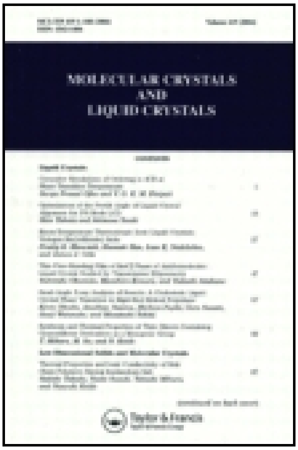

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Local Field Anisotropy in Nematic Liquid Crystals

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LOCAL FIELD ANISOTROPY IN NEMATIC LIQUID CRYSTALS

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The anisotropy of the local electric field in the interior of ordered fluids provides a measure of the anisotropy of the molecular distribution. In nematics, both the orientational order parameter and the anisotropy of the local field can be calculated from refractive index and density measurements; results are presented for the liquid crystal butyl p-(p-ethoxyphenoxycarbonyl) phenyl carbonate. It is found that the anisotropy of the local field is very nearly proportional to the orientational order parameter. A simple model incorporating steric intermolecular repulsion predicts this behaviour. The ratio of the local field anisotropy to the uniaxial and biaxial order parameters is simply related to the length-to-breadth ratio of the effective molecular hard core.

1. INTRODUCTION

Measurements of refractive indices of liquid crystals are frequently analysed to yield information about the degree of orientational order of the constituent molecules. In order to carry out such an analysis, assumptions must be made regarding the local electric field which acts to polarise the molecules. Temperature dependent density and refractive index data is usually interpreted using either Vuks'[1] or Neugebauer's[2] method of relating these bulk properties to the molecular polarisability. In Vuks' approach it is assumed that the local electric field is isotropic; for an anisotropic fluid such as a liquid crystal this assumption lacks theoretical justification. Neugebauer's results, which allow for the anisotropy of the local field, have been derived for a system of particles which are, unlike the constituents of a liquid crystal, arranged in a lattice. The relative merits of the two approaches, as applied to the interpretation of refractive index and density data, have been discussed in the literature[3-5]. Because of its firmer theoretical basis, Neugebauer's method is preferable, however, it is not clear how the lattice sums associated with the anisotropy of the local field can be interpreted in the case of liquid crystals. Although it has been shown that the local field in certain molecular crystal lattices is equivalent to that of an elliptical cavity in a continuum model[6], the eccentricity of this cavity is not necessarily that of the molecular hard core and is therefore not fully known.

It has been shown recently[7] that for an anisotropic fluid model, the relation between refractive indices, density and polarisability is formally identical with Neugebauer's result; the local field factors, however, are obtained from the radial distribution function rather than from lattice sums. In this approach it is shown that in the interior of a polarised anisotropic fluid, it is possible to construct a surface having the property that the contribution of the dipoles within the surface to the electric field at the origin is zero. The shape of this generalised Lorentz cavity and the associated local field factors are simply obtained from the radial distribution function.

In this paper we construct the simplest possible radial distribution for liquid crystal molecules consistent with an elongated cylindrically symmetric effective molecular hard core. On the basis of this model, we show that the local field anisotropy is proportional to the orientational order parameters, and that the proportionality constant is simply related to the length-to-breadth ratio of the molecular hard core. This proportionality has been predicted[8] and observed[9] for EBBA and other materials[10]; more recently it has been also proposed[11] on the basis of a generalised Onsager approach to anisotropic dielectrics. Experimental data on BEPC (butyl-p(p-ethoxyphenoxycarbonyl) phenyl carbonate) is analysed to obtain the orientational order parameter and the local field anisotropy factor; it is proposed that the local field anisotropy may provide a useful measure of the axial ratio of the molecular hard core.

2. THEORY

2.1 The Local Field

The relation between refractive indices n_{ii}, number density ρ and effective molecular polarisability α_{ii} is[9], in SI units,

$$\frac{n_{ii}^2-1}{n_{ii}^2+2}\left(1-\frac{\rho}{\varepsilon_o}\eta_{ii}\alpha_{ii}\right) = \frac{\rho\alpha_{ii}}{3\varepsilon_o} \qquad (1)$$

where i = x,y,z refers to directions in a laboratory fixed coordinate system and η_{ii} is the local field anisotropy tensor . Eq.(1) is valid if the dielectric tensor ($\varepsilon_{ii} = n^2_{ii}$), the anisotropy tensor and the polarisability tensor are all diagonal in the same laboratory fixed coordinate system x,y,z. This is expected to be the case for some phases (e.g. nematic, smectic A) but not necessarily for others (e.g. smectic C). The anisotropy tensor is given by[7]

$$\eta_{ii} = \frac{-1}{4\pi}\int \ln\left(R_c(\hat{r})\right)\ (3r_i^2 - 1)d\Omega \qquad (2)$$

where $\hat{r}$ is a unit vector in the laboratory fixed coordinate system with components r_i; $d\Omega$ is the element of solid angle and $R_c(\hat{r})$ is the distance from the origin to a point on the surface of the generalised Lorentz cavity in the direction $\hat{r}$. The equation of this surface is[7]

$$\ln\left(R_c(\hat{r})\right) = \ln b - \int_0^b \frac{g(r\hat{r})dr}{r} + \int_b^\infty \frac{\left(1-g(r\hat{r})\right)dr}{r} \qquad (3)$$

where $g(r\hat{r})$ is the radial distribution function and b is an arbitrary constant. It is interesting to note that $R_c(\hat{r})$ does not depend on b, since $\frac{\partial R_c(\hat{r})}{\partial b} = 0$ for all b. If $g(r\hat{r})$ is independent of the direction $\hat{r}$, $R_c(\hat{r})$ is a constant and the cavity is a sphere with $\eta_{ii} = 0$. In a nematic liquid crystal, the average molecular repeat distance is expected to be different in the direction parallel to the nematic director and in directions perpendicular to it; this anisotropy of $g(r\hat{r})$ gives rise to a non-spherical cavity. It is worth noting in eq. (2) that η_{ii} is independent of the size of the cavity.

The local field E_i^L responsible for polarising the molecules depends on η_{ii}, and is given by[7]

$$E_i^L = [\tfrac{1}{3}(\varepsilon_{ii} + 2) + \eta_{ii}(\varepsilon_{ii} - 1)]E_i \qquad (4)$$

where E_i is the average electric field inside the material.

2.2 Estimate of the Radial Distribution

In principle, the radial distribution $g(r\hat{r})$ can be obtained directly from the partition function if the intermolecular interactions are known. In practice, however, an exact solution is difficult even for a system of hard spheres and appears prohibitively difficult for liquid crystals. We therefore attempt instead to construct the simplest approximate radial distribution function consistent with a system of orientationally ordered prolate hard particles.

We assume that a molecule may be represented by a prolate spheroid as shown on Fig. 1. with semi-major and semi-minor axes $R_\parallel$ and $R_\perp$. If $\hat{n}$ is a unit vector along the symmetry axis of the spheroid and $\bar{R} = R\hat{R}$ is a vector from its center to a point on its surface, the equation of the surface may be written as

$$\bar{R} = R_\perp \hat{R}\left(1 - e^2(\hat{R}\cdot\hat{n})^2\right)^{-1/2} \qquad (5)$$

where the eccentricity is $e = \sqrt{1 - (\frac{R_\perp}{R_\parallel})^2}$. Alternately, if the unit normal to the surface at $\bar{R}$ is $\hat{N}$, eq.(5) may be written as

$$\bar{R} = R_\perp\left(\hat{N} + c^2(\hat{N}\cdot\hat{n})\hat{n}\right)/\left(1+c^2(\hat{N}\cdot\hat{n})^2\right)^{1/2} \qquad (6)$$

where $c^2 = \dfrac{e^2}{1-e^2}$. If $\hat{r}$ is again a unit vector with components r_i in a laboratory fixed coordinate system, the

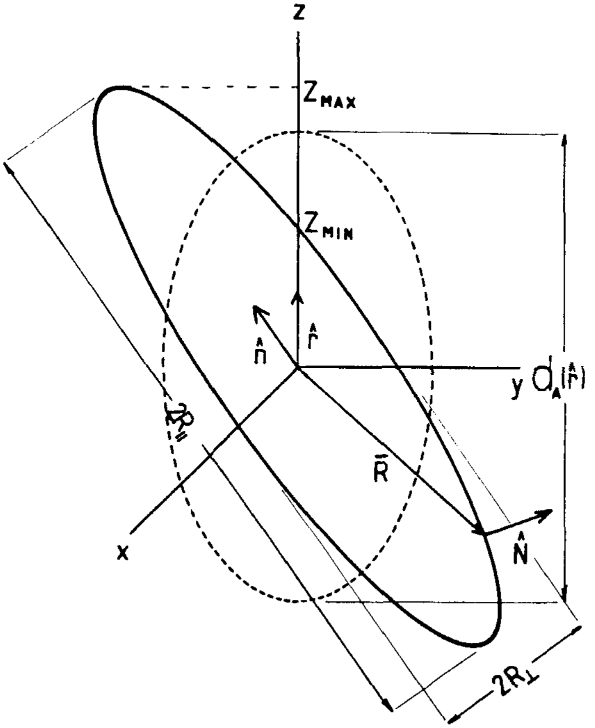

FIGURE 1. The prolate spheroid representing the hard core is shown with a solid line. The dashed line represents the orientationally averaged hard core. The nematic director is along the z-axis.

extent of the molecular hard core in direction $\hat{r}$ can be readily estimated from eqs.(5) and (6). (For simplicity, in Fig. 1 $\hat{r}$ has been chosen along the z-axis). The coordinate Z_{MIN} where the positive z-axis intecepts the spheroid is given, from eq.(5), by $Z_{MIN} = R_{\perp}\left(1-e^2(\hat{r}\cdot\hat{n})^2\right)^{-1/2}$, while the projection of the spheroid onto the z-axis is from eq.(6), $Z_{MAX} = R_{\perp}\left(1+c^2(\hat{r}\cdot\hat{n})^2\right)^{1/2}$. The extent of the spheroid of orientation $\hat{n}$ in the direction $\hat{r}$ is bounded by these quantities; clearly no particle can approach the center of the spheroid along the z-axis closer than Z_{MIN} nor can the hard core interfere with the approach of a particle along the z-axis at distances greater than Z_{MAX}. In order to avoid having to deal with orientational correlations between adjacent molecules as well as for simplicity we assume that the effective extent Z_{AV} of the spheroid in the direction $\hat{r}$ is the linear approximation to the average of Z_{MIN} and Z_{MAX}; that is,

$$Z_{AV} = R_\perp\left(1 + \frac{R_\parallel - R_\perp}{R_\perp}(\hat{r}\cdot\hat{n})^2\right).$$

As required, $Z_{MIN} < Z_{AV} < Z_{MAX}$, and $Z_{MIN} = Z_{MAX} = Z_{AV}$ if $\hat{r}\cdot\hat{n} = 1$ or 0. The hard-core diameter $d(\hat{r})$ in the direction $\hat{r}$ is $2Z_{AV}$; and since $(\hat{r}\cdot\hat{n})^2 = r_\alpha n_\alpha n_\beta r_\beta$ where summation is implied over repeated greek indices,

$$d(\hat{r}) = 2\left(\frac{R_\parallel + 2R_\perp}{3} + \frac{2}{3}(R_\parallel - R_\perp)\left(\frac{1}{2}(3n_\alpha n_\beta - \delta_{\alpha\beta})r_\alpha r_\beta\right)\right) \quad (7)$$

Since the orientational order parameter $Q_{\alpha\beta} = \left\langle \frac{1}{2}(3n_\alpha n_\beta - \delta_{\alpha\beta})\right\rangle$ where $\langle\ \rangle$ denotes the average value, the orientationally averaged hard core diameter becomes

$$d_A(\hat{r}) = \frac{2}{3}R_\perp\left[(\kappa+2) + 2(\kappa-1)\,Q_{\alpha\beta}r_\alpha r_\beta\right] \quad (8)$$

where κ is the length-to-breadth ratio $\frac{R_\parallel}{R_\perp}$. If the order parameter $Q_{\alpha\beta}$ is diagonal in the laboratory frame, eq.(8) becomes

$$d_A(\hat{r}) = \frac{2(R_\parallel + 2R_\perp)}{3}\left[1 + 2\left(\frac{\kappa-1}{\kappa+2}\right)\left(S\,\frac{1}{2}(3\cos^2\Theta_r - 1) + \frac{P}{3}\,\frac{3}{2}\sin^2\Theta_r\cos 2\phi_r\right)\right] \quad (9)$$

where $S = \left\langle\frac{1}{2}(3\cos^2\Theta - 1)\right\rangle$, $P = \left\langle\frac{3}{2}(\sin^2\Theta\cos 2\phi)\right\rangle$

and Θ, ϕ, Θ_r, ϕ_r are the polar angles specifying the directions $\hat{n}$ and $\hat{r}$ respectively. The orientationally averaged hard core in the laboratory fixed coordinate system, given by eq.(9), is a sixth-degree surface resembling an ellipsoid, which becomes a sphere in the limit as the order parameters S and P go to zero. The simplest approximation to $g(r\hat{r})$ consistent with such a hard core is to let

$$g(r\hat{r}) = \begin{cases} 0 \text{ if } r < d_A(\hat{r}) \\ 1 \text{ if } r > d_A(\hat{r}) \end{cases} \tag{10}$$

Substitution into eq.(3) gives $R_c(\hat{r}) = d_A(\hat{r})$, thus the generalised Lorentz cavity has the same shape as the orientationally averaged hard core. A more realistic $g(r\hat{r})$, even for the same hard core, would in general lead to a somewhat different cavity shape. The local field factors can now be calculated from eqs.(2) and (9) giving, to second order,

$$\begin{aligned} \eta_{xx} &= \frac{2}{5}\left(\frac{\kappa-1}{\kappa+2}\right)(S-P) - \frac{4}{35}\left(\frac{\kappa-1}{\kappa+2}\right)^2\left(S^2+2SP-\frac{P^2}{3}\right) \\ \eta_{yy} &= \frac{2}{5}\left(\frac{\kappa-1}{\kappa+2}\right)(S+P) - \frac{4}{35}\left(\frac{\kappa-1}{\kappa+2}\right)^2\left(S^2-2SP-\frac{P^2}{3}\right) \\ \eta_{zz} &= \frac{-4}{5}\left(\frac{\kappa-1}{\kappa+2}\right)S + \frac{8}{35}\left(\frac{\kappa-1}{\kappa+2}\right)^2\left(S^2-\frac{P^2}{3}\right) \end{aligned} \tag{11}$$

Since for molecules with axial ratio $\kappa \lesssim 2$ the first order terms will dominate, η_{zz} is expected to be nearly proportional to the order parameter with slope $\frac{-4}{5}\left(\frac{\kappa-1}{\kappa+2}\right)$.

If the molecular polarisability is $\alpha_{\parallel}$ along $\hat{n}$ and $\alpha_{\perp}$ perpendicular to $\hat{n}$, the orientationally averaged molecular polarisability is

$$\alpha_{\alpha\beta} = \left\langle \frac{(\alpha_{\parallel}+2\alpha_{\perp})}{3}\,\delta_{\alpha\beta} + \frac{2}{3}(\alpha_{\parallel}-\alpha_{\perp})\left(\frac{1}{2}(3n_{\alpha}n_{\beta}-\delta_{\alpha\beta})\right)\right\rangle$$
$$= \bar{\alpha}\delta_{\alpha\beta} + \frac{2}{3}\Delta Q_{\alpha\beta} \tag{12}$$

where $\bar{\alpha} = \left(\frac{\alpha_{\parallel} + 2\alpha_{\perp}}{3}\right)$ and $\Delta = \alpha_{\parallel} - \alpha_{\perp}$. If $\alpha_{\alpha\beta}$ is diagonal in the laboratory frame, then

$$\alpha_{xx} = \bar{\alpha} - \frac{1}{3}\Delta(S-P)$$
$$\alpha_{yy} = \bar{\alpha} - \frac{1}{3}\Delta(S+P)$$
$$\alpha_{zz} = \bar{\alpha} + \frac{2}{3}\Delta S \tag{13}$$

2.3 Density

It is possible to estimate the dependence of the density on the order parameters from eq.(9). The volume of a macroscopic sample is expected to be proportional to the product of the average repeat distances of molecules along the x,y and z directions, and these in turn are expected to be proportional to the orientationally averaged hard core diameter $d_A(\hat{r})$ in that direction. Thus the volume V is given, from eq.(9), by

$$V = V(o)\left[1 - 3\left(\frac{\kappa-1}{\kappa+2}\right)^2\left(S^2+\frac{P^2}{3}\right) + 2\left(\frac{\kappa-1}{\kappa+2}\right)^3(S^3-SP^2)\right] \tag{14}$$

where V(o) is the volume of the isotropic phase. For a uniaxial (P=0) nematic, the discontinuous relative volume change across the N-I transition is

$$\frac{\Delta V}{V(o)} \simeq -3\left(\frac{\kappa-1}{\kappa+2}\right)^2 S_c^2 \tag{15}$$

where S_c is the value of S in the nematic phase at the transition. Eq.(14) gives the volume variation due to changes in the order parameters alone; volume changes associated with normal thermal expansion must also be included. This results in the following expression for the mass density ρ_M, to second order :

$$\frac{\rho_M(o)}{\rho_M} = 1 - 3\left(\frac{\kappa-1}{\kappa+2}\right)^2 \left(S^2+\frac{P^2}{3}\right) + \gamma(T_{NI}-T) \qquad (16)$$

where T_{NI} is the N-I transition temperature, $\rho_M(o)$ is the density of the isotropic phase at T_{NI} and γ is the coefficient of thermal expansion of volume of the isotropic phase.

3. EXPERIMENTAL RESULTS

The material BEPC (butyl-p(p-ethoxyphenoxycarbonyl) phenyl carbonate) was obtained from Eastman Kodak and was used without purification. The refractive indices shown in Fig. 2 were measured using interferometric methods[9,12,13]; absolute values were also measured with an Abbe refractometer. Density measurements were carried out using an Anton-Paar Digital Densimeter; results are shown in Fig. 3. The average polarisability $\bar{\alpha} = \left(\frac{\alpha_\parallel+2\alpha_\perp}{3}\right)$ can be obtained from eq.(1); in the isotropic phase

$$\bar{\alpha} = \frac{3\varepsilon_o}{\rho}\,\frac{n^2-1}{n^2+2}$$

and experimental values yield

$$\bar{\alpha} = 42.7 \pm .7 \times 10^{-40}\ \mathrm{Fm}^2 .$$

Letting $\delta = \frac{\Delta}{3\bar{\alpha}} = \frac{\alpha_\parallel-\alpha_\perp}{3\bar{\alpha}}$ and eliminating the traceless tensor η_{ii} from eqn.(1) gives

$$4\delta S = 1 - 3A + (9A^2 - 30A + 9)^{1/2} \qquad (17)$$

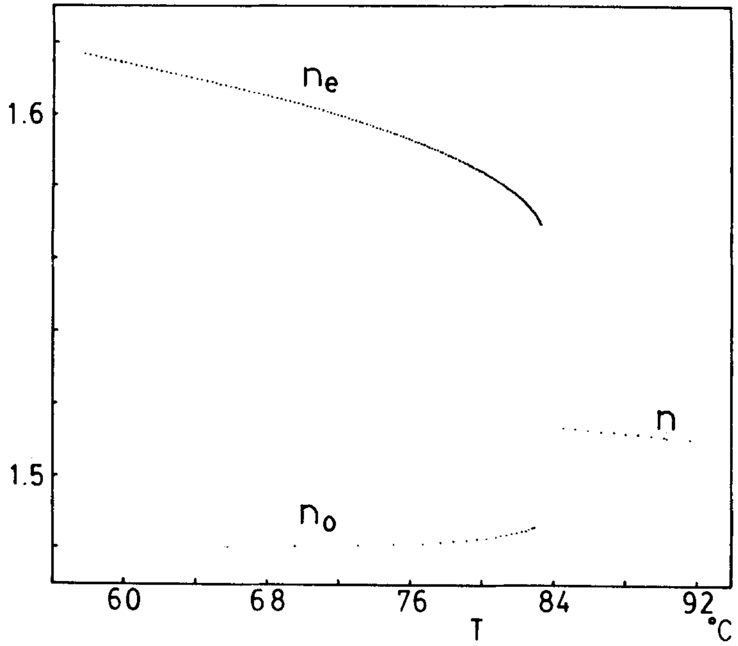

FIGURE 2. The refractive indices of BEPC as functions of temperature.

where $\frac{1}{A} = \frac{\bar{\alpha}\rho}{3\varepsilon_o}\left(\frac{n_e^2+2}{n_e^2-1} + 2\frac{n_o^2+2}{n_o^2-1}\right)$. To determine δ, we have used Haller's method[14] of extrapolating to zero temperature a linear fit to the points $\ln(\delta S)$, $\ln(1-T/T_{NI})$. As suggested by recent work[15], we applied the same extrapolation procedure to the points $\ln(\delta S-\delta S_c)$, $\ln(1-T/T_{NI})$; the two methods agreed to give $\Delta = 16.0 \pm 1.3 \times 10^{-40}$ Fm^2. The order parameter calculated from eq.(17) is shown on Fig. 4 as function of temperature. The local field tensor η_{zz} is obtained from eq.(1),

$$\eta_{zz} = \frac{\varepsilon_o}{\rho\bar{\alpha}\,(1+2\delta S)} - \frac{1}{3}\frac{n_e^2+2}{n_e^2-1}.$$

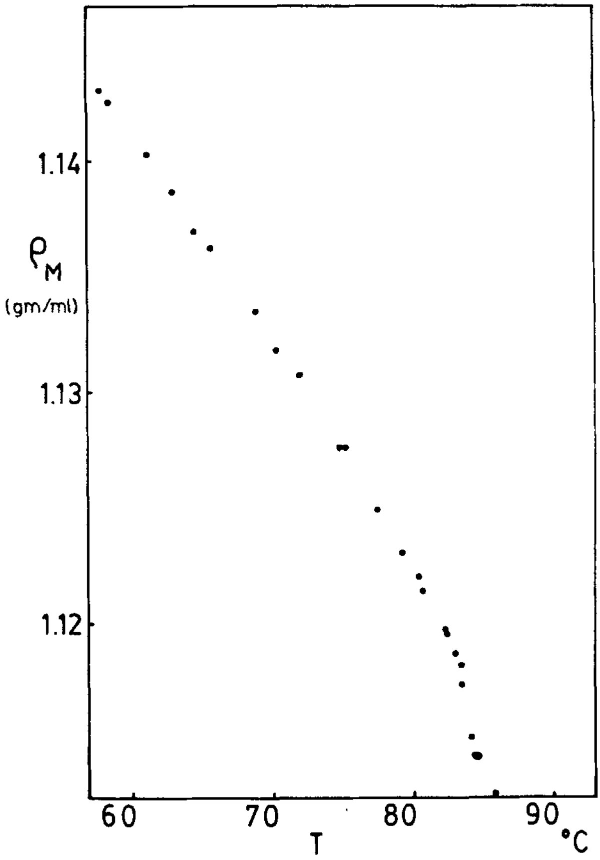

FIGURE 3. The mass density of BEPC as function of temperature.

η_{zz} is shown in Fig. 4 as a function of the order parameter S. To a good approximation, η_{zz} is proportional to S. From eq.(11), the length-to-breadth ratio κ can be obtained from the slope of η_{zz} vs. S; this gives $\kappa = 1.25 \pm .03$. Although this might appear somewhat low for the length-to-breadth ratio of the molecular hard core, it is not unreasonable for a flexible molecule averaged over

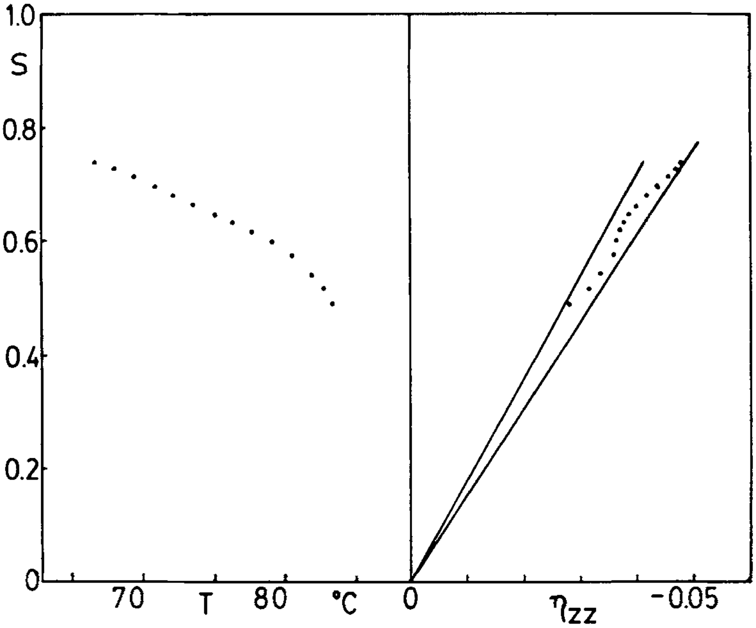

FIGURE 4. Order parameter S as function of temperature and as function of the local field factor η_{zz}.

molecular configurations. It is consistent with the small relative polarisability anisotropy $\frac{\alpha_\parallel - \alpha_\perp}{\bar{\alpha}} = .375$. By comparison, similar analysis for EBBA[9] gives $\kappa = 1.75$ while $\frac{\alpha_\parallel - \alpha_\perp}{\bar{\alpha}} = .800$. An independent estimate of κ may be obtained from density and order parameter data; eq.(16) suggests that a plot of $\frac{1-\rho_M(o)/\rho_M}{T-T_{NI}}$ vs. $\frac{S^2}{T-T_{NI}}$ should be approximately linear with slope $3\left(\frac{\kappa-1}{\kappa+2}\right)^2$. Such a plot is shown in Fig. 5, the slope is $1.10 \pm .15 \times 10^{-2}$, giving $\kappa = 1.19 \pm .02$.

proportionality constant and the molecular length-to-breadth ratio is reasonably accurate. Additional analysis of accurate refractive index and density data is required to further test this hypothesis.

Work to extend this approach to smectic phases is currently under way.

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consequently conclusions regarding κ from density data must be treated with caution.

4. CONCLUSIONS

Our experimental results indicate that the local field anisotropy factor for the liquid crystal BEPC is approximately proportional to the orientational order parameter. This behaviour is in agreement with theoretical predictions[11,8] and experimental results on other systems[9,10]. We have proposed a simple model for the orientationally averaged hard core, and constructed an anisotropic radial distribution consistent with this. Expressions for the local field factors were obtained for the case of a biaxial nematic; comparison with experimental data suggested that the length-to-breadth ratio of BEPC molecules is $\kappa = 1.25 \pm .03$. Analysis of density data based on the same hard core model yields a similar result. The model presented for the hard core is greatly oversimplified. It is expected, for example, that changes in the local environment of a molecule will produce changes in its conformation, hence in a more realistic model, the effective molecular length-to-breadth ratio κ should depend on the order parameter S. The approximations responsible for the simple form of the radial distribution function are expected to be of less importance, since the local field factors depend primarily on the anisotropy of $g(r\hat{r})$ and only to a lesser extent on its detailed structure[16].

Our model incorporates the essential features of an anisotropic molecular distribution and on this basis predicts the observed proportionality between the order parameters and the local field factor. It is expected therefore that the proposed relation between this

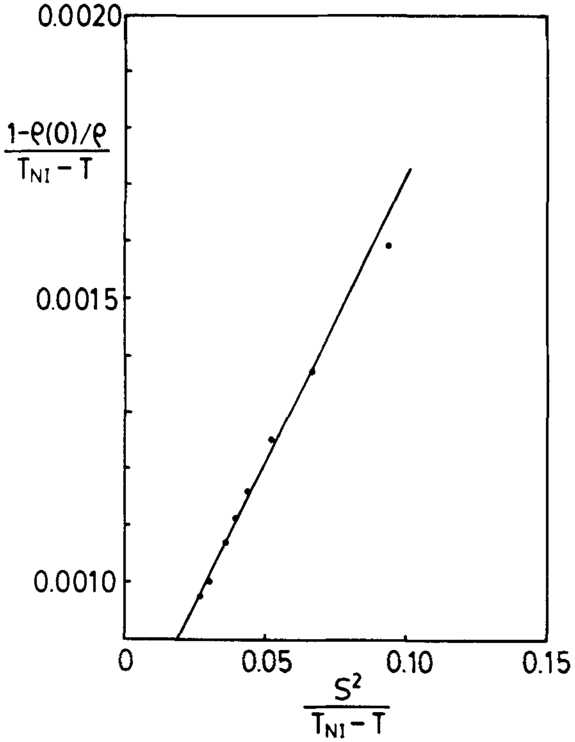

FIGURE 5. Plot of $(1-\rho(o)/\rho)/(T_{NI} - T)$ versus $S^2/(T_{NI} - T)$.

The expected discontinuous volume change across the N-I transition can be estimated from eq.(15),

$$\frac{\Delta V}{V(o)} \simeq 3\left(\frac{\kappa-1}{\kappa+2}\right)^2 S_c^2 = 0.28\ \%$$

for $\kappa = 1.2$ and $S_c = 0.49$. Due to the coexistence of the nematic and isotropic phases in a 0.1°C temperature interval at the transition, the discontinuous volume change is difficult to estimate. Although 0.28% seems not incompatible with the density data, this agreement is fortuitous, since for $\kappa = 1.3$ eq.(15) predicts 0.60% while for EBBA it predicts 1.3 %. Hence eq.(15) overestimates the volume change across the transition and