

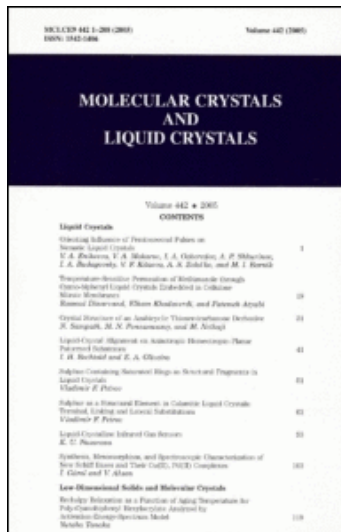
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Polarization Field and Orientational Order in Liquid Crystals

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Optical birefringence is a conveniently measurable quantity that is often used for determining the orientational order in uniaxial liquid crystals. The orientational order parameter is given by

$$S = \frac{\alpha_e - \alpha_o}{\alpha_{\parallel} - \alpha_{\perp}} \quad (1)$$

where α_e and α_o are the polarizabilities of the medium corresponding to the extraordinary and ordinary refractive indices, α_{\parallel} and α_{\perp} are the corresponding values for a perfectly oriented medium with $S = 1$.

Mainly two methods have been used to relate the polarizabilities with the measured refractive indices. The first, due to Neugebauer¹⁻³ (hereafter abbreviated to N) makes use of an anisotropic internal field. The relevant equations are:

$$n_{e,o}^2 - 1 = \frac{4\pi v \alpha_{e,o}}{1 - v \alpha_{e,o} \gamma_{e,o}} \quad (2)$$

where v is the number of molecules per unit volume and γ are the internal field constants. Now $\gamma_e + 2\gamma_o = 4\pi$, and therefore

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi v}{3} \left[\frac{n_e^2 + 2}{n_e^2 - 1} + 2 \frac{n_o^2 + 2}{n_o^2 - 1} \right] \quad (3)$$

Further, the average polarizability is assumed to be the same in all phases and can be derived from the data for the isotropic liquid phase:

$$\alpha_e + 2\alpha_o = \frac{9}{4\pi v} \left(\frac{n^2 - 1}{n^2 + 2} \right) \quad (4)$$

Eq. (3) and (4) can be used to calculate α_e and α_0 in the liquid crystal. Similar calculations can be carried out in the crystalline phase to determine α_{\parallel} and α_{\perp} (see Ref. 2 and 3 for details). Some extrapolation procedures have also been suggested to estimate $(\alpha_{\parallel} - \alpha_{\perp})$ from the data in the nematic phase.^{3,4}

In the second approach due to Vuks^{5,6} (hereafter abbreviated to V), it is assumed that the local field is isotropic and polarizabilities are calculated using the relations

$$\frac{n_{e,0}^2 - 1}{n^2 + 2} = \frac{4\pi v}{3} \alpha_{e,0} \quad (5)$$

where $\bar{n}^2 = (n_e^2 + 2n_0^2)/3$.

Calculations of α_{\parallel} and α_{\perp} have shown that the N -method gives a better agreement with the values obtained from the addition of bond polarizabilities. The V -method gives somewhat high values for the anisotropy $(\alpha_{\parallel} - \alpha_{\perp})$.³

However, if one is interested in determining the order parameters using Eq. (1), the two methods yield practically identical values.^{3,7} (This indicates that the V -method overestimates the anisotropy of polarizability to about the same extent in both the nematic and crystalline phases.^{3,4}) As a consequence, since the first application of the V -method to liquid crystals⁶ a large number of workers⁸⁻¹⁷ have used it for calculating the order parameter from the refractive index data.

The purpose of the present note is to consider certain practical aspects of such calculations. In particular we wish to point out that the N -method is very sensitive to the accuracy of measurement of the density. To illustrate this point, let us consider the case of PAA. In the nematic phase, at $T_c - T = 42^\circ$, the density $\rho = 1.1868$,⁶ $n_e = 1.894$ and $n_0 = 1.558$ for $\lambda 5893 \text{ \AA}$,¹⁸ and in the isotropic phase at $T_c + 1^\circ$, $\rho = 1.143$ and $n = 1.642$. Using these values and the N -approach, $(\alpha_e - \alpha_0) = 15.40 \times 10^{-24} \text{ cc}$ at $T_c - 42^\circ$. If the density is increased by 1% in the nematic phase, the value of $(\alpha_e - \alpha_0)$ and hence the calculated value of S increase by about 11.5%. This is essentially because $\gamma_{e,0}$ also depend on ρ . On the other hand, $(\alpha_e - \alpha_0)$ as determined by the V -relation (5) is simply inversely proportional to ρ and hence *decreases* by just 1% when the density is increased by 1%. Therefore, if the accuracy of the density data is suspect, it is in fact preferable to use the V -method to calculate the order parameters.

Another source of experimental error arises if the orientation of the sample is not perfect. To take a simple example, let us suppose that the director is not strictly parallel to the glass surface but tilted at an angle of 10° to it. Then, one would measure an effectively lower value of n_e , which in the case of PAA at $T_c - 42^\circ$ would be 1.880 instead of 1.894; n_0 would still be 1.558. The N -method, leads to $(\alpha_e - \alpha_0) = 15.92 \times 10^{-24} \text{ cc}$ or an effective S

which is about 3.4% *higher* than the value measured for the truly homogeneous sample. A similar calculation using the V -method, gives a value of S which is $\sim 4.4\%$ *lower* for the misaligned sample—a trend which is more reasonable. This source of error becomes particularly important when considering measurements on smectic phases, for which it is quite difficult to achieve a truly homogeneous alignment. What one observes is only a gross alignment, and the order parameters calculated from measurements on such a sample will obviously be unsatisfactory.

We can illustrate these points by referring to a recent paper by Sarna *et al.*¹⁹ The authors have measured the refractive indices of HBT in the nematic and smectic B phases and of OBT in the nematic and smectic A phases. In both cases, they found that though the order parameters calculated using the N - and the V -methods agree with each other reasonably well in the nematic phase, the former gives considerably higher values for the smectic phases. Thus in the smectic B phase of HBT, they get $S = 0.85$ using the N -method and 0.68 using the V -method, and conclude that the former value is more realistic. But in view of our earlier discussion, it would appear that this difference is almost certainly due to the inaccuracy of their data. To check this point, we can make use of the assumption stated earlier that the average polarizability of the material is constant in all the phases. From the V -relation the average polarizability can be expressed in the form

$$\frac{4\pi}{3} v\bar{\alpha} = \frac{\bar{n}^2 - 1}{n^2 + 2}, \quad (6)$$

which has been tested to hold good in a number of cases.^{6,17} Krishnamurti and Subramhanyam²⁰ have shown that Eq. (6) holds good to a very good approximation even when the N -relations are used, and have, in fact, applied it in their discussion of the polarizabilities of several compounds in the smectic phase. From the data of Sarna *et al.* in the smectic B phase of HBT, the density calculated from Eq. (6) is nearly 2% lower than the measured value, which has been claimed to be accurate to $\pm 0.01\%$. (In fact, this calculated density is slightly lower even than the measured density of the nematic phase just above the smectic B-nematic transition point.) Assuming that the density measurements are correct, one is forced to the conclusion that the alignment of the sample is poor. In fact if we use the density derived from Eq. (6) for the smectic B phase of HBT, the N -relations lead to $S \simeq 0.70$, which is very close to the value calculated by the V -method. This value is in fact more realistic for the *misaligned* sample. Thus, a comparison with the results derived from the two methods may even be used to assess the reliability of the experimental data.

NOTE ADDED IN PROOF

The points raised in the note apply to the results published recently by Gasparoux *et al.* [*Mol. Cryst. Liq. Cryst.*, **51**, 229 (1979)]. For example, they claim that their density data is accurate to $\pm 2\%$, whereas in fact their values for 104 differ from the precise data of Press and Arrott [*Phys. Rev.*, **8**, 1459 (1973)] and Gulari and Chu [*J. Chem. Phys.*, **62**, 795 (1975)] by $\sim 6\%$. In the circumstances, it is not surprising that they found considerable discrepancy between the results using N and V formulae. Moreover, the calculations appear to give far too low values of the order parameters; e.g., as low as 0.06 near T_{NI} for 404. In view of these experimental uncertainties, some of their conclusions have to be taken with caution.

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