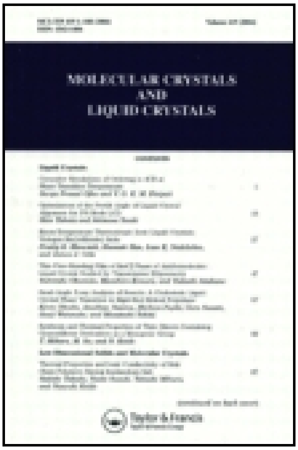

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On the Refractive Indexes of Nematic Liquid Crystal

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On the Refractive Indexes of Nematic Liquid Crystals†

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A new theory of the optical properties of a nematic liquid crystal is developed. Each molecule is assumed to be spherical, but anisotropic with respect to its electric polarisability. The local field is evaluated through a generalization of the procedure employed by one of the authors (1976) in connection with the dielectric properties of simpler liquids. The agreement between theoretical and experimental refractive indexes of MBBA is found to be higher for this theory than for previous theories developed in the framework of the Lorentz-field approximation (Vuks, Neugebauer).

1 INTRODUCTION

The description of the optical properties of a nematic liquid crystal has found two conflicting formulations in the theories due to Neugebauer[1,2] and to Vuks,[3] respectively: both these theories extend to ordered fluids the classical Lorenz–Lorentz formula for the refractive index, to which they reduce in the particular case of an isotropic liquid. Their common starting point is therefore the Lorentz-field approximation, which is known to be not fully satisfactory in describing the dielectric behaviour of a liquid: in non polar liquids, where it does not meet the Onsager's criticism[4] and is consequently applied in all the frequency range, it leads for the static case to the Clausius–Mossotti equation, whose validity has been questioned since a long time.[5] For instance,

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as shown by Mopsik,[6] this equation fails to explain the pressure dependence of the dielectric constant of such simple liquids like carbon tetrachloride and carbon disulfide. No better understanding of Mopsik data is obtained through Böttcher's formula, which is a particular case of Onsager's theory applied to non polar liquids. On the contrary, the above data find a natural explanation in the theory due to one of the authors,[7] based on a truncated Fourier-expansion of the dipole-dipole interaction. Such a theory has been also successfully extended to the static dielectric constant of polar liquids,[8] and finally to dielectric relaxation phenomena.[9] As it provides a satisfactory and unitary treatment of both the static and the dynamic properties of an isotropic liquid, it seems interesting to see how it works in the more complicated case of non-isotropic fluids.

In the optical range of frequencies, where the permanent dipoles of the molecules are out of role because they cannot follow the oscillations of the electric field, we can treat a polar liquid like a non polar one: in this way the problem is essentially reduced to the calculation of the polarisation vector **P** for a system of non polar molecules, under the effect of a macroscopic electric field **E**: once **P** is determined, the fundamental equation $\mathbf{P} = (\varepsilon - 1)\mathbf{E}/4\pi$ provides the dielectric constant tensor ε (expressed by a 3×3 matrix with diagonal elements $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_\perp$ and $\varepsilon_{zz} = \varepsilon_\parallel$) and therefore the refractive indexes through the relations $\sqrt{\varepsilon_\parallel} = n_\parallel$ $\sqrt{\varepsilon_\perp} = n_\perp$.

The theory presented in this paper is limited to the case of spherical molecules, so that the pair distribution function can be taken as spherically symmetric: each sphere, however, is assumed to be anisotropic with respect to the polarisation, in the sense that its polarisability is $\alpha_\parallel$ along a preferential axis (hereafter called the major axis of the molecule), and $\alpha_\perp$ ($<\alpha_\parallel$) along any other direction normal to it. This simple model is shown to predict the refractive indexes of MBBA in a very satisfactory way, such that the discrepancies between experimental and theoretical values are only of the order of a few parts over thousand. The theory is compared with both the Vuks' and the Neugebauer's treatments, under the same simplifying assumption of a spherical distribution of matter around a given molecule. This means that in Neugebauer's equations we put all the depolarisation factors for the Lorentz field equal to $4\pi/3$. The result for MBBA is that the agreement between theory and experiment is higher for Neugebauer's than for Vuks' equations, but even higher for our theory.

2 THEORY

Moving along the lines followed in Refs. 7 and 8, we take the origin 0 of the reference frame coincident with the position occupied by a molecule with major axis ζ_0. Let now $n_j(\mathbf{r})$ be the average number density of molecules at a distance $\mathbf{r}$ from 0 having major axis $\boldsymbol{\zeta}_j$: if $\mathbf{E}^*(\mathbf{r})$ and $\mathbf{E}_0^*$ are the average local fields acting on a molecule at $\mathbf{r}$, and on the central molecule at 0, respectively, we can write

$$\mathbf{E}^*(\mathbf{r}) = \mathbf{E} + \mathscr{D}(\mathbf{r})[\alpha^{(0)}\mathbf{E}_0^*] + \sum_j \int d^3r' n_j(\mathbf{r}')\mathscr{D}(\mathbf{r} - \mathbf{r}')[\alpha^{(j)}\mathbf{E}^*(\mathbf{r}')] \tag{1}$$

where $\mathbf{E}$ is the macroscopic electric field, $\alpha^{(j)}$ the polarisability tensor for the molecule with axis $\boldsymbol{\zeta}_j$, and $\mathscr{D}(\mathbf{r})$ is the dipole operator, defined in such a way that $\mathscr{D}(\mathbf{r} - \mathbf{r}')\boldsymbol{\mu}$ gives the electric field arising in vacuo at $\mathbf{r}$ when a dipole $\boldsymbol{\mu}$ is placed at $\mathbf{r}'$. Equation (1) has to be associated with the constraint

$$\mathbf{E}_0^* = \mathbf{E} + \sum_j \int d^3r' n_j(\mathbf{r}')\mathscr{D}(\mathbf{r}')[\alpha^{(j)}\mathbf{E}^*(\mathbf{r}')]$$

which, owing to Eq. (1) itself, can be rewritten in the form

$$\mathbf{E}_0^* = \{\mathbf{E}^*(\mathbf{r}) - \mathscr{D}(\mathbf{r})[\alpha^{(0)}\mathbf{E}_0^*]\}_{\mathbf{r}\to 0}. \tag{2}$$

At any point $\mathbf{r}$ of the liquid we assume that the dependence of $n_j(\mathbf{r})$ upon the orientation index j can be factorized, namely

$$n_j(\mathbf{r}) = f_j n(\mathbf{r}) \tag{3}$$

where f_j is independent of $\mathbf{r}$, and $n(\mathbf{r})$ stays for the total number density of molecules at $\mathbf{r}$, so that $\sum_j f_j = 1$.

The meaning of the approximation (3), which is shown to be consistent with the Maier and Saupe approximation,[10] is discussed in the Appendix.

If now $\boldsymbol{\zeta}_j$ is assumed to be an axis of rotational symmetry for the molecule, one can write

$$\alpha^{(j)}\mathbf{E}^* = \alpha_\perp \mathbf{E}^* + \Delta\alpha(\mathbf{E}^* \cdot \boldsymbol{\zeta}_j)\boldsymbol{\zeta}_j \tag{4}$$

where

$$\Delta\alpha = \alpha_\parallel - \alpha_\perp \tag{5}$$

is the difference between the principal values of the polarisability along the major axis, and any axis normal to it, respectively.

Using now the equations $\mathbf{E}^*(\mathbf{r}) = \mathbf{E} + \mathscr{E}(\mathbf{r})$ and $n(r) = n^0 + \mathscr{N}(r)$ to define the deviations $\mathscr{E}(\mathbf{r})$ and $\mathscr{N}(r)$ from the macroscopic electric field $\mathbf{E}$ and from the macroscopic number density $n^0 = N/\Omega$, respectively (both $\mathscr{E}(\mathbf{r})$ and $\mathscr{N}(r)$ being assumed to vanish for $r \to \infty$), we can now use the theory developed in Ref. 7 to rewrite Eq. (1) in the form

$$\begin{aligned}\mathscr{E}(\mathbf{r}) = {} & \mathscr{D}(\mathbf{r})[\alpha^{(0)}\mathbf{E}_0^*] + n^0 \sum_j f_j \int d^3r' \mathscr{D}(\mathbf{r} - \mathbf{r}')[\alpha^{(j)}\mathscr{E}(\mathbf{r}')] \\ & + \sum_j f_j \int d^3r' \mathscr{N}(r')\mathscr{D}(\mathbf{r} - \mathbf{r}')[\alpha^{(j)}\mathbf{E}] + \sum_j f_j \int d^3r' \mathscr{N}(r')\mathscr{D}(\mathbf{r} - \mathbf{r}')[\alpha^{(j)}\mathscr{E}(\mathbf{r}')]\end{aligned} \tag{6}$$

Equation (6) is a generalization of the relation discussed in Ref. 7 in connection with the isotropic case. Applying the method of solution adopted there, we introduce a set $\{\mathbf{q}\}$ containing a finite number Σ of vectors, whose components are integer multiples of the basic wave number $q_0 = 2\pi/L$ for the periodic cube with volume $\Omega = L^3$ where the liquid is contained. Since the representative points of the vectors are stuffed in the reciprocal space with the highest possible density, namely $\Omega/(2\pi)^3$, their maximum length Q is related to Σ by the equation

$$\tfrac{4}{3}\pi Q^3 \frac{\Omega}{(2\pi)^3} = \Sigma \tag{7}$$

Calling χ the isothermal compressibility of the liquid, and using for $\mathcal{N}(r)$ (assumed spherically symmetric) and for $\mathcal{D}(\mathbf{r})$ the representations given in Ref. 7, we get

$$\Sigma/N = \gamma = (1 - n^0 \chi \kappa_B T)^{-1} \tag{8}$$

and $\mathscr{E}(\mathbf{r}) = \sum_{\{q\}} \mathscr{E}_{\mathbf{q}} \exp i\mathbf{q}\cdot\mathbf{r}$, where the coefficients $\mathscr{E}_{\mathbf{q}}$ are seen to be related by the set of equations

$$\begin{aligned}\mathscr{E}_{\mathbf{q}} = {} & -\frac{4\pi}{\Omega}[\alpha^{(0)}\mathbf{E}_0^* \cdot \mathbf{q}]\frac{\mathbf{q}}{q^2} + \frac{4\pi n^0}{\Sigma}\sum_j f_j \frac{[\alpha^{(j)}\mathbf{E}\cdot\mathbf{q}]\mathbf{q}}{q^2} \\ & -4\pi n^0 \sum_j f_j \frac{[\alpha^{(j)}\mathscr{E}_{\mathbf{q}}\cdot\mathbf{q}]\mathbf{q}}{q^2} + \frac{4\pi n^0}{\Sigma}\sum_j f_j \sum_{\mathbf{q}'}{}^{*} [\alpha^{(j)}\mathscr{E}_{\mathbf{q}'}\cdot\mathbf{q}]\frac{\mathbf{q}}{q^2}\end{aligned} \tag{9}$$

Here the symbol $\sum_{\mathbf{q}'}^*$ means that $\mathbf{q}'$ runs over the set $\{\mathbf{q}\}$ under the constraint $|\mathbf{q} - \mathbf{q}'| \leq Q$.

In Ref. 7 it was shown that the last term on the right hand side of Eq. (9), in the isotropic case, brings a very small contribution, affecting the refractive index by only one part over thousand. The weight of this correction is smaller than the uncertainty inherent in the published data for MBBA, as one can see by comparing refractive indexes coming from different sources (see Ref. 11 and 16). Therefore the mentioned term on the right hand side of Eq. (9) will be neglected. Such an approximation, which allows a considerable simplification of the whole theory, amounts to using for the isotropic case the equation

$$n^2 - 1 = 3Z \frac{1 + 4Z}{(1 + 3Z)(1 - \gamma Z) + \gamma Z} \tag{10}$$

instead of the more complex equation given in Ref. 7.

Owing to Eq. (4), Eq. (9) then becomes

$$\begin{aligned}\mathscr{E}_{\mathbf{q}} = &-\frac{4\pi\alpha_\perp}{\Omega}\frac{(\mathbf{E}_0^*\cdot\mathbf{q})\mathbf{q}}{q^2} - 4\pi\frac{\Delta\alpha}{\Omega}(\mathbf{E}_0^*\cdot\boldsymbol{\zeta}_0)\frac{(\boldsymbol{\zeta}_0\cdot\mathbf{q})\mathbf{q}}{q^2}\\ &+\frac{4\pi n^0}{\Sigma}\alpha_\perp\frac{(\mathbf{E}\cdot\mathbf{q})\mathbf{q}}{q^2} + \frac{4\pi n^0\Delta\alpha}{\Sigma}\sum_j f_j(\mathbf{E}\cdot\boldsymbol{\zeta}_j)\frac{(\boldsymbol{\zeta}_j\cdot\mathbf{q})\mathbf{q}}{q^2}\\ &-4\pi n^0\alpha_\perp(\mathscr{E}_{\mathbf{q}}\cdot\mathbf{q})\frac{\mathbf{q}}{q^2} - 4\pi n^0\Delta\alpha\sum_j f_j\frac{(\mathscr{E}_{\mathbf{q}}\cdot\boldsymbol{\zeta}_j)(\boldsymbol{\zeta}_j\cdot\mathbf{q})\mathbf{q}}{q^2}\end{aligned} \tag{11}$$

The solution of this equation is of the form

$$\mathscr{E}_{\mathbf{q}} = (\mathbf{R}_{\mathbf{q}}\cdot\mathbf{q})\frac{\mathbf{q}}{q^2} \tag{12}$$

where the vector $\mathbf{R}_{\mathbf{q}}$ is seen to be given by

$$\mathbf{R}_{\mathbf{q}} = \frac{4\pi}{X(\mathbf{u}_{\mathbf{q}})}\left\{-\frac{\alpha_\perp}{\Omega}\mathbf{E}_0^* - \frac{\Delta\alpha}{\Omega}(\mathbf{E}_0^*\cdot\boldsymbol{\zeta}_0)\boldsymbol{\zeta}_0 + \frac{n^0}{\Sigma}\alpha_\perp\mathbf{E} + \frac{n^0\Delta\alpha}{\Sigma}\sum_j f_j(\mathbf{E}\cdot\boldsymbol{\zeta}_j)\boldsymbol{\zeta}_j\right\} \tag{13}$$

Here we have introduced the quantities $\mathbf{u}_{\mathbf{q}}$ and $X(\mathbf{u}_{\mathbf{q}})$ defined by

$$\begin{aligned}\mathbf{u}_{\mathbf{q}} &= \mathbf{q}/q\\ X(\mathbf{u}_{\mathbf{q}}) &= 1 + 4\pi n^0\alpha_\perp + 4\pi n^0\Delta\alpha\sum_j f_j(\mathbf{u}_{\mathbf{q}}\cdot\boldsymbol{\zeta}_j)^2\end{aligned} \tag{14}$$

The constraint (2) can now be written

$$\mathbf{E}_0^* = \mathbf{E} + \sum_{\mathbf{q}}\mathscr{E}_{\mathbf{q}} + \frac{4\pi}{\Omega}\alpha_\perp\sum_{\mathbf{q}}(\mathbf{E}_0^*\cdot\mathbf{q})\frac{\mathbf{q}}{q^2} + \frac{4\pi\Delta\alpha}{\Omega}(\mathbf{E}_0^*\cdot\boldsymbol{\zeta}_0)\sum_{\mathbf{q}}(\boldsymbol{\zeta}_0\cdot\mathbf{q})\frac{\mathbf{q}}{q^2} \tag{15}$$

or also, owing to Eqs. (12) and (13)

$$\begin{aligned}\mathbf{E}_0^* = \mathbf{E} &+ \frac{4\pi}{3}n^0\gamma\alpha_\perp\mathbf{E}_0^* + \frac{4\pi}{3}n^0\Delta\alpha\gamma(\mathbf{E}_0^*\cdot\boldsymbol{\zeta}_0)\boldsymbol{\zeta}_0\\ &+\frac{4\pi n^0}{\Sigma}\sum_{\mathbf{q}}\left\{-\gamma\alpha_\perp\mathbf{E}_0^* - \gamma\Delta\alpha(\mathbf{E}_0^*\cdot\boldsymbol{\zeta}_0)\boldsymbol{\zeta}_0 + \alpha_\perp\mathbf{E} + \Delta\alpha\sum_j f_j(\mathbf{E}\cdot\boldsymbol{\zeta}_j)\boldsymbol{\zeta}_j\right\}\cdot\mathbf{q}\\ &\times\frac{\mathbf{q}}{q^2X(\mathbf{u}_{\mathbf{q}})}\end{aligned} \tag{16}$$

In accomplishing the step from (15) to (16) use has been made of the formula

$$\sum_{\mathbf{q}}\frac{\mathbf{A}\cdot\mathbf{q}}{q^2}\mathbf{q} = \tfrac{1}{3}\Sigma\mathbf{A}$$

which is a direct consequence of the isotropic distribution of the **q**-vectors in the reciprocal space (see Ref. 7). Equation (16) is the fundamental relation defining the local field $\mathbf{E}_0^*$ on the reference molecule.

3 SOLUTION OF EQUATION (16)

The first step to solve Eq. (16) concerns the explicit evaluation of the sums over j entering Eqs. (14) and (16). One has

$$\sum_j f_j(\mathbf{u_q}\cdot\boldsymbol{\zeta}_j)^2 = \sin^2(\mathbf{u_q},\boldsymbol{\kappa})\sum_j \sin^2\theta_j\cos^2\varphi_j f_j + \cos^2(\mathbf{u_q},\boldsymbol{\kappa})\sum_j \cos^2\theta_j f_j$$
$$+ 2\sin(\mathbf{u_q},\boldsymbol{\kappa})\cos(\mathbf{u_q},\boldsymbol{\kappa})\sum_j \sin\theta_j\cos\theta_j\cos\varphi_j f_j$$

where $\boldsymbol{\kappa}$ is a unit vector along the director, and θ_j, φ_j are polar angles used to specify the orientation of $\boldsymbol{\zeta}_j$. Since f_j is assumed to be independent of φ_j, one has finally

$$\sum_j f_j(\mathbf{u_q}\cdot\boldsymbol{\zeta}_j)^2 = \tfrac{1}{2}\sin^2(\mathbf{u_q},\boldsymbol{\kappa})[1 - \langle\cos^2\Theta\rangle] + \cos^2(\mathbf{u_q},\boldsymbol{\kappa})\langle\cos^2\Theta\rangle \quad (17)$$

where $\langle\cos^2\Theta\rangle = \sum_j f_j\cos^2\theta_j$ is related to the order parameter S by the equation

$$S = \frac{3\langle\cos^2\Theta\rangle - 1}{2} \quad (18)$$

As to the sum over j required by Eq. (16), it is easy to verify that

$$\sum_j f_j(\mathbf{E}\cdot\boldsymbol{\zeta}_j)\boldsymbol{\zeta}_j = \tfrac{1}{2}[1 - \langle\cos^2\Theta\rangle]E_x\mathbf{i} + \langle\cos^2\Theta\rangle E_z\boldsymbol{\kappa} \quad (19)$$

where E_x and E_z are the components of the macroscopic field **E** normal and parallel to the director, respectively.

We are now in a position to evaluate a sum of the form

$$\frac{1}{\Sigma}\sum_{\mathbf{q}}\frac{(\mathbf{A}\cdot\mathbf{q})\mathbf{q}}{q^2X(\mathbf{u_q})}$$

as required by Eq. (16). Owing to Eq. (7), the sum under study can be transformed into the following integral over the sphere of radius Q:

$$\frac{1}{\Sigma}\frac{\Omega}{(2\pi)^3}\int_0^Q q^2dq\int_0^\pi \sin\theta\,d\theta\int_0^{2\pi}d\varphi$$
$$\times\frac{A_x\sin^2\theta\cos^2\varphi\mathbf{i} + A_y\sin^2\theta\sin^2\varphi\mathbf{j} + A_z\cos^2\theta\boldsymbol{\kappa}}{1 + 4\pi n^0\alpha_\perp + 4\pi n^0\Delta\alpha[\frac{1}{2}\sin^2\theta(1 - \langle\cos^2\Theta\rangle) + \cos^2\theta\langle\cos^2\Theta\rangle]}$$

where A_x, A_y, A_z are the components of $\mathbf{A}$ with respect to the reference frame used for Eq. (19), with the x-axis lying normally to the director $\boldsymbol{\kappa}$ in the plane formed by $\boldsymbol{\kappa}$ and $\mathbf{E}$. We easily get

$$\frac{1}{\Sigma}\sum_{\mathbf{q}}\frac{(\mathbf{A}\cdot\mathbf{q})\mathbf{q}}{q^2X(\mathbf{u_q})} = C_\perp(A_x\mathbf{i} + A_y\mathbf{j}) + C_\parallel A_z\boldsymbol{\kappa} \tag{20}$$

where

$$\begin{aligned} C_\parallel &= \int_0^1 dx\,\frac{x^2}{1+3z-u+3ux^2} \\ &= \frac{1}{3u}\left[1 - \sqrt{\frac{1+3z-u}{3u}}\,tg^{-1}\sqrt{\frac{3u}{1+3z-u}}\right] \\ C_\perp &= \frac{1}{2}\int_0^1 dx\,\frac{1-x^2}{1+3z-u+3ux^2} \\ &= \frac{1}{6u}\sqrt{\frac{3u}{1+3z-u}}\,tg^{-1}\sqrt{\frac{3u}{1+3z-u}} - \frac{1}{2}C_\parallel \end{aligned} \tag{21}$$

having defined the dimensionless parameters

$$Z = \tfrac{4}{3}\pi n^0\bar{\alpha} = \tfrac{4}{3}\pi n^0\,\frac{2\alpha_\perp + \alpha_\parallel}{3} \tag{22}$$

$$u = \tfrac{4}{3}\pi n^0 S\Delta\alpha \tag{23}$$

Now going back to Eq. (16), we can rewrite it in the form

$$\begin{aligned} E_{0x}^* &= E_x + 4\pi n^0 C_\perp\left\{-\gamma m_{0x} + \alpha_\perp E_x + \Delta\alpha\,\frac{1-\langle\cos^2\Theta\rangle}{2}E_x\right\} + \tfrac{4}{3}\pi n^0\gamma m_{0x} \\ E_{0y}^* &= -4\pi n^0\gamma[C_\perp - \tfrac{1}{3}]m_{0y} \\ E_{0z}^* &= E_z + 4\pi n^0 C_\parallel\{-\gamma m_{0z} + \alpha_\perp E_z + \Delta\alpha\langle\cos^2\Theta\rangle E_z\} + \tfrac{4}{3}\pi n^0\gamma m_{0z} \end{aligned} \tag{24}$$

where m_{0x}, m_{0y}, m_{0z} are the components of the dipole moment induced on the reference molecule, namely

$$\mathbf{m}_0 = \alpha_\perp\mathbf{E}_0^* + \Delta\alpha(\mathbf{E}_0^*\cdot\boldsymbol{\zeta}_0)\boldsymbol{\zeta}_0 \tag{25}$$

Eq. (25) is equivalent to the system

$$m_{0x} = \alpha_\perp E_{0x}^* + \Delta\alpha(E_{0x}^*\zeta_{0x} + E_{0y}^*\zeta_{0y} + E_{0z}^*\zeta_{0z})\zeta_{0x},\ \text{etc.} \tag{26}$$

which in principle can be solved with respect to E_{0x}^*, E_{0y}^* and E_{0z}^*. Substituting the resulting solutions (expressed as linear combinations of m_{0x}, m_{0y}, m_{0z}) into the left hand sides of Eqs. (24), we finally obtain a system of three linear equations connecting the components m_{0x}, m_{0y}, m_{0z} of the vector $\mathbf{m}_0$ to the components E_x, E_z of the macroscopic electric field $\mathbf{E}$. The matrix $\mathcal{O}_0$ connecting

$\mathbf{m}_0$ to $\mathbf{E}$, i.e. $\mathbf{m}_0 = \mathscr{O}_0\mathbf{E}$, turns out to be a very complicated function of the polar angles θ_0, φ_0 specifying the orientation of $\boldsymbol{\zeta}_0$, namely $\zeta_{0x} = \sin\theta_0 \cos\varphi_0$, $\zeta_{0y} = \sin\theta_0 \sin\varphi_0$, $\zeta_{0z} = \cos\theta_0$. At this point the evaluation of the average dipole moment $\langle\mathbf{m}_0\rangle$ requires an average over all the orientations $\boldsymbol{\zeta}_0$ taken by a reference molecule, i.e. $\langle\mathbf{m}_0\rangle = \sum_0 \mathbf{m}_0 f_0 = \sum_0 f_0 \mathscr{O}_0 \mathbf{E}$. Owing to the non-linear dependence of $\mathscr{O}_0$ upon $\cos^2\theta_0$, the average matrix $\langle\mathscr{O}_0\rangle = \sum_0 f_0 \mathscr{O}_0$ cannot be expressed in terms of the quantity $\sum_0 f_0 \cos^2\theta_0 = (2S + 1)/3$ alone, but involves all the higher order moments of the angular distribution ($\langle\cos^4\Theta\rangle$, etc....). Ultimately, this procedure leads to expressing the refractive indexes of a liquid crystal in terms of an infinite set of order parameters, each of them being related to a particular multipole averaged over the angular distribution of the molecular axes.

In the present paper, we will carry out the calculation in the lowest degree of approximation of the theory, i.e. when only the quadrupole term $\langle\cos^2\Theta\rangle$ is called into play. The reason for this choice is not only a matter of simplicity, but derives primarily from the need of comparing our theoretical predictions with those of the classical theory, which is worked out in the same degree of approximation.[1-3] Moreover, the remarkable agreement between theory and experiment (see below, Sect. 4) will justify, a posteriori, the legitimacy of our simplified description.

To this purpose we can directly average over $\boldsymbol{\zeta}_0$ the system (24), obtaining in this way a tensor relation connecting $\langle\mathbf{E}_0^*\rangle$ to $\langle\mathbf{m}_0\rangle$ via the desired quadrupole term $\langle\cos^2\Theta\rangle$. Therefore, the requirement of a theory expressing $\langle\mathbf{m}_0\rangle$ only in terms of $\langle\cos^2\Theta\rangle$ is equivalent to assessing that also the remaining equation (25) can be averaged in such a way to provide an independent relation between $\langle\mathbf{m}_0\rangle$, $\langle\mathbf{E}_0^*\rangle$ and $\langle\cos^2\Theta\rangle$. Of course, this cannot be true, unless we introduce the approximation $\langle(\mathbf{E}_0^* \cdot \boldsymbol{\zeta}_0)\boldsymbol{\zeta}_0\rangle \simeq \langle[\langle\mathbf{E}_0^*\rangle \cdot \boldsymbol{\zeta}_0]\boldsymbol{\zeta}_0\rangle$. In fact in this case we get from (25)

$$\langle\mathbf{m}_0\rangle = \alpha_\perp\langle\mathbf{E}_0^*\rangle + \Delta\alpha\left\{\frac{1 - \langle\cos^2\Theta\rangle}{2}\langle E_{0x}^*\rangle\mathbf{i} + \langle\cos^2\Theta\rangle\langle E_{0z}^*\rangle\boldsymbol{\kappa}\right\} \tag{27}$$

or also

$$\begin{aligned}
\langle E_{0x}^*\rangle &= \frac{\langle m_{0x}\rangle}{\alpha_\perp + \Delta\alpha\dfrac{1 - \langle\cos^2\Theta\rangle}{2}} \\
\langle E_{0y}^*\rangle &= \frac{1}{\alpha_\perp}\langle m_{0y}\rangle \\
\langle E_{0z}^*\rangle &= \frac{\langle m_{0z}\rangle}{\alpha_\perp + \Delta\alpha\langle\cos^2\Theta\rangle}
\end{aligned} \tag{28}$$

By equating the right hand sides of Eqs. (28) and (24) (the latter also averaged over ζ_0), one gets the final equations expressing $\langle m_{0x}\rangle$ and $\langle m_{0z}\rangle$ in terms of E_x and E_z, respectively. The result is

$$\langle m_{0x}\rangle = \left[\alpha_\perp + \Delta\alpha\frac{1-\langle\cos^2\Theta\rangle}{2}\right] \times \frac{1+4\pi n^0 C_\perp\left[\alpha_\perp + \Delta\alpha\dfrac{1-\langle\cos^2\Theta\rangle}{2}\right]}{1+4\pi\gamma n^0(C_\perp - \frac{1}{3})\left[\alpha_\perp + \dfrac{\Delta\alpha}{2}(1-\langle\cos^2\Theta\rangle)\right]}E_x \tag{29}$$

$$\langle m_{0y}\rangle = 0$$

$$\langle m_{0z}\rangle = [\alpha_\perp + \Delta\alpha\langle\cos^2\Theta\rangle]\frac{1+4\pi n^0 C_\parallel[\alpha_\perp + \Delta\alpha\langle\cos^2\Theta\rangle]}{1+4\pi\gamma n^0(C_\parallel - \frac{1}{3})[\alpha_\perp + \Delta\alpha\langle\cos^2\Theta\rangle]}E_z$$

The dielectric constant tensor ε is now obtained by the relation $n^0\langle\mathbf{m}_0\rangle = (\varepsilon - 1)\mathbf{E}/4\pi$, and is obviously represented by a diagonal matrix with $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_\perp$, $\varepsilon_{zz} = \varepsilon_\parallel$. The corresponding refractive indexes for ordinary and extraordinary rays are given by $n_\perp^2 = \varepsilon_\perp$, and $n_\parallel^2 = \varepsilon_\parallel$, respectively. One obtains in this way the final equations

$$n_\perp^2 - 1 = (3z - u)\frac{1 + C_\perp(u,z)[3z-u]}{1+\gamma[C_\perp(u,z) - \frac{1}{3}][3z-u]} \tag{30'}$$

$$n_\parallel^2 - 1 = (3z + 2u)\frac{1 + C_\parallel(u,z)[3z+2u]}{1+\gamma[C_\parallel(u,z) - \frac{1}{3}][3z+2u]} \tag{30''}$$

4 COMPARISON WITH EXPERIMENT

a) *Brunet Germain's* (*B.G.*) *data*—Eqs. (30′) and (30″) will be used to discuss the refractive indexes of MBBA in its nematic range. Experimental data for this liquid are available from 22°C up to 43°C[11] at the following wavelengths: 4678 Å, 4800 Å, 5086 Å, 5890 Å, and 6438 Å.

It has to be pointed out that the parameter z is automatically fixed through the knowledge of the refractive index n_{iso} of the isotropic phase, at a given temperature. In fact in this way Eq. (10) provides the corresponding isotropic value z_{iso} which, inserted into the relation $z(T) = z_{\text{iso}}\rho(T)/\rho_{\text{iso}}$, allows to determine z at any desired temperature, when the corresponding density is known.† For MBBA, according to the data of Press and Arrott,[12] we take

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† Such a relation follows from Eq. (24) when $\bar{\alpha}$ is assumed to be temperature-independent.

$\rho_{\mathrm{iso}}\,(45^\circ\mathrm{C}) = 1.0263\ \mathrm{g/cm^3}$, and

$$\rho(T) = 1.049[1 - 8.5 \times 10^{-4}(t - 22)]\ \mathrm{g/cm^3} \quad (t \text{ in } {}^\circ\mathrm{C})$$

The lack of compressibility data in the literature can be approximately overcome by using for χ in Eq. (8) a representative value resulting from measurements of sound velocities ($\chi \sim 1/[\rho v^2]$). This amounts to confusing the isothermal with the adiabatic compressibility: the error is certainly negligible as the dependence of γ upon χ is very weak. Using for the sound velocity at $t = 22^\circ\mathrm{C}$ ($\gamma = 2$ MHz) the value 1.54×10^5 cm/s,[13] and for the molecular weight of MBBA $M = 267$, we find in this way

$$\gamma \simeq 1.0044$$

Once z and γ are known, Eqs. (30′) and (30″) express $n_\parallel$ and $n_\perp$ in terms of the parameter u, defined by Eq. (23). In principle, this means that we could predict both the ordinary and the extraordinary index of refraction if we had at our disposal a reliable value of $\Delta\alpha$. However, this is not the case at all, and we must check the theory in some other way. For instance, by eliminating u between (30′) and (30″), we can predict for any experimental value of $n_\perp$ the corresponding value of $n_\parallel$, and compare it directly with the experiment. Alternatively, we can determine, at a given temperature, the value of u for which the theory reproduces exactly the experimental value of $\Delta n = n_\parallel - n_\perp$: in this case both the theoretical values $n_\parallel(u)$ and $n_\perp(u)$ are comparable with those deduced experimentally. This latter procedure seems more significant than the former, because it emphasizes the role of the birefringence Δn, which is the most characteristic parameter of the nematic phase. Therefore it will be used here to test the three competing theories, i.e. the present one and those developed

TABLE I

$\lambda = 4678$ Å; $(Z_{22^\circ\mathrm{C}})$ Present $= 0.396936$; $(Z_{22^\circ\mathrm{C}})$ Neugebauer $= (Z_{22^\circ\mathrm{C}})$ Vuks $=$ 0.375075 (B.G. data)

		Present		Neugebauer		Vuks	
t (°C)	$(\Delta n)_{BG}$	u	$n_\parallel$	u	$n_\parallel$	u	$n_\parallel$
22	0.268	0.1338	1.854	0.1123	1.858	0.1848	1.875
25	0.262	0.1310	1.848	0.1100	1.852	0.1808	1.868
28	0.252	0.1262	1.839	0.1062	1.843	0.1742	1.859
31	0.240	0.1205	1.829	0.1015	1.832	0.1659	1.847
34	0.228	0.1147	1.819	0.0968	1.821	0.1577	1.836
37	0.212	0.1069	1.806	0.0904	1.808	0.1468	1.822
39	0.200	0.1011	1.796	0.0855	1.798	0.1386	1.812
41	0.181	0.0917	1.782	0.0777	1.783	0.1256	1.796
43	0.158	0.0803	1.765	0.0681	1.766	0.1097	1.777

by Vuks and by Neugebauer in the classical framework of the Lorentz field approximation.

The theoretical indexes $n_{\parallel}$ listed in Tables I to V have been determined so as to render the differences $n_{\parallel}(u) - n_{\perp}(u)$ equal to the corresponding experimental values $(\Delta n)_{BG}$ deducible from Ref. 11. The above tables list also the values of u for which the equality $(\Delta n)_{\text{theor}} = (\Delta n)_{\text{exp}}$ is found (these values are given with four significant figures, in the same way as the experimental refractive indexes of Ref. 11). For the theories of Vuks and of Neugebauer we have used the equations, written in terms of our dimensionless parameters u and z:

$$\begin{aligned}
&\frac{n_{\parallel}^2 - 1}{n_{\parallel}^2 + n_{\perp}^2 + 4} = \tfrac{1}{2}[z + \tfrac{2}{3}u] \\
&\frac{n_{\perp}^2 - 1}{n_{\parallel}^2 + n_{\perp}^2 + 4} = \tfrac{1}{2}[z - \tfrac{1}{3}u] \qquad \text{(Vuks)} \qquad (31) \\
&\frac{n_{\text{iso}}^2 - 1}{n_{\text{iso}}^2 + 2} = z_{\text{iso}}
\end{aligned}$$

and

$$\begin{aligned}
&n_{\parallel}^2 - 1 = \frac{2u + 3z}{1 - z - \frac{2}{3}u} \\
&n_{\perp}^2 - 1 = \frac{3z - u}{1 - z + \frac{1}{3}u} \qquad \text{(Neugebauer)} \qquad (32) \\
&\frac{n_{\text{iso}}^2 - 1}{n_{\text{iso}}^2 + 2} = z_{\text{iso}}
\end{aligned}$$

respectively.

TABLE II

$\lambda = 4800$ Å; $(Z_{22°C})$ Present = 0.392262; $(Z_{22°C})$ Neugebauer = $(Z_{22°C})$ Vuks = 0.370993 (B.G. data)

		Present		Neugebauer		Vuks	
t (°C)	$(\Delta n)_{BG}$	u	$n_{\parallel}$	u	$n_{\parallel}$	u	$n_{\parallel}$
22	0.261	0.1310	1.840	0.1103	1.844	0.1803	1.860
25	0.255	0.1282	1.834	0.1080	1.838	0.1762	1.853
28	0.245	0.1234	1.825	0.1041	1.828	0.1694	1.844
31	0.235	0.1186	1.816	0.1002	1.819	0.1626	1.834
34	0.223	0.1128	1.806	0.0954	1.809	0.1545	1.823
37	0.208	0.1055	1.794	0.0894	1.796	0.1442	1.810
39	0.195	0.0991	1.783	0.0841	1.785	0.1353	1.799
41	0.178	0.0906	1.770	0.0770	1.772	0.1236	1.785
43	0.154	0.0786	1.753	0.0669	1.754	0.1071	1.765

TABLE III

$\lambda = 5086$ Å; $(Z_{22°C})$ Present = 0.384945; $(Z_{22°C})$ Neugebauer = $(Z_{22°C})$ Vuks = 0.364586 (B.G. data)

		Present		Neugebauer		Vuks	
t (°C)	$(\Delta n)_{BG}$	u	$n_\parallel$	u	$n_\parallel$	u	$n_\parallel$
22	0.245	0.1241	1.815	0.1050	1.818	0.1696	1.833
25	0.239	0.1213	1.809	0.1027	1.812	0.1656	1.827
28	0.230	0.1169	1.800	0.0991	1.803	0.1594	1.818
31	0.220	0.1121	1.792	0.0951	1.794	0.1526	1.808
34	0.208	0.1062	1.781	0.0902	1.784	0.1444	1.797
37	0.194	0.0992	1.770	0.0845	1.772	0.1348	1.785
39	0.182	0.0933	1.760	0.0795	1.762	0.1265	1.774
41	0.166	0.0852	1.748	0.0728	1.750	0.1155	1.761
43	0.144	0.0741	1.732	0.0634	1.733	0.1003	1.743

Table VI shows, for each wavelength, the relative deviations

$$\frac{\delta n_\parallel}{n_\parallel} = \frac{n_\parallel(u) - (n_\parallel)_{\text{exp}}}{(n_\parallel)_{\text{exp}}}, \qquad \frac{\delta n_\perp}{n_\perp} = \frac{n_\perp(u) - (n_\perp)_{\text{exp}}}{(n_\perp)_{\text{exp}}}$$

which represent the most significant parameters to describe the agreement between theory and experiment. As seen by inspection of the table, this agreement is systematically higher for our theory: it is especially pronounced at long wavelengths, where the error affecting our theoretical predictions, not too far from the clearing point, is of the order of magnitude of the uncertainty affecting the experimental data.

Since $\Delta\alpha$ and S enter the theory only through their product $S\Delta\alpha$ (see Eq. (23)), it is obviously not possible to deduce both the parameters from a set of

TABLE IV

$\lambda = 5890$ Å: $(Z_{22°C})$ Present = 0.373860; $(Z_{22°C})$ Neugebauer = $(Z_{22°C})$ Vuks = 0.354841 (B.G. data)

		Present		Neugebauer		Vuks	
t (°C)	$(\Delta n)_{BG}$	u	$n_\parallel$	u	$n_\parallel$	u	$n_\parallel$
22	0.220	0.1130	1.776	0.0963	1.779	0.1529	1.792
25	0.215	0.1106	1.770	0.0943	1.773	0.1495	1.786
28	0.207	0.1067	1.763	0.0911	1.766	0.1440	1.778
31	0.198	0.1022	1.755	0.0874	1.757	0.1378	1.770
34	0.187	0.0967	1.746	0.0828	1.748	0.1302	1.759
37	0.173	0.0897	1.734	0.0769	1.736	0.1206	1.747
39	0.162	0.0841	1.725	0.0722	1.727	0.1130	1.738
41	0.148	0.0770	1.715	0.0661	1.716	0.1033	1.726
43	0.126	0.0657	1.698	0.0566	1.699	0.0880	1.708

TABLE V

$\lambda = 6438$ Å; $(Z_{22°C})$ Present = 0.369603; $(Z_{22°C})$ Neugebauer = $(Z_{22°C})$ Vuks = 0.350615 (B.G. data)

		Present		Neugebauer		Vuks	
t (°C)	$(\Delta n)_{BG}$	u	$n_{\parallel}$	u	$n_{\parallel}$	u	$n_{\parallel}$
22	0.210	0.1084	1.761	0.0927	1.762	0.1461	1.775
25	0.205	0.1060	1.755	0.0907	1.757	0.1427	1.769
28	0.197	0.1020	1.748	0.0874	1.749	0.1372	1.761
31	0.189	0.0981	1.741	0.0841	1.742	0.1317	1.753
34	0.179	0.0930	1.732	0.0799	1.733	0.1248	1.744
37	0.166	0.0865	1.721	0.0744	1.722	0.1158	1.732
39	0.156	0.0814	1.713	0.0698	1.713	0.1089	1.724
41	0.143	0.0747	1.703	0.0644	1.703	0.0999	1.713
43	0.123	0.0644	1.688	0.0556	1.688	0.0860	1.697

optical measurements. Instead, it is possible to predict the temperature dependence of the order parameter S, if $\Delta\alpha$ is assumed, as usual, to be temperature independent. In this case the ratio $u/z = S(\Delta\alpha/\alpha)$, normalized to unity at $t = 22$°C, can be directly compared with the experimental curve $S(t)/S(22°\mathrm{C})$ as deducible from N.M.R. data.

The values of $f(t) = (u/z)_t/(u/z)_{22°\mathrm{C}}$, averaged for each temperature over the five different wavelengths, are shown for the three theories in Table VII, with the corresponding root mean square deviations σ affecting the results of the averages. As seen by inspection of the table, the results of the three theories are substantially undistinguishable. The conclusion is that we cannot choose between the competing formulae (30), (31) and (32) only on the basis of order parameter data: all the theories give essentially the same answer, in good agreement with the experimental N.M.R. curve of $f(t)$ (the reliability of Vuks equations in interpreting the temperature dependence of S is well known, see for instance Ref. 14). However, the circumstance that the values of σ are of the order of the approximation by which our theory predicts also the refractive indexes plays obviously in favour of its internal consistence. In spite of the simple model treating the molecules as spherical particles, we can say that our description of the optical properties of a nematic liquid crystal is fully reliable within some parts over thousand.

The identity of the answers in the particular case of the function $f(t)$ does not mean that a similar result has be to expected for any other information deducible from the three theories. The most relevant difference concerns the ratio $\Delta\alpha/\alpha$, describing the anisotropy of the molecular polarisability. Although the wavelength dependence of this ratio, as described by the function

$$\varphi(\lambda) = \left(\frac{\Delta\alpha}{\alpha}\right)_{\lambda} \bigg/ \left(\frac{\Delta\alpha}{\alpha}\right)_{4678\,\text{Å}} = \left(\frac{u}{z}\right)_{\lambda} \bigg/ \left(\frac{u}{z}\right)_{4678\,\text{Å}}$$

TABLE VI

Relative errors $\delta n_{\parallel}/n_{\parallel}$ and $\delta n_{\perp}/n_{\perp}$, showing the discrepancies between theoretical and experimental refractive indexes for B.G. data.

		22	25	28	31	34	37	39	41	43	°C / Å
Present	$\frac{\delta n_{\parallel}}{n_{\parallel}} \times 10^3$	6.0	6.0	5.5	5.5	5.5	5.0	4.5	4.5	2.8	4678
		4.9	4.9	4.4	3.9	3.9	3.4	2.8	2.3	1.7	4800
		3.9	3.9	3.3	3.4	2.3	2.3	1.7	1.1	1.2	5086
		4.0	3.4	3.4	3.4	3.5	2.3	1.7	1.8	1.2	5890
		4.0	3.4	3.4	3.5	2.9	2.3	1.7	1.2	0.6	6438
	$\frac{\delta n_{\perp}}{n_{\perp}} \times 10^3$	7.0	7.0	6.3	6.3	6.3	5.7	5.0	5.0	3.1	4678
		5.7	5.7	5.1	4.5	4.4	3.8	3.2	2.5	1.9	4800
		4.5	4.5	3.8	3.8	2.6	2.5	1.9	1.3	1.3	5086
		4.5	3.9	3.9	3.9	3.9	2.6	1.9	1.9	1.3	5890
		4.5	3.9	3.9	3.9	3.2	2.6	1.9	1.3	0.6	6438
Neugebauer	$\frac{\delta n_{\parallel}}{n_{\parallel}} \times 10^3$	8.1	8.2	7.7	7.2	6.6	6.1	5.6	5.1	3.4	4678
		7.1	7.1	6.1	5.5	5.6	4.5	3.9	3.4	2.3	4800
		5.5	5.6	5.0	4.5	3.9	3.4	2.8	2.3	1.7	5086
		5.7	5.1	5.1	4.6	4.6	3.5	2.9	2.3	1.8	5890
		4.6	4.6	4.0	4.0	3.5	2.9	1.8	1.2	0.6	6438
	$\frac{\delta n_{\perp}}{n_{\perp}} \times 10^3$	9.5	9.5	8.9	8.2	7.6	6.9	6.3	6.7	3.8	4678
		8.3	8.3	7.0	6.4	6.4	5.1	4.4	3.8	2.5	4800
		6.4	6.4	5.8	5.1	4.5	3.8	3.2	2.5	1.9	5086
		6.5	5.8	5.8	5.2	5.2	3.9	3.2	2.6	1.9	5890
		5.2	5.2	4.5	4.5	3.9	3.2	1.9	1.3	0.6	6438
Vuks	$\frac{\delta n_{\parallel}}{n_{\parallel}} \times 10^3$	17.4	16.9	16.4	15.4	14.9	13.9	13.4	12.4	9.7	4678
		15.8	15.3	14.9	13.8	13.3	12.3	11.8	10.8	8.6	4800
		13.8	13.9	13.4	12.3	11.3	10.8	9.7	8.6	7.5	5086
		13.0	12.5	12.0	12.0	10.9	9.8	9.3	8.2	7.1	5890
		12.0	11.4	10.9	10.4	9.8	8.7	8.2	7.0	5.9	6438
	$\frac{\delta n_{\perp}}{n_{\perp}} \times 10^3$	20.3	19.7	19.0	17.7	17.1	15.8	15.1	13.8	10.6	4678
		18.5	17.8	17.2	15.9	15.2	13.9	13.3	12.0	9.4	4800
		16.0	16.0	15.4	14.0	12.8	12.1	10.8	9.5	8.2	5086
		14.8	14.2	13.6	13.5	12.2	10.9	10.3	9.0	7.6	5890
		13.6	13.0	12.3	11.6	11.0	9.7	9.0	7.7	6.4	6438

(averaged over the temperature range) is not very dissimilar in the three theories (see Table VIII), nevertheless the resulting values of $\Delta\alpha/\alpha$ turn out to be quite different. Taking the absolute value of S at 22°C from the N.M.R. data reported in Ref. 15, we get

$$\frac{\Delta\alpha}{\alpha} = \frac{1}{S(22^\circ\mathrm{C})}\left(\frac{u}{z}\right)_{22^\circ\mathrm{C}} \simeq \frac{1}{0.60}\left(\frac{u}{z}\right)_{22^\circ\mathrm{C}}$$

TABLE VII

Temperature dependence of the order parameter (normalized to unity at t = 22°C) for MBBA (from B.G. data)

	t (°C)	22	25	28	31	34	37	39	41	43
Present	$f(t)$	1	0.9807	0.9474	0.9105	0.8664	0.8093	0.7625	0.6981	0.6053
	$\sigma \times 10^3$	—	0.89	1.25	1.80	2.28	4.27	4.90	4.06	7.96
Neugebauer	$f(t)$	1	0.9817	0.9495	0.9137	0.8706	0.8145	0.7678	0.7045	0.6120
	$\sigma \times 10^3$	—	0.92	1.30	1.69	2.42	4.51	5.71	4.29	8.41
Vuks	$f(t)$	1	0.9797	0.9455	0.9074	0.8623	0.8043	0.7571	0.6922	0.5994
	$\sigma \times 10^3$	—	0.88	1.53	1.89	2.23	4.11	4.69	3.98	7.71

TABLE VIII

Wavelength dependence of the ratio $\Delta\alpha/\alpha$ (normalized to unity at λ = 4678 Å) for MBBA (from B.G. data)

	λ	4678 Å	4800 Å	5086 Å	5890 Å	6438 Å
Present	$\varphi(\lambda)$	1	0.9938	0.9556	0.8912	0.8692
	$\sigma \times 10^3$	—	3.79	2.57	9.68	4.17
Neugebauer	$\varphi(\lambda)$	1	0.9956	0.9605	0.9002	0.8811
	$\sigma \times 10^3$	—	3.71	2.63	10.15	5.07
Vuks	$\varphi(\lambda)$	1	0.9887	0.9430	0.8688	0.8447
	$\sigma \times 10^3$	—	4.00	2.58	9.20	4.04

At λ = 4678 Å, Table I gives

$$\left(\frac{\Delta\alpha}{\alpha}\right)_{\text{present}} = 0.56, \qquad \left(\frac{\Delta\alpha}{\alpha}\right)_{\text{Vuks}} = 0.82, \qquad \left(\frac{\Delta\alpha}{\alpha}\right)_{\text{Neugebauer}} = 0.50$$

Our result is therefore much lower than the value of Vuks, and slightly higher than the value of Neugebauer.

b) *Chang's data*—Very recently Chang,[16] starting from optical interference measurements, re-evaluated the refractive indexes of MBBA at 22°C using the exact formula for wavelength dispersion. Chang's data for $n_{\parallel}$ and Δn, interpolated to the wavelengths discussed in Sect. 4a, are listed in Table IX. The same table gives the values of u (with the corresponding theoretical indexes $n_{\parallel}(u)$) obtained by solving Eqs. (30), (32) and (31), respectively, under the constraint $n_{\parallel}(u) - n_{\perp}(u) = (\Delta n)_{\text{Chang}}$. The calculations were made by using

TABLE IX

Theoretical values of u and $n_{\|}$ as obtained by solving Eqs. (30), (32) and (31), respectively, for Chang's data at 22°C.

			Present		Neugebauer		Vuks	
λ (Å)	$(\Delta n)_{\text{Chang}}$	$(n_{\|})_{\text{Chang}}$	u	$n_{\|}$	u	$n_{\|}$	u	$n_{\|}$
4678	0.302	1.871	0.1503	1.878	0.1258	1.883	0.2079	1.900
4800	0.290	1.858	0.1452	1.860	0.1219	1.865	0.2000	1.881
5086	0.265	1.826	0.1340	1.829	0.1132	1.832	1.1833	1.848
5890	0.230	1.779	0.1181	1.783	0.1005	1.786	0.1597	1.799
6438	0.219	1.764	0.1130	1.767	0.0966	1.769	0.1523	1.782

TABLE X

Relative deviations $\delta n_{\|}/n_{\|}$ and $\delta n_{\perp}/n_{\perp}$ for Chang's data at 22°C.

	Present		Neugebauer		Vuks	
λ (Å)	$\frac{\delta n_{\|}}{n_{\|}} \times 10^3$	$\frac{\delta n_{\perp}}{n_{\perp}} \times 10^3$	$\frac{\delta n_{\|}}{n_{\|}} \times 10^3$	$\frac{\delta n_{\perp}}{n_{\perp}} \times 10^3$	$\frac{\delta n_{\|}}{n_{\|}} \times 10^3$	$\frac{\delta n_{\perp}}{n_{\perp}} \times 10^3$
4678	3.7	4.5	6.4	7.6	15.5	18.5
4800	1.1	1.3	3.8	4.5	12.4	14.7
5086	1.6	1.9	3.3	3.8	12.0	14.1
5890	2.2	2.6	3.9	4.5	11.2	12.9
6438	1.7	1.9	2.8	3.2	10.2	11.7

Brunet-Germain's data for the refractive indexes in the isotropic phase, i.e. the same values of z previously employed for Tables I-V. The agreement between theoretical and experimental indexes, as shown in Table X, is confirmed to be systematically higher for our theory than for Neugebauer's and Vuks' theories.

CONCLUSIONS

The theory developed in this paper under the simplifying assumption of a spherically symmetric distribution of matter around a molecule has been shown to represent a step forward with respect to both the Neugebauer's and Vuks' theories in explaining the experimental refractive indexes of MBBA. Our analysis has also confirmed the superiority of Neugebauer's with respect to Vuks' equations, in agreement with the conclusions of Subramhanyam *et al.*[17,18]

In spite of the crudness of the model adopted here, the remarkable agreement between theoretical and experimental indexes can be considered as a further proof of the theory developed in Refs. 7, 8, and 9. It is also encouraging for extending the theory to non-spherical molecules, in which case the spherically symmetric function $\mathcal{N}(r)$ taken from Ref. 7 must be relinquished. In such a refined calculation, the contribution of the last term on the right hand side of Eq. (9) should be probably accounted for.

Finally, the theory is able to express the refractive indexes in terms of all the successive moments of the angular distribution of the molecular axes: although in the present paper the approximation (27) has been adopted, for which only the second moment contained in S is called into play, however we emphasize that such an approximation is not necessary at all, and that the rigorous analysis along the lines shown by Eq. (26), though troublesome, would be in principle perfectly possible. Especially in its capability of being improved and generalized, so as to predict higher order parameters than rank two,† the present theory seems to be decidedly superior to the models developed by Vuks and Neugebauer.

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APPENDIX

Splitting the pair interaction between two molecules with orientation indexes i and j, respectively, into a spherically symmetric part $\psi(r)$ (containing a hard-core term) and an anisotropic part $A_{ij}(\mathbf{r})$ responsible for the angular correlations, we can write the distribution function $n_j(\mathbf{r})$ in the form

$$n_j(\mathbf{r}) = C \exp\left[-\frac{u_j(\mathbf{r}) + V(\mathbf{r})}{\kappa_B T}\right] \qquad \text{(A1)}$$

where

$$V(\mathbf{r}) = \int d^3r' \psi(\mathbf{r} - \mathbf{r}') n(\mathbf{r}')$$

$$u_j(\mathbf{r}) = \sum_i \int d^3r' A_{ij}(\mathbf{r} - \mathbf{r}') n_i(\mathbf{r}')$$

---

† We begin to see experimental work on higher rank order parameters in the literature, as for example in the Raman scattering work of Ref. 15.

Since $\sum_i n_j(\mathbf{r}) = n(\mathbf{r})$ (total number density), this means that

$$n_j(\mathbf{r}) = \frac{\exp\left[-\dfrac{1}{\kappa_B T} u_j(\mathbf{r})\right]}{\sum\limits_i \exp\left[-\dfrac{1}{\kappa_B T} u_i(\mathbf{r})\right]} n(\mathbf{r}) \tag{A2}$$

The step from Eq. (A2) to Eq. (3) requires the energy term $u_j(\mathbf{r})$ to be independent of $\mathbf{r}$: strictly, this cannot be true, because for $\mathbf{r} \to 0$ u_j depends upon the direction ζ_0 of the central molecule, while at large distances from the origin no memory is left of this particular orientation, and u_j takes the value (independent of $\mathbf{r}$) appropriate to a molecule with axis ζ_j in the average field of the other molecules. This picture, however, would lead us too far: it would require the introduction of two particles—angular—correlation functions—a problem that should compete first to the theory of the order parameter. The simplest expression of this theory, due to Maier and Saupe,[10] uses the molecular field approximation, as introduced by Weiss a long time ago for ferromagnets: each molecule is assumed to be oriented by the average field created by the other molecules. In this way all the particles of the liquid are treated at equal strength, irrespectively of their distance from the central molecule: in other words, the dependence of u_j upon the position of the molecule is neglected.

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