributed to the scattering. Detailed studies have been made [130] on the light scattering in a mixture of a chiral CE2 liquid crystal and the nonchiral 7S5 nematic. By varying the concentration of the mixture, it was possible to vary the parameter $p_0 = 4\pi L_1/d$, which determines the pitch of the cholesteric helix. The measurements were carried out at a fixed scattering angle $\theta_{\mathrm{sc}} = 170°$. Such measurements are convenient because, as follows from Eqn (4.26), the modes with $l = \pm 1$ do not contribute to the scattering for $\theta_{\mathrm{sc}} = 180°$ ($\psi = 90°$). The linearly polarised light of the He–Ne laser was passed through a quarter-wave plate rotated about 45° relative to the plane of polarisation. The light back-scattered from the specimen passed through the same plate and another polariser and entered a photomultiplier. Two positions of the quarter-wave plate were used. For one position, the right-

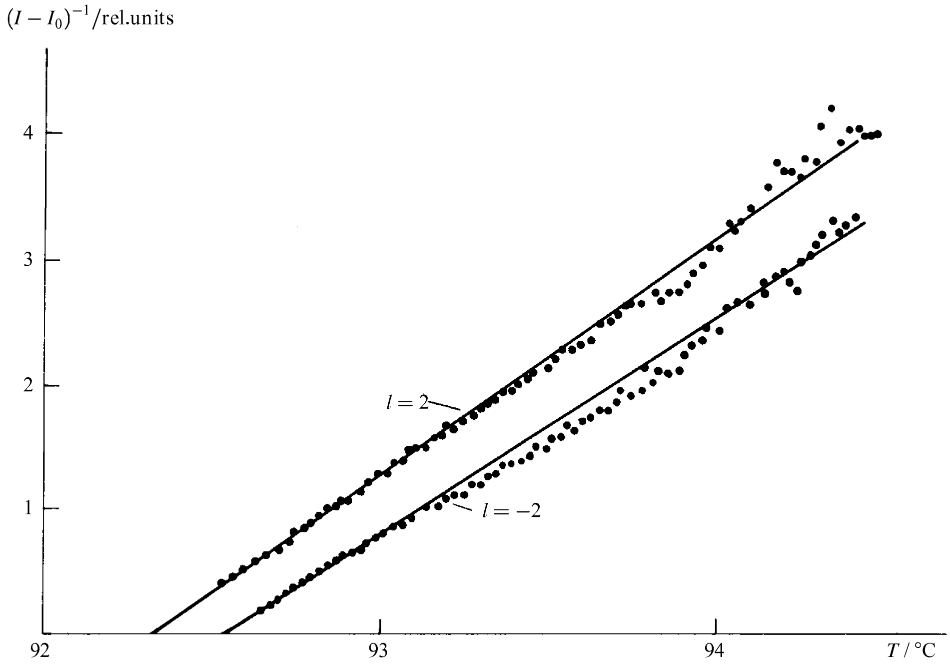

Figure 23. Temperature variation of the reciprocal of the scattering intensity $(I-I_0)^{-1}$ for a 40% solution of CE2 in 7S5. The data for different modes have been obtained with the aid of different orientations of a quarter-wave plate. Continuous lines were fitted by Eqn (3.27) using the least squares method [130].

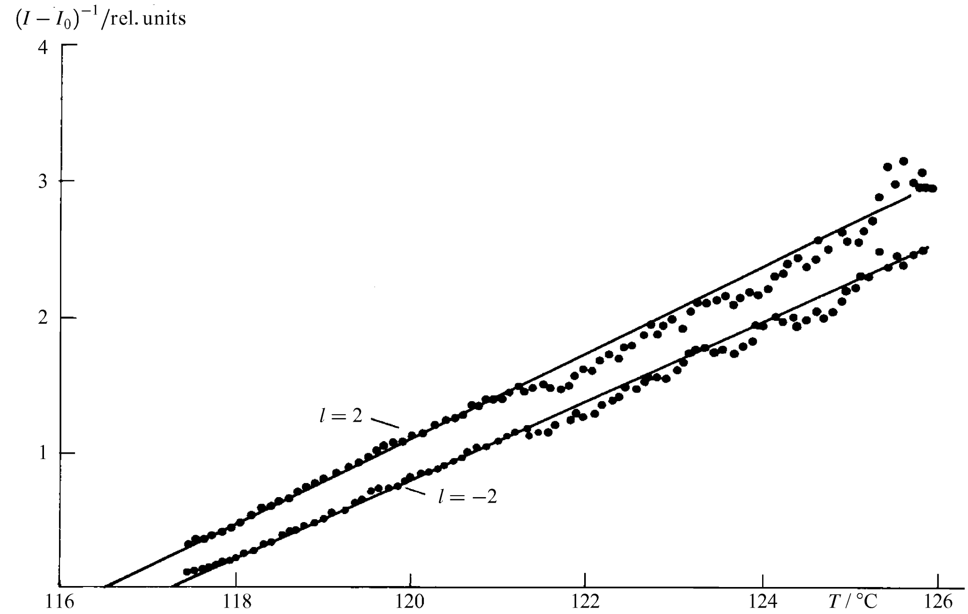

Figure 24. Temperature variation of the reciprocal of the scatteringi ntensity in pure CE2. The continuous lines were fitted by Eqn (3.27). In the case where $l = -2$, only the high-temperature data were used [130].

polarised light was incident on the specimen and the right-polarised [left-polarised? (Translator)] light was incident on the photomultiplier. For the second position, the polarisations of the two beams were reversed. Thus, it follows from Eqn (4.26) that these two positions yielded information about the contributions of the modes with $l = 2$ and -2 respectively. The nonuniformity of the temperature in the specimen did not exceed 0.01 K. The measurements were performed at CE2 concentrations in the solvent $c_0 = 40$, 60, 80, and 100 wt%. The results of the measurements for the 40 wt% $(p_0 = 250\,\mathrm{nm})$ and 100 wt% $(p_0 = 100\,\mathrm{nm})$ solutions are presented in Figs 23 and 24. Evidently, as in the isotropic phase of a nematic, the reciprocal of the intensity varies linearly with temperature over a fairly wide range. The difference consists in the fact that a specific temperature of the loss of stability $T^*_{(l)}$ corresponds to each mode. In the immediate vicinity of T_c, a deviation from linearity is observed in pure CE2 after a change in temperature of ~1 K. The experimental data were treated by the method of least squares in terms of the formula

$$I(\pm 2, \pm 2) = I_B + K_0\left[T - T^*_{\pm 2}(q)\right]^{-1}, \tag{4.27}$$

where $T^*_{\pm 2}(q) = T^* - (L_1/A')(q^2_{\mp} 2qd/L_1)$ and I_B and K_0 are adjustable parameters (q is the modulus of the scattering vector). The dependence of the difference $T_{-2(q)} - T_{2(q)} = -4qd/A'$ on the concentration c_0 is presented in Fig. 25 [130]. The theoretical difference between these temperatures must be proportional to the reciprocal of the pitch of the cholesteric helix if it is assumed that all the remaining parameters remain unchanged. Although the experimental data do not demonstrate a linear relation, nevertheless an increase in the temperature difference with increase in concentration is clearly seen.

In the case of experiments using linear polarisations, it is necessary to take into account the rotation of the plane of polarisation before and after scattering. The corresponding expressions have been obtained [126]. The temperature variation of the polarised and depolarised components of

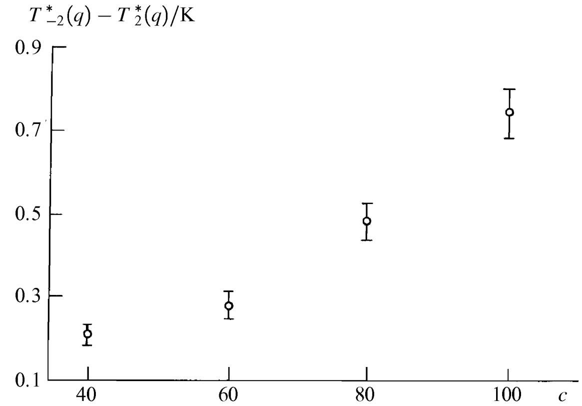

Figure 25. The difference between the temperatures $T^*_{-2}(q)$ and $T^*_2(q)$ in CE2 solutions at the concentrations $c = 40$, 60, 80, and 100 wt% corresponding to different chiralities [130].

the integral scattered light intensity in the isotropic phase of cholesteryl oleate $(T_c = 308.1\ \mathrm{K})$ has been investigated [131]. The intensity was measured at a scattering angle of 90° to within 1%. The source of light was a He–Ne laser. The temperature was varied in the range 308.2–325.0 K. The accuracy of the measurement and of the stabilisation of temperature was at least to within 0.01 K. The results of the measurements are presented in Fig. 26. Interpretation of the experimental data shows that, if $T > 310\ \mathrm{K}$, the reciprocal of the intensity for an experimental accuracy specified *a priori* behaves as const $\times (T - T^*)$, where $T^* = 307.1\ \mathrm{K}$. At $T < 310\ \mathrm{K}$, a deviation from the linear relation is observed. In contrast to the situation which obtains with a nematic liquid crystal, this deviation can be due not only to the interaction of the fluctuations but also to the difference between the temperatures corresponding to the breakdown of stability T^*_l, since at $\theta_{sc} = 90°$ several modes contribute to the scattering: the modes with $l = \pm 2$, ± 1 contribute to the

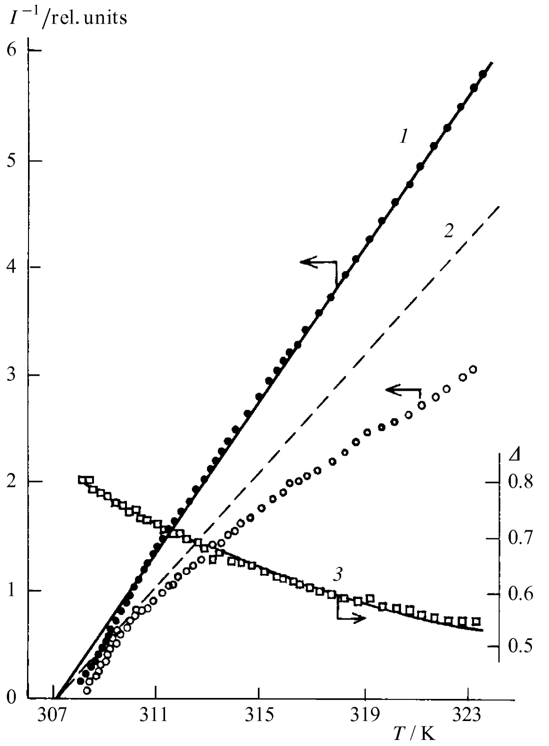

Figure 26. Temperature variation of the $(I_V^V)^{-1}$ and $(I_H^V)^{-1}$ components of the scattered light and of the degree of depolarisation $\Delta = I_H^V/I_V^V$ (□) in the isotropic phase of a cholesteric liquid crystal — cholesteryl oleate. Extrapolation of the remote points for the quantity $(I_H^V)^{-1}$ along straight line *1* affords $T^* = 307.1$ K. The discrepancy between the experimental values of the $(I_V^V)^{-1}$ component and the dashed straight line directed towards the same temperature demonstrates the contribution to the scattering by the fluctuations of other thermodynamic quantities, in particular the density [131].

I_V^V component and the modes with $l = \pm 2$, 0 contribute to the I_H^V component [122, 126].

Thus measurements under the conditions of both circular and linear polarisations confirmed the applicability of the Landau theory over a wide temperature range in the isotropic phase of cholesteric liquid crystals. The deviation of the temperature variation of the reciprocal of the scattering intensity from linearity in the critical region may be described with the aid of the theory taking into account the fluctuation-dependent corrections due to the interaction of the fluctuations of the type examined in Section 2.2 [133].

Thus the principal studies on the isotropic phase of a cholesteric have been devoted to the effects distinguishing cholesterics from nematics: the anomalously large rotation (compared with molecular rotation) of the plane of polarisation and circular dichroism. It was shown that these effects are caused by fluctuations and are particularly large in the vicinity of the transition to the ordered phase. The difficulty of describing these effects in the case of highly chiral cholesterics is associated with the existence of an intermediate fog phase [164] (see Section 5.3 below), the structure of which has been only slightly investigated. This may account for the lack of studies in which combined investigations of the phase transition are made by measuring the temperature variation of the heat capacity and susceptibility (as has been done in the isotropic phase of nematics) and the results are subjected to a joint interpretation. Such studies would be of great interest.

Measurements under the conditions of circular polarisations, which makes it possible to isolate pseudoscalar parameters of cholesteric liquid crystals, constitute a method which is not traditional for molecular optics. These measure-ments have been performed only for the integral intensity of the scattered light. Measurements of the spectral intensity, which would make it possible to obtain information about the kinetics of the fluctuations of the order parameter, are of considerable interest.

5. The ordered phase of cholesterics

In an ordered cholesteric liquid crystal, the equilibrium director $\boldsymbol{n}^0$ is not a constant vector, as in nematic liquid crystals, but rotates as the given point migrates along the axis of the helix (the z axis). Thus these crystals are homogeneous in the plane orthogonal to the z axis and periodic along it with the period equal to the pitch of the helix. Such a structure leads to completely unique optical properties. Firstly, light is reflected selectively [12]. Secondly, the rotation of the plane of polarisation observed in the ordered phase of cholesteric liquid crystals attains several thousand degrees per millimetre [13]. The eigenwaves in such a medium have a periodic amplitude (Bloch waves) determined in the general case by an infinite set of Fourier coefficients [12]. An exact expression is available only for waves propagated along the optical axis [134]. In the case of an inclined incidence, fairly effective approximate methods have been developed for the description of the propagation of light in a cholesteric [12, 13, 134, 165], using the anisotropy ε_a as a small parameter. The complexity of the eigenwaves hinders the description of the scattering by the fluctuations of the medium.

As in other homogeneous media, both the field of the point source and the correlation function of the relative permittivity fluctuations must be known for the determination of the scattering intensity. Each of these problems is of independent interest. A characteristic feature of Green's function and the correlation function for an ordered cholesteric is that they are translationally noninvariant. In particular, the field of the point source depends not only on the distance from it but also on its position [135]. This leads to significant mathematical difficulties and the analytical expressions for them can be obtained only in the presence of small parameters [136 – 138]. In the case of Green's function, the optical anisotropy $\varepsilon_a/\varepsilon_\perp$ is such a parameter [12], while in the case of the correlation function the parameter is the ratio $q_\perp/p_0$ [136, 138], where $q_\perp$ is the component of the wave vector at right angles to the axis of the helix and $2\pi/p_0$ is the pitch of the helix.

5.1 Fluctuations of the director in an ordered cholesteric

All the known cholesteric liquid crystals are uniaxial and their equilibrium order parameters $S^0_{\alpha\beta}(\boldsymbol{r})$ is determined by the director $\boldsymbol{n}^0 = \boldsymbol{n}^0(\boldsymbol{r})$:

$$S^0_{\alpha\beta}(\boldsymbol{r}) = S_0\left[n^0_\alpha(\boldsymbol{r})n^0_\beta(\boldsymbol{r}) - \tfrac{1}{3}\delta_{\alpha\beta}\right],$$

where the vector $\boldsymbol{n}^0(\boldsymbol{r})$ rotates as the given point migrates along the axis of the helix:

$$\boldsymbol{n}^0(\boldsymbol{r}) = \boldsymbol{n}^0(z) = \left[\cos(p_0 z),\ \sin(p_0 z),\ 0\right].$$

As in the case of a nematic liquid crystal, the fluctuations $\delta\widehat{S} = \widehat{S} - \widehat{S}^0$ can be divided into three groups: longitudinal fluctuations (one mode), fluctuations of the director (two modes), and biaxial fluctuations (two modes). In order to find the correlation function for the fluctuations, it is necessary to formulate an expression for the thermodynamic potential, which is the sum of all the possible invariants made up of the order parameter and its derivatives. Assuming that the inhomogeneities are fairly smooth, one can restrict the treatment to derivatives not greater than those of the second order [Eqns (1.10)–(1.12)]. In the Gaussian approximation, this expression has a quadratic form in $\delta\widehat{S}$. The correlation function is obtained by inverting the operator which enters into this quadratic form.

The local order in the majority of the known cholesteric liquid crystals is fairly close to the nematic local order. This factor makes it possible to reach a conclusion about the magnitude of the longitudinal and biaxial fluctuations. The biaxial fluctuations in nematics are small and their correlation radius $r_{\mathrm{c}\perp}$ is of the order of magnitude of the intermolecular distance r_{m}. The longitudinal fluctuations behave critically on passing to the isotropic phase. However, owing to the break caused by the first-order transition, their correlation radius $r_{\mathrm{c}\|}$ is also small, although it can be appreciably greater than $r_{\mathrm{c}\perp}$. Since $r_{\mathrm{c}\perp}$ and $r_{\mathrm{c}\|}$ are much smaller than the pitch of the cholesteric helix, it follows that in a cholesteric these fluctuations remain virtually the same as in nematics. As regards the fluctuations of the director, the situation is different. In an unbounded nematic in the absence of an external field, both modes have an infinite correlation radius and their amplitudes exceed by several orders of magnitude the amplitudes of the longitudinal and biaxial modes. In cholesterics, one of the director modes is singular and the other has a finite correlation radius of the order of magnitude of the pitch of the helix, which is large compared with $r_{\mathrm{c}\perp}$ and $r_{\mathrm{c}\|}$ [17]. Therefore we can limit the treatment, to a first approximation, to the allowance for only the director fluctuations. (The biaxial and longitudinal fluctuations in cholesterics have been considered elsewhere [136].) The relative permittivity fluctuations are related to the director fluctuations by the expression

$$\delta\varepsilon_{\alpha\beta}(\boldsymbol{r}) = \varepsilon_{\mathrm{a}}\left[\delta n_{\alpha}(\boldsymbol{r})\, n^0_{\beta}(z) + \delta n_{\alpha}(\boldsymbol{r})\, n^0_{\beta}(z)\right] . \tag{5.1}$$

For the relative permittivity fluctuation correlation function $G_{\alpha\beta\delta\gamma}(\boldsymbol{r}-\boldsymbol{r}', z+z')$, one can write

$$G_{\alpha\beta\delta\gamma}(\boldsymbol{r}-\boldsymbol{r}', z+z') = \varepsilon_{\mathrm{a}}\left[n^0_{\alpha}(z)n^0_{\delta}(z)G_{\beta\gamma} + n^0_{\beta}(z)n^0_{\gamma}(z)G_{\alpha\delta}\right.$$
$$\left. + n^0_{\alpha}(z)n^0_{\gamma}(z)G_{\beta\delta} + n^0_{\beta}(z)n^0_{\delta}(z)G_{\alpha\gamma}\right], \tag{5.2}$$

where $G_{\alpha\beta}$ is the correlation function for the director fluctuations:

$$G_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{r}', z+z') = \langle\delta n_{\alpha}(\boldsymbol{r})\delta n_{\beta}(\boldsymbol{r}')\rangle . \tag{5.3}$$

By virtue of the symmetry of the medium, $G_{\alpha\beta\delta\gamma}$ and $G_{\alpha\beta}$ are periodic functions of the second argument.

In order to determine the correlation function $G_{\alpha\beta}$, we make use of the expression for the thermodynamic potential of the cholesteric as a functional of $n(\boldsymbol{r})$ [9]:

$$\Phi = \Phi_0 + \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\Big\{K_{11}(\nabla\cdot\boldsymbol{n})^2 + K_{22}\left[\boldsymbol{n}\times(\nabla\times\boldsymbol{n}) + p_0\right]^2$$
$$+ K_{33}\left[(\boldsymbol{n}\cdot\nabla)\boldsymbol{n}\right]^2\Big\} . \tag{5.4}$$

This expression differs from Eqn (3.1) by the presence of a pseudoscalar p_0. The field $\boldsymbol{n} = \boldsymbol{n}^0(z)$ in Eqn (5.1) is known to ensure a minimum in the free energy defined by Eqn (5.4). The free energy change associated with a small deviation $\delta\boldsymbol{n}(\boldsymbol{r})$ of the director field from $\boldsymbol{n}^0(\boldsymbol{r})$ assumes the following form in the quadratic approximation:

$$\delta\Phi = \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\Big\{K_{11}(\nabla\cdot\delta\boldsymbol{n})^2 + K_{22}\left[\boldsymbol{n}^0(\nabla\times\delta\boldsymbol{n})\right]^2$$
$$+ K_{33}\left[(\delta\boldsymbol{n}\cdot\nabla)\boldsymbol{n}^0 + (\boldsymbol{n}^0\cdot\nabla)\delta\boldsymbol{n}\right]^2\Big\} . \tag{5.5}$$

The correlation function $G_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{r}', z+z')$ is the kernel of the operator equal to the reciprocal of the operator of the quadratic form defined by Eqn (5.5). The most logical calculation of the director fluctuations has been carried out in a study [138] where the zero harmonic in terms of the second argument of this correlation function was found in terms of the single constant approximation $K_{jj} = K$ ($j = 1-3$):

$$G^0_{\alpha\beta}(\boldsymbol{q}) = V^{-1}\int \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'\exp[-\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}')]G_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{r}', z+z') .$$

In the x, y, z coordinate system, it has the form

$$G^0_{\alpha\beta}(\boldsymbol{q}) = \frac{k_{\mathrm{B}}T}{p_0^2 K g(\boldsymbol{q})}$$
$$\times\begin{pmatrix} p_0^2 & q_{\perp}p_0 & 0 \\ -\mathrm{i}q_{\perp}p_0 & q_{\perp}p_0 + g(\boldsymbol{q})/2 & 0 \\ 0 & 0 & g(\boldsymbol{q})/2 \end{pmatrix}, \tag{5.6}$$

where

$$g(\boldsymbol{q}) = \left\{q_{\|}^2 + \left[\frac{1}{2}\left(\frac{q_{\|}}{p_0}\right)^2 + \frac{3}{8}\left(\frac{q_{\perp}}{p_0}\right)^2\right]q_{\perp}^2\right\}^{-1} . \tag{5.7}$$

Eqns (5.6) and (5.7) are valid only subject to the condition $q_{\perp} \ll p_0$. We may draw attention to the unusual nature of the correlation function (5.6). For $q_{\|} = 0$, it has a singularity $q_{\perp}^{-4}$. This is a manifestation of a general property of one-dimensionally periodic systems — the Landau–Peierls instability [18]. Such dependence on $\boldsymbol{q}$ leads to an infinite mean square fluctuation at a point and a crystal with an infinite volume cannot therefore exist. However, the smearing of the crystal by fluctuations would occur only for astronomical dimensions [138].

5.2 Green's function of the electromagnetic field

The equilibrium relative permittivity tensor $\varepsilon^0_{\alpha\beta}$ for an ordered cholesteric can be resolved into longitudinal and transverse components relative to the director:

$$\varepsilon^0_{\alpha\beta}(z) = \varepsilon_{\|}n^0_{\alpha}(z)n^0_{\beta}(z) + \varepsilon_{\perp}\left[\delta_{\alpha\beta} - n^0_{\alpha}(z)n^0_{\beta}(z)\right] . \tag{5.8}$$

Since the direction of the vector $\boldsymbol{n}^0$ varies as the given point migrates along the z axis, it follows that instead of the basis vectors $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$, it is more convenient to go over to a triad of unit vectors:

$$\boldsymbol{m}^{(\pm 1)} = (\boldsymbol{e}_1 \pm \mathrm{i}\boldsymbol{e}_2)/\sqrt{2}, \quad \boldsymbol{n}^0 = \boldsymbol{e}_3 .$$

In terms of this basis, the relative permittivity tensor has the form

$$\varepsilon_{\alpha\beta}(z) = \begin{pmatrix} \bar{\varepsilon} & 0 & \frac{1}{2}\varepsilon_{\mathrm{a}}\mathrm{e}^{2\mathrm{i}p_0 z} \\ 0 & \varepsilon_{\perp} & 0 \\ \frac{1}{2}\varepsilon_{\mathrm{a}}\mathrm{e}^{-2\mathrm{i}p_0 z} & 0 & \bar{\varepsilon} \end{pmatrix}, \tag{5.9}$$

where $\bar{\varepsilon} = (\varepsilon_{\perp} + \varepsilon_{\|})/2$. Evidently the period of the variation of the relative permittivity tensor is smaller by a factor of two than the pitch of the helix. This is associated with the fact that the directions of the director $\boldsymbol{n}$ and $-\boldsymbol{n}$ are equivalent.

Green's function $\widehat{T}$ must satisfy the equation

$$\left[\nabla\times\nabla\times - \frac{\omega^2}{c^2}\widehat{\varepsilon}(z)\right]\widehat{T}(\boldsymbol{r}, \boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}') . \tag{5.10}$$

The differentiation in the left-hand side of this equation is carried out with respect to the components of $\boldsymbol{r}$. Like the correlation function for the director fluctuations, the propagator $\widehat{T}$ depends not only on $\boldsymbol{r}-\boldsymbol{r}'$ but also on $z+z'$ and is a periodic function of $z+z'$ with the period $2\pi/p_0$. According to Peterson [135], the two-wave approximation [12, 13], which was effective in the propagation problem, is unsuitable for the determination of Green's function in the scattering problem.

In Peterson's study [135], the problem of finding the propagator reduces to the determination of the eigenwaves in the medium and an effective numerical method is proposed for this purpose. In following the procedure in the above study, we shall consider the operator $\widehat{L}=\widehat{\varepsilon}^{-1}(z)\nabla\times\nabla\times$, acting in the space of the functions $\boldsymbol{E}(\boldsymbol{r})$ with the scalar product

$$(\boldsymbol{E}', \boldsymbol{E})_{\hat{\varepsilon}} = \frac{1}{(2\pi)^3}\int \mathrm{d}\boldsymbol{r}\, E_{\alpha}^{'*}(\boldsymbol{r})\varepsilon_{\alpha\beta}(z)E_{\beta}(\boldsymbol{r})\,. \tag{5.11}$$

This is a Hermitian operator. We shall designate by $\boldsymbol{E}_{\boldsymbol{k}}^{j}(\boldsymbol{r})$ the eigenfunctions of this operator. The discrete index j numbers the types of waves in the medium. If the normalisation conditions $(\boldsymbol{E}_{\boldsymbol{k}'}^{j'}, \boldsymbol{E}^{j}) = \delta_{jj'}(\boldsymbol{k}-\boldsymbol{k}')$ holds, then Green's function can be represented in the form

$$T_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{r}') = \frac{1}{(2\pi)^3}\sum_{j}\int \mathrm{d}\boldsymbol{k}\, \frac{E_{\alpha\boldsymbol{k}}^{j}(\boldsymbol{r})D_{\beta\boldsymbol{k}}^{j*}(\boldsymbol{r}')}{[\omega_j(\boldsymbol{k})/c]^2-\chi}\,, \tag{5.12}$$

where $\boldsymbol{D}_{\boldsymbol{k}}^{j} = \widehat{\varepsilon}\boldsymbol{E}_{\boldsymbol{k}}^{j}$, $\chi=(\omega/c)^2$, and $\omega_j(k)$ satisfies the dispersion relation. By virtue of the transverse nature of the field $\boldsymbol{D}$, there exist only two types of waves ($j=1,2$). For large distances r, the propagator can be found by the stationary phase method [139]:

$$T_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{r}') = \sum_{j} M_{j}^{-1} E_{\alpha\boldsymbol{k}_{\mathrm{st}}}^{j}(\boldsymbol{r}) D_{\beta\boldsymbol{k}_{\mathrm{st}}}^{j*}(\boldsymbol{r}')\,, \tag{5.13}$$

where

$$M_j = 4\pi\left|\frac{\partial\omega_j^2}{\partial k_{\perp}^2}\right| \left|\boldsymbol{k}_{\perp\mathrm{st}}\left(\frac{\partial^2\boldsymbol{k}}{\partial k_{\parallel}^2}\right)_{\chi}\right|^{1/2} r_{\perp}\,. \tag{5.14}$$

The derivatives are calculated at the point $\boldsymbol{k}_{\mathrm{st}}$ on the surface $\omega_j^2(\boldsymbol{k}) = \chi c^2$, where the external normal is directed along $\boldsymbol{r}$. The eigenwaves $\boldsymbol{E}_{\boldsymbol{k}}^{j}(\boldsymbol{r})$ in Eqn (5.13) are of the Bloch type. Their amplitudes can be sought in the form of a Fourier series. The problem is how to solve the sequence of recurrence relations for the coefficients of the series. A numerical algorithm has been proposed [135] for the calculation of these coefficients, based on the ideas usually employed in the solution of the Mathieu equation [140].

One of the characteristics of the propagation of waves in periodic media is the existence of forbidden gaps [12]. This leads to the situation where at a fixed frequency ω the dispersion surface $k=k^{(j)}(\boldsymbol{k},\omega)$ is nonconvex [141]. As a result of the presence of points of inflection, M_j in Eqn (5.14) becomes zero for certain directions. This means that in these directions the field of the point source decreases more slowly than r^{-1}. This behaviour of Green's function has been considered [142] for the case of a scalar field and it has been shown that in these directions the field decreases as $r^{-5/6}$.

5.3 Blue phases of cholesterics

For cholesterics with a high degree of chirality over a narrow temperature range between the isotropic and the usual helical phases, the so-called blue phases are observed. At the present time not less than three phases are distinguished: BPI, BPII, and the fog phase BPIII. They appear in the above sequence as the temperature is raised [164]. The structures of BPI and BPII have been thoroughly investigated both theoretically [164, 166, 167] and experimentally [168], while the structure of the fog phase still remains a subject of investigation. The symmetry of the BPI and BPII phases is characterised by the cubic groups O^8 and O^2 respectively. The fog phase apparently constitutes an amorphous macroscopic nonordered state of the substance with a large correlation length in the orientation order. We shall discuss below the properties of BPI and BPII. The blue phases possess interesting optical properties: a selective light scattering (which usually in fact leads to the blue colour), a marked optical activity, circular and linear dichroisms, and the absence of linear double refraction. We may note that, in contrast to the ordered phase of cholesterics, here one observes not one but several comparable Bragg reflections. The presence of these reflections permits the conclusion that the blue phases have a periodic structure.

The nature of the polarisation dependence of the diffraction leads to the conclusion that this periodicity is associated primarily with the orientation degrees of freedom [164]. Therefore, the symmetrical traceless tensor $\widehat{S}$ [Eqn (1.1)] can be used for the description of the order in blue phases. The equilibrium order parameter $\widehat{S}^{0}(\boldsymbol{r})$ can be expressed in the form

$$\widehat{S}^{0}(\boldsymbol{r}) = \sum_{\boldsymbol{\tau}} \widehat{S}_{\boldsymbol{\tau}}^{0}\,\mathrm{e}^{\mathrm{i}\boldsymbol{\tau}\cdot\boldsymbol{r}}\,, \tag{5.15}$$

where $\boldsymbol{\tau} = 2\pi(h\boldsymbol{x}+k\boldsymbol{y}+l\boldsymbol{z}\})/d$, $\boldsymbol{x}$, $\boldsymbol{y}$, and $\boldsymbol{z}$ are the unit vectors of the axes, h, k, and l are integers, and d is the lattice constant. The tensors $\widehat{S}_{\tau}$ are Fourier coefficients, which can be expanded in terms of the tensors basis (4.3):

$$\widehat{S}_{\boldsymbol{\tau}}^{0} = \sum_{j=-2}^{2} S^{0}(\boldsymbol{\tau}, j)\widehat{\pi}^{(j)}(\boldsymbol{\tau}/\tau)\,. \tag{5.16}$$

The periodic order defined by Eqn (5.15) leads to Bragg peaks on diffraction of light by the structure, the peaks corresponding to the scattering vector $\boldsymbol{q}=\boldsymbol{\tau}$. However, apart from the scattering by regular structural inhomogeneities $\widehat{S}^{0}$ (diffraction), scattering by the thermal fluctuations of the order parameters $\delta\widehat{S}$ also occurs. Since the shift of the system as a whole takes place without the expenditure of energy, fluctuations corresponding to the shear deformations of the lattice are the most intense. The presence of fluctuations should lead to the 'spreading' of the Bragg peaks.

The scattering by fluctuation-induced lattice deformation has been examined theoretically [169]. The change in the thermodynamic potential Φ associated with the deformation in the crystal is

$$\Phi = \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\,\lambda_{\alpha\beta\gamma\rho}u_{\alpha\beta}u_{\gamma\rho}\,, \tag{5.17}$$

where

$$u_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_{\alpha}}{\partial r_{\beta}} + \frac{\partial u_{\beta}}{\partial r_{\alpha}}\right)$$

is the deformation tensor, $\boldsymbol{u}$ the displacement vector, and $\lambda_{\alpha\beta\gamma\delta}$ the tensor of the moduli of elasticity [170]. The correlator of the fluctuations of the displacements can be easily found from Eqn (5.17):

$$\langle u_{\alpha}u_{\gamma}\rangle_{\boldsymbol{q}} = k_{\mathrm{B}}T(\lambda_{\cdot\beta\cdot\rho}q_{\beta}q_{\rho})_{\alpha\gamma}^{-1}\,. \tag{5.18}$$

The Goldstone nature of the displacement fluctuations ($\langle uu \rangle_q \sim q^{-2}$ at $q \to 0$) makes it possible to use the principle of the conservation of the modulus [7] (cf Sections 3.1 and 3.2): in large scale slow fluctuations $\boldsymbol{u}$, there is sufficient time for the fast degrees of freedom $S^0(\boldsymbol{\tau}, j)$ to attain the equilibrium and to become adjusted to the new state of the system. This leads to the appearance of a contribution to the fluctuations of the order parameter tensor by the displacement fluctuations: $\delta\widehat{S}(r)_u = \widehat{S}^0(\boldsymbol{r}+\boldsymbol{u}) - \widehat{S}^0(\boldsymbol{r})$. In terms of the lowest orders in u, we have from Eqn (5.15)

$$\delta\widehat{S}(\boldsymbol{r})_u = \mathrm{i}u_\alpha \sum_{\boldsymbol{\tau}} \boldsymbol{\tau}_\alpha \widehat{S}^0_{\boldsymbol{\tau}} \mathrm{e}^{\mathrm{i}\boldsymbol{\tau}\cdot\boldsymbol{r}} . \tag{5.19}$$

We may draw attention to the fact that in the given instance the contribution of the 'principle of the conservation of the modulus' is of first order in terms of the Goldstone variable and not the second, as was the case in nematics (and also in magnetic materials [7]). The reason for this is the spatial inhomogeneity of the blue phase. As a result, the correlator $\langle \delta\widehat{S}_u \delta\widehat{S}_u \rangle_q$ is also of the Goldstone type.

Naturally, apart from the displacement-induced fluctuations $\delta\widehat{S}_u$, there is a possibility in the blue phase also of the usual spontaneous fluctuations $\delta\widehat{S}$. However, they are not of the Goldstone type and we shall not be interested in them.

The single scattering intensity in the lowest approximation in terms of $S^0(\boldsymbol{\tau}, j)$ can be found from Eqn (2.8). For the wave vector $\boldsymbol{k}^{(s)} - \boldsymbol{k}^{(i)} = \boldsymbol{\tau} + \boldsymbol{p}$ near the reflection $\boldsymbol{\tau}$ (for $\boldsymbol{p} \ll \boldsymbol{\tau}$), we have

$$I(\boldsymbol{e}^{(\mathrm{i})}, \boldsymbol{e}^{(\mathrm{s})}) = Z_0^{(i)} |\boldsymbol{e}^{(\mathrm{i})} \widehat{S}^0_{\boldsymbol{\tau}} \boldsymbol{e}^{(\mathrm{s})*}|^2 \tau_\alpha \tau_\gamma (\lambda_{\cdot\beta\cdot\rho}\, p_\beta p_\rho)^{-1}_{\alpha\gamma} . \tag{5.20}$$

Here the notation is the same as in Eqn (2.8). This formula shows that, by measuring the distribution of the intensity in the vicinity of the Bragg reflection, it is possible to determine the moduli of elasticity of the blue phase. It is noteworthy that, according to Eqn (5.20), the intensity in the vicinity of the peak falls as p^{-2}.

If, following Dmitrienko [169], one postulates that the entire change in $\widehat{S}$ is associated with the shear deformation $\boldsymbol{r} \to \boldsymbol{r} + \boldsymbol{u}(\boldsymbol{r})$ in Eqn (5.15), then the Landau theory [Eqn (4.1)] makes it possible to express the modulus of elasticity tensor $\lambda_{\alpha\beta\gamma\delta}$ in terms of the coefficients of the expansion of the thermodynamic potential A, L_1, L_2, d, and the amplitude of the harmonics of the equilibrium order parameter $S^0_{\boldsymbol{\tau}}$ in Eqn (5.16). Allowance for the principal modes ($j = \pm 2$) leads to the expression

$$\lambda_{\alpha\beta\gamma\rho} = 2L_1 p_0 \sum_{\boldsymbol{\tau}} |S^0(\boldsymbol{\tau}, 2)|^2 \tau^{-3} \tau_\alpha \tau_\beta \tau_\gamma \tau_\rho . \tag{5.21}$$

The broadening of the Bragg peaks was apparently first observed experimentally by Marcus [171].

The light scattering by fluctuations in BPII has been investigated [172] in a 27.5% solution of 60CB in the CN cholesteric. A laser with a frequency of 5145 A was employed. Interpretation of experimental data led to the following dependence of the scattering intensity on the scattering vector q_{sc} and the frequency ω:

$$I(q_{\mathrm{sc}}, \omega) = A(q_{\mathrm{sc}}) s(\omega) , \tag{5.22}$$

where in the frequency range 4 – 3500 Hz the quantity $s(\omega)$ is the sum of two Lorentzians plus a constant:

$$s(\omega) = \mathrm{const} \left[\frac{1}{1 + (\omega/125)^2} + \frac{0.214}{1 + (\omega/360)^2} + 0.0013 \right] . \tag{5.23}$$

Therefore, according to Marcus [172], the fluctuations in BPII do not constitute a simple diffusion mode. As regards the behaviour of $A(q_{\mathrm{sc}})$, Marcus's data [172] demonstrate the presence of a certain characteristic dimension of the order of 8 μm (i.e. approximately 50 times greater than the lattice constant), in terms of which the fluctuations are correlated throughout the frequency range investigated. The scattering in BPII has also been investigated [173] both for light and for soft X-rays. It was shown that the structure constants defining the positions of the maxima in the dependence of the intensity $I(q_{\mathrm{sc}})$ on the scattering vector q_{sc} are the same in the optical and X-ray experiments, although the causes of the scattering are different. According to Aliev et al. [173], the size of the uniformly ordered regions in BPII amounts to 8 – 10 lattice periods. A similarity of the q_{sc} dependence of the scattering intensity in the blue phase of liquid crystals and in microporous glasses has also been observed.

Very interesting results have been obtained in a study [174] of the influence of smectic fluctuations on the structure of supercooled BPI with the aid of the scattering of X-rays and visible light. It was shown, in particular, that, as the temperature is induced, the Bragg scattering pattern reveals the appearance, apart from the main peak, of an additional peak associated with processes involving a rearrangement of the lattice. Furthermore, a new BPS phase was observed between BPI and the cholesteric phase. It exhibits two types of order: chiral long-range BP order and smectic short-range order. The BPS phase is regarded as a candidate for an analogue of the smectic A* liquid crystal (a liquid crystal analogue of the Abrikosov lattice in superconductors observed by Goodby et al. [175]).

Thus the zero harmonic in terms of the $z + z'$ parameter of the correlation function for the director fluctuations $\langle \delta n_\alpha(\boldsymbol{q}_\perp, z) \delta n_\beta(\boldsymbol{q}_\perp, z') \rangle$ in the case where $q_\perp \ll p_0$ has now been calculated. The correlator for one of the modes (the so-called umbrella mode $\delta\boldsymbol{n}||z$) has a singularity of the type $\sim (q^2)_{||} + \mathrm{const}\, q_\perp^4)^{-1}$.

A detailed analysis of the scattering intensity taking into account the real correlation function for the fluctuations of the relative permittivity in cholesterics has not been carried out. This is apparently due to the fact that, firstly, there is no analytical expression for Green's function and, secondly, only the zero harmonic of the correlation function in terms of the argument $z + z'$ has been calculated, although higher harmonics may also contribute to the scattering. There are no fundamental difficulties in a logical analysis because there exists an effective numerical algorithm for the evaluation of Green's function [135] and the method employed [138] to determine the zero harmonic makes it possible to find also harmonics of higher orders.

Studies on cholesterics with a very large pitch of the helix (twisted nematic liquid crystals) are promising. In the calculation of Green's function for the electromagnetic field, it is possible to employ in this instance the 'adiabatic' approximation [9, 10, 176] and the problem consists solely in the evaluation of the correlation function for the fluctuations in the limit $q_\perp \gg p_0$.

We may note that the presence of the director fluctuations in an ordered cholesteric should lead to the smearing of the Bragg reflections due to diffuse scattering. Measurements of this effect would make it possible to determine the elastic constants of cholesterics and also to obtain information about the dynamics of the fluctuations. It would be of interest to elucidate the role of the scattering by fluctuations in the experimentally observed deviation of the transmission coefficient from unity for a wave propagated along the axis of the helix and not diffracted by the structure of the cholesteric.

Additional studies are apparently still required for the blue phases. In particular, more detailed investigations of the dynamics of the BPI and BPII fluctuations are necessary. For a final conclusion concerning the nature of the fog and the new BPS phases, more detailed measurements of the X-ray structure factors are required.

6. Smectic liquid crystals (SLC)

6.1 Fluctuations of the director in an ordered smectic A

From the optical point of view, the equilibrium smectic A liquid crystal is an anisotropic medium with the relative permittivity tensor defined by Eqn (3.31). From the microscopic point of view, smectics are layered systems with a one-dimensionally periodic structure along a specified z axis. The structure period $2\pi/q_0$ is of the order of magnitude of the intermolecular distance. In a smectic A, the long molecular axes in the state of equilibrium are directed along the normal to the layers, i.e. the director vector $\boldsymbol{n}_0 || z$.

If one is interested in light scattering, only the fluctuations of the relative permittivity tensor $\delta\hat{\varepsilon}$ need be investigated. This tensor has six fluctuation modes of the symmetrical fluctuations. Firstly, the scalar mode [$\mathrm{Sp}(\delta\hat{\varepsilon})$ fluctuations], the allowance for which in a smectic is essential, in contrast to a nematic, because the equilibrium periodic structure (1.2) is described in a smectic precisely by a scalar degree of freedom — the density. Secondly, as in nematics, there are orientation degrees of freedom here: one longitudinal mode, two biaxial transverse modes (director fluctuations), and two biaxial transverse modes. However, the scattering by scalar, longitudinal, and biaxial fluctuations in the ordered phase of the smectic liquid crystal should be comparatively small — of the order of magnitude of the scattering in the usual organic liquids. For biaxial and longitudinal fluctuations, this claim appears evident (the scattering by longitudinal fluctuations in the A → I transition and by biaxial fluctuations in the A → C transition may be an exception). For a scalar mode, this follows from the fact that the period of the equilibrium structure is much smaller than the wavelength λ and the long-wave fluctuations of the smooth complex amplitude [Eqn (1.14)] of the density wave are hardly manifested in light scattering with a transmitted momen-tum $q_{\mathrm{sc}} \leqslant 2k_0$ (see also Lyuksyutov [143]). Therefore in the case of smectics A the treatment is usually restricted to the consideration of only the scattering by the director fluctuations $\delta\boldsymbol{n}$.

We spoke above about spontaneous fluctuations. In a smectic A, which is a degenerate system, there is also a possibility of nonclassical fluctuations due to the principle of conservation of the modulus, of the type considered in Sections 3.1 and 3.2 for nematics and in Section 5.3 for cholesterics. The nonclassical contribution to the scalar mode is most specific for smectics [143].

For smectics A, the fluctuations of the director can arise due to two physically different causes. Firstly, these are purely spontaneous thermal fluctuations of the long molecular axes. In contrast to nematics, the appearance of these fluctuations requires a fairly large amount of energy, because they are associated with deviations of the local director from the normal to the layer (the so-called tilt mode). Secondly, the director fluctuations can arise owing to a change in the direction of the normal to the layer in local displacements of the layers $\boldsymbol{u}(\boldsymbol{r})$ (the dilation mode). We may note that the latter mechanism constitutes in a certain sense allowance for the 'principle of the conservation of the modulus': for sufficiently smooth and slow displacements $\boldsymbol{u}(\boldsymbol{r})$, the director has sufficient time to become arranged along the new local direction of the normal to the layer. The only component of the displacement vector $\boldsymbol{u}(\boldsymbol{r})$ the fluctuations of which in smectics A are not small is the component u_z, henceforth designated by u [9].

From this point of view, the elastic energy of the distortion of the smectic A contains contributions of three types. Firstly, this is the Frank elastic energy $\Phi_{\mathrm{N}} = \Phi$ in Eqn (3.1), which takes into account the deviations of the field of the director $\boldsymbol{n}(\boldsymbol{r})$ from the homogeneous state with $n^0 = \mathrm{const}$. The second contribution is the elastic energy Φ_{S} in the layered structure proper of the smectic and, thirdly, it is the energy Φ_{SN} associated with the deviations of the director from the normal to the layers.

The following model is most often used for the sum of the second and third contributions [20]:

$$\Phi_{\mathrm{S}} + \Phi_{\mathrm{SN}} = \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\,\left(a|\psi|^2 + \frac{1}{2}b|\psi|^4 + L_{\|}|\nabla_{\|}\psi|^2 \right.$$
$$\left. + L_{\perp}|(\nabla + \mathrm{i}\boldsymbol{q}_0\cdot\delta\boldsymbol{n})\psi|^2\right)\,. \tag{6.1}$$

Here the parameter ψ has been defined in Eqn (1.14). A special form of the formulation of the interaction of ψ and $\delta\boldsymbol{n}$ in the fourth term of Eqn (6.1) takes into account the constancy of the energy in the simultaneous uniform rotation of the layers and of the field of the directors and also the energy equivalence of the uniform rotations of the layers or the director relative to the equilibrium configuration.

It is also possible to take into account an additional contribution to Φ_{S} associated with the higher-order gradients of ψ:

$$\Phi'_{\mathrm{S}} = \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\,\left[d_1|\nabla_{\perp}^2\psi|^2 + d'|\nabla_{\|}^2\psi|^2 + d''|\nabla_{\perp}\nabla_{\|}\psi|^2\right]. \tag{6.2}$$

In Eqns (6.1) and (6.2), $a = a'(T - T_{\mathrm{NA}})$, T_{NA} is the temperature of the N → A transition, and a', b, $L_{\|}$, $L_{\perp}$, d_1, d', and d'' are constants which are assumed to be positive with the exception of d''; $d_1 d' > (d'')^2$.

In the Gaussian approximation in terms of small deviations from equilibrium $\eta(\boldsymbol{r}) - |\psi(\boldsymbol{r})| = \psi_0$ and $u(\boldsymbol{r})$, we have from Eqn (6.1), (6.2) and (1.14)

$$\Phi_{\mathrm{S}} + \Phi_{\mathrm{SN}} + \Phi'_{\mathrm{S}} = \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\,\left[A\eta^2 + L_{\|}(\nabla_{\|}\eta)^2 + L_{\perp}(\nabla_{\perp}\eta)^2\right.$$
$$+ B(\nabla_{\|}u)^2 + D(\nabla_{\perp}u + \delta\boldsymbol{n})^2 + K_{\mathrm{S}}(\nabla_{\perp}^2 u)^2$$
$$\left. + K'_{\mathrm{S}}(\nabla_{\|}^2 u)^2 + K''_{\mathrm{S}}\nabla_{\perp}^2 u\nabla_{\|}^2 u\right], \tag{6.3}$$

where

$$A = -2a,\quad B = L_{\|}q_0^2\psi_0^2,\quad D = L_{\perp}q_0^2\psi_0^2\,,$$
$$K_{\mathrm{S}} = d_1 q_0^2\psi_0^2,\quad K'_{\mathrm{S}} = d' q_0^2\psi_0^2,\quad K''_{\mathrm{S}} = d'' q_0^2\psi_0^2\,; \tag{6.4}$$

here $\psi_0 = \langle|\psi(\boldsymbol{r})|\rangle$ is the equilibrium value of the order param-eter, which in the mean field approximation has the form $\psi_0^2 = -a'(T - T_{\mathrm{NA}})/b$. In Eqn (6.4), we neglected the fourth-order term in ∇ as a function of η. It follows from Eqn (6.3) that in the given model $\eta(\boldsymbol{r})$ does not interact with the dis-placement fluctuations $u(\boldsymbol{r})$ and the director fluctuations $\delta\boldsymbol{n}(\boldsymbol{r})$.

In the limit $D \to \infty$, we can assume the identity

$$\delta\boldsymbol{n}(\boldsymbol{r}) = -\nabla_{\perp} u(\boldsymbol{r}) \tag{6.5}$$

in Eqn (6.3). This approximation corresponds to the situation usually considered where the local director is rigorously perpendicular to the layers and its fluctuations are determined solely by the fluctuations of the layered structure [9, 11]. According to Eqns (3.1) and (6.3), in this case the total contribution to the elastic energy of the smectic A liquid crystal $\Phi_{\mathrm{A}} = \Phi_{\mathrm{N}} + \Phi_{\mathrm{S}} + \Phi_{\mathrm{SN}} + \Phi'_{\mathrm{S}}$, associated with the fluctuations of the displacements of the layers, has the following form with an accuracy to within surface terms:

$$\Phi_{\mathrm{A}}(u) = \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\, \Big[B(\nabla_{\parallel} u)^2 + K_1(\nabla_{\perp}^2 u)^2 + K'(\nabla_{\parallel}^2 u)^2 + 2K''\nabla_{\perp}^2 u \nabla_{\parallel}^2 u\Big]\,, \tag{6.6}$$

where

$$K_1 = K_{11} + K_{\mathrm{S}}\,, \quad K' = K'_{\mathrm{S}}\,, \quad K'' = K_{33} + K''_{\mathrm{S}}\,. \tag{6.7}$$

The term $K_{22}|\boldsymbol{n}\cdot\operatorname{curl}\boldsymbol{n}|^2$ from Eqn (3.1) does not then contribute to Φ_{A}.

For finite values of D, Eqn (6.3) makes it possible to consider the deviations of the director from the normal to the layer. On substituting the director fluctuations δn in Eqns (3.1) and (6.3), as in the case of nematics in the form (3.3), we obtain the contribution to the elastic energy Φ_{A} by the modes with the given $\boldsymbol{q}$:

$$\begin{aligned}\Phi_{\mathrm{A}}(\eta_{\boldsymbol{q}}, u_{\boldsymbol{q}}, \boldsymbol{n}_{\boldsymbol{q}}) = \tfrac{1}{2}\big[&(A + L_{\parallel}q_{\parallel}^2 + L_{\perp}q_{\perp}^2)|\eta_{\boldsymbol{q}}|^2 \\ &+ (B + K_{11}q_{\perp}^2 + K_{33}q_{\parallel}^2)|\delta n_{1\boldsymbol{q}}|^2 \\ &+ (D + K_{22}q_{\perp}^2 + K_{33}q_{\parallel}^2)|\delta n_{2\boldsymbol{q}}|^2 \\ &+ (Bq_{\parallel}^2 + Dq_{\perp}^2 + K_{\mathrm{S}}q_{\perp}^4 + K'_{\mathrm{S}}q_{\parallel}^4 + K''_{\mathrm{S}}q_{\parallel}^2 q_{\perp}^2)|u_{\boldsymbol{q}}|^2 \\ &+ \mathrm{i}Dq_{\perp}(u_{\boldsymbol{q}}\delta n_{1\boldsymbol{q}}^{*} - u_{\boldsymbol{q}}^{*}\delta n_{1\boldsymbol{q}})\big]\,.\end{aligned} \tag{6.8}$$

Only the terms in the first nonvanishing orders in q have been left here in the coefficients of $\delta n_{j\boldsymbol{q}}$ and $\eta_{\boldsymbol{q}}$. Evidently, only the δn_1 mode interacts with the displacement fluctuations u. From the quadratic form (6.8), it is easy to find all the nonzero correlators for the fluctuation modes:

$$\begin{aligned}&\langle\eta^2\rangle_{\boldsymbol{q}} = \beta(A + L_{\parallel}q_{\parallel}^2 + L_{\perp}q_{\perp}^2)^{-1}\,, \\ &\langle\delta n_j^2\rangle_{\boldsymbol{q}} = \beta(A_j + \mathcal{K}_{\mathrm{N}j})^{-1}\,, \\ &\langle u^2\rangle_{\boldsymbol{q}} = \beta(A_3 + \mathcal{K}_{\mathrm{S}})^{-1}\,, \\ &\langle u\delta n_1^{*}\rangle_{\boldsymbol{q}} = \mathrm{i}\beta q_{\perp}D\big[BDq_{\perp}^2 + D\mathcal{K}_{\mathrm{S}} + (Bq_{\parallel}^2 + Dq_{\perp}^2)\mathcal{K}_{\mathrm{N}1}\big]^{-1}\,,\end{aligned} \tag{6.9}$$

where

$$\begin{aligned}&\beta = \mathrm{k_B}T\,, \quad A_1 = A_1(\boldsymbol{q}) = \frac{D(Bq_{\parallel}^2 + \mathcal{K}_{\mathrm{S}})}{Bq_{\parallel}^2 + Dq_{\perp}^2 + \mathcal{K}_{\mathrm{S}}}\,, \quad A_2 = D\,, \\ &A_3 = A_3(\boldsymbol{q}) = Bq_{\parallel}^2 + q_{\perp}^2(D^{-1} + \mathcal{K}_{\mathrm{N}j}^{-1})^{-1}\,, \quad j = 1, 2\,, \\ &\mathcal{K}_{\mathrm{S}} = \mathcal{K}_{\mathrm{S}}(\boldsymbol{q}) = K_{\mathrm{S}}q_{\perp}^4 + K'_{\mathrm{S}}q_{\parallel}^4 + K''_{\mathrm{S}}q_{\parallel}^2 q_{\perp}^2\,, \\ &\mathcal{K}_{\mathrm{N}j} = \mathcal{K}_{\mathrm{N}j}(\boldsymbol{q}) = K_{jj}q_{\perp}^2 + K_{33}q_{\parallel}^2\,, \quad j = 1, 2\,.\end{aligned} \tag{6.10}$$

(cf Brochard's study [144] where is was assumed that $K_{\mathrm{S}} \equiv 0$.)

The typical values of the parameters of smectic A liquid crystals in the region remote from the transition point $T = T_{\mathrm{NA}}$ are $B \sim 2 \times 10^7\ \mathrm{g\,cm^{-2}\,s^{-1}}$, $K_{11} \sim 10^{-6}$ dyn [9, 10], and $K_{33} \sim 10^2 K_{11}$ [145, 146]. For estimates, one may assume that $D \sim B$, $K_{22} \sim K_{33}$, and $K'_{\mathrm{S}} \sim K''_{\mathrm{S}} \sim K_{33}$. In the usual situation in smectics A with the optical values of the wave vectors $q \sim 10^5\ \mathrm{cm^{-1}}$, the contributions to the elastic energy associated with the changes in the interlayer distance (the coefficient B) and with the deviations of the director from the normal to the layer (the coefficient D) are much greater than the energy associated with the deviation of the field of the directors from the homogeneous state $\boldsymbol{n}^0$ (the coefficients K_{11}, K_{22}, and K_{33}) and with the distortion of the form of the layers (the coefficients K_{S}, K'_{S}, and K''_{S}). This indicates the validity of the inequalities

$$B,\ D \gg \mathcal{K}_{\mathrm{N}j}(\boldsymbol{q})\,, \tag{6.11}$$

$$Bq_{\parallel}^2 + Dq_{\perp}^2 \gg \mathcal{K}_{\mathrm{S}}(\boldsymbol{q})\,. \tag{6.12}$$

As a result, in terms of the lowest orders in B and D, we have

$$\begin{aligned}&\langle\delta n_1^2\rangle_{\boldsymbol{q}} = \beta(B^{-1}q_{\perp}^2 q_{\parallel}^{-2} + D^{-1})\,, \quad \langle\delta n_2^2\rangle_{\boldsymbol{q}} = \beta D^{-1}\,, \\ &\langle u^2\rangle_{\boldsymbol{q}} = \beta B^{-1}q_{\parallel}^{-2}\,, \quad \langle u\delta n_1^{*}\rangle_{\boldsymbol{q}} = \mathrm{i}\beta B^{-1}q_{\perp}q_{\parallel}^{-2}\,.\end{aligned} \tag{6.13}$$

For $q_{\parallel} \to 0$, Eqns (6.13) (except the $\langle\delta n_2^2\rangle_{\boldsymbol{q}}$ equation) cease to apply. In this case, it is necessary to take into account the correction terms $K_{\mathrm{S}}q_{\perp}^4$ and $K_{11}q_{\perp}^2$ in Eqns (6.9) and (6.10). For $q_{\parallel} \to 0$, we have

$$\begin{aligned}&\langle\delta n_1^2\rangle_{\boldsymbol{q}} = \beta(Bq_{\parallel}^2 q_{\perp}^{-2} + K_1 q_{\perp}^2)^{-1}\,, \\ &\langle u^2\rangle_{\boldsymbol{q}} = \beta(Bq_{\parallel}^2 + K_1 q_{\perp}^4)^{-1}\,, \\ &\langle u\delta n_1^{*}\rangle_{\boldsymbol{q}} = \beta(Bq_{\parallel}^2 + K_1 q_{\perp}^4)^{-1}\,.\end{aligned} \tag{6.14}$$

The first two equations (6.14) are frequently used in a simplified description of the displacement and director fluctuations in smectics A on the basis of expressions of the type (6.5) and (6.6) [9, 10]. The only difference between Eqn (6.14) and the results in the literature [9, 144] consists in the fact that K_1 is determined by Eqn (6.7) and is not fully identical with the Frank modulus K_{11}.

The previous discussion referred to an unbounded smectic A. The fluctuation-induced displacements of the layers u in the case of a thin smectic film have been analysed in a study [177], where a numerical algorithm for the calculation of the correlation function was proposed. An analytical expression, obtained by a method analogous to that described in Section 3.4, has been published [178]. The influence of the boundary conditions, in particular of the surface tension, on the fluctuations and scattering was studied in the above investigation, the case of different boundary conditions on the surfaces of the film being examined.

We shall now discuss the region of the $T = T_{\mathrm{NA}}$ phase transition. Although a considerable number of experimental and theoretical studies have been devoted to the N → A phase transition, its nature has still not been ultimately elucidated. Various theoretical models for this transition have been analysed in Lubensky's review [147]. The presence of two correlation radii of the fluctuations of the ordered parameter η is characteristic of smectic A liquid crystals:

$$r_{\mathrm{c}\|} = (L_{\|}/A)^{1/2}, \quad r_{\mathrm{c}\perp} = (L_{\perp}/A)^{1/2}. \tag{6.15}$$

Their behaviour as a function of temperature in the vicinity of the transition point $T = T_{\mathrm{NA}}$ is described by the power laws

$$r_{\mathrm{c}\|} \sim \tau^{-\nu_{\|}}, \quad r_{\mathrm{c}\perp} \sim \tau^{-\nu_{\perp}}, \tag{6.16}$$

where $\tau = |T - T_{\mathrm{NA}}|/T_{\mathrm{NA}}$. The behaviour of the coefficients B and D as a function of temperature is also described by power laws:

$$B \sim \tau^{\varphi}, \quad D \sim \tau^{\varphi'}. \tag{6.17}$$

In addition, singular contributions to the Frank modulus arise in the N-phase as a result of the fluctuation corrections arising from the smectic fluctuations η:

$$\delta K_{22} \sim \tau^{-\rho_2}, \quad \delta K_{33} \sim \tau^{-\rho_3}. \tag{6.18}$$

The existing theoretical models predict different values of the indices. In the mean field model [Eqn (6.1)], $\nu_{\|} = \nu_{\perp} = 0.5$, $\varphi = \varphi' = 1.0$, and $\rho_2 = \rho_3 = 0$. The scaling relations yield

$$\varphi = \rho_2 = 2\nu_{\perp} - \nu_{\|}, \quad \varphi' = \rho_3 = \nu_{\|}, \quad 2 - \alpha = \nu_{\|} + 2\nu_{\perp}, \tag{6.19}$$

where α is the heat capacity index. If the N → A transition belongs to the same class of universality as the three-dimensional inverse XY model [148] or an isotropic type II conductor [20], then $\nu_{\|} = \nu_{\perp} = 0.67$. In the case of anisotropic scaling [149], $\nu_{\|} = 2\nu_{\perp}$. The numerical values of the indices $\nu_{\|}$ and $\nu_{\perp}$ are not then predicted. There is also a possibility of versions of the anisotropic scaling model with the nonuniversal relation $\nu_{\|} > \nu_{\perp}$.

Experiments (see below) yield φ, $\varphi' > 0$ and hence near the $T = T_{\mathrm{NA}}$ transition point we have $B, D \to 0$. In this case, inequality (6.11) becomes invalid. If inequality (6.12) continues to hold [as happens, for example, in the mean field theory, where according to Eqn (6.4) the coefficients B, D, K_{S}, K'_{S}, and K''_{S} exhibit the same temperature dependence], we obtain

$$A_1(\boldsymbol{q}) = BDq_{\|}^2(Bq_{\|}^2 + Dq_{\perp}^2)^{-1}, \tag{6.20}$$

and the temperature dependence of $A_1(\boldsymbol{q})$ is determined by the behaviour of the coefficients B and D. In particular,

$$\begin{aligned} A_1(\boldsymbol{q}) &= Bq_{\|}^2 q_{\perp}^{-2}, \quad \text{if } q_{\|} \ll q_{\perp}, \\ &= D, \qquad\quad \text{if } q_{\|} \gg q_{\perp}. \end{aligned} \tag{6.21}$$

Otherwise the temperature dependence of A_1 is determined by the entire set of coefficients B, D, K_{S}, K'_{S}, and K''_{S}.

The correlation function for the relative permittivity fluctuations, determined by the director fluctuations, can be found, as in the case of a nematic, from Eqn (3.21), in which it is sufficient to put $\xi_j = \varepsilon_{\mathrm{a}}\delta n_j$. It follows from the previous discussion that, under conditions remote from the $T = T_{\mathrm{NA}}$ transition point, both modes of the director fluctuations, $\langle \delta n_1^2 \rangle_{\boldsymbol{q}}$ and $\langle \delta n_2^2 \rangle_{\boldsymbol{q}}$, are of the same order of magnitude, provided that $q_{\|} \sim q_{\perp}$. However, when $q_{\|} \to 0$, the correlator $\langle \delta n_2^2 \rangle_{\boldsymbol{q}}$ hardly changes, while the correlator $\langle \delta n_1^2 \rangle_{\boldsymbol{q}}$ increases sharply. In the vicinity of $T = T_{\mathrm{NA}}$ for $q_{\|} = 0$, both correlators increase in a critical manner. If $q_{\|} \to 0$ under these conditions, then the behaviour becomes of the Goldstone type: $\langle \delta n_1^2 \rangle_{\boldsymbol{q}} \sim q_{\perp}^{-2}$.

6.2 Light scattering by director fluctuations in smectics A

The intensity of light scattering in smectics, which constitute an optically anisotropic medium is determined by Eqn (3.36). Convolution of the correlation function (3.21) with the polarisation vectors is of the form

$$e_{\nu}^{(i)} e_{\mu}^{(i)} G_{\nu\alpha\mu\beta} e_{\alpha}^{(s)} e_{\beta}^{(s)} = \sum_{j=1,2} \langle \delta n_j^2 \rangle_{\boldsymbol{q}} Q_j(\boldsymbol{e}^{(i)}, \boldsymbol{e}^{(s)}, \boldsymbol{q}), \tag{6.22}$$

where

$$Q_j(\boldsymbol{e}^{(i)}, \boldsymbol{e}^{(s)}, \boldsymbol{q}) = \left[(\boldsymbol{e}^{(i)} \cdot \boldsymbol{e}_j)(\boldsymbol{e}^{(s)} \cdot \boldsymbol{n}^0) + (\boldsymbol{e}^{(s)} \cdot \boldsymbol{e}_j)(\boldsymbol{e}^{(i)} \cdot \boldsymbol{n}^0) \right]^2. \tag{6.23}$$

As already mentioned in Section 6.1, under conditions remote from the phase transition point the mode $\langle \delta n_1^2 \rangle_{\boldsymbol{q}}$ increases sharply when $q_{\|} \to 0$:

$$\langle \delta n_1^2 \rangle_{\boldsymbol{q}} = \frac{k_{\mathrm{B}} T q_{\perp}^2}{Bq_{\|}^2 + K_1 q_{\perp}^4} \approx \frac{\pi k_{\mathrm{B}} T}{(K_1 B)^{1/2}} \delta(q_{\|}). \tag{6.24}$$

In this region, the mode $\langle \delta n_2^2 \rangle_{\boldsymbol{q}} \approx k_{\mathrm{B}} T/D$ may be neglected. Eqn (6.24) implies that during light scattering in a smectic A an interesting effect should be observed: virtually the entire scattered light is concentrated in the region of the $\boldsymbol{k}_{(s)}$ directions, for which $q_{\|} = 0$, where $\boldsymbol{q} = \boldsymbol{k}^{(s)} - \boldsymbol{k}^{(i)}$, i.e. $\boldsymbol{k}_{\|}^{(s)} = \boldsymbol{k}_{\|}^{(i)}$. The latter condition has the geometrical implication that $\boldsymbol{k}^{(s)}$ should be located on the surface of one of two coaxial circular cones with the axis $\boldsymbol{n}^0$ $(s = 1, 2)$. This effect was first predicted theoretically by de Gennes [150]. It follows from the analysis of the angular factors Q_j in Eqn (6.23) that only the depolarisation contributions to scattering of the (0) → (e) or (e) → (0) types are nonzero for $q_{\|} = 0$.

The theoretical prediction reduces to the fact that, when observations are made in a plane perpendicular to $\boldsymbol{n}^0$, a relatively bright narrow ring of scattered light with the type of polarisation opposite to that of the incident light should be observed. The distribution of intensity along the ring is of the form

$$I_{(s)}^{(i)} \sim \sin^2(\varphi) f_{(s)}^{(i)}(\varphi), \tag{6.25}$$

where the azimuthal angle $0 \leqslant \varphi \leqslant 2$ is reckoned from the plane $\{\boldsymbol{n}^0, \boldsymbol{k}^{(i)}\}$ and $f_{(s)}^{(i)}(\varphi)$ is a smooth function which does not become zero. For $\varphi = 0°$ or $90°$, the intensity is $I_{(s)}^{(i)}(\varphi) = 0$ and we have the so-called sickle-shaped distribution [9, 150] of the intensity along the ring.

An experimental test of this effect has been carried out [151 – 153]. In the first studies [151, 152], scattering by static inhomogeneities associated with the displacement of the layers caused by the imperfection of the orienting substrate, was observed. The angular distribution pattern of the scattering should then be the same as in scattering by the thermal fluctuations of the layer displacements, i.e. it should be described by Eqns (6.22) and (6.24). In particular, a study was made [152] of the scattering of a laser beam with $\lambda = 6328$ Å in a homeotropically oriented specimen of a BBAA (*p*-butoxybenzylidene-*N*-anilinoacetophenone) smectic A liquid crystal at $T = 89$ °C. The thickness of the specimen varied from 50 to 500 μm. The substrate was polished to within $\lambda/10$. The angle between the direction of the incident ray and the director was varied in the range 0°–70°. The (0) → (e) and (e) → (0) types of scattering were observed. Fig. 27 presents a photograph of the sickle-shaped scattering pattern. In a subsequent study [153], the sickle-shaped distribution of the intensity of scattering by thermal fluctuations was observed by correlation spectroscopic methods in *N*-(*p*-cyanobenzylidene)-*p*-octyloxyaniline smectic A liquid crystals with a thickness d from 200 to 800 μm and a substrate polished to within $\lambda/30$ at $T = 75$ °C.

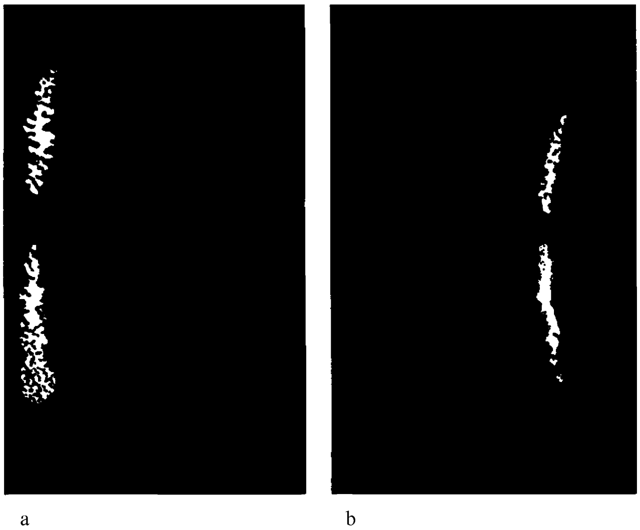

Figure 27. The sickle-shaped distribution of the scattered light in a BBAA smectic liquid crystal: (a) (e) → (0) scattering; (b) (0) → (e) scattering [152].

In light scattering by a thin film of a smectic liquid crystal, the problem arises of taking into account the boundary conditions not only in the calculation of fluctuations but also for the electromagnetic field. Multiple reflection and refraction of the incident and scattered rays at the boundaries may prove significant in such a specimen. Green's function for the electromagnetic field, taking into account also reflections at the boundary with an optically uniaxial medium, has been obtained in a study [178] where the intensity of the light scattered by a smectic film in the case of normal incidence was also calculated.

6.3 Scattering in the vicinity of the N – A phase transition

At the present time, the majority of experiments on light scattering in smectic A liquid crystals are devoted to the investigation of the vicinity of the $T = T_{\mathrm{NA}}$ phase transition point in order to obtain information about the indices φ and φ' in Eqns (6.16)–(6.18). For this purpose, use is usually made of the experimental geometries permitting the separate observation of scattering by the δn_{1q} and δn_{2q} modes. These isolated geometries are determined by the condition that one of the two geometrical factors Q_j in Eqn (6.22) becomes zero. Complete analysis of such geometries, similar to that specified by Eqns (3.39) for nematics has not been carried out yet. We may note that, as in nematics, the (0) → (0) type scattering intensity is zero. Special cases of the following geometries have been used:

G1: (0) → (e) scattering; the vectors $\boldsymbol{k}^{(i)}$, $\boldsymbol{k}^{(s)}$, and $\boldsymbol{n}^0$ belong to one plane (in this geometry, $Q_1 = 0$).

G2: (0) → (e) scattering; the projections of the vectors $\boldsymbol{k}^{(i)}$ and $\boldsymbol{k}^{(s)}$ onto the unit vector perpendicular to $\boldsymbol{n}^0$ and located in the plane $\{\boldsymbol{n}^0, \boldsymbol{k}^{(i)}\}$ are equal ($Q_2 = 0$).

G3: (e) → (0) scattering; the projections of the vectors $\boldsymbol{k}^{(i)}$ and $\boldsymbol{k}^{(s)}$ onto the unit vector perpendicular to $\boldsymbol{n}^0$ and located in the plane $\{n^0, k^{(s)}\}$ are equal ($Q_2 = 0$).

The G1 geometry was applied, for example by Fromm [146], Huang and Ho [154], and Lewis et al. [155], the G2 geometry was used by Fromm [146] and Lewis et al. [155], and the G3 geometry was also employed by Lewis et al. [155]. [The (e) → (0) type geometries with $Q_1 = 0$ and also the (e) → (e) type geometries have not been used in the experiments known to us.] Furthermore, a 'degeneracy geometry', in which $\boldsymbol{q}_\perp = 0(\boldsymbol{q}||\boldsymbol{n}^0)$, has been used [145, 146]. In this case, the formal definition of the vectors $\boldsymbol{e}_j$ and of the modes δn_j in Eqn (3.3) loses its significance, but it follows from Eqns (6.9) and (6.10) that, for $\boldsymbol{q}_\perp \to \boldsymbol{0}$, we have

$$\langle\delta n_1^2\rangle_q = \langle\delta n_2^2\rangle_q = k_{\mathrm{B}}T\left(D + K_{33}q_\parallel^2\right)^{-1}. \qquad (6.26)$$

When Eqn (6.26) is substituted in Eqn (3.21) taking into account the identity $e_{1\alpha}e_{1\beta} + e_{2\alpha}e_{2\beta} = \delta_{\alpha\beta} - n_\alpha^0 n_\beta^0$, the degeneracy is eliminated. In this geometry, the scattering intensity is determined by the parameters D and K_{33}.

Before discussing the results of experiments on light scattering in smectics A in the vicinity of $T = T_{\mathrm{NA}}$, we may note that, according to Eqns (6.18) and (6.19), information about the critical indices is contained also in the behaviour of the Frank moduli K_{22} and K_{33} as a function of temperature at $T \to T_{\mathrm{NA}}$ on the side of the N-phase. In numerous investigations, the scattering intensities have been measured in the vicinity of $T = T_{\mathrm{NA}}$ in both A- and N-phases. Therefore here we shall consider simultaneously the scattering at $T \to T_{\mathrm{NA}}$ in both phases. We may note here the Jäning – Brochard cross-over formula [156], taking into account the interaction of the fluctuations of the smectic order parameter ψ and the director $\boldsymbol{n}$, which is frequently used in the interpretation of experiments on the temperature variation of the light scattered by the δn_2 mode:

$$\langle\delta n_2^2\rangle_q \sim \Bigg\{K_{22}^0 q_\perp^2 + K_{33}^0 q_\parallel^2 + \frac{k_{\mathrm{B}}Tq_0^2 X}{4\pi r_{\mathrm{c}\parallel}}\left[\left(1 + X^{-2}\right)\tan^{-1}X - X^{-1}\right]\Bigg\}^{-1}, \qquad (6.27)$$

where $X = \left[(r_{\mathrm{c}\parallel}q_\parallel)^2 + (r_{\mathrm{c}\perp}q_\perp)^2\right]/2$ and K_{22}^0 and K_{33}^0 are the components of the Frank moduli which are regular with respect to temperature.

In the discussion of experiments on light scattering in smectics and nematics, the following terminology, associated with the names of the types of distortions corresponding to the Frank moduli has been adopted: K_{11} (splay), K_{22} (twist), and K_{33} (bend). δn_1 is a bend-splay mode and δn_2 is a bend-twist mode. In the case where $q_\parallel = 0$, the δn_1 and δn_2 modes are referred to respectively as the splay and twist modes and, when $q_\perp = 0$, both modes are bend modes according to Eqn (6.26).

The thickness of smectic specimens usually employed is of the order of 25–250 μm. The following data provide an idea about the level of current experiments on light scattering in smectics A. In interpreting the experimental results, account is taken of the discrete nature of the Fourier spectrum $q_\parallel = \pi l/d$ $(l = \pm1, \pm2, \ldots)$ in a finite system [153, 157]. In order to check the influence of the size of the specimen, measurements have been frequently performed for two

Table 1. The indices $\rho_2(K_{22})$, $\rho_3(K_{33})$, $\varphi(B)$, and $\varphi'(D)$ obtained for smectic A liquid crystals with different widths of the nematic phase (the table from Lewis et al. [155] and the data of Fromm [146],[a] Huang and Ho [154],[b] Vithana et al. [157],[c] and Solomon and Litster [160][d] have been used).

SLC	ρ_2	φ	ρ_3	φ'	T_{NA}/T_{NI}
CBBOA	0.47 ± 0.07	0.33 ± 0.05	0.65 ± 0.05	0.50 ± 0.02	0.94
	—	—	0.74 ± 0.04	—	
8OCB	0.35 ± 0.05	0.33 ± 0.04	0.67 ± 0.05	0.50 ± 0.05	0.96
	0.47 ± 0.11	—	0.75 ± 0.04	—	
	—	0.26 ± 0.08	0.66 ± 0.04	—	
	0.67 ± 0.06 [a]	—	0.71 ± 0.04 [a]	0.52 ± 0.04 [a]	
8CB	0.34 ± 0.13	0.26 ± 0.06	0.72 ± 0.05	—	0.977
	—	—	0.62 ± 0.03	—	
	0.53 [d]		0.72 [d]		
9CB	0.45 [c]		0.60 [c]		0.993 [c]
40.8	—	0.32 ± 0.02	0.69 ± 0.03	0.54 ± 0.04	0.96
	—	0.44 ± 0.04	—	—	
$\bar{8}$S5	0.37 ± 0.06	0.44 ± 0.02	0.68 ± 0.03	—	0.94
	0.57 ± 0.13	—	0.89 ± 0.05	—	
	—	—	0.82 ± 0.02 [b]	—	
$\bar{6}$O9	0.46 ± 0.03	0.44 ± 0.05	0.66 ± 0.02	—	0.93
	0.48 ± 0.03	—	—	—	
DHAOB	0.66 ± 0.03 [c]	—	—	—	0.885

specimens with different thicknesses d: 25 and 50 μm in the study of Huang and Ho [154], 125 and 250 μm in the study of Lewis et al. [155], and 58.4 and 216 μm in the study of Vithana et al. [157]. The purity of the specimens reaches 99.99% and above [157]. The accuracy of thermal stabilisation exceeds 10^{-4} K [155, 157]. Account was taken of the drift of the transition temperature T_{NA} as a function of time which reached 10^{-2} K h^{-1} (in the study of von Kanell and Litster [145], while in that of Vithana et al. it was 0.3 mK day^{-1} for $d = 58.4$ μm and 0.4 mK day^{-1} for $d = 216$ μm) and the corrections were applied for it.

The incident laser beam is centred on the symmetry point of the temperature gradient of the cell in order to reduce to a minimum the nonuniformity of the temperature across the beam (the nonuniformity in the study of Vithana et al. [157] was 0.03 – 0.04 mK). The heating of the specimen by the laser beam is monitored [155, 157]. Correlation spectroscopy is the most frequently used experimental technique.

Despite such high sophistication of the experiments, an appreciable scatter of the indices obtained for different smectic A liquid crystals is characteristic of the $N \rightarrow A$ phase transition. A clear idea about this is provided by Table 1. It shows that the inequalities $\varphi' > \varphi$ and $\rho_3 > \rho_2$ hold for the experimentally measured indices. The quantities φ and φ' are very different from the values obtained by analogy with superconductors: $\varphi = \varphi' = 0.67$. Generally speaking, the scaling relations (6.19) do not hold either.

The nonuniversality of the indices is most strikingly manifested in experiments on mixtures of two smectic liquid crystals with a variable concentration. In particular, Huang and Ho [154] found that ρ_3 varied from 0.82 ± 0.02 to 1.00 ± 0.03 in the $\bar{7}\text{S5}_{1-x}\bar{8}\text{S5}_x$ mixture for x varying from 1 to 0.638) and from 0.8 ± 0.04 to 0.88 ± 0.01 in the $\bar{\text{S}}\text{5}_{1-x}\bar{8}\text{OCB}_x$ mixture (for x varying from 0.0473 to 0.0232), while Fromm [146] found that the index ρ_3 varied from 0.71 ± 0.04 to 0.78 ± 0.04 and the index φ' varied from 0.52 ± 0.04 to 0.56 ± 0.04 in the $\text{6OCB}_x\text{8OCB}_{1-x}$ mixture for $y = x/(1-x)$ varying from 0 to 0.4046.

Fig. 28 illustrates the temperature dependence of the scattering intensity for the $\boldsymbol{q}_\perp = \mathbf{0}$ geometry [i.e. according to Eqn (6.26), the temperature variation of the quantity $(D + K_{33}q_\parallel^2)^{-1}$] [146]. Under these conditions, above T_c we have the coefficient $D = 0$ and the scattering intensity in

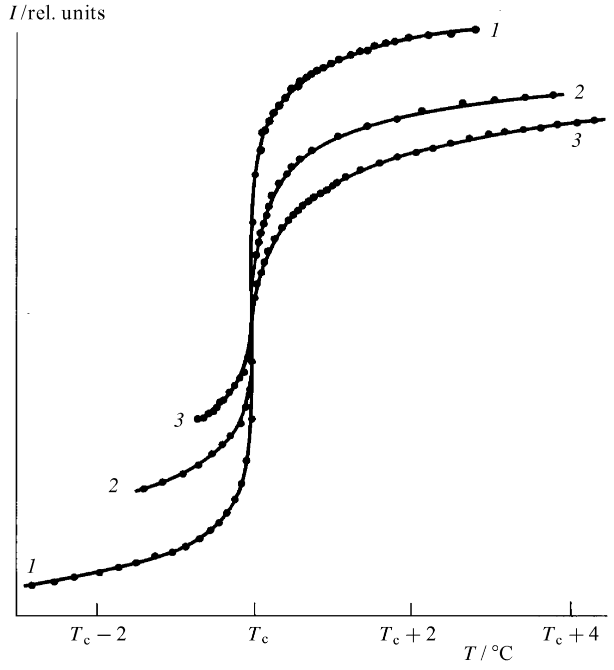

Figure 28. Temperature dependence of the intensity I of the scattering by the bend mode in the vicinity of the $N \leftrightarrow A$ transition point for the $\text{6OCB}_x\text{8OCB}_{1-x}$ mixture for different values of $y = x/(1-x)$: (1) $y = 0.2$; (2) $y = 0.3327$; (3) $y = 0.4046$ [146].

Fig. 28 determines directly the temperature variation of K_{33}, i.e. the index ρ_3. A similar situation [145] occurs also for the pure smectic liquid crystal 40.8. Evidently the value of K_{33} at $T = T_c$ exceeds the values of this quantity characteristic of the bulk of the N-phase by approximately two orders of magnitude. The comparative roles of D and $K_{33}q_{\parallel}^2$ in the denominator of Eqn (6.26) can be inferred from Fig. 28 — the role of the term $K_{33}q_{\parallel}^2$ in the A-phase becomes significant only in the region $|T - T_c| \leqslant 10^{-2}$ K. Unfortunately, such direct measurement of the index ρ_2 from the temperature variation of the mode $\langle \delta n_2^2 \rangle_q$ in the N-phase at $T \to T_{\mathrm{NA}}$ is made difficult by the fact that the fluctuation correction δK_{22} in Eqn (6.18) is approximately 50 times smaller than δK_{33} and it is difficult to isolate it against the background of the regular contribution to K_{22}. This difficulty has been overcome [146] by virtue of the fact that the mixture used in the above study has the phase diagram illustrated in Fig. 29. The presence of the reentrant N-phase at low temperatures made it possible to determine the regular components of K_{22} and K_{33} with a sufficiently high accuracy by interpolation between the two N-phases (Fig. 30). As a result, the index ρ_2 varied from 0.67 ± 0.05 to 0.62 ± 0.06 as the concentration x varied from 0 to 0.4046, while the index φ' varied from 0.60 ± 0.05 to 0.55 ± 0.05 as x varied from 0.3327 to 0.4243.

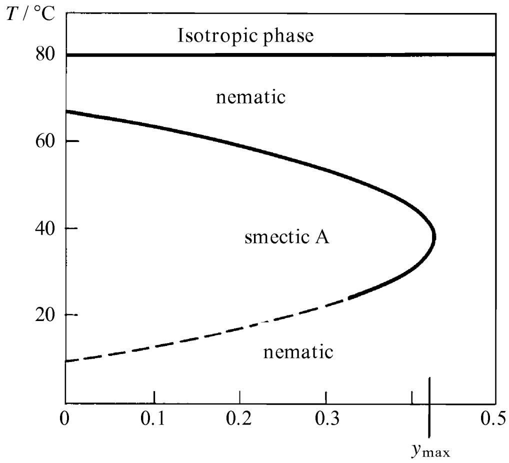

Figure 29. Phase diagram for the 6OCB$_x$8OCB$_{1-x}$ mixture at variable temperatures T; $y = x/(1-x)$ [146].

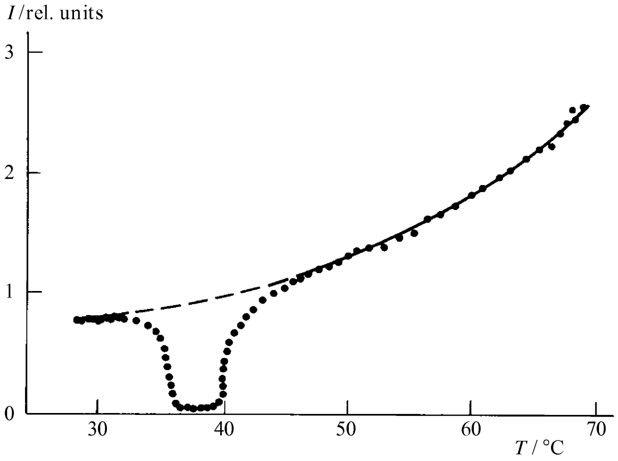

Figure 30. Temperature variation of the intensity I of the scattered light for the twist mode in the presence of a reentrant nematic phase. Dashed line — interpolation of the intensity between two nematic phases; $y = 0.4243$ [146].

The modulus K_1 does not manifest a pronounced temperature variation in the N → A transition. The result obtained by von Kanell and Litster [145], who investigated a monolayer smectic (the majority of smectics are of the bilayer type, i.e. the period of their structure is approximately equal to two molecular lengths) is an exception.

The absence of the universality of the exponents shows apparently that only certain effective indices are actually measured. The view that these exponents describe the cross-over behaviour between critical and tricritical behaviour is in our view fairly realistic [146, 155, 157]. In order to diminish the influence of the tricritical behaviour, it is necessary to carry out experiments on specimens with a wide range of existence of the nematic phase. Such an experiment has been carried out [157] on a DHAOB (dihexylazoxybenzene) specimen for which $\tau_{\mathrm{IA}} = (T_{\mathrm{IN}} - T_{\mathrm{NA}})/T_{\mathrm{NA}} = 0.115$, where T_{IN} is the N → I transition temperature. An important feature is that measurements of the magntic anisotropy [158] did not reveal in this liquid crystal any kind of anomalies of the nematic order parameter S_0 in the N → A transition. The correlation time function of the number of photons was measured. Fig. 31 presents a plot of the scattering intensity as a function of temperature. Interpretation of the experimental data yielded $\rho_2 = 0.66 \pm 0.03$ over a range corresponding to four decades of the temperature $\tau = (T - T_{\mathrm{NA}})/T_{\mathrm{NA}}$, in agreement with the helium analogy. The values of ρ_2 obtained are greater than those found for specimens with a narrower nematic phase. This is illustrated in Fig. 32, where the index ρ_2 is plotted as a function of the width of the nematic zone. The authors' principal conclusion [157] is as follows: all the previous experimental studies were performed under conditions where the interaction of the nematic (S) and smectic ($|\psi|$) order parameters is significant. For this reason, the measurements in these investigations yielded effective exponents associated with the tricritical–critical cross-over.

We shall discuss briefly the pretransitional effect associated with the presence of the smectic C phase. Above the A–C transition, in the region remote from the N–A–C tricritical point, the experimental temperature dependence of

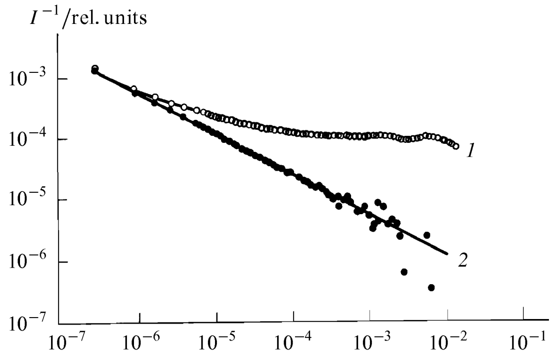

Figure 31. Temperature variation of the reciprocal of the scattering intensity in a specimen of the DHAOB smectic 216 μm thick ($T_{\mathrm{NA}} = 289.7966$ K) on the logarithmic scale. The data were interpreted in terms of the formula $I^{-1} = At^{-\rho_2} + B$, where B is a constant component: (1) experimental values; (2) result of the exclusion of B [157].

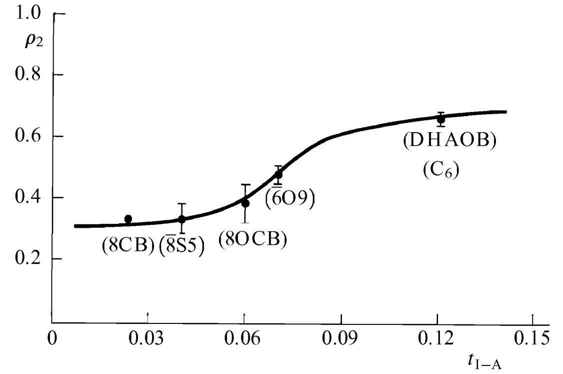

Figure 32. Dependence of the index ρ_2 on the thickness of the nematic zone $t_{\mathrm{I-A}} = (T_{\mathrm{NI}} - T_{\mathrm{NA}})/T_{\mathrm{NA}}$ for different liquid crystals [157].

the scattering intensity agrees with the prediction of the mean field model: $D \sim (T - T_{\mathrm{AC}})^{\gamma}$ with $\gamma = 1.0$ (Fig. 33) [159]. Above the N–C transition, the experimental behaviour of I_{sc} agrees [154] with the predictions of the Chen–Lubensky model [19] (Fig. 34). In particular, according to estimates the absolute value of δK_{11} was $\sim$2% of δK_{33} under these conditions.

The most interesting effects are observed at the N–A–C tricritical point. The scattering intensity in a series of nCB homologues has been investigated [160]. With increase in n, the width of the N-phase diminishes and the system approaches the tricritical point. By selecting appropriate mixtures of different homologues, it was possible to obtain effectively fractional values of n. According to the authors' estimate [160], the tricritical point corresponded to $n = 9.1$. Eqn (6.27) was used in interpreting the experimental data. A decrease in the indices ρ_2 and ρ_3 was observed — from $\rho_3 = 0.72$ and $\rho'_2 = 0.53$ for $n = 8$ to $\rho_3 = 0.50$ and $\rho'_2 = 0.34$ for $n = 9.07$. The behaviour of scattering by bend, bend-twist, and splay modes of fluctuations has been investigated for the $\overline{7}\mathrm{S5}_{1-x}\overline{8}\mathrm{S5}_x$ and $\overline{7}\mathrm{S5}_x\mathrm{8OCB}_x$ mixtures in which it was possible to approach the concentration of N–A–C point (Fig. 35). It was found that, in the vicinity of this point, the integral intensity of the light scattering by the bend and bend-twist modes has an anomalous minimum as a function of temperature. For the splay mode, the behaviour of the intensity is normal (Fig. 36) [154]. The kinetics of the fluctuations have been investigated [161] for the same mixtures by correlation spectroscopic methods. No anomalies were observed in the kinetics of the splay mode. On the other hand, it was found for the bend mode that the time correlation function requires two relaxation times for its description. The amplitude of the unusual 'fast' contribution had an unusual minimum 0.5 °C before the transition point. The authors [161] attribute the presence of this 'fast' contribution to scattering by smectic-like tilt-fluctuation formations.

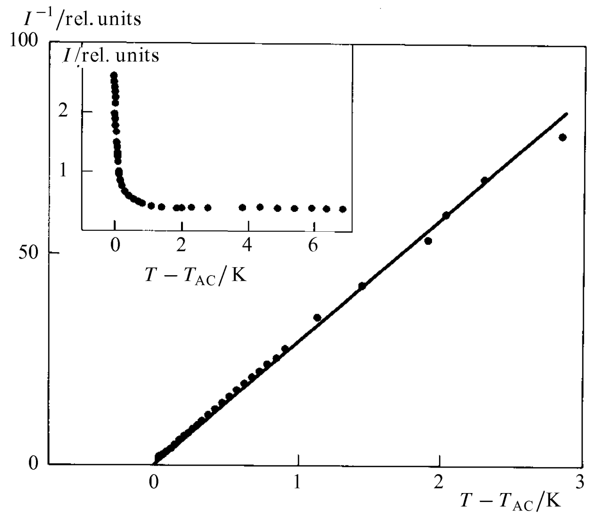

Figure 33. Temperature variation of the intensity I of the scattering by the bend mode and of its reciprocal above the A → C transition in a $\overline{8}$S5 liquid crystal; continuous line — linear fit [154].

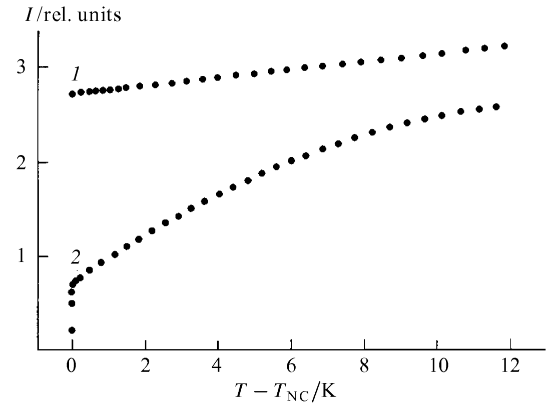

Figure 34. Temperature variation of the intensity I of scattering by the bend and splay modes in a $\overline{7}$S5 liquid crystal above the N ↔ C transition: (*1*) splay mode; (*2*) bend mode [154].

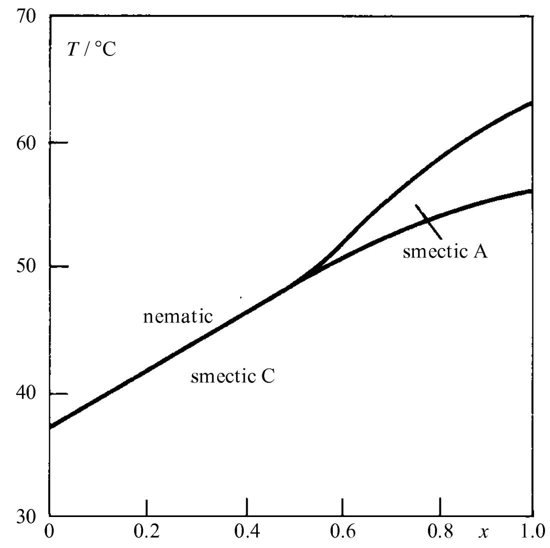

Figure 35. Phase diagram for the $\overline{7}\mathrm{S5}_{1-x}\overline{8}\mathrm{S5}_x$ mixture [154].

A smectic liquid crystal is of interest primarily as a layered one-dimensionally periodic system with strongly developed fluctuations of the layer displacements and the Landau–Peierls instability. However, fluctuations of the director and not those of the displacements are most strongly manifested in light scattering. The former fluctuations can be of two types: those induced by the displacements of the layers and spontaneous fluctuations (deviations of the director from the normal to the layer). The induced director fluctuations are

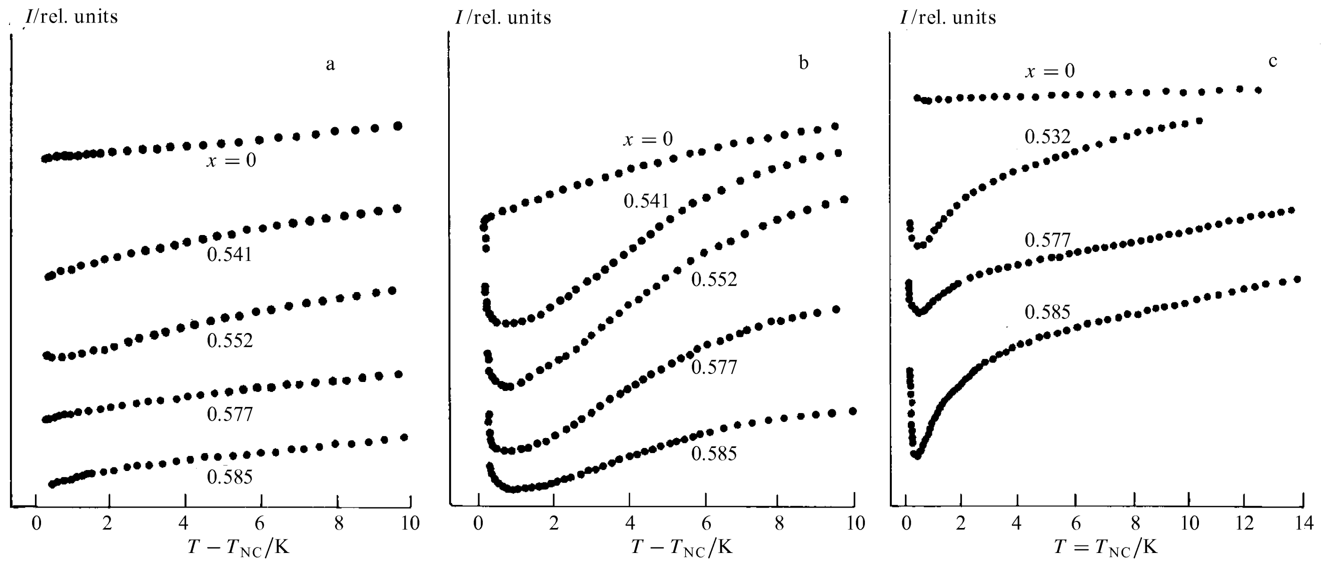

Figure 36. Temperature variation of the light scattering intensity I in the $\bar{7}S5_{1-x}\bar{8}S5_x$ mixture at different concentrations x: (a) splay mode; (b) bend mode; (c) bend-twist mode [154].

the most intense. The indicatrix of the light scattering associated with these fluctuations has a strikingly pronounced sickle shape in the region remote from the point of transition to the nematic phase. Near the A–N critical point, both modes of director fluctuations become comparable in magnitude.

Much interest has been shown in the behaviour of smectic A liquid crystals near the N–A transition to the nematic liquid crystal. Numerous careful studies on the scattering of light and X-rays and studies involving the measurement of the heat capacity have been carried out in this field. As a result, the absence of universality in the values of the critical exponents for different smectics A can be regarded as firmly established.

We shall list certain problems which, in our view, need to be tackled in the case of smectic liquid crystals. In the first place this is allowance for the interaction of the tensor nematic order parameter S with the smectic density wave ψ in the description of fluctuations and also allowance for the finiteness of the system and the Landau–Peierls instability in the interpretation of experiments in the vicinity of the A–N transition point. In smectic A liquid crystals, it is easier than in nematics to isolate experimentally the scattering by biaxial and longitudinal fluctuations against the background of the weaker, than in nematics, scattering by director fluctuations. The use of the light scattering method for thin layers of a smectic as a procedure for the investigation of surface phenomena and, in particular, as a method for the determination of the surface tension of smectics appears promising.

Successive calculation of the contribution of displacement fluctuations to density and biaxial and longitudinal fluctuations on the basis of the principle of conservation of the modulus and the observation of this contribution in light scattering experiments are also of interest.

7. Conclusions

From the standpoint of the study of light scattering in liquid crystals, the latter proved to be unique objects. In order to obtain results for liquid crystals permitting a quantitative comparison with experiment, it was necessary to take into account a whole series of additional factors which have been almost always neglected in the scattering theory. These are, in the first place, optical anisotropy (both uniaxial and biaxial), optical activity, the presence of a regular periodic structure, and the influence of the finite nature of the specimen. On the other hand, fluctuations in liquid crystals are frequently anomalously large, resembling critical phenomena in this respect but with the difference that the parameter kr_c for liquid crystals can reach 10^4 and above, which is much greater than the value experimentally attainable in the critical region.

Although the light scattering method has proved useful in many instances as an effective procedure for gaining information about the system, it is still used insufficiently widely for liquid crystals. Apparently one of the significant reasons for this is the existence of numerous complicating factors in the light scattering process. In the present review, we have endeavoured to show that these complexities can be overcome both by the appropriate modification of the theory and by using in certain cases nontraditional experimental methods (such as measurements of the scattering intensity under the conditions of circular polarisations or the determination of the extinction coefficient from the degree of coherence of the transmitted ray.

The selection of the subject was associated primarily with the choice of those objects where, in the authors view, the problems of fluctuations and light scattering have been developed in greatest detail. The range of the authors' scientific interest naturally played a by no means subsidiary role in such selection.

In particular we were not concerned with scattering in smectics C [181], the scattering in exotic smectics, and also in discotics [182]. The optical properties of ferroelectric liquid crystals, the characteristics of the scattering in the vicinity of instability thresholds of the type of the magnetic or optical

Freédericksz transitions [183], and the influence of all possible distortions of liquid crystals on light scattering were not discussed. Nor were lyotropic and polymeric liquid crystals considered, because the symmetry of the liquid crystal and not the nature of its molecular structure is important for our purposes.

Physical phenomena observed comparatively recently, the study of which is being actively prosecuted and in which fluctuations play an undoubtedly important role — the formation of the twist-grain-boundary (TGB) phases near the nematic – smectic A – smectic C tricritical point — also remained outside the limits of our discussion. A theoretical analysis of the TGB phases has been carried out with the aid of the Landau theory [184] and was based on the analogy with the phase transition to the Abrikosov superconducting eddy lattice [185]. Such a phase has been observed experimentally, for example in the studies of Goodby et al. [175] and Ihn et al. [186]. The influence of the fluctuations of the order parameter in TGB phases has apparently not been studied in detail.

From the standpoint of the general physical picture of liquid crystals, in which the difficulties associated with both liquid phases, involving large fluctuations of various types, and with solid phases, involving complex optical properties, are combined, liquid crystals constitute very convenient objects for the development of both theoretical models and new methods in light scattering. Although the first quantitative measurements of the scattering intensity in liquid crystals were performed more than 50 years ago (see, for example, Chatelain [77]), serious studies on scattering have still not been performed for a whole series of different types of liquid crystals and a wide field for further investigations exists.

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