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# Pretransitional optical rotation in the isotropic phase of cholesteric liquid crystals*

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We discuss the phenomenon of a pretransitional enhancement in the optical rotatory power of the isotropic phase of cholesteric liquid crystals. The effect is viewed theoretically as the modulation of dielectric properties of the isotropic liquid by chiral orientational correlations which destroy local inversion symmetry in a way that produces circular birefringence. De Gennes's theory of short-range order is applied to derive a quantitative result. This is experimentally tested with a system of "chiral-nematic" liquid crystals, achieving good rapport in the pretransition region. The existence of chiral orientational order in the isotropic phase is confirmed.

## I. INTRODUCTION

In an earlier publication,[1] we reported the observation of an enhancement in the optical rotatory power of the isotropic phase of a cholesteric liquid crystal near the isotropic-cholesteric phase transition. This effect was interpreted in the framework of de Gennes's theory of orientational short-range order in the isotropic phase[2] and constitutes the first experimental confirmation for the existence of chiral orientational order in the isotropic liquid. In this picture of the isotropic liquid, fluctuations in the orientation of the long axes of different molecules within a coherence distance are coupled due to chiral interactions in a manner which destroys local inversion symmetry. The resulting structure preserves a local spiral conformation of molecular orientations reminiscent of the long-range helical structure of the ordered phase. Phenomenologically, orientational coupling contributes to spatial variations in the internal local fields, as manifested by a wave-vector dispersion in the polarizability tensor characterizing the dielectric properties of the medium. The chiral aspects of the coupling append a skew Hermitian component to the polarizability, causing the medium to become circularly birefringent and thus optically active. The strength of the optical rotation increases in proportion to the extent of the local skew symmetry, which appears to become divergent as the temperature approaches a quasi-second-order transition temperature, $T^*$, but is curtailed by the occurrence of a first-order transition at a slightly higher temperature, $T_k$. A preliminary discussion of this phenomenon was offered in our earlier letter.[1] We will now present the detailed theoretical formulation and a discussion of the experimental results.

Section II develops the theoretical framework by casting the problem in the language of order-disorder effects. The Landau-de Gennes theory is discussed with emphasis on its chiral aspects. Parallels are drawn to elastic theories of the ordered phase to elucidate the role of the chiral coupling term. Section III formulates the dielectric properties of a system of oriented optically active molecules in the liquid state, incorporating the presence of spatial orientational correlations and molecular optical activity into the local fields. It is shown that the medium is circularly birefringent, and quantitative results are derived using the de Gennes model of short-range order. Section IV discusses the experimental considerations and results, followed by the Conclusion, in which rapport between theory and experiment is established. It is emphasized that the dielectric theory of anisotropic liquids is still an open question. Many assumptions, particularly those involving the form of the local field, remain in doubt and are justifiable only on empirical grounds, some of which are discussed in the text.

## II. PHENOMENOLOGY OF SHORT-RANGE ORDER IN ISOTROPIC PHASE

### A. Order parameter

The state of alignment of a rigid rodlike molecule can be described by the traceless symmetric bilinear form

$$S_{\alpha\beta}^{(i)} = \tfrac{3}{2}\left(\nu_{\alpha}^{(i)}\nu_{\beta}^{(i)} - \tfrac{1}{3}\delta_{\alpha\beta}\right), \tag{1}$$

where $\hat{\nu}^{(i)}$ is a unit vector defining the orientation of a molecule located at $\vec{x}_i$ and subscripts refer to axes in the laboratory coordinate system. The molecular electric and magnetic susceptibilities $\underline{\alpha}_E^{(i)}$ and $\underline{\alpha}_M^{(i)}$ in this coordinate system can be written

$$\begin{aligned} \underline{\alpha}_E^{(i)} &= \overline{\alpha}_E \overleftrightarrow{1} + \tfrac{2}{3}\Delta\alpha_E^0 \underline{S}^{(i)}(\hat{\nu}^{(i)}), \\ \underline{\alpha}_M^{(i)} &= \overline{\alpha}_M \overleftrightarrow{1} + \tfrac{2}{3}\Delta\alpha_M^0 \underline{S}^{(i)}(\hat{\nu}^{(i)}), \end{aligned} \tag{2}$$

with $\overline{\alpha} = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$ and $\Delta\alpha^0 = \alpha_{\parallel} - \alpha_{\perp}$, where $\alpha_{\parallel}$

and $\alpha_\perp$ are, respectively, the components parallel and perpendicular to the molecular axis. Since molecular orientations vary over space and time, it is useful to adopt a continuum order parameter to characterize the local orientation:

$$NQ_{\alpha\beta}(\vec{x},t)=\sum_i S^{(i)}_{\alpha\beta}(\hat{\nu}^{(i)})\delta(\vec{x}-\vec{x}_i(t)) \tag{3}$$

($N$ is the number of molecules per volume). For a locally uniaxial liquid crystal with axis $\hat{n}(\vec{x})$, the statistical average of $Q_{\alpha\beta}$ is

$$\langle Q_{\alpha\beta}(\vec{x},t)\rangle=\tfrac{3}{2}S[n_\alpha(\vec{x})n_\beta(\vec{x})-\tfrac{1}{3}\delta_{\alpha\beta}], \tag{4}$$

where $0\leqslant S\leqslant 1$ measures the extent of ordering. For a cholesteric, $\hat{n}(\vec{x})$ traces out a spiral as $\vec{x}$ proceeds in a direction perpendicular to $\hat{n}(\vec{x})$.

Order can also be defined via the anisotropy in macroscopic tensor properties, e.g., the electric susceptibility $\underline{\chi}$:

$$Q'_{\alpha\beta}=(\chi_{\alpha\beta}-\tfrac{1}{3}\delta_{\alpha\beta}\,\mathrm{Tr}\underline{\chi})/\tfrac{2}{3}\Delta\alpha^0. \tag{5}$$

In general, the two definitions are not equivalent unless the definitive macroscopic property does not involve intermolecular interactions. The electric susceptibility entails effective field effects which produce a nonlinear relationship between macroscopic and microscopic susceptibilities, and consequently (3) and (5) are not equivalent. For our formulation of dielectric behavior, it will be essential that we define order via (3) and (2), using the electric susceptibility $\underline{\alpha}_E$.

### B. de Gennes theory of short-range order

Mesophase-isotropic liquid transitions display latent heats diminutive compared to the heats of fusion of crystalline solids, suggesting a more continuous change of symmetry characteristic of second-order phase transitions. A major consequence of this fact is that the orientational order of the mesophase and all related properties do not change abruptly from order to disorder at the transition. While the average order of the isotropic phase is zero, characteristics of the ordered phase appear *locally* long before the transition is reached, giving rise to pretransitional phenomena in the isotropic phase.

Using the Landau theory of order-disorder transition,[3,4] de Gennes proposed a theory of short-range order in the isotropic phase of mesophases.[2] Details of this theory are well expounded in the literature and will not be duplicated here. Summarily, the orientational free-energy density is expanded as a series in powers of the order parameter $Q_{\alpha\beta}$, as defined earlier. For a nematic liquid we have

$$\begin{aligned}F_{\mathrm{nem}}&=F_0+\tfrac{1}{2}A\,\mathrm{Tr}Q^2-\tfrac{1}{3}B\,\mathrm{Tr}Q^3+O(Q^4)\\&\quad+\tfrac{1}{2}L_1\partial_\alpha Q_{\beta\gamma}\partial_\alpha Q_{\beta\gamma}+\tfrac{1}{2}L_2\partial_\alpha Q_{\alpha\gamma}\partial_\beta Q_{\beta\gamma}.\end{aligned} \tag{6}$$

The phenomenological coefficients $A$, $B$, $L_1$, and $L_2$ are each expanded as a series in powers of the reduced temperature $T_r=(T-T^*)/T^*$, where $T^*$ is the second-order transition temperature. To the lowest-order approximation, $A(T)=a'(T-T^*)$, and $B$, $L_1$, and $L_2$ are constants. The appearance of a cubic term in $Q$ implies that the transition is really of first order, albeit weakly so, associated with the inequivalence of states or orientation characterized by $Q$ and $-Q$. $L_1$ and $L_2$ may be construed as elastic moduli governing the spatial distortions of the local orientational order in the isotropic phase. Since $\underline{Q}$ is a symmetric, traceless tensor of rank 2, it may be written as

$$\underline{\mathrm{Q}}=\begin{bmatrix}\dfrac{-S+P}{2} & Q_{xy} & Q_{xz}\\ Q_{xy} & \dfrac{-S-P}{2} & Q_{yz}\\ Q_{xz} & Q_{yz} & S\end{bmatrix}. \tag{7}$$

It is easily seen that $F_{\mathrm{nem}}$ leaves the five independent components of $Q_{\alpha\beta}$ uncoupled, indicative of a lack of correlation between different components of the order, in distinct contrast to the cholesteric case, as we will see.

Cholesteric molecules lack a center of symmetry and thus exhibit optical activity. If chiral orientational order exists in the isotropic phase, the requirement of macroscopic inversion symmetry must be relaxed, at least over the extent of the coherence distance of the short-range order. This allows additional pseudoscalar terms to be added to $F_{\mathrm{nem}}$, the lowest-order term coupling of the order $Q_{\alpha\beta}$ to its spatial variations curl$\underline{\mathrm{Q}}$:

$$\begin{aligned}F_{\mathrm{chol}}&=F_{\mathrm{nem}}+2q_0L'\underline{\mathrm{Q}}\cdot\mathrm{curl}\underline{\mathrm{Q}}\\&=F_{\mathrm{nem}}+2q_0L'\epsilon_{\alpha\beta\gamma}Q_{\alpha\mu}\partial_\gamma Q_{\beta\mu}.\end{aligned} \tag{8}$$

Since curl$\underline{\mathrm{Q}}$ is an axial vector, $q_0$ is a pseudoscalar, changing sign under inversion, indicative of a change in chirality from the right- to left-handed helix. The collective constant $(2q_0L')$ is a phenomenological constant which needs to have no physical meaning. However, we can elucidate the roles played by $q_0$ and $L'$ by rewriting (8) in a way that similates the form of the Frank elastic energy[7]:

$$\begin{aligned}F&=F_0+\tfrac{1}{2}K_{11}(\nabla\cdot\hat{n})^2+\tfrac{1}{2}K_{22}(\hat{n}\cdot\mathrm{curl}\hat{n}+t_0)^2\\&\quad+\tfrac{1}{2}K_{33}(\hat{n}\times\mathrm{curl}\hat{n})^2+K_{24}[\nabla\hat{n}:\nabla\hat{n}-(\nabla\cdot\hat{n})^2],\end{aligned} \tag{9}$$

where $\hat{n}$ is the local orientation; $t_0=2\pi/p$ ($p$ = pitch) is the torsion; $K_{11}$, $K_{22}$, and $K_{33}$ are the splay, twist, and bend elastic constants, respectively; and $K_{24}$ is a surface elastic modulus. To affect the similarity between (8) and (9), we calculate (8) for a cholesteric material near the transition (small $S$), which can be characterized as locally uniaxial with the order parameter given by (4). Thus $F_{\text{chol}}$ has the form

$$F_{\text{chol}} = F_0 + \tfrac{9}{4}(L_1 + \tfrac{1}{2}L_2)S^2(\nabla\cdot\hat{n})^2 + \tfrac{9}{4}L_2 S^2(\hat{n}\times\text{curl}\hat{n})^2 + \tfrac{9}{4}L_1 S^2[\hat{n}\cdot\text{curl}\hat{n} + (L'/L_1)q_0]^2 + \tfrac{9}{4}L_1 S^2[\nabla\hat{n}:\nabla\hat{n} - (\nabla\cdot\hat{n})^2]\,. \tag{10}$$

Comparison of (9) and (10) suggests these correspondences:

$$\begin{aligned} &(L'/L_1)q_0 \rightarrow t_0,\\ &\tfrac{9}{4}L_1 S^2 \rightarrow K_{22}. \end{aligned} \tag{11}$$

"Correspondence" should not be construed as an equivalence relation. Our purpose in this exercise is to compare the role of $q_0$ to that of $t_0$ in the ordered phase. By a judicious choice of $L' = L_1$, we obtain from (11), that $q_0 = t_0$. Thus $q_0^{-1}$ measures the extent of the short-range chiral ordering in the same way that $t_0^{-1}$ measures the pitch of the long-range helical order. The correspondence between $t_0$ and $q_0$ does indeed have further justification. Experimental measurements of $q_0$ by "Bragg scattering" in the isotropic phase of cholesteric cholesteryl 2-(2-ethoxyethoxy)-ethyl-carbonate (CEEEC),[5] for example, and of the cholesteric pitch $t_0^{-1}$ near $T_k$ show comparable values, with the association of $L'$ to $L_1$. Further support for this interpretation of $q_0$ will emerge later in our work. Note that $L_1 S^2$ plays the role of elastic constant $K_{22}$, which is known to have an $S^2$ dependence from the Maier-Saupe Theory.[6] In the ordered phase, it is known that $K_{22}t_0 = K_2$ is not temperature dependent[7]; whether or not this is also true of $q_0 L'$ will be tested experimentally.

Several thermodynamic relations can be inferred from the de Gennes free energy. Using the order parameter (4), with $\hat{n}(\vec{x}) = (0,0,1)$ for the nematic and $\hat{n}(\vec{x}) = (\cos\theta(z), \sin\theta(z), 0)$ for cholesteric, the free energies obtain the forms

$$\begin{aligned} F_{\text{nem}} &= F_0 + \tfrac{3}{4}a'(T - T^*)S^2 - \tfrac{1}{4}BS^3 + \tfrac{9}{16}CS^4 + \cdots,\\ F_{\text{chol}} &= F_{\text{nem}} + \tfrac{27}{4}L_1 q_0^2 S^2 + \cdots. \end{aligned}$$

From these it is straightforward to calculate the latent heat $H$, the order parameter $S_k$ at $T_k$, and the difference $(T_k - T^*)$:

$$\begin{aligned} &H = \tfrac{3}{4}a' T_k S_k^2,\\ &S_k = 2B/9C,\\ &(T_k - T^*)_{\text{nem}} = BS_k/6a',\\ &(T_k - T^*)_{\text{chol}} = BS_k/6a' - 9L_1 q_0^2/a'. \end{aligned} \tag{12}$$

Inasmuch as the validity of Landau theory at $T_k$ is questionable, no quantitative rigor is implied in (12), which does show qualitatively that the proximity of approach to $T^*$ differs for cholesterics and nematics by a factor associated with their difference in twist elastic energy. Equation (12) also shows that as the transition becomes more second order, the values of $B$, $H$, $S_k$, and $T_k - T^*$ become vanishingly small.

### C. Correlation spectrum and implications of theory

From the Fourier spectrum of the free energy (8), we can calculate the orientational correlations via the equipartition theorem, and thence derive the scattering intensity corresponding to a fluctuation with wave vector $\vec{q}$. The presence of chiral coupling in cholesterics causes different components of $\underset{=}{\tilde{Q}}$ to be coupled in $\tilde{F}(\vec{q})$, and its decomposition into normal modes of fluctuations is difficult to do for an arbitrary $\vec{q}$. For $\vec{q}$ directed along the laboratory $z$ axis, de Gennes calculated these nonzero averages:

$$\begin{aligned} \langle|\tilde{S}|^2\rangle &= \frac{2KT}{3A(T)}\,\frac{1}{1+(q\xi_0)^2}\,,\\ \langle|\tilde{Q}_{xy}|^2\rangle &= \langle|\tfrac{1}{2}\tilde{P}|^2\rangle\\ &= \frac{KT}{2A(T)}\,\frac{1+(q\xi_1)^2}{[1+(q\xi_1)^2]^2-(\gamma_1 q\xi_1)^2}\,,\\ \langle|\tilde{Q}_{xz}|^2\rangle &= \langle|\tilde{Q}_{xz}|^2\rangle\\ &= \frac{KT}{2A(T)}\,\frac{1+(q\xi_2)^2}{[1+(q\xi_2)^2]^2-(\gamma_2 q\xi_2)^2}\,,\\ \langle\tilde{P}''\tilde{Q}'_{xy}\rangle &= -\langle\tilde{Q}''_{xy}\tilde{P}'\rangle\\ &= \frac{KT}{2A(T)}\,\frac{\gamma_1 q\xi_1}{[1+(q\xi_1)^2]^2-(\gamma_1 q\xi_1)^2}\,,\\ \langle\tilde{Q}'_{xz}\tilde{Q}''_{yz}\rangle &= -\langle\tilde{Q}''_{xz}Q'_{yz}\rangle\\ &= \frac{KT}{4A(T)}\,\frac{\gamma_2 q\xi_2}{[1+(q\xi_2)^2]^2-(\gamma_2 q\xi_2)^2}\,, \end{aligned} \tag{13}$$

where

$$\begin{aligned} &\xi_0^2 = \frac{L_1+\frac{1}{3}L_2}{A(T)}\,, \quad \gamma_1 = \frac{4L'}{L_1}\,q_0\xi_1 = 4q_0\xi_1,\\ &\xi_1^2 = \frac{L_1}{A(T)}\,, \quad \gamma_2 = \frac{2L'}{L_1}\,\frac{q_0\xi_1^2}{\xi_2} = \frac{2\xi_1}{\xi_2}\,(q_0\xi_1),\\ &\xi_2^2 = \frac{L_1+\frac{1}{2}L_2}{A(T)} \end{aligned}$$

($\underline{\tilde{Q}}'$ and $\underline{\tilde{Q}}''$ are the real and imaginary parts of the Fourier transform of $\underline{Q}$).

For $\vec{q}$ oriented along an arbitrary direction with respect to the laboratory $(x, y, z)$ system, the orientational averages can be derived from those for $\vec{q} = q_z$ by a coordinate transformation. If the $z$ and $z'$ axes are defined by $\vec{k}_0$ and $\vec{q}$, respectively, as shown in Fig. 1, then the $(x', y', z')$ system can be obtained from the $(x, y, z)$ system by a sequence of Euler rotations by angles $\phi$, $\theta$, $\psi$, in that order, i.e.,

$$\vec{x}' = \underline{R}(\phi, \theta, \psi) \circ \vec{x},$$

$$\underline{R} = \begin{pmatrix} \cos\phi\cos\psi - \cos\theta\sin\phi\sin\psi & \cos\psi\sin\phi + \cos\theta\cos\phi\sin\psi & \sin\psi\sin\theta \\ -\sin\psi\cos\phi - \cos\theta\sin\phi\cos\psi & -\sin\psi\sin\phi + \cos\theta\cos\phi\cos\psi & \cos\psi\sin\theta \\ \sin\theta\sin\phi & -\sin\theta\cos\phi & \cos\theta \end{pmatrix} . \tag{14}$$

The averages in the primed coordinate system are those given by (13). The tensor $Q_{\alpha\beta}$ in the unprimed system is related to those of the primed system by a similarity transformation:

$$[Q_{\alpha\beta}]_{\vec{x}} = R^{\dagger}_{\alpha\mu}[Q_{\mu\nu}]_{\vec{x}'} R_{\nu\beta} . \tag{15}$$

It then follows that the correlations in the unprimed system will be related to those of (13) by tensor transformations of rank 4:

$$\langle Q_{\alpha\beta} Q_{\gamma\delta} \rangle_{\vec{x}} = R^{\dagger}_{\alpha\alpha'} R^{\dagger}_{\beta\beta'} R^{\dagger}_{\gamma\gamma'} R^{\dagger}_{\delta\delta'} \langle Q_{\alpha'\beta'} Q_{\gamma'\delta'} \rangle_{\vec{x}'} . \tag{16}$$

By this method, the averages can be calculated for any $\vec{q}$; the details are straightforward but cumbersome and will be omitted.

The cholesteric features of these correlations emerge in three ways: Firstly, as predicted by de Gennes[2] and measured by Yang,[5] the scattering intensity shows a maxima for $q = (\gamma_1 - 1)^{1/2}$ or $q = (\gamma_2 - 1)^{1/2}$ in the temperature regime where $2 > \gamma_1, \gamma_2 > 1$. The broad peak is reminiscent of Bragg scattering in the ordered phase, suggesting a strong tendency to build up a spiral at these temperatures. This effect was observed in a long-pitch cholesteryl ester over a narrow range of temperatures $0.68\,^\circ\mathrm{K} > T - T^* > 0.11\,^\circ\mathrm{K}$; at higher temperatures, the average extent of fluctuations become too small to yield an observable intensity. Secondly, and more dramatically, coupling of different components of $Q_{\alpha\beta}$ gives rise to a large optical rotatory power. Thirdly, orientational averages become singular when $\gamma_1, \gamma_2 > 2$, or $2q_0\xi > 1$, below which temperature the isotropic phase becomes absolutely unstable against fluctuations. This implies that the transition temperature $T_k$ is to some extent limited by the torsion $q_0$, which is unique to cholesterics.

Yang's measurement of the Rayleigh linewidth was the only previous attempt to investigate the chiral short-range ordering in cholesterics. Apart from the Bragg peaks, the cholesteric features of the isotropic liquid failed to emerge when $T$ is only 0.7°C above the transition. This underscores the fact that the diminutive chiral coupling is very quickly dominated by the nematic coupling in the isotropic phase. Thus any meaningful probe of the chiral short-range order must be able to obscure the nematic nature of the correlations. The most obvious property in which chirality alone emerges is the optical rotatory power of the isotropic phase.

## III. THEORY OF OPTICAL ROTATORY POWER IN ISOTROPIC PHASE OF CHOLESTERICS

It is well known that the long-range spiral orientational order of cholesterics produces a large optical rotatory power,[7] and that all cholesteric molecules show natural optical activity in dilute solutions. The long-range order dominates the rotatory power of the ordered phase, and in its

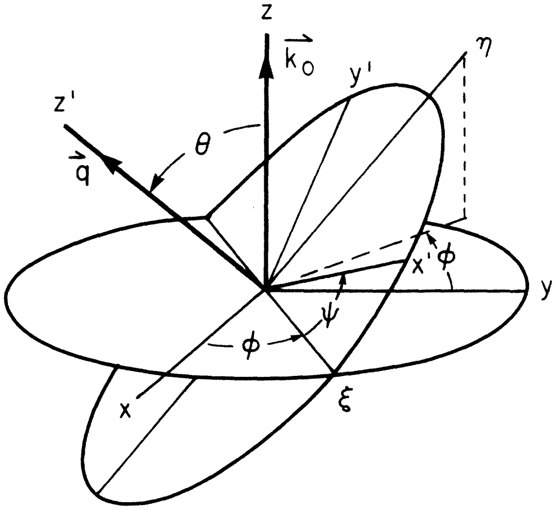


FIG. 1. Definition of coordinate systems. The primed system ($z'$ axis defined by $\vec{q}$) is related to unprimed laboratory system ($z$ axis defined by $\vec{k}_0$) via Euler rotations by $\phi$, $\theta$, $\psi$, in that order.

absence only natural optical activity appears in the isotropic liquid. The presence of persistent order produces an enhancement in the rotatory power of the isotropic liquid, the magnitude of which gauges the degree of short-range chiral order.

We shall interpret this precursor effect by showing that in a medium governed by short-range chiral orientational correlations, the induced polarization density $\vec{P}$ is related to the electric field $\vec{E}$ in a way which results in circular birefringence, or equivalently, the electric susceptibility contains a skew Hermitian wave-vector-dependent component.

### A. Preliminary remarks

The dielectric theory of an ordered anisotropic fluid is still largely a matter of conjecture, and local field effects are not completely understood. The work of Maier and co-workers[8,9] on nematic liquid crystals predicted that each component of the polarizability $\underline{\alpha}$ is related to the corresponding index of refraction $\underline{n}$ by a Clausius-Mossotti equation of the form

$$\begin{aligned}(n_i^2-1)/(n_i^2+2)&=\tfrac{4}{3}\pi N\alpha_i\\&=\tfrac{4}{3}\pi N[\overline{\alpha}+(\alpha_i-\overline{\alpha})S]\,.\end{aligned}\qquad(17)$$

This implies that the form of the effective field $\vec{F}_i=\frac{1}{3}(n_i^2+2)\vec{E}_i$ differs for each component. The Maier-Saupe predictions (17) were not experimentally verified. Vuks,[10] in studying the crystals of strongly anisotropic organic molecules, found the components of the polarizability to satisfy equations of the form

$$\begin{aligned}&(n_i^2-1)/(\langle n^2\rangle+2)=\tfrac{4}{3}\pi N\alpha_i\quad(i=\parallel\text{ or }\perp),\\&\langle n^2\rangle=\tfrac{1}{3}(n_\parallel^2+2n_\perp^2).\end{aligned}\qquad(18)$$

These relations imply that the effective field assumes the same functional form $\vec{F}=\frac{1}{3}(\langle n^2\rangle+2)\vec{E}$ independent of direction. The Vuks relations were experimentally verified by Chandrasekhar and Madhusudana[11] for nematic liquid crystals and their mixtures.

We now examine the implications of the Vuks findings in the context of dielectric theory. The effective field seen by a molecule at the center of the Lorentz cavity is a sum of the external field $\vec{E}_0$, the fields $\vec{E}_{\mathrm{DP}}$ emanating from all dipoles in the volume excluding the cavity, and $\vec{E}_C$ from those in the cavity. As is well-known from the extinction theorem,[12] the fields $\vec{E}_0+\vec{E}_{\mathrm{DP}}$ combine to extinguish the external field and generate fields which propagate with the characteristic velocities of the medium. Thus $\vec{E}+\vec{E}_{\mathrm{DP}}$ becomes a sum of the macroscopic field $\vec{E}$ in the medium and a contribution $\vec{E}_\sigma$ from the surface of the Lorentz cavity. For molecules distributed with cubic symmetry or with a random disposition, it is known[13] that $E_C=0$. Thus the effective field, in the case of a uniform polarization, is given by $\vec{E}+\vec{E}_\sigma$ and is strongly dependent on the choice of cavity chosen. An anisotropic cavity, e.g., a rodlike one, leads to an angle-dependent $\vec{E}$ which obtains its minimum value in the long direction and maximum in the short direction. This is in contradiction with the Maier-Saupe predictions according to which the long molecular axis should experience the largest effective field $\frac{1}{2}(n_\parallel^2+2)\vec{E}$. The Vuks-Chandrasekhar results imply that $\vec{E}_\sigma$, and thus the effective field, is independent of direction, i.e., the cavity is spherical, corresponding to an effective field $\vec{F}=\frac{1}{3}(\langle n^2\rangle+2)\vec{E}$.

This conclusion is of course empirical, and rigorous theoretical justification is difficult. Moreover, fluctuations did not enter this discussion of the ordered phase, in which the mean order parameter predominates over all higher-order orientational averages. This is no longer true in the isotropic phase, in which the mean order parameter is zero and fluctuations become the dominant effects, and must be incorporated into the dielectric theory. Nevertheless, we expect that the Vuks-Chandrasekhar hypothesis to remain valid and assume a spherical cavity.

### B. Dielectric formulation of effective susceptibility in presence of chiral orientational correlations

Phenomenologically, an optically active medium is characterized by a circular birefringence. Microscopically, the phase of the electromagnetic wave varies over the finite extent of the molecule and gives rise to a wave-vector dispersion in the dielectric permeability. Furthermore, the intrinsic chirality of the molecule requires that this $\vec{k}$-dispersion contains a skew Hermitian component. Thus we can either expand the electromagnetic field in its spatial derivatives to account for the variation of phase, deriving the induced moments

$$\begin{aligned}&\langle\vec{\mu}_E\rangle=\alpha_E\vec{E}+\beta\nabla\times\vec{E}+O(\nabla^2),\\&\langle\vec{\mu}_M\rangle=\alpha_M\vec{H}+\beta\nabla\times\vec{H}+O(\nabla^2)\end{aligned}\qquad(19)$$

or expand the permeability in wave vector $\vec{k}$[18]:

$$\begin{aligned}&\tilde{\epsilon}_{\alpha\beta}(\vec{k})=\epsilon_{\alpha\beta}^0+i\beta k_\gamma\epsilon_{\gamma\alpha\beta}+O(k^2),\\&\tilde{\mu}_{\alpha\beta}(\vec{k})=\mu_{\alpha\beta}^0+i\beta k_\gamma\epsilon_{\gamma\alpha\beta}+O(k^2).\end{aligned}\qquad(20)$$

The usual theories of natural optical activity[14,15] follow the former approach, deriving, e.g., the Rosenfeld relations:

$$\begin{pmatrix}\vec{D}\\ \vec{B}\end{pmatrix}=\begin{pmatrix}\bar{\epsilon} & i4\pi\beta\bar{N}k_0\dfrac{\bar{\epsilon}+2}{3}\\ -i4\pi\beta\bar{N}k_0\dfrac{\bar{\epsilon}+2}{3} & \bar{\mu}\end{pmatrix}\begin{pmatrix}\vec{E}\\ \vec{H}\end{pmatrix}, \tag{21}$$

which lead to circular birefringence and the optical rotation:

$$\phi_0=4\pi\bar{N}k_0^2\beta\frac{\bar{n}^2+2}{3}\,, \tag{22}$$

where $\bar{\epsilon}=\bar{n}^2$, and $\bar{\mu}\cong 1$. The theories of natural optical activity are well expounded in the literature.[15-17]

The optical rotatory power of the isotropic phase is a cooperative phenomenon arising from chiral correlations in the molecular orientations. While this means that the spatial variations of the fields must be considered over a much larger expanse, the essential features of optical activity remain the same, and the fields $\vec{D}$ and $\vec{B}$ must again be related to $\vec{E}$ and $\vec{H}$ in such a way that circular birefringence results. Pursuant to the foregoing remarks, we will incorporate the contributions of orientational correlations into a description of the medium via the $\vec{k}$-dispersive permeabilities $\underline{\epsilon}(\vec{k})$ and $\underline{\mu}(\vec{k})$.

The temporal behavior of the liquid's response will be neglected by allowing an implicit frequency dispersion in the molecular polarizability $\underline{\alpha}(\omega)$. Intermolecular relaxation effects are unimportant at optical frequencies in any case. The incident field $\vec{E}_0(\vec{x})e^{-i\omega t}$ propagates with wave vector $\vec{k}_0$ along the $z$ axis. It polarizes the molecules in the isotropic phase, each having a polarizability tensor $\underline{\alpha}(\vec{x},\vec{\Psi};\,\omega)$ which depends on the orientation $\vec{\Psi}$ of the molecular long axis (the set of Euler angles defined in Fig. 1). The coordinates and orientations of all the molecules specify a $6N$-dimensional configuration, $\Omega$, the set of which constitutes a statistical ensemble.

A molecule at $\vec{x}_i$ sees an effective field $\vec{F}(\vec{x}_i,\Omega)$ which contains the incident field plus the sum of the radiated dipole fields of all other molecules in a particular configuration, $\Omega$. Its induced dipole moment is

$$\vec{\mu}^{(i)}(\vec{x}_i,\vec{\Psi}_i)=\underline{\alpha}(\vec{x}_i,\vec{\Psi}_i,\omega)\cdot\vec{F}(\vec{x}_i,\Omega),$$

with

$$\vec{F}(\vec{x}_i,\Omega)=\vec{E}_0(\vec{x}_i)+\sum_{j=i}^{N}\underline{G}(\vec{x}_i,\vec{x}_j;\,k_0)\cdot\vec{\mu}^{(j)}(\vec{x}_j,\vec{\Psi}_j). \tag{23}$$

$\underline{G}(\vec{x}_i,\vec{x}_j;\,k_0)$ is the Green's function describing the field generated at $\vec{x}_i$ by a unit point dipole at $\vec{x}_j$, which has the well-known form

$$\begin{aligned}G_{\mu\nu}(\vec{x},\vec{x}';\,k_0)&=(\partial_\mu\partial_\nu+k_0^2\delta_{\mu\nu})(e^{ik_0R}/R)\\&=G_{\mu\nu}(\vec{R};\,k_0),\end{aligned} \tag{24}$$

where $\vec{R}=\vec{x}-\vec{x}'=R\hat{n}$. $\underline{G}$ is approximately a static dipole field in the near zone and a spherical wave in the radiation zone. Since coherence distances in the isotropic phase are about 100 Å in range, the major contributions will come from a static dipolar coupling.

To convert to a continuum description of polarization, the induced dipoles are averaged over a volume $\Delta V$ surrounding $\vec{x}$ which contains many molecules but is macroscopically small:

$$\vec{p}(\vec{x},\vec{\Psi})=\sum_{\{i\in\Delta V\}}\delta(\vec{x}-\vec{x}_i)\delta(\vec{\Psi}-\vec{\Psi}_i)\vec{\mu}^{(i)}(\vec{x}_i,\Psi_i).$$

Similarly we define a *local* polarizability $\underline{\alpha}(\vec{x},\vec{\Psi},\omega)$ which must, however, be distinguished from the macroscopic polarizability $\underline{\chi}$ that relates $\vec{P}$ and $\vec{E}$. Thus (23) becomes

$$\begin{aligned}\vec{p}(\vec{x},\vec{\Psi})&=\underline{\alpha}(\vec{x},\vec{\Psi})\cdot\vec{F}(\vec{x},\Omega)\\&=\underline{\alpha}(\vec{x},\vec{\Psi})\cdot\left(\vec{E}_0+\int d^3x'\,\underline{G}(\vec{x}-\vec{x}';k_0)\cdot\vec{p}(\vec{x}',\vec{\Psi}')\right)\end{aligned} \tag{25}$$

According to Eqs. (2) and (3),

$$\alpha_{\mu\nu}^{(i)}=\overline{\alpha}\delta_{\mu\nu}+\tfrac{2}{3}\Delta\alpha^0S_{\mu\nu}^{(i)}(\vec{x}_i,\vec{\Psi}_i),$$

$$N(\vec{x})Q_{\mu\nu}(\vec{x},\vec{\Psi})=\sum_{\{i\in\Delta V\}}S_{\mu\nu}^{(i)}(\vec{x}_i,\vec{\Psi}_i)\delta(\vec{x}-\vec{x}_i)\delta(\vec{\Psi}-\vec{\Psi}_i),$$

which allows us to relate $\underline{\alpha}(\vec{x},\vec{\Psi})$ and $\underline{Q}(\vec{x},\vec{\Psi})$:

$$\alpha_{\mu\nu}(\vec{x},\vec{\Psi};\,\omega)=N(\vec{x})[\overline{\alpha}\delta_{\mu\nu}+\tfrac{2}{3}\Delta\alpha^0Q_{\mu\nu}(\vec{x},\vec{\Psi})]\,. \tag{26}$$

To incorporate the presence of molecular optical activity, we make the following modification of (26) based on the Rosenfeld equations (19), in which the effective field is expanded in its spatial derivatives:

$$\begin{aligned}\vec{\mu}^{(i)}(\vec{x}_i,\vec{\Psi}_i)=&\,\underline{\alpha}(\vec{x}_i,\vec{\Psi}_i)\cdot\vec{F}(\vec{x}_i,\Omega)\\&+\beta\nabla\times\vec{F}(\vec{x}_i,\Omega)+O(\nabla^2).\end{aligned} \tag{27}$$

Using the explicit spatial dependence of $\vec{E}$, we have

$$\begin{aligned}\vec{\mu}^{(i)}_\lambda(\vec{x}_i,\vec{\Psi}_i)&=[\alpha_{\lambda\nu}(\vec{x}_i,\vec{\Psi}_i)+i\bar{n}\beta(k_0)_\gamma\epsilon_{\gamma\lambda\nu}]F_\nu(\vec{x}_i,\Omega)\\&\equiv\alpha'_{\lambda\nu}(\vec{x}_i,\vec{\Psi}_i)F_\nu(\vec{x}_i,\Omega),\end{aligned} \tag{28}$$

with

$$\begin{aligned}\alpha'_{\mu\nu}(\vec{x},\vec{\Psi})&=\alpha_{\mu\nu}(\vec{x},\Psi)+iN(\vec{x})\bar{n}\beta(k_0)_\gamma\epsilon_{\gamma\mu\nu}\\&\equiv\alpha_{\mu\nu}+iN(\vec{x})\Gamma_{\mu\nu}.\end{aligned} \tag{29}$$

Thus the integral equation (25) preserves its form in the presence of natural optical activity if $\underline{\alpha}$ is replaced by $\underline{\alpha}'(\vec{x},\vec{\Psi})$.

In solving (25) in conjunction with Eqs. (26) and (29), iteration yields an expansion in orders of $N\overline{\alpha}$, which may not converge when the density $N$ is high. For nematic PAA, $N = 2\times 10^{21}/\text{cm}^3$, $\overline{\alpha} = 3.25\times 10^{-23}$ cm$^3$, giving $N\overline{\alpha} = 0.07$, which may be sufficiently small. However, we can avert this question by the decomposition:

$$\vec{\mathrm{p}}(\vec{\mathrm{x}}, \vec{\Psi}) = \vec{\mathrm{P}}_0(\vec{\mathrm{x}}) + \delta\vec{\mathrm{P}}(\vec{\mathrm{x}}, \vec{\Psi}).$$

$\vec{\mathrm{P}}_0$ is the solution in the absence of natural optical activity and orientational correlations, i.e., $\beta = 0$ and $Q_{\mu\nu} = 0$. $\delta\vec{\mathrm{P}}$ will be treated as a small correction since its contribution to the susceptibility $\underline{\chi}$ is at least five orders of magnitude smaller than that given by the Lorentz solution. The formal relations governing $\delta\vec{\mathrm{P}}$ will be independent of the validity of the solution $\vec{\mathrm{P}}_0$ of the Born-Rosenfeld theory,[13,19] thereby circumventing the convergence question.

Both $\vec{\mathrm{p}}(\vec{\mathrm{x}}, \vec{\Psi})$ and $N(\vec{\mathrm{x}})$ are governed by statistical fluctuations. From (25), $\vec{\mathrm{P}}_0$ satisfies

$$\vec{\mathrm{P}}_0(\vec{\mathrm{x}}) = N(\vec{\mathrm{x}})\,\overline{\alpha}\left(\vec{\mathrm{E}}_0(\vec{\mathrm{x}}) + \int_{v(\vec{\mathrm{x}})}^{V} d^3x'\,\underline{\mathrm{G}}(\vec{\mathrm{x}} - \vec{\mathrm{x}}'; k_0)\cdot\vec{\mathrm{P}}_0(\vec{\mathrm{x}}')\right), \tag{30}$$

where $v(\vec{\mathrm{x}})$ is the Lorentz cavity, which by previous discussions does not contribute to the effective field, and $V$ is the total volume. The solution of (30) is very well known from the work of Born and Wolf[13] and Rosenfeld,[19] according to which Eq. (30) separates into two equalities, one of which expresses the Ewald-Oseen extinction theorem[12] and the other gives the Clausius-Mossotti equation:

$$(\overline{n}^2 - 1)/(\overline{n}^2 + 2) = \tfrac{4}{3}\pi\overline{N}\overline{\alpha}. \tag{31}$$

The effective field is given by

$$\begin{aligned}\vec{\mathrm{F}} &= \vec{\mathrm{E}}_0 + \overline{N}\overline{\alpha}\int_{v}^{V} d^3x'\,\underline{\mathrm{G}}(\vec{\mathrm{R}}; k_0)\cdot\langle\vec{\mathrm{P}}_0(\vec{\mathrm{x}}')\rangle \\ &= \frac{4\pi}{(\overline{n}^2 - 1)}\vec{\mathrm{P}}_0 + \tfrac{4}{3}\pi\vec{\mathrm{P}}_0 \\ &= \tfrac{1}{3}(\overline{n}^2 + 2)\vec{\mathrm{E}}(\vec{\mathrm{x}}).\end{aligned} \tag{32}$$

The fields $\vec{\mathrm{E}}$ and $\vec{\mathrm{P}}$ will propagate a new wave velocity $\overline{n}\vec{\mathrm{k}}_0$ as a result of the extinction theorem.

Next we look at the corrections $\delta\vec{\mathrm{P}}$ to $\vec{\mathrm{p}}(\vec{\mathrm{x}}, \vec{\Psi})$ due to orientational effects and optical activity. From Eqs. (25), (30), and (32) it easily follows that $\delta\vec{\mathrm{P}}$ satisfies

$$\begin{aligned}\delta\vec{\mathrm{P}}(\vec{\mathrm{x}}, \vec{\Psi}) &= \delta\,\underline{\alpha}'(\vec{\mathrm{x}}, \vec{\Psi})\cdot\left(\vec{\mathrm{E}}_0(\vec{\mathrm{x}}) + \int_{v}^{V} d^3x'\,\underline{\mathrm{G}}(\vec{\mathrm{x}} - \vec{\mathrm{x}}'; k_0)\cdot[\langle\vec{\mathrm{P}}_0\rangle + \delta\vec{\mathrm{P}}(\vec{\mathrm{x}}', \vec{\Psi}')]\right) \\ &= \delta\,\underline{\alpha}'\left(\vec{\mathrm{F}}(\vec{\mathrm{x}}) + \int_{v}^{V} d^3x'\,\underline{\mathrm{G}}(\vec{\mathrm{x}} - \vec{\mathrm{x}}'; k_0)\cdot\delta\vec{\mathrm{P}}(\vec{\mathrm{x}}', \vec{\Psi}')\right),\end{aligned} \tag{33}$$

where

$$\delta\,\underline{\alpha}' = N(\vec{\mathrm{x}})[\tfrac{2}{3}\Delta\alpha^0\underline{\mathbf{Q}}(\vec{\mathrm{x}}, \vec{\Psi}) + i\underline{\Gamma}].$$

Iteration of (33), and taking the ensemble averages defined by

$$\langle\langle A(\vec{\mathrm{x}}, \vec{\Psi})\rangle\rangle_{x,\Psi} = \int\prod_{k}\frac{d^3x_k\,d^3\Psi_k}{V}A(\vec{\mathrm{x}}, \vec{\Psi}; \{\Omega\})f(\{\Omega\})$$

($f(\{\Omega\})$ is the ensemble's statistical distribution), we obtain

$$\begin{aligned}\langle\langle\delta\vec{\mathrm{P}}\rangle\rangle &= \langle\langle\delta\,\underline{\alpha}'(\vec{\mathrm{x}}, \vec{\Psi})\rangle\rangle\cdot\vec{\mathrm{F}}(\vec{\mathrm{x}}) + \int_{v}^{V} d^3x'\langle\langle\delta\,\underline{\alpha}'(\vec{\mathrm{x}}, \vec{\Psi})\cdot\underline{\mathrm{G}}(\vec{\mathrm{x}} - \vec{\mathrm{x}}'; k_0)\cdot\delta\,\underline{\alpha}'(\vec{\mathrm{x}}', \vec{\Psi}')\rangle\rangle\cdot\vec{\mathrm{F}}(\vec{\mathrm{x}}') \\ &\quad + \int_{v(x)}^{V} d^3x'\int_{v(x')}^{V} d^3x''\langle\langle\delta\,\underline{\alpha}'\cdot\underline{\mathrm{G}}\cdot\delta\,\underline{\alpha}'\cdot\underline{\mathrm{G}}\cdot\delta\,\underline{\alpha}'\rangle\rangle\cdot\vec{\mathrm{F}}(\vec{\mathrm{x}}'') + \cdots.\end{aligned} \tag{34}$$

Since $\langle\langle\underline{\mathrm{Q}}(\vec{\mathrm{x}}, \vec{\Psi})\rangle\rangle \equiv 0$ in the isotropic phase, the first term of (34) is

$$\langle\langle\delta\alpha'_{\mu\nu}\rangle\rangle = \langle N(\vec{\mathrm{x}})i\Gamma_{\mu\nu}\rangle = i\overline{N}\Gamma_{\mu\nu}. \tag{35}$$

The second term, using $\vec{\mathrm{F}}(\vec{\mathrm{x}}) \sim e^{i\overline{n}\vec{\mathrm{k}}_0\cdot\vec{\mathrm{x}}}$, is

$$\left(\int_{v(\vec{\mathrm{x}})}^{V} d^3x'\langle\langle\delta\,\underline{\alpha}'(\vec{\mathrm{x}}, \vec{\Psi})\cdot\underline{\mathrm{G}}(\vec{\mathrm{x}} - \vec{\mathrm{x}}')\cdot\delta\,\underline{\alpha}'(\vec{\mathrm{x}}', \vec{\Psi}')\rangle_x\rangle_\Psi\, e^{i\overline{n}\vec{\mathrm{k}}_0\cdot(\vec{\mathrm{x}} - \vec{\mathrm{x}}')}\right)\cdot\vec{\mathrm{F}}(\vec{\mathrm{x}})$$

which, with the help of conditional probabilities, becomes

$$\left(\int_{v(x)}^{V} d^3x' \langle N(\vec{x})N(\vec{x}')\rangle_x \underline{G}(\vec{x}-\vec{x}')\cdot\langle[\tfrac{2}{3}\Delta\alpha^0\underline{Q}(\vec{x},\vec{\Psi})+i\underline{\Gamma}][\tfrac{2}{3}\Delta\alpha^0\underline{Q}(\vec{x}',\Psi')+i\underline{\Gamma}]\rangle_{\Psi|X}\, e^{i\bar{n}\vec{k}_0\cdot(\vec{x}-\vec{x}')}\right)\cdot\vec{F}(\vec{x})$$

$$\cong \int_{v(x)}^{V} d^3x'\, \bar{N}^2\underline{G}(\vec{x}-\vec{x}')[(\tfrac{2}{3}\Delta\alpha^0)^2\langle\underline{Q}(\vec{x},\vec{\Psi})\underline{Q}(\vec{x}',\vec{\Psi}')\rangle-\underline{\Gamma}\cdot\underline{\Gamma}]\, e^{i\bar{n}\vec{k}_0\cdot(\vec{x}-\vec{x}')}\cdot\vec{F}(\vec{x}). \quad (36)$$

[The conditional probability $f(\vec{\Psi}|\vec{X})$ is the probability of a given relative orientation given that the molecules are separated by $\vec{R}=\vec{x}-\vec{x}'$.] The term in $\underline{\Gamma}^2$ is of order $(\beta k_0)^2\sim(10^{-7}\bar{\alpha})^2$ and is negligible compared to the first term of (36), which is of order $10^{-5}\bar{\alpha}$. Thus the natural optical activity is uncoupled from the contribution from short-range order up to this order of approximation.

The third- and higher-order terms, which involve correlations between three or more molecules, are of the form

$$\int_{v(x)}^{V} d^3x' \int_{v(\vec{x}')}^{V} d^3x'' \langle N(\vec{x})N(\vec{x}')N(\vec{x}'')\rangle \underline{G}(\vec{x}-\vec{x}')\, e^{i\bar{n}\vec{k}_0\cdot(\vec{x}-\vec{x}')}\underline{G}(\vec{x}'-\vec{x}'')\, e^{i\bar{n}\vec{k}_0\cdot(\vec{x}'-\vec{x}'')}$$

$$\cdot\vec{F}(\vec{x})\cdot\{-i\underline{\Gamma}^3+i\underline{\Gamma}(\tfrac{2}{3}\Delta\alpha^0)^2[\langle\underline{Q}(\vec{x})\underline{Q}(\vec{x}')\rangle+\langle\underline{Q}(\vec{x})\underline{Q}(\vec{x}'')\rangle+\langle\underline{Q}(\vec{x}')\underline{Q}(\vec{x}'')\rangle]$$

$$+(\tfrac{2}{3}\Delta\alpha^0)^3\langle\underline{Q}(\vec{x},\vec{\Psi})\cdot\underline{Q}(\vec{x}',\vec{\Psi}')\cdot\underline{Q}(\vec{x}'',\vec{\Psi}'')\rangle\}.$$

To the extent that terms of order $\underline{Q}^3$ or higher are neglected in the second-order Landau expansion, correlations between three or more molecules can be neglected as long as we are not too close to $T_k$. The term in $\underline{\Gamma}(\frac{2}{3}\Delta\alpha^0)^2$ which couples the short-range order and optical activity, is of order $\beta k_0(10^{-5}\bar{\alpha})\sim10^{-11}\bar{\alpha}^2$ and is also negligible, as is the $\underline{\Gamma}^3$ term. Thus the third order, and in like fashion all higher-order terms, can be discarded.

In summary, the polarization density is

$$\vec{p}(\vec{x})=\langle\vec{P}_0(\vec{x})\rangle+\delta\vec{P}(\vec{x})$$

$$=\left(\bar{N}\bar{\alpha}\vec{1}+i\bar{N}\underline{\Gamma}+\int_{v(\vec{0})}^{V} d^3R\,\bar{N}^2\underline{G}(\vec{R};\,k_0)\,e^{i\bar{n}\vec{k}_0\cdot\vec{R}}\cdot(\tfrac{2}{3}\Delta\alpha^0)^2\langle\underline{Q}(0,\Psi)\circ\underline{Q}(\vec{R},\Psi')\rangle\right)\cdot\vec{F}(\vec{x})+\cdots$$

$$\equiv\underline{\tilde{\chi}}_{\rm eff}(\bar{n}\vec{k}_0)\cdot\vec{E}(\vec{x}). \quad (37)$$

(We have invoked translational invariance above.) By expressing the integral in terms of Fourier components of various quantities, $\underline{\tilde{\chi}}_{\rm eff}(\bar{n}k_0)$ can be written

$$\underline{\tilde{\chi}}_{\rm eff}(\bar{n}k_0)\cong\frac{\bar{n}^2+2}{3}\;(\tfrac{2}{3}\bar{N}\Delta\alpha^0)^2\int\frac{d^3q}{(2\pi)^3}\,\underline{\tilde{G}}(\bar{n}\vec{k}_0+\vec{q})\cdot\langle\underline{\tilde{Q}}^*(\vec{q}):\underline{\tilde{Q}}(\vec{q})\rangle+\frac{\bar{n}^2+2}{3}\,(\bar{N}\bar{\alpha}\vec{1}+i\bar{N}\Gamma)$$

$$\equiv\underline{\Lambda}+(\bar{N}\bar{\alpha}\vec{1}+i\bar{N}\Gamma)\frac{\bar{n}^2+2}{3}. \quad (38)$$

$\underline{\tilde{\chi}}_{\rm eff}$ summarizes the effects of optical activity and short-range orientational order, which produce a $\vec{k}$ dispersion in the electric susceptibility [Eq. (38)] characterizing the spatial dispersion of electromagnetic fields in the medium. Before exploring the symmetries of $\underline{\tilde{\chi}}_{\rm eff}$, a few comments on this derivation are needed.

In the course of this development, we have had occasions to invoke the assumption that molecules *within* the Lorentz cavity $v(\vec{x})$ do not contribute to the local field, which arises entirely from regions outside a judiciously chosen cavity where microscopic variations can be overlooked as it assumes its mean value $\langle\vec{P}_0\rangle$. We have also tacitly accepted the assumption of a spherical cavity. Furthermore, the de Gennes free energy is really addressed to slow (long-wavelength) elastic distortions of the orientational order. When the coherence distance $\xi$ approaches molecular dimensions, or when $R\rightarrow0$, this characterization of the local molecular environment invites doubt. As discussed at length earlier in this section, the ultimate justification for these assumptions rests with empirical results, which strongly suggest that the local fine structure of the molecular distribution has negligible importance in the local field, either in the ordered or isotropic phase; thus contributions from $v(\vec{x})$ can be neglected.

$\underline{\tilde{\chi}}_{\rm eff}$ has some important symmetry properties. It is obvious from the definitions [Eqs. (29) and (38)] that $(\tilde{\chi}_{\rm eff})_{\mu\nu}$ is Hermitian, i.e., $[\tilde{\chi}_{\mu\nu}]^*=\tilde{\chi}_{\nu\mu}$, so that the medium is nonabsorbing. More importantly, we have

$$\tilde{\chi}^{\rm eff}_{\mu\nu}=-\tilde{\chi}^{\rm eff}_{\nu\mu}=[\tilde{\chi}^{\rm eff}_{\nu\mu}]^* \quad \text{if } \mu\neq\nu, \quad (39)$$

i.e., the off-diagonal components of $\tilde{\chi}_{\mu\nu}$ are purely imaginary. Putting it in other words, $\tilde{\chi}^{\rm eff}_{\mu\nu}$ has a skew Hermitian component. To prove this, it is only necessary to show that the chiral term in the free energy (6) couples *only real and imaginary parts of different components* of $\tilde{Q}_{\mu\nu}(\vec{q})$, for it would then follow that (if $\alpha \neq \beta$)

$$\tilde{G}_{\mu\nu}\langle \tilde{Q}^*_{\alpha\mu}\tilde{Q}_{\nu\beta}\rangle = i\tilde{G}_{\mu\nu}[\langle \tilde{Q}'_{\alpha\mu}\tilde{Q}''_{\nu\beta}\rangle - \langle \tilde{Q}''_{\alpha\mu}\tilde{Q}'_{\nu\beta}\rangle]$$

and since $\tilde{G}_{\mu\nu}(\vec{q})$ is real, it follows from definition (38) that the off-diagonal terms are skew symmetric. [That $\Gamma_{\mu\nu}$ is skew-symmetric is obvious from definition (29).] To prove the above claim, we recognize that

$$\begin{aligned} F_{\text{chiral}} &= \int (2q_0L'\underline{\mathrm{Q}} : \mathrm{curl}\underline{\mathrm{Q}})\, d^3x \\ &\sim \int d^3q\, e^{i\vec{q}\cdot\vec{x}}[2q_0L'\underline{\tilde{\mathrm{Q}}}^*(\vec{q})\cdot i\vec{q}\times\underline{\tilde{\mathrm{Q}}}(\vec{q})] \\ &\sim \int d^3q\, e^{i\vec{q}\cdot\vec{x}}\tilde{F}_{\text{chiral}}(\vec{q}), \\ \tilde{F}_{\text{chiral}}(\vec{q}) &= 2iq_0L'\epsilon_{\alpha\gamma\beta}\tilde{Q}^*_{\alpha\mu}q_\gamma\tilde{Q}_{\beta\mu}. \end{aligned} \tag{40}$$

Since $\epsilon_{\alpha\gamma\beta}=0$ if any pair of indices is equal, $\tilde{F}_{\text{chiral}}(\vec{q})$ cannot involve products of different components of $\tilde{Q}_{\mu\nu}(\vec{q})$. Secondly, for every choice of $\gamma$, there are two choices for $(\alpha, \beta)$, and $\tilde{F}_{\text{chiral}}$ becomes

$$\begin{aligned} 2iL'q_0q_\gamma(\epsilon_{\alpha\gamma\beta}\tilde{Q}^*_{\alpha\mu}\tilde{Q}_{\beta\mu} + \epsilon_{\beta\gamma\alpha}\tilde{Q}^*_{\beta\mu}\tilde{Q}_{\alpha\mu}) &= 2iL'q_0q_\gamma[\tilde{Q}^*_{\alpha\mu}\tilde{Q}_{\beta\mu} - (\tilde{Q}^*_{\alpha\mu}\tilde{Q}_{\beta\mu})^*]\epsilon_{\alpha\gamma\beta} \\ &= 4L'q_0q_\gamma\epsilon_{\alpha\beta\gamma}(\tilde{Q}'_{\alpha\mu}\tilde{Q}''_{\beta\mu} - \tilde{Q}''_{\alpha\mu}Q'_{\beta\mu}), \end{aligned} \tag{41}$$

so that $\tilde{F}_{\text{chiral}}$ couples only the real and imaginary parts of different components of $\tilde{Q}_{\mu\nu}$. Since $\tilde{F}_{\text{nem}}$ contains only terms of the form $|\tilde{Q}_{\mu\nu}|^2 = (\tilde{Q}'_{\mu\nu})^2 + (\tilde{Q}''_{\mu\nu})^2$, it is obvious that the total free energy $\tilde{F}_{\text{chol}}$ couples only real and imaginary parts of different $\tilde{Q}_{\mu\nu}$'s, so that all correlations of the form $\langle \tilde{Q}'_{\alpha\mu}\tilde{Q}'_{\beta\mu}\rangle$ and $\langle \tilde{Q}''_{\alpha\mu}\tilde{Q}''_{\beta\mu}\rangle$ are zero, proving our contention.

The last claim is also reasonable from a physical standpoint. For optical activity to occur, it is essential that different components of the induced electric moment sees the field with a different phase. Since $\tilde{Q}_{\mu\nu}(\vec{q})$ corresponds to an induced polarization wave propagating along $\vec{q}$, due to chirality it must be coupled to the *out-of-phase* component of a different component of $\underline{\tilde{\mathrm{Q}}}(\vec{q})$. This means that chiral short-range order involves the coupling of in-phase and out-of-phase components, or real and imaginary parts of different components of $\underline{\tilde{\mathrm{Q}}}$.

To complete the optical characterization of the active medium, we need to supplement (38) with a description of the magnetic properties. Fortunately $\bar{\alpha}_M \sim 10^{-6}\bar{\alpha}_E$, so that the effects of orientational order are six orders of magnitude smaller than those in the electric case and hence will be neglected. There is, however, the contribution of natural optical activity which must be included as in the Rosenthal theory:

$$\vec{\mathrm{B}} = \bar{\mu}\vec{\mathrm{H}} + i\,\frac{4\pi\bar{N}\beta}{\bar{\epsilon}}\,\frac{\bar{n}^2+2}{3}\,\bar{n}\vec{\mathrm{k}}_0\times\vec{\mathrm{H}}$$

or (42)

$$\mu_{\alpha\beta} = \bar{\mu}\delta_{\alpha\beta} + i\,\frac{\bar{n}^2+2}{3}\,\frac{\Gamma_{\alpha\beta}}{\bar{\epsilon}}\,.$$

Equations (38) and (42) provide a complete material description of the medium.

### C. Modes of propagation and optical rotatory power

The modes of propagation are found from Maxwell's equations and the constitutive relations (38) and (42):

$$\begin{aligned} &\vec{\mathrm{k}}_0\cdot\vec{\mathrm{D}} = 0, \quad n\vec{\mathrm{k}}_0\times\vec{\mathrm{E}} = k_0\vec{\mathrm{B}}, \\ &\vec{\mathrm{k}}_0\cdot\vec{\mathrm{B}} = 0, \quad n\vec{\mathrm{k}}_0\times\vec{\mathrm{H}} = -k_0\vec{\mathrm{D}} \end{aligned} \tag{43}$$

($n$ is the index of the medium). $\vec{\mathrm{D}}$ and $\vec{\mathrm{B}}$ are transverse to $\vec{\mathrm{k}}_0$, so that $D_z = B_z = 0$ allow us to express $E_z$ and $H_z$ in terms of the transverse components, thereby reducing to a two-dimensional problem:

$$\begin{aligned} &\vec{\mathrm{D}}_\perp = \underline{\epsilon}_\perp\cdot\vec{\mathrm{E}}_\perp, \quad \vec{\mathrm{B}}_\perp = \underline{\mu}_\perp\circ\vec{\mathrm{H}}_\perp, \\ &(\underline{\epsilon}_\perp)_{\alpha\beta} = \epsilon^{\text{eff}}_{\alpha\beta} - \epsilon^{\text{eff}}_{\alpha z}\epsilon^{\text{eff}}_{z\beta}/\epsilon^{\text{eff}}_{zz}, \\ &(\underline{\mu}_\perp)_{\alpha\beta} = \mu_{\alpha\beta} - \mu_{\alpha z}\mu_{z\beta}/\mu_{zz}, \end{aligned} \tag{44}$$

where

$$\begin{aligned} \epsilon^{\text{eff}}_{\alpha\beta} &= \delta_{\alpha\beta} + 4\pi\tilde{\chi}^{\text{eff}}_{\alpha\beta} \\ &= \bar{\epsilon}\delta_{\alpha\beta} + i\bar{N}\left(\frac{\bar{n}^2+2}{3}\right)\Gamma_{\alpha\beta} + \Lambda_{\alpha\beta}; \end{aligned} \tag{45}$$

more explicitly, $\epsilon^{\text{eff}}_{\alpha\beta}$ and $\mu_{\alpha\beta}$ are given by

$$\epsilon^{\text{eff}}_{\alpha\beta} = \begin{bmatrix} \bar{\epsilon}+\Lambda'_{xx} & i(q+\Lambda''_{xy}) & i\Lambda''_{xz} \\ -i(q+\Lambda''_{xy}) & \bar{\epsilon}+\Lambda'_{yy} & i\Lambda''_{yz} \\ -i\Lambda''_{xz} & -i\Lambda''_{yz} & \bar{\epsilon}+\Lambda'_{zz} \end{bmatrix}, \tag{46}$$

$$\mu_{\alpha\beta} = \begin{bmatrix} \bar{\mu} & ig/\bar{\epsilon} & 0 \\ -ig/\bar{\epsilon} & \bar{\mu} & 0 \\ 0 & 0 & \bar{\mu} \end{bmatrix}, \tag{47}$$

with $g = \bar{N}[(\bar{n}^2+2)/3]4\pi\bar{n}k_0\beta$, $\bar{\epsilon} = \bar{n}^2$. [We have also invoked the symmetries of $\Lambda_{\alpha\beta}$ in (46).] Maxwell's equations yield

$$\begin{aligned} &nH_y = D_x, \quad nE_x = B_y, \\ &nH_x = -D_y, \quad nE_y = -B_x, \end{aligned}$$

which can be solved in conjunction with (44), yielding the secular equation for the index $n$, with roots

$$n_\pm^2 \cong \bar{\mu}(\bar{\epsilon}+\Lambda'_{xx}) \pm (2g+\Lambda''_{xy}) + O(g^2,\Lambda^2)$$
$$\cong (\bar{n}^2+\Lambda'_{xx}) \pm (2g+\Lambda''_{xy}). \qquad (48)$$

This can be written in the more interesting form

$$\frac{n_\pm^2-1}{\bar{n}^2+2} = \frac{\bar{n}^2-1}{\bar{n}^2+2} + \frac{\Lambda'_{xx} \pm (2g+\Lambda''_{xy})}{\bar{n}^2+2}$$
$$= \tfrac{4}{3}\pi \bar{N}\bar{\alpha} + \frac{\Lambda'_{xx} \pm (2g+\Lambda''_{xy})}{\bar{n}^2+2}$$
$$\equiv \tfrac{4}{3}\pi \bar{N}\alpha_\pm , \qquad (49)$$

where

$$\alpha_\pm \equiv \bar{\alpha} \pm (2\bar{n}k_0\beta)$$
$$+ \frac{(\frac{2}{3}\Delta\alpha^0)^2\bar{N}}{4\pi} \int \frac{d^3q}{(2\pi)^3} \tilde{G}_{\mu\nu}(\bar{n}\vec{k}_0+\vec{q})$$
$$\times [\mathrm{Re}\langle \tilde{Q}^*_{x\mu}\tilde{Q}_{\nu x}\rangle \pm \mathrm{Im}\langle \tilde{Q}^*_{x\mu}\tilde{Q}_{\nu y}\rangle]. \qquad (50)$$

Since the average index $\bar{n}'$ now satisfies $\bar{n}'^2 \approx \frac{1}{2}(n_+^2+n_-^2) = \bar{n}^2+\Lambda_{xx} \cong \bar{n}^2$, Eq. (49) approximates the Vuks form of the Clausius-Mosotti equations (18) for a system with two principal indices $n_+$ and $n_-$, corresponding to circularly polarized modes of propagation $\vec{E}_+$ and $\vec{E}_-$, respectively:

$$\vec{E}_\pm \cong \begin{pmatrix} 1 \\ \mp i[1+O(\Lambda''_{xy})] \end{pmatrix} E_0 . \qquad (51)$$

For an electric field in either mode propagating through the medium, the effective field experienced by each molecule has the same form $\vec{F}_\pm = \frac{1}{3}(\bar{n}^2+2)\vec{E}_\pm$, which follows from (49) by comparing

$$\vec{P}_\pm = \bar{N}\alpha_\pm \vec{F}_\pm$$
$$\vec{P}_\pm \equiv \frac{\epsilon_\pm - 1}{4\pi}\vec{E}_\pm = \frac{\bar{n}^2+2}{3}\bar{N}\alpha_\pm \vec{E}_\pm$$

(where $\epsilon_\pm = n_\pm^2$).

The medium thus exhibits circular birefringence and possesses an optical rotatory power:

$$\phi = \tfrac{1}{2}k_0(n_+ - n_-) \cong \frac{k_0}{2\bar{n}}(2g+\Lambda''_{xy})$$
$$= \Big\{ 4\pi\bar{N}k_0^2\beta\frac{\bar{n}^2+2}{3} + 2\pi k_0\frac{\bar{n}^2+2}{3}$$
$$\times (\tfrac{2}{3}\bar{N}\Delta\alpha^0)^2 \mathrm{Im}[\tilde{G}_{\mu\nu}\otimes\langle \tilde{Q}^*_{x\mu}\tilde{Q}_{\nu y}\rangle]_{\bar{n}\vec{k}_0} \Big\}$$
$$= \phi_0 + \phi_c \qquad (52)$$

($\otimes$ stands for the convolution). This is the principal result of the theory, and states that the rotatory power of the isotropic phase is a sum of the molecular contribution $\phi_0$ and a term $\phi_c$ related to chiral orientational correlations in the isotropic phase. $\phi_0$ is, of course, the Rosenfeld result (24) for natural optical activity. Note that the effect $\phi_c$ depends quadratically on the anisotropy in the molecular polarizability.

Apart from the definitions (2) and (3) in which the effect of orientation is manifested by a linear

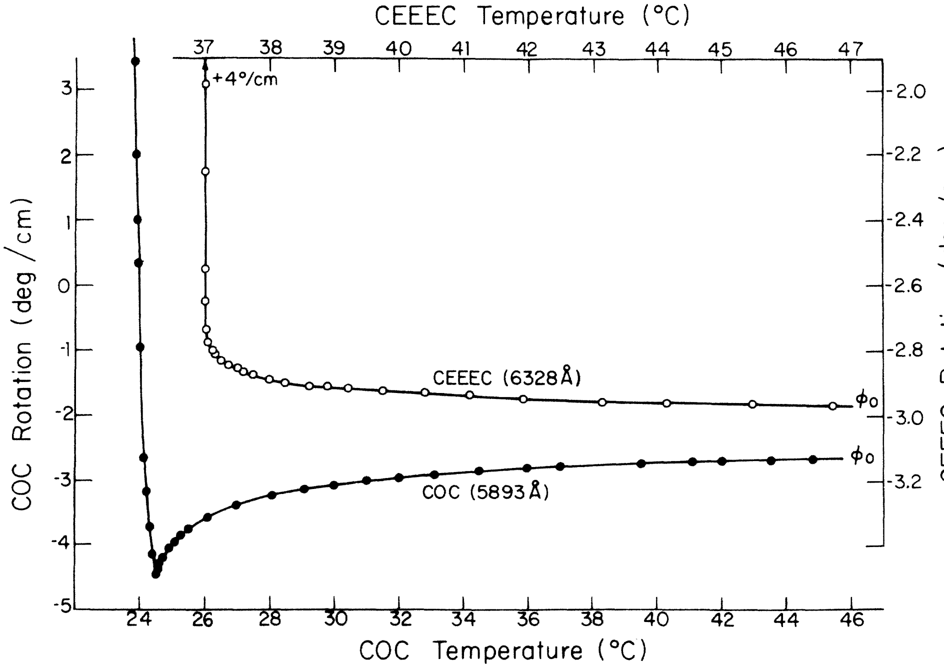


FIG. 2. Temperature dependence of optical rotatory power for two typical cholesteryl esters: right-handed CEEEC and left-handed COC.

modulation of the average local electric polarizability, the result (52) has not relied upon any specific model of orientational correlation. We will now use de Gennes's model to give (52) a quantitative result. The correlations $\langle \tilde{Q}^*_{x\mu}(\vec{q}) \times \tilde{Q}_{\nu y}(\vec{q})\rangle$ can be calculated in accordance with procedures described in Sec. II C. The transform $\tilde{G}_{\mu\nu}$ of the dipole propagator (24) is easily found to be

$$\tilde{G}_{\mu\nu}(\vec{q}) = -4\pi \frac{k_0^2\delta_{\mu\nu} - q_\mu q_\nu}{k_0^2 - q^2} . \tag{53}$$

The integration $\int d^3q$ over all fluctuations cannot be perpetrated in closed form. As an approximation, we recognize that the factor $\zeta = \bar{n}k_0\xi_1$ is of the order of 0.1 at $T_k$ and much smaller at higher temperatures. Expanding the integral in powers of $\zeta$, it is found that successive terms decrease by a factor, $\zeta^2 < 0.01$. The details are given in the Appendix, with the result

$$\phi_c \cong \tfrac{8}{105}\pi k_0^2(q_0\xi_1)(KT/L_1)(\tfrac{2}{3}\bar{N}\Delta\alpha^0)^2\left(\frac{\bar{n}^2+2}{3}\right) \times [1 + \tfrac{5}{2}(1 + L_2/L_1)^{-3/2}] + O(\zeta^3). \tag{54}$$

Thus the predicted temperature dependence is due mainly to $q_0\xi_1$. If $L_1$ and $q_0$ are assumed not to depend on temperature, then the dependence is of the form $(T - T^*)^{-1/2}$. There is, however, no *a priori* reason for these assumptions, which will be tested experimentally.

## IV. EXPERIMENT AND ANALYSIS

### A. Experimental considerations

The choice of an appropriate system to study the effect discussed in previous sections turns out to be a crucial one. For a preliminary probe of this phenomenon, we carried out a series of crude experiments using a standard Perkin-Elmer-141 polarimeter and a variety of cholesteryl esters as samples. Without belaboring the crude experimental details, we discuss some of the qualitative observations.

Figure 2 presents some representative results. An effect is indeed observed in each case, albeit a small one amidst an overwhelming background of natural optical activity $\phi_0$. If this $\phi_0$ is removed, the residual optical rotation has an intrinsic sense of chirality which varies from ester to ester, being negative for aliphatic cholesteryl esters such as cholesteryl oleyl carbonate (COC), and positive for cholesteryl chloride and CEEEC. Furthermore, the sense of the rotation reverses in some esters but not others as it enters the ordered phase. We know that the rotatory power of the ordered phase is influenced by two factors: (i) the sign of $t_0$, i.e., the sense of the helix, and (ii) whether the ratio of wavelength to optical pitch $\lambda' = \lambda_0/\bar{n}p$ is $\gtrless 1$. This is summarized by[20]

$$\phi_{\text{chol}} = (\text{const})\frac{t_0}{(1 - \lambda'^2)} . \tag{55}$$

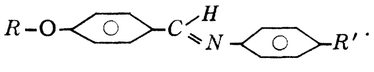
The ratio $\lambda'$ can either be measured or estimated for each sample. From the signs of $(1 - \lambda'^2)$ and of the rotation, the sign of $t_0$ can be determined and compared with the sign of the pretransitional rotatory power of the isotropic phase. Such an analysis showed complete correspondence, supporting the suggestion that the same intermolecular interactions are responsible for the chiral structure in both phases.

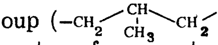
Heuristically, these observations suggest the following.

(i) The order of magnitude of $\phi_c$ is rather small for cholesteryl esters, which, with the presence of a large $\phi_0$, makes quantitative accuracy difficult. Since our theoretical result is proportional to $(\Delta\alpha^0)^2$, it seems *apropos* to measure the effect with molecules of greater anisotropy, perhaps more nematogenic molecules.

(ii) Since the rotatory powers of both phases are rooted in a common origin, it is natural to question to what extent does $\phi_c$ also depend on the "periodicity" of the short-range helical structure. It is pertinent to find a way of varying the "effective pitch" while leaving other physical parameters intact to monitor this dependence.

The dilution of cholesteric materials with nematogenic dopants will increase $\Delta\epsilon^0$ at the expense of decreasing the strength of the chiral interaction as gauged by $t_0 = 2\pi/p$, and incurring the risk of introducing mixed states due to incomplete miscibility. It is therefore better to implement the chirality on the molecular level by preparing nematogens with an optically active end group, e.g., compounds of the form



in which the radical $R'$ contains an active amyl group ( $-\mathrm{CH_2-CH(CH_3)-CH_2-CH_3}$). Such a molecule lacks a center of symmetry and is optically active. The Schiff's base structure endows it with properties comparable to those of nematics. In particular, $(\Delta\alpha^0)^2$ is hundreds of times larger than those of cholesteryl esters, so all effects related to the modulation of the dielectric tensor by orientational fluctuations will be correspondingly increased by two to three orders of magnitude. The strength of the chirality compares with that of esters, both showing a pitch in the 200 nm range in the ordered phase.

These "chiral nematic" compounds can be prepared in dextro-rotatory or racemic (50%-dextro–50%-laevo mixture) forms. They form, respectively, a one-component cholesteric and nematic compound. As a result of their chemical equivalence, both forms have identical physical and thermodynamic parameters (except for those depending on chirality). Furthermore, they are completely miscible, and their mixtures consist of uncompensated dextro and laevo molecules of the same constitution, which consequently differ from the pure dextro-compound only in chirality. The pitch of mixtures can be varied by adding varying concentrations $C$ of "dextro" molecules to the racemic solvent, according to a *linear* dependence of $t_0$ on $C$. All these properties are documented in a previous publication.[21] Thus we can produce cholesterics of arbitrary pitch, all of which are otherwise identical.

### B. Experimental details and results

The compound we studied is the "chiral nematic" system: $p$-ethoxybenzal-$p'$-($\beta$-methylbutyl) aniline, abbreviated EBMBA, chosen because it is a room-temperature cholesteric with the lowest clearing temperature (60°C). The compounds were prepared by D. Dolphin and F. Muljiani. Their purification is of a rather meticulous nature Schiff's bases are sensitive to moisture and gaseous pollutants, which must be expelled and the samples must be sealed to ensure a constant $T_k$, throughout the duration of the experiment. There are three steps in the purification: (i) large particulate matter is filtered by millipores and some gases adsorbed by charcoal, (ii) chemical impurities are removed by several low-temperature recrystallization cycles from appropriate solvents, (iii) remaining solvents and gases are removed under high vacuum ($10^{-6}$ Torr). Details of the procedure are given in (Ref. 22). Samples are sealed in cells 5 cm long and saturated by an argon environment which prevents further exposure to gases. Samples so prepared showed negligible degradation over periods of months.

The experimental setup is shown in Fig. 3. The polarimetry is based on synchronous detection of a modulated optical signal with a PAR model No. 124 lock-in amplifier. Temperature control of the samples is critical and is achieved by two independent regulating systems. A primary heater maintains the ambient environment at a few degrees below the operating temperature, which is regulated by a second heating system that controls the sample temperature. This control system utilizes the principle that thermal exchange between two reservoirs is smallest when their temperature difference is small. The temperature is stabilized to within ±0.001°C for durations far exceeding the time required for measurements.

We studied the optical rotatory power of two samples: (I) pure dextro-rotatory EBMBA, with a pitch of 218 nm, and (II) a 30.15%-dextro-69.85%-racemic mixture, with a pitch of 728 nm. These correspond to $\lambda' = \lambda_0/\bar{n}p$ of 1.80 and 0.54, respectively, so that for $\lambda_0 = 6328$ Å the signs of their optical rotatory power in the ordered phase

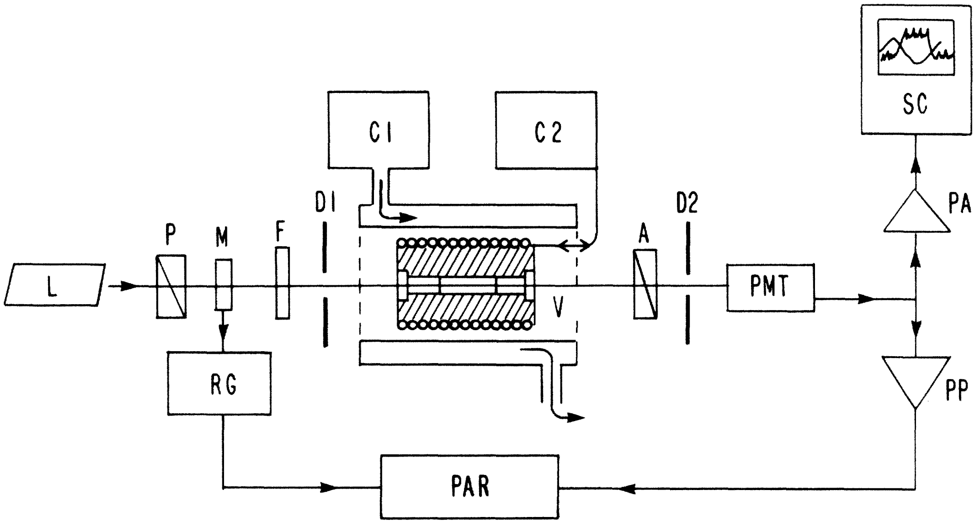


FIG. 3. Experimental arrangement for the measurement of optical rotatory power: L, helium-neon laser; P, polarizer; M, light chopper; F, filter; A, analyzer; D1 and D2, diaphrams; V, oven-cell assembly; PMT, photomultiplier; C1 and C2, proportional temperature controllers; PAR, lock-in amplifier; PP, photometric preamp; PA, preamp, SC oscilloscope; RG, reference signal generator.

differ in accordance with (62). The signs of $\phi_c$ in the isotropic phase, however, should be the same since both depend only on the chirality of $q_0$. All mixtures are homogeneous and thermotropic, with differential scanning calorimetry showing no phase separation or mixed phase formation.

Measurements are made on cooling from temperatures far into the isotropic phase, and intervals of 1 h were allowed at each temperature for the sample to thermally equilibrate prior to measurement. The clearing temperature $T_k$, as its name suggests, is determined by monitoring the transmitted light intensity. At temperatures below $T_k$ the medium is opaque to the light beam, so that $T_k$ is the temperature at which nontransmission occurs. The change is rather easily detected since the transition is first order and discontinuous. This method shows a hysteresis of 0.03°C in $T_k$ as determined on heating and cooling, possibly due to a slight supercooling of the sample. Results were reproducible, and $T_k$ is 60.57°C and 60.46°C for samples I and II, respectively. The small difference may reflect the difference in chiral energy of the samples, but is more likely to have resulted from slight differences in purity.

To account for the natural optical activity of molecules, dilute solutions of EBMBA in various solvents were prepared in known concentrations, and their optical activity were measured at several frequencies as a function of concentration. The results showed little temperature dependence. The measured activity was extrapolated to 100% concentration in each case, and the results showed little variation with concentration. Concentrations ranged from 2% to 10%, and solvents included benzene and carbon tetrachloride. The value of $\phi_0$ was 1.03°/cm in benzene and 0.98°/cm in CCl at $\lambda_0 = 6328$ Å. In view of the much larger magnitude of $\phi_c$ expected, the approximation $\phi_0 = 1.00°/\text{cm}$ should entail negligible error.

The measured optical rotatory power of the isotropic phase is shown in Fig. 4. We have scaled the rotatory power of the mixture by its concentration in active EBMBA (i.e., $\phi_c/0.3015$) and shifted its temperature scale by the difference in $T^*$ of samples I and II (as determined by procedures to be discussed). The adjusted data plot of sample II then overlaps the data of pure (100% dextro) active EBMBA, each rising more than a decade as the transition is approached and subtending a range of temperatures broader than 55°C in which signifi-

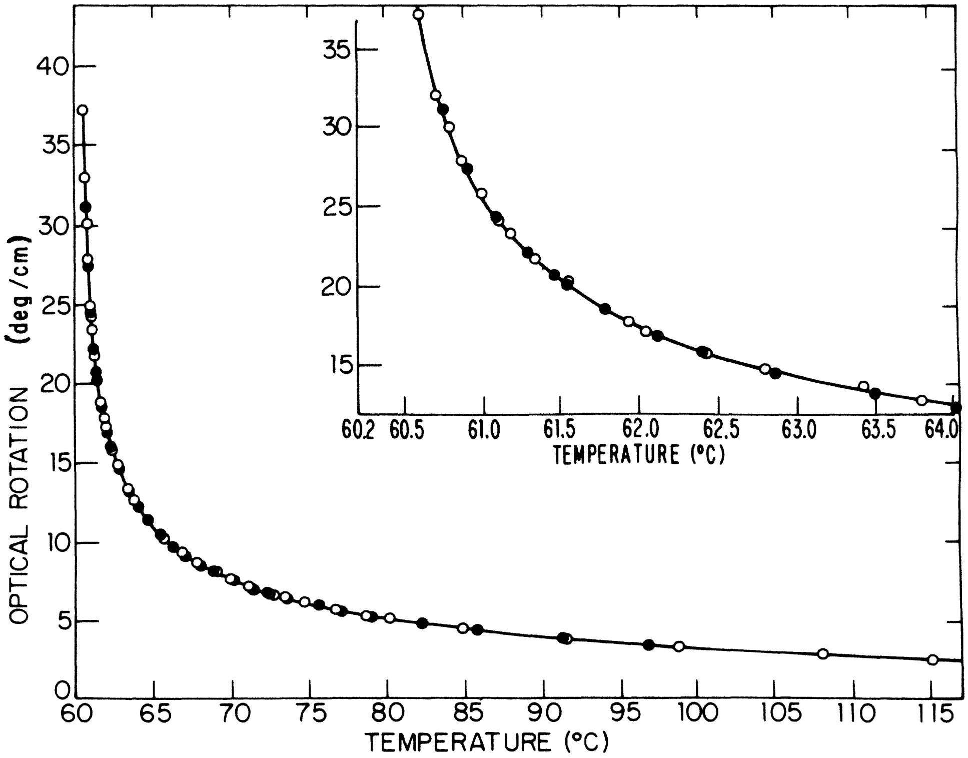


FIG. 4. Open circles: optical rotation of sample I; closed circles: sample II, as a function of temperature in the isotropic phase. Rotations of II have been divided by 0.3015 and its temperature shifted by 0.25°K. Insert gives magnified view of pretransition region ($\lambda_0 = 6328$ Å).

cant temperature dependence is exhibited.

To fit these results to the theoretical prediction (54), we assume that $L_1$ and $L_2$ are rather stable with temperature, so that the major temperature dependence is embodied by the factor $q_0\xi_1(T)$. This assumption is supported by the work of Stinson and Litster[23] on $N$-($p$-methoxybenzylidene)-$p'$-butylaniline (MBBA) (nematic) and that of Yang[5] on CEEEC (cholesteric). There is no *a priori* reason for overlooking the temperature dependence of $q_0$. In fact, the dependence of pitch on temperature in the ordered phase very much indicates the dependence of $q_0$ on the nature and extent of the orientational ordering.[22] If we do, however, assume that $q_0$ is equal to a constant, then the rotatory power is of the form

$$\phi = \phi_0 + \text{const} \times (T - T^*)^{-\gamma} KT. \qquad (56)$$

If indeed the fitted data deviates from this dependence in some temperature regime, it may serve to denote the temperature dependence of $q_0$, assuming our theory is valid. Fitting the data to (56) involves the adjustable parameters $\phi_0$, $T^*$, and $\gamma$. With the result $\phi_0 = 1.00°/\text{cm}$ measured, we can vary $T^*$ to obtain the best linear fit to a $\ln(\phi - \phi_0)$-vs-$\ln(T - T^*)$ plot, the slope of which yields $-\gamma$. It turns out that no linear slope can be obtained over the entire 55°C range measured. Since the pretransitional region is the range of interest, we insist that the best fit be one which obtains near $T_k$. With this criterion, we obtained a fit with $T^* = 60.15°\text{C}$, which gives a linear fit over a 6°C range above $T_k$ with a slope of $-0.495$ for sample I. For sample II, $T^* = 59.90°\text{C}$ and slope $= -0.498$. The fit is presented for sample I in Fig. 5. The fit appears to be quite good near $T_k$, but fails at higher temperatures. We will discuss the implications of these results and account for the deviations in Sec. IV C.

### C. Analysis and discussions

From the overlapping of the curves for samples I and II in Fig. 5, the following can be inferred: (i) The temperature dependence of the rotatory power is independent of the magnitude of the parameter $q_0$, or the "effective pitch" of the isotropic phase. (ii) The magnitude of $\phi_c$ is linearly proportional to the concentration of active EBMBA in the mixture, which in turn is proportional to the torsion $q_0$,[19] in agreement with theoretical predictions. (iii) The sense of the rotatory power depends only on the chirality of the intermolecular interactions, i.e., on the sign of $q_0$ but not its magnitude nor the ratio $\lambda' = q_0/k_0$, in marked contrast to the case of the ordered phase, in which the dispersion (62) is a result of the long-range order. (iv) The signs of $t_0$ and $q_0$ agree, which supports the notion that the rotatory power of the two phases share a common origin.

To account for the deviation of the data fit from the form (56), we propose these explanations.

(i) The assumption of a temperature independent $q_0$ is unjustified. The parameter $q_0$ is not a molecular property, but relates to the chiral interactions between molecules, which must depend on the positional and orientational distribution of the surrounding molecules, quantities which are expectably dependent on temperature. This is certainly true of $t_0$, for instance, near a cholesteric-smectic transition.[24] The deviation from (56) thus expresses a decrease in chiral coupling in a more highly randomized molecular environment. The chiral interactions derive from higher-order multipolar coupling between molecules[25] than the dipole dispersion coupling which gives rise to nematic order, and accordingly must be shorter in range. In the ordered phase, the molecular ordering is sufficiently strong to maintain its structure against the disruptive effects of thermal fluctuations; consequently $t_0$ changes little with temperature (except near a smectic phase). In the isotropic phase, the breakdown of long-range order gives thermal fluctuations greater importance in altering the molecular environment, so that the chiral coupling is decreased at higher temperature, as does $q_0$.

(ii) Each coefficient in the Landau expansion is itself expanded as a series in powers of the reduced temperature $T_r \approx (T - T^*)/T^*$. When $T_r$ is small it is adequate to approximate the coefficients by the lowest order in $T_r$. Thus we obtain $A(T) = a'(T - T^*)$, and $B$, $C$, $L_1$, $L_2$, $q_0$ are constants for small $T_r$. For large $T_r$, these approximations become doubtful. While the Landau expansion remains valid as an expansion in the order

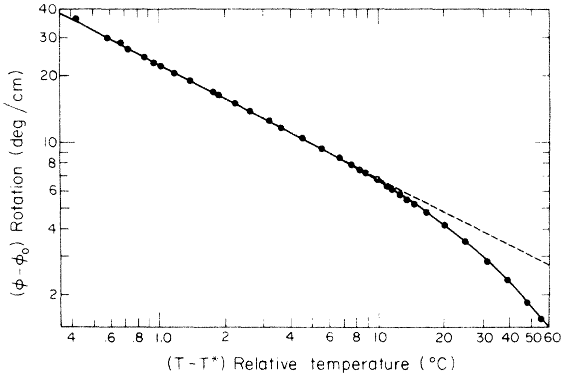


FIG. 5. $\ln(\phi - \phi_0)$ as a function of $\ln(T - T^*)$, showing a slope of $-0.50$ in the pretransition region. The sample is pure dextro-rotatory EBMBA, and $\lambda_0 = 6328$ Å.

parameter, it becomes suspect as an expansion in $T_r$. Indeed the approach may break down at sufficiently large $T_r$, and the dependence of $q_0$ on temperature is a particular exemplification of this point.

(iii) Conceptually, the de Gennes free energy is a product of symmetry considerations and as such may be viewed abstractly. As a physical description of the isotropic phase, it resembles the Frank energy in that it describes continuous long-wavelength distorsions of the order parameter from its equilibrium structure. As such it must depend on the existence of gradual deformations as well as a well-defined structure. When $\xi$ decreases to the dimension of a few molecules, variations in the orientational structure are probably more abrupt than the elastic description warrants, and the simple approximate form of the chiral energy may become inadequate at higher temperatures. This question runs in the same vein as those raised regarding the form of the local field when the coherence distance is diminished to molecular dimensions, for which speculations can only be spurious and a deeper analysis is required of the structure of the molecular environment in these circumstances.

(iv) Finally, we emphasize that EBMBA exhibits a first-order transition at $T_k$, with $T_k - T^* = 0.42\,^\circ\mathrm{C}$ and a latent heat of 0.41 cal/g. Since the transition is not of second order, it may be necessary to include the $BQ^3$ terms in the theory. This is probably not too important unless $T$ is near $T_k$.

To lend some credibility to the theoretical result, we calculate $\phi_c$ using some estimated parameters as follows:

(a) For $L_1$, we borrow Stinson's value of $0.734 \times 10^{-6}$ dyn for MBBA.[23]

(b) From measurements of the induced magnetic birefringence of EBMBA[26] by the authors, for both active and racemic samples, we have the Cotton-Mouton coefficient

$$\alpha(T) = \frac{\Delta\epsilon^0 \Delta\chi_m^0}{9\bar{n}a'}\,\frac{1}{T - T^*}. \qquad (57)$$

The measured slope of $\alpha^{-1}$ vs $T - T^*$ is $0.734 \times 10^{14}$ erg/cm$^3$ °K, and the mean index $\bar{n} = 1.559$ at $T_k$, so that $a'$ can be determined from (57) if $\Delta\chi_m^0$ and $\Delta\epsilon^0$ are known.

(c) For the magnetic anisotropy $\Delta\chi_m^0$ we again borrow the values for MBBA,[27] which is justified since it is known that the aliphatic tails of the compounds to not contribute to $\Delta\chi_m$ significantly. The measured value of $\Delta\chi_m$ at $T_k$ is $0.802 \times 10^{-7}$, so that from the Maier-Saupe theory $\Delta\chi_m^0 = \Delta\chi_m(T_k)/S_k$, where $S_k$ is the order parameter at $T_k$, a rather controversial quantity varying from sample to sample, and is 0.42 for the Maier-Saupe theory.

(d) $\Delta\alpha^0$ can be obtained in terms of $\Delta\epsilon^0$ via the Vuks-Chandraseknar relations (18), which give $\Delta\epsilon^0/(\bar{n}^2 + 2) = \frac{4}{3}\pi\bar{N}\Delta\alpha^0$. $\Delta\epsilon^0$ itself is derived from measurements of the ordinary and extraordinary indices of the racemic EBMBA sample via the relation

$$\Delta\epsilon(T) = \epsilon_e(T) - \epsilon_o(T) = 2(n_o + n_e)\Delta n(T).$$

From the Maier-Saupe theory we have

$$\Delta\epsilon^0 = \Delta\epsilon(T)/S(T) = \Delta\epsilon_k/S_k.$$

In particular, we can let $T = T_k$, at which $\Delta\epsilon_k = 0.329$. Again, the result for $\Delta\epsilon^0$ depends on the value used for $S_k$.

(e) $q_0$ is approximated by the value $t_0 = 2\pi/p$ for the ordered phase near $T_k$, i.e., $t_0 = 2.90 \times 10^5\ \mathrm{cm}^{-1}$. There is no reason to expect $p = 2\pi/t_0$ to equal $p' = 2\pi/q_0$, i.e., that the torsion $t_0$ changes continuously at the transition. There is one bit of evidence which suggests that this may be the case. We know that Bragg scattering occurs in the isotropic phase when the condition $\frac{1}{2} < 2q_0\xi_1 < 1$ is satisfied. From the measured Bragg angle $\theta_B$, the pitch $p'$ can be calculated:

$$\lambda_0 = \bar{n}p' \sin\tfrac{1}{2}\theta_B.$$

For CEEEC sample near $T_k$, Yang[5] measured $\theta_B = 33°$ for $\lambda_0 = 6328$ Å, from which $\bar{n}p' = 2.23\ \mu$m. This is in good agreement with our measurements of the pitch of the same samples in the ordered phase by Bragg scattering techniques.

(f) Estimates of $L_2$ are not available, although

TABLE I. Estimates of the optical rotatory power ($T = T^* + 1.17\,^\circ$K).

| $S_k$ | $\Delta\epsilon^0$ | $\Delta\chi_m^0$ | $a'$ (erg/°K cm$^3$) | $\phi_c$ ($L_2 = 0$) (deg/cm) | $\phi_c$ ($L_2 = L_1$) (deg/cm) |
|---|---|---|---|---|---|
| 0.30 | 1.097 | $2.67 \times 10^{-7}$ | $1.53 \times 10^{-6}$ | 12.61 | 8.51 |
| 0.33 | 0.997 | $2.43 \times 10^{-7}$ | $1.27 \times 10^{-6}$ | 11.46 | 7.73 |
| 0.36 | 0.914 | $2.23 \times 10^{-7}$ | $1.06 \times 10^{-6}$ | 10.51 | 7.09 |
| 0.39 | 0.844 | $2.06 \times 10^{-7}$ | $9.07 \times 10^{-5}$ | 9.70 | 6.54 |
| 0.42 | 0.783 | $1.91 \times 10^{-7}$ | $7.82 \times 10^{-5}$ | 9.01 | 6.08 |
| 0.45 | 0.731 | $1.78 \times 10^{-7}$ | $6.81 \times 10^{-5}$ | 8.40 | 5.67 |

Stinson[23] showed that $L_2 < 1.10 L_1$ for MBBA.

Thus, with an appropriate choice of $S_k$ we can estimate all of the parameters as outlined above. Measured values of $S_k$ can vary anywhere from 0.31 to 0.45. Instead of trying to guess the value of $S_k$, Table I presents a sampling of results obtained with different values of $S_k$ at a temperature 1.17°K above $T^*$, at which the measured value of $\phi_c = 20.75°/\text{cm}$. The results can be seen to be within a factor of 2 of the measured value, which is quite good considering that some of the parameters are either unknown or questionable.

According to de Gennes's theory, the isotropic phase becomes absolutely unstable against fluctuations if $2q_0\xi_1$ exceeds 1. This imposes an upper limit on the coherence range of the isotropic phase. Strictly speaking, the effect we have observed is nonsingular, an unimportant distinction since $T^*$ is never reached. The condition $2q_0\xi_1 < 1$ implies that $\xi_1 < 172$ Å. In the absence of measurements of $L_1$, we cannot determine how this restricts $T - T^*$. An estimate with $L_1$ from MBBA yields $(T - T^*) > 0.32°\text{K}$. The measured value of $T_k - T^*$ is 0.43°C for sample I and 0.56°C for sample II. Using the same value of $L_1$, we obtain $\xi_1(T_k) \simeq 151$ Å and $2q_0\xi_1(T_k) = 0.87$ for sample I, and $\xi_1(T_k) \simeq 131$ Å and $2q_0\xi_1 = 0.23$ for sample II. These estimates show that at $T^* + 6°\text{C}$, $\xi_1 \simeq 42$ Å, the range in which a temperature-dependence starts to appear in $q_0$ (a typical molecule is 25×5 Å).

Finally, we can obtain estimates for the parameters $B$, $C$, and $L_1$ using (13) and our measurements of $T_k - T^*$, the latent heat $H$, and an estimate of $S_k$. The last two relations of (12) imply that the proximity to $T^*$ at $T_k$ for samples I and II differ as a result of the difference in chiral energies, which differ because of their difference in the net dextro-rotatory molecule concentration $C$. Thus

$$(T_k - T^*)_{\text{II}} - (T_k - T^*)_{\text{I}} = (9L_1 t_0^2/a')(1 - C^2)$$
$$= 0.14°\text{K},$$

using $C = 0.3015$, $t_0 = 2.9 \times 10^5\ \text{cm}^{-1}$, and $a' = 7.82 \times 10^5\ \text{erg}/°\text{K cm}^3$ (for $S_k = 0.42$), and we obtain $L_1 = 1.55 \times 10^{-7}$ dyn, which is quite reasonable compared to the values of $K_{11} \simeq K_{33} = 1.84 \times 10^{-7}$ measured[28] for MBBA near $T_k$. $B$ and $C$ are then estimated to be

$$B \simeq 0.64 \times 10^7\ \text{ergs/cm}^3,$$
$$C = 2B/9S_k \cong 0.34 \times 10^7\ \text{ergs/cm}^3.$$

One must not infer too much rigor from these estimates, since the relations (12) were derived assuming that higher-order terms in order parameter $Q$ are negligible in the Landau expansion, which may be questionable at $T_k$.

## CONCLUSIONS

A theory has been proposed for the enhancement of optical rotatory power in the isotropic phase of cholesteric liquid crystals in the pretransition region. The effect is associated with the modulation of dielectric properties of the medium by short-range correlations of the orientational order. The theory predicts that the effect depends on $q_0\xi_1$, which has a $(T - T^*)^{-1/2}$ temperature dependence if the "effective pitch" $2\pi/q_0$ of the isotropic phase is independent of temperature. Experiments verified this for temperatures in the pretransition region. Deviation from the $(T - T^*)^{-1/2}$ behavior at higher temperatures is interpreted as a temperature dependence of the chiral coupling $q_0$ between molecules in the isotropic phase. Thus the theory provides a plausible explanation of this pretransitional effect. Further work on this subject might utilize samples with longer coherence lengths or a more nearly second-order transition. In conclusion, our work confirms the existence of chiral short-range order in the isotropic liquid and supports the de Gennes interpretation of the isotropic phase in cholesterics.

## ACKNOWLEDGMENTS

We thank Professor Y. R. Shen and Professor P. Pershan for valuable comments, and Professor D. Dolphin and Dr. Z. Muljiani for preparing the samples.

## APPENDIX

According to (52) and (53), $\phi_c$ is given by

$$\frac{4\pi k_0}{\bar{n}}\left(\frac{\bar{n}^2+2}{3}\right)\left(\frac{2}{3}\bar{N}\Delta\alpha^0\right)^2 \int \frac{d^3q}{(2\pi)^3} \times \left(-4\pi \frac{k_0^2\delta_{\mu\nu} - (\bar{n}\vec{\mathrm{k}}_0 + \vec{\mathrm{q}})_\mu (\bar{n}\vec{\mathrm{k}}_0 + \vec{\mathrm{q}})_\nu}{k_0^2 - (\bar{n}\vec{\mathrm{k}}_0 + \vec{\mathrm{q}})^2} \operatorname{Im}\langle \tilde{Q}^*_{x\mu}\tilde{Q}_{\nu y}\rangle\right). \tag{A1}$$

By the procedure outlined in Sec. IIC, and using the symmetries of the correlations discussed in Sec. IIIB, it is simple to show that $\operatorname{Im}\langle \tilde{Q}^*_{x\mu}\tilde{Q}_{\nu y}\rangle$, for any $\vec{\mathrm{q}}$, consists of a sum of the cross-correlation averages given by (14), i.e.,

$$f_1(\theta, \phi)\langle \tilde{Q}'_{xy}\tilde{P}''\rangle + f_2(\theta, \phi)\langle \tilde{Q}'_{xz}\tilde{Q}''_{yz}\rangle,$$

where $\theta$, $\phi$ are the Euler angles defined in Fig. 1. $\tilde{G}_{\mu\nu}(\bar{n}\vec{\mathrm{k}}_0 + \vec{\mathrm{q}})$ has a locus of singularities at $\theta = \theta_s(\vec{\mathrm{q}})$ defined by

$$(1 - \bar{n}^2)k_0^2 - q^2 - 2\bar{n}k_0 q \cos\theta_s(\vec{\mathrm{q}}) = 0. \tag{A2}$$

This is a sphere in $\vec{\mathrm{q}}$ space with radius $k_0$ and center at $\bar{n}\vec{\mathrm{k}}_0$. Clearly, $\tilde{G}_{\mu\nu}$ can only be singular if $(\bar{n} - 1)k_0 \leqslant \|\vec{\mathrm{q}}\| \leqslant (\bar{n} + 1)k_0$, with $\theta_s(q)$ given by (A2).

Let us examine the function

$$H(\mu)=\frac{1}{q'^2+2\bar{n}\zeta q'\mu+(\bar{n}^2-1)\zeta^2}=\frac{1}{2\bar{n}\zeta q'}\,\frac{1}{\mu-\mu_0(q')},$$

where $\mu=\cos\theta$, $q'=q\xi_1$, $\zeta=\bar{n}k_0\xi_1$, and where $\mu_0(q')=\cos\theta_s(q')$ makes $H(\mu)$ singular. $H(\mu)$ is nonsingular in regions I and III, in which $q'\geqslant(\bar{n}+1)\zeta$ and $q'\leqslant(\bar{n}-1)\zeta$, respectively, and is singular in region II, where $(\bar{n}-1)k_0\leqslant\|\vec{q}\|\leqslant(\bar{n}+1)k_0$. In region II, where $H(\mu)$ is singular at $\mu_0(q')$, the integration of (A1) over $\mu$ (or $\theta$) nevertheless converges, and the subsequent integration over $q'$ in the range $[(\bar{n}-1)k_0, (\bar{n}+1)k_0]$ yields a term of order $\zeta^4\lesssim10^{-4}$. The nonsingular region III yields a contribution of the same order. The contribution of region I is of order $\zeta$, so that the other terms are negligible.

In region I, where $x\approx\zeta/q'\leqslant1/(\bar{n}+1)<1$, we can expand $\tilde{G}_{\mu\nu}(\zeta+q')$, which is now nonsingular, in orders of $x$, yielding a series of the form

$$\tilde{G}_{\mu\nu}=\sum_{m=0}^{\infty}(\zeta/q')^m f_m(\theta,\phi). \qquad \text{(A3)}$$

The justification of this procedure requires that each term in (A3) contributes to a convergent integral, and that the integrated series itself converges. It is easy to show that the integrals converge. To show that the approximation converges, we note that $f_m(\theta,\phi)$ has alternating odd and even parity in $\theta$, so that successive terms are smaller by a factor, $\zeta^2<10^{-2}$, and the series converges rapidly.

The lowest-order contribution to $\phi_c$ is thus

$$\phi_c\cong\frac{8\pi}{105}k_0^2(q_0\xi_1)\frac{KT}{L_1}\left(\frac{2}{3}\bar{N}\Delta\alpha^0\right)^2\times\left(\frac{\bar{n}^2+2}{3}\right)\left[1+\frac{5}{2}\left(1+\frac{L_2}{L_1}\right)^{-3/2}\right]+O(\zeta^3).$$

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