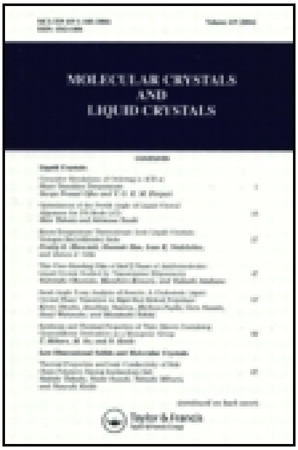

# Molecular Crystals and Liquid Crystals

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# Polarization Field and Molecular Order in Nematic Liquid Crystals

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# Polarization Field and Molecular Order in Nematic Liquid Crystals†

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**Abstract**—In a nematic medium, as a result of the anisotropic distribution of the molecules, the average local electric field is of the form $E+\gamma P$, where $E$ is the applied field, $P$ the polarization, and $\gamma$ is a factor which is different for the directions parallel and perpendicular to the optic axis. For the nematic medium, the Neugebauer's relation

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

is valid. Here, $n_e$ and $n_o$ are the principal refractive indices, $N$ the number of molecules per unit volume and $\alpha_e$ and $\alpha_o$ are respectively the effective average polarizabilities along the optic axis and perpendicular to it. For the crystalline phase wherein the long axes of the molecules are parallel, a similar relation is there connecting the principal indices with $\alpha_{||}$ and $\alpha_{\perp}$, the polarizabilities along the long axis and perpendicular to it. Using these relations along with the Lorenz-Lorentz relation for the liquid phase $\alpha_e$, $\alpha_o$, $\alpha_{||}$, $\alpha_{\perp}$ and the $\gamma$ and $S$-factors are calculated for PAA and PAP for different wavelengths and temperatures from the latest refractive index data of Germain. The values of $\gamma$ and $S$ are consistent. The $S$-factors are in good agreement with the values reported previously by Chandrasekhar and Madhusudana. The anisotropic molecular distribution in these compounds, as deduced from the values of $\gamma$, is discussed.

## 1. Introduction

The principal polarizabilities of the molecules, the anisotropic nature of the polarization field in the medium and the orientational order parameter $S$, determine the birefringence of nematic liquid crystals. For calculations of the polarizabilities of the molecules and of the order parameter $S$ from birefringence data the Lorenz–Lorentz formula cannot be employed because its validity is restricted to

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cases where there is spherical (or cubic) symmetry associated with the molecular arrangement. The Vuks formula⁽¹⁾ had been used by Chandrasekhar and Madhusudana⁽²⁾ for calculations in the cases of *p*-azoxyanisole, *p*-azoxyphenetole and their mixtures, using the refractive index data reported by Chatelain and Germain.⁽³⁾ According to the Vuks formula the ratio of the average local electric field to the applied field is the same for the two cases when the applied field is (i) parallel and (ii) perpendicular to the optic axis of the medium. Such a situation need not necessarily prevail when the molecular distribution is anisotropic. Neugebauer⁽⁴,⁵⁾ has considered in detail the form of the polarization field in anisotropic media. Saupe and Maier⁽⁶,⁷⁾ had applied the Neugebauer relations for calculation of the order parameter in PAA and PAP. However, at that time the birefringence data in these compounds were inadequate and calculations could not be made to verify if the Neugebauer relations would lead to consistent results. In the present paper, we make use of the more recent and extensive data of Germain⁽⁸⁾ for PAA and PAP and it is found that the use of the Neugebauer relations leads to results which are consistent and that the calculated internal field constants confirm the anisotropic nature of molecular distribution in nematic liquid crystals. In the following section, a brief summary of the results of Neugebauer's approach is given in order to indicate how the calculations have been made. For further details of the theory the earlier papers⁽⁴⁻⁷⁾ may be referred to. Notation and formulae given in this paper are in a more convenient form for purposes of calculation.

## 2. Neugebauer relations

It is well known that in the crystalline phase of PAA and PAP the molecules are arranged with their long axes parallel to one another. This direction corresponds to one of the principal directions of the refractive index ellipsoid. When the applied field is along each one of the principal axes of the ellipsoid, the average local electric field is given by expressions of the form, $E_{\mathrm{loc}} = E + \gamma P$, where $\gamma$ is the internal field constant. For an anisotropic molecular distribution, $\gamma \neq 4\pi/3$, because the contribution of the dipoles within the cavity to the local field does not vanish. The expression for $\gamma$, when the electric field is along the principal direction $x$, is given by

$$\gamma_x = 4\pi/3 + [\sum_i (3x_i^2 - r_i^2) r_i^{-5}]/N_c \tag{1}$$

and correspondingly similar expressions give $\gamma_y$ and $\gamma_z$. In the above, $N_c$ is the number of molecules per unit volume of the crystal and $x_i$, $y_i$, $z_i$ and $r_i$ represent the coordinates of the molecules and their distance from the centre of the fictitious spherical cavity at the centre of which the average local field is calculated. The summations are to be carried out over all the molecules inside the spherical cavity except the one at the centre of the cavity.

If $\alpha_x$, $\alpha_y$, $\alpha_z$ are the principal polarizabilities of the molecules and $n_x$, $n_y$ and $n_z$ are the three principal refractive indices, they are related by expressions of the type, as e.g.,

$$n_z^2 - 1 = 4\pi N_c \alpha_z (1 - N_c \alpha_z \gamma_z)^{-1}. \tag{2}$$

Using the result $\gamma_x + \gamma_y + \gamma_z = 4\pi$, the expressions for $n_x$, $n_y$, $n_z$ may be combined to give the following Neugebauer relation for the crystal.

$$\frac{1}{\alpha_x} + \frac{1}{\alpha_y} + \frac{1}{\alpha_z} = \frac{4\pi N_c}{3}\left[\frac{n_x^2+2}{n_x^2-1} + \frac{n_y^2+2}{n_y^2-1} + \frac{n_z^2+2}{n_z^2-1}\right]. \tag{3}$$

From now on we denote $\alpha_z$, the polarizability of the molecules parallel to the long axis, by $\alpha_\parallel$ and the average polarizability perpendicular to the long axis by $\alpha_\perp = (\alpha_x + \alpha_y)/2$. When $\alpha_x$ and $\alpha_y$ are nearly equal, Eq. (3) reduces to

$$\frac{1}{\alpha_\parallel} + \frac{2}{\alpha_\perp} = \frac{4\pi N_c}{3}\left[\frac{n_x^2+2}{n_x^2-1} + \frac{n_y^2+2}{n_y^2-1} + \frac{n_z^2+2}{n_z^2-1}\right]. \tag{4}$$

For the liquid phase, the Lorenz–Lorentz relation given below is valid.

$$(\alpha_\parallel + 2\alpha_\perp) = \frac{9}{4\pi N_1}\left(\frac{n^2-1}{n^2+2}\right). \tag{5}$$

Here $N_1$ is the number of molecules per unit volume of the liquid and $n$ is the refractive index of the liquid. Equations (4) and (5) are used to calculate $\alpha_\parallel$ and $\alpha_\perp$. The solution which gives $\alpha_\parallel > \alpha_\perp$ is chosen.

In the nematic phase, the effective polarizabilities of the molecules $\alpha_e$ and $\alpha_0$, corresponding to the electric vector being parallel and perpendicular to the optic axis respectively, are given by

$$\alpha_e = \tfrac{1}{3}(\alpha_\parallel - \alpha_\perp)(2S+1) + \alpha_\perp$$

and

$$\alpha_o = \tfrac{1}{3}(\alpha_\parallel - \alpha_\perp)(1-S) + \alpha_\perp,$$

so that the order parameter $S$ may be expressed as

$$S = (\alpha_e - \alpha_o)/(\alpha_\parallel - \alpha_\perp).$$

The expressions for the extraordinary and ordinary indices of the nematic phase, are:

$$n_e^2 - 1 = 4\pi N\alpha_e(1 - N\alpha_e\gamma_e)^{-1} \tag{6}$$

$$n_o^2 - 1 = 4\pi N\alpha_o(1 - N\alpha_o\gamma_o)^{-1}. \tag{7}$$

Here $N$ is the number of molecules per unit volume of the nematic phase and $\gamma_e$ and $\gamma_o$ are the corresponding internal field constants similar to the case of the crystal given by expressions of the type shown in Eq. (1) and they satisfy the relation $\gamma_e + 2\gamma_o = 4\pi$. The Neugebauer relation for the nematic phase is hence given by

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N}{3}\left[\frac{n_e^2+2}{n_e^2-1} + \frac{2(n_o^2+2)}{n_o^2-1}\right]. \tag{8}$$

For the liquid, the Lorenz–Lorentz relation may be written as

$$\alpha_e + 2\alpha_o = \frac{9}{4\pi N_1}\left(\frac{n^2-1}{n^2+2}\right). \tag{9}$$

Using Eqs. (8) and (9), and remembering that $\alpha_e > \alpha_o$, $\alpha_e$ and $\alpha_o$ may be calculated. Before concluding this section it may be pointed out that in the theory developed by Neugebauer, as is often done in simple dielectric theory, it is assumed that the induced dipoles may be treated as point dipoles for purposes of evaluating the field due to the dipoles within the spherical cavity. It is this simplifying assumption which leads to the result that $\gamma_x + \gamma_y + \gamma_z = 4\pi$. This approximation does not influence the consistency of the results, evidently because the contribution to the local field by the dipoles within the cavity is only a small fraction of the total.

## 3. Calculation of the $\gamma$- and $S$-values and Discussion

The refractive indices for liquid and liquid crystalline PAA and PAP for a number of wavelengths in the visible region of the spectrum, as also the densities of these compounds at different temperatures, have been reported recently by Germain.(8) Using these data, $\alpha_e$ and $\alpha_o$ for the different wavelengths were calculated. From Eq. (6), $\gamma_e$ was also calculated using the data at each wavelength. Since $\gamma_e$ is just a parameter depending on the molecular distribution, the values of $\gamma_e$ calculated from the birefringence data for various wavelengths (at any given temperature) should all be equal. A typical set of values so calculated for PAA is shown in Table 1

TABLE 1 Calculations made for PAA $T = 100\,°\mathrm{C}$

| $\lambda$ in Å | $\alpha_e \times 10^{24}$ | $\alpha_o \times 10^{24}$ | $\gamma_e$ |
|---|---|---|---|
| 6438 | 41.31 | 26.81 | 3.57 |
| 5890 | 42.17 | 27.16 | 3.60 |
| 5086 | 45.17 | 28.00 | 3.55 |
| 4800 | 47.08 | 28.48 | 3.54 |
| 4678 | 48.14 | 28.79 | 3.55 |

and the reasonably good constancy of $\gamma_e$ confirms the validity of the Neugebauer relation. For the sake of consistency, at each temperature we have adopted the averages of the values of $\gamma_e$ and of $\gamma_o$, and obtained the values of $\alpha_e$ and $\alpha_o$ from Eqs. (6) and (7). These values are shown in Tables 3 and 4.

The calculated $\gamma$-factor for the case when the electric vector is parallel to the optic axis is always less than $4\pi/3$, and for the other case when the electric vector is perpendicular to the optic axis, it is more than $4\pi/3$. A physical interpretation of this result can be given as follows. The molecules close to the centre of the cavity contribute most to the sums $\sum(3x_i^2 - r_i^2)r_i^{-5}$, etc. For the nematic medium with an imbricated structure, if we consider a constant distance $r$ from the centre of the cavity, many molecules would have their $z$ coordinates smaller than the $x$ and/or $y$ coordinates, so that the sum $(3z_i^2 - r_i^2)r_i^{-5}$ (for the case of the electric vector parallel to the optic axis) is negative, leading to a $\gamma_e$ value less than $4\pi/3$. Similarly, for the case of the electric vector perpendicular to the optic axis the sums of $(3x_i^2 - r_i^2)r_i^{-5}$ and $(3y_i^2 - r_i^2)r_i^{-5}$ would be positive leading to a $\gamma_o$ value greater than $4\pi/3$.

The values of the densities of crystalline PAA and PAP used in our calculations are the same as those used by Chandrasekhar and Madhusudana.(2) The refractive indices of PAA and PAP in the crystalline phase have been determined by Chatelain.(9,10) at a few wavelengths in the visible region. The data of Germain(8) are not for exactly the same set of wavelengths and they extend to lower wavelengths, in which region the dispersion is large. In these circumstances, the following procedure was adopted for calculating $\alpha_\parallel$ and $\alpha_\perp$ for all wavelengths. In the case of PAA we used the data for the crystal for 5890 and 5461 Å and calculated the values of $\alpha_\parallel$ and $\alpha_\perp$ at these two wavelengths. The average polarizability in the liquid phase for 5461 Å was arrived at by using the data for the liquid phase given by Germain at other wavelengths and fitting a three-term Cauchy formula. By using Eq. (2), $\gamma_z$ was calculated from the data for the above two wavelengths and it was found that the two values were practically the same, viz., 3.172 and 3.176 for PAA. For the sake of consistency, the average of these two $\gamma_z$ values was used to recalculate $\alpha_\parallel$ and $\alpha_\perp$ at 5890 and 5461 Å. The two pairs of values of $\alpha_\parallel$ and $\alpha_\perp$ were fitted by two separate dispersion formulae of the type $\alpha = A/(\omega_0^2 - \omega^2)$ and from these the $\alpha_\parallel$ and $\alpha_\perp$ values were calculated for all wavelengths. In the case of PAP the data for the crystal for the wavelengths 5890 and 4920 Å were used for similar calculations of $\alpha_\parallel$ and $\alpha_\perp$ for all the wavelengths. The value of $\gamma_z$ for PAP was found to be very close to that for PAA, the two values being 3.207 and 3.174, although the refractive indices of these two compounds are different. The absorption wavelengths associated with the dispersion of $\alpha_\parallel$ in PAA and PAP are calculated to be respectively 2447 and 2465 Å. For $\alpha_\perp$ the values of the absorption wavelengths are 1289 and 1232 Å. This close agreement between the values for PAA and PAP is to be expected in view of the close similarity between their molecular structures.

The $S$-factors and the polarizabilities calculated for different wavelengths are shown in Tables 2, 3 and 4. The $S$-factors for each

TABLE 2 Polarizabilities and $\gamma_z$-factors calculated from crystal and liquid refractive index data

| | PAA: $\gamma_z = 3.174$ | | PAP: $\gamma_z = 3.207$ | |
|---|---|---|---|---|
| $\lambda$ in Å | $\alpha_\parallel \times 10^{24}$ | $\alpha_\perp \times 10^{24}$ | $\alpha_\parallel \times 10^{24}$ | $\alpha_\perp \times 10^{24}$ |
| 6438 | 47.64 | 23.52 | 52.67 | 27.39 |
| 5890 | 49.24 | 23.71 | 54.48 | 27.59 |
| 5086 | 53.01 | 24.12 | 58.74 | 28.01 |
| 4800 | 55.04 | 24.33 | 61.04 | 28.21 |
| 4678 | 56.07 | 24.43 | 62.22 | 28.31 |

TABLE 3 Calculated values in the case of PAA[a]

| | $T\,°\mathrm{C}$ | 95 | 100 | 105 | 110 | 115 | 120 | 125 | 130 | 134 |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\gamma_e$ | 3.53 | 3.56 | 3.59 | 3.63 | 3.67 | 3.72 | 3.79 | 3.87 | 3.90 |
| 6438 Å | $\alpha_e$ | 41.57 | 41.33 | 41.01 | 40.67 | 40.29 | 39.82 | 39.20 | 38.39 | 37.59 |
| | $\alpha_o$ | 26.66 | 26.80 | 26.93 | 27.10 | 27.29 | 27.55 | 27.86 | 28.27 | 28.67 |
| | $S$ | 0.618 | 0.602 | 0.584 | 0.563 | 0.539 | 0.509 | 0.470 | 0.419 | 0.370 |
| 5890 Å | $\alpha_e$ | 42.64 | 42.36 | 42.01 | 41.64 | 41.22 | 40.72 | 40.06 | 39.21 | 38.24 |
| | $\alpha_o$ | 26.97 | 27.12 | 27.28 | 27.49 | 27.69 | 27.95 | 28.31 | 28.72 | 29.20 |
| | $S$ | 0.614 | 0.597 | 0.577 | 0.554 | 0.530 | 0.500 | 0.460 | 0.411 | 0.354 |
| 5086 Å | $\alpha_e$ | 45.48 | 45.14 | 44.59 | 44.36 | 43.91 | 43.35 | 42.61 | 41.63 | 40.59 |
| | $\alpha_o$ | 27.86 | 28.01 | 28.18 | 28.40 | 28.61 | 28.91 | 29.23 | 29.68 | 30.17 |
| | $S$ | 0.610 | 0.593 | 0.568 | 0.552 | 0.530 | 0.499 | 0.463 | 0.414 | 0.360 |
| 4800 Å | $\alpha_e$ | 47.31 | 46.94 | 46.56 | 46.14 | 45.63 | 45.03 | 44.19 | 43.15 | 42.07 |
| | $\alpha_o$ | 28.31 | 28.51 | 28.68 | 28.90 | 29.19 | 29.49 | 29.89 | 30.43 | 30.99 |
| | $S$ | 0.619 | 0.600 | 0.582 | 0.561 | 0.535 | 0.506 | 0.465 | 0.414 | 0.360 |
| 4678 Å | $\alpha_e$ | 48.42 | 48.06 | 47.43 | 47.42 | 46.66 | 46.03 | 45.23 | 44.19 | 43.16 |
| | $\alpha_o$ | 28.65 | 28.81 | 28.98 | 29.25 | 29.49 | 29.76 | 30.17 | 30.75 | 31.27 |
| | $S$ | 0.625 | 0.608 | 0.583 | 0.574 | 0.542 | 0.514 | 0.475 | 0.425 | 0.376 |

[a] $\alpha_e$ and $\alpha_o$ are in units of $10^{-24}$ cm$^3$.

TABLE 4 Calculated values in the case of PAP[a]

|  | $T$ °C | 135 | 140 | 145 | 150 | 155 | 160 | 165 |
|---|---|---|---|---|---|---|---|---|
|  | $\gamma_e$ | 3.51 | 3.56 | 3.59 | 3.64 | 3.68 | 3.70 | 3.77 |
| 6438 Å | $\alpha_e$ | 47.95 | 47.56 | 47.20 | 46.69 | 46.13 | 45.54 | 44.59 |
|  | $\alpha_o$ | 29.95 | 30.17 | 30.36 | 30.61 | 30.85 | 31.15 | 31.61 |
|  | $S$ | 0.712 | 0.688 | 0.666 | 0.636 | 0.604 | 0.569 | 0.514 |
| 5890 Å | $\alpha_e$ | 49.18 | 48.70 | 48.31 | 47.79 | 47.24 | 46.62 | 45.63 |
|  | $\alpha_o$ | 30.24 | 30.46 | 30.65 | 30.90 | 31.19 | 31.55 | 32.06 |
|  | $S$ | 0.704 | 0.678 | 0.656 | 0.628 | 0.597 | 0.560 | 0.504 |
| 5086 Å | $\alpha_e$ | 52.45 | 51.93 | 51.46 | 50.87 | 50.29 | 49.56 | 48.36 |
|  | $\alpha_o$ | 31.05 | 31.28 | 31.53 | 31.79 | 32.14 | 32.49 | 33.05 |
|  | $S$ | 0.696 | 0.672 | 0.648 | 0.621 | 0.591 | 0.555 | 0.498 |
| 4800 Å | $\alpha_e$ | 54.57 | 54.05 | 53.54 | 52.92 | 52.27 | 51.48 | 50.25 |
|  | $\alpha_o$ | 31.52 | 31.80 | 32.11 | 32.42 | 32.72 | 33.08 | 33.69 |
|  | $S$ | 0.702 | 0.678 | 0.653 | 0.625 | 0.595 | 0.560 | 0.504 |
| 4678 Å | $\alpha_e$ | 55.84 | 55.28 | 54.74 | 54.09 | 53.36 | 52.58 | 51.28 |
|  | $\alpha_o$ | 31.85 | 32.14 | 32.39 | 32.70 | 33.06 | 33.42 | 33.84 |
|  | $S$ | 0.708 | 0.683 | 0.659 | 0.631 | 0.599 | 0.565 | 0.514 |

[a] $\alpha_e$ and $\alpha_o$ are in units of $10^{-24}$ cm$^3$.

temperature shown in each column of Tables 3 and 4 agree to within about 1% of the mean value. Especially for the middle three wavelengths the agreement is excellent. For the two extreme wavelengths there are small discrepancies which may be attributed to the fact that we have used a simple single-term dispersion formula for $\alpha_{\parallel}$ and $\alpha_{\perp}$. Tables 5 and 6 show the close agreement of the values of $S$ calculated by us with those calculated by Chandrasekhar and Madhusudana.(2) However, the values of the polarizabilities calculated by us are very different from their values by about 10%. In spite of this, the ratio $(\alpha_e - \alpha_o)/(\alpha_{\parallel} - \alpha_{\perp})$ is not changed significantly. Tables 5 and 6 also show the values of $S$ obtained by Rowell *et al.*(11) from NMR studies. There is broad agreement, but the values of $S$ obtained from birefringence data are somewhat different from those obtained from NMR studies.

TABLE 5 PAA $T_f = 135\,°\mathrm{C}$

| $T_f - T$ | $S$ (calc) | $S$ (SC & NVM) | $S$ (NMR) |
|---|---|---|---|
| 1 | 0.364 | 0.370 | — |
| 4 | 0.404 | 0.414 | 0.409 |
| 7 | 0.437 | 0.447 | 0.496 |
| 12 | 0.483 | 0.484 | 0.538 |
| 17 | 0.518 | 0.512 | 0.568 |
| 27 | 0.568 | 0.553 | — |
| 37 | 0.607 | 0.584 | — |

TABLE 6 PAP $T_f = 167\,°\mathrm{C}$

| $T_f - T$ | $S$ (calc) | $S$ (SC & NVM) | $S$ (NMR) |
|---|---|---|---|
| 1 | 0.496 | 0.494 | — |
| 4 | 0.529 | 0.535 | 0.533 |
| 8 | 0.569 | 0.574 | 0.583 |
| 13 | 0.603 | 0.609 | 0.639 |
| 18 | 0.634 | 0.637 | 0.671 |
| 28 | 0.685 | 0.680 | 0.721 |

Mueller(12) has theoretically considered the calculation of the $\gamma$-factors for different lattices, as e.g., the case of tetragonal lattices with different axial ratios. Similar detailed calculations with cylindrical distribution functions are required before one can correlate the $\gamma$-factors with the anisotropy of molecular distribution in nematic liquid crystals. The present calculations show that $\gamma_e$ which is less than $4\pi/3$ increases slowly with increase of temperature, although close to the transition point the value is still very different from $4\pi/3$. The change from the anisotropic to the isotropic distribution apparently occurs over a very narrow range of temperature abruptly. The close correspondence between the values of $\gamma_e$ for PAA and PAP indicates that the anisotropic molecular distributions in the two cases are very similar, as is to be expected from the similarity of their molecular structures. In fact, this similarity was assumed by Chandrasekhar *et al.*(13) in their paper dealing with the relationship between elasticity and orientational order in nematic liquid crystals. In conclusion, it may be stated that the use of the Neugebauer relations leads to consistent results and at the same time provides indirect information regarding the anisotropic nature of the molecular distribution in nematic liquid crystals.

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