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DEPENDENCE OF POLARIZABILITY AND DIAMAGNETIC SUSCEPTIBILITY ON THE ORDER PARAMETER D

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ABSTRACT

In nematic liquid crystals consisting of molecules which deviate from cylindrical symmetry the molecular order cannot be completely characterized by the order parameter S alone, but the order parameter D is required additionally. It is shown here, that the diamagnetic susceptibility, the polarizability, and hence the refractive index depend on S as well as on D, and that the usually applied evaluation gives a combination of these.

INTRODUCTION

The theory of nematic state by Maier and Saupe[1] has been derived with the assumption of cylindrically symmetric molecules. In reality however, the two transverse axes of the molecules will usually be different. To account for this fact, Alben, McColl, and Shih[2] introduced an additional order parameter D, which was interpreted later by Straley[3] in terms of Euler angles as $D = \frac{3}{2}\sin^2\theta\cos 2\phi$. Luckhurst et al.[4]

derived the pseudo-potential which allows to calculate D as function of S quantitatively. For the first time, experimental evidence of D was found in NMR measurements[3,4]. Very recently the dependence of the dichroic ratio on D has been discussed, and such measurements have been evaluated for D of non-mesogenic molecules dissolved in nematic liquid crystal[5,6].

The probably most frequently employed method to evaluate the order parameter is that which uses molecular polarizabilities derived from the related, experimentally determined refractive indices[7]. Another suitable experimental observable is the diamagnetic susceptibility[7]. In the following it will be shown that in both cases S cannot be evaluated separately but a combination of S and D.

CALCULATIONS

If an electrical field of strength E_z parallel to the z axis of the laboratory axes system x,y,z is applied on a nematic sample, it produces therein a polarization P_z. It is assumed, that the molecular axes system x',y',z' coincides with the main axes of the molecular polarizability α (main values $\alpha_{z'}$, $\alpha_{y'}$, $\alpha_{x'}$). Describing the mutual orientation of the two frames by the Euler angles θ, ψ, and ϕ, P_z is given by

$$P_z = E_z(\alpha_{z'} n_{zz'}^2 + \alpha_{y'} n_{zy'}^2 + \alpha_{x'} n_{zx'}^2)$$

with

$$n_{zz'} = \cos\theta$$
$$n_{zy'} = \sin\theta \sin\phi$$
$$n_{zx'} = \sin\theta \cos\phi$$

Averaging over the ensemble and substituting $\overline{\sin^2\theta} = \frac{2}{3}(1 - S)$ and $\overline{\sin^2\theta \cos 2\phi} = \frac{2}{3}D$ result in

$$\overline{P_z} = \frac{E_z}{3}\{\alpha_{z'} + \alpha_{y'} + \alpha_{x'} + 2(\alpha_{z'} - \frac{1}{2}(\alpha_{y'} + \alpha_{x'}))S + (\alpha_{y'} - \alpha_{x'})D\}$$

Similarly, the application of a field parallel to y gives

$$P_y = E_y(\alpha_{z'} n^2_{yz'} + \alpha_{y'} n^2_{yy'} + \alpha_{x'} n^2_{yx'})$$

with

$$n_{yz'} = -\sin\theta\cos\psi$$
$$n_{yy'} = -\sin\psi\sin\phi + \cos\theta\cos\psi\cos\phi$$
$$n_{yx'} = \sin\psi\cos\phi + \cos\theta\cos\psi\sin\phi$$

By averaging and taking into account that for uniaxial phases $\overline{(1 + \cos^2\theta)\cos 2\psi\cos 2\phi - 2\cos\theta\sin 2\psi\cos 2\phi}$ and $\overline{\sin^2\theta\cos 2\psi}$ vanish,[3] we get

$$\overline{P_y} = \frac{E_y}{3}\{\alpha_{z'} + \alpha_{y'} + \alpha_{x'} - (\alpha_{z'} - \frac{1}{2}(\alpha_{y'} + \alpha_{x'}))S - (\alpha_{y'} - \alpha_{x'})\frac{D}{2}\}$$

The same procedure for P_x results in $\overline{P_x} = \overline{P_y}$ in this special case of a uniaxial phase. Hence, the macroscopically measurable polarizabilities $\alpha_e = \overline{P_z}/E_z$ and $\alpha_o = \overline{P_y}/E_y$ (where o and e stand for ordinary and extraordinary, respectively) can be written as

$$\alpha_e = \alpha_m + 2(\alpha_a S + \alpha_f D) \qquad (1)$$
$$\alpha_o = \alpha_m - (\alpha_a S + \alpha_f D)$$

with

$$\alpha_m = (\alpha_{z'} + \alpha_{y'} + \alpha_{x'})/3$$
$$\alpha_a = (\alpha_{z'} - \frac{1}{2}(\alpha_{y'} + \alpha_{x'}))/3$$
$$\alpha_f = (\alpha_{y'} - \alpha_{x'})/6$$

The expression used to evaluate S from experimentally determined polarizabilities in the case of cylindrically symmetric molecules now reads as

$$\frac{\alpha_e - \alpha_o}{3\alpha_a} = S + \frac{\alpha_f}{\alpha_a} D \qquad (2)$$

In the same manner, the diamagnetic susceptibility χ can be treated. Using a corresponding notation, the molar susceptibilities are given by

$$\begin{aligned} \chi_e &= \chi_m + 2(\chi_a S + \chi_f D) \\ \chi_o &= \chi_m - (\chi_a S + \chi_f D) \end{aligned} \qquad (3)$$

In analogy to Eq. (2) it follows

$$\frac{\chi_e - \chi_o}{3\chi_a} = S + \frac{\chi_f}{\chi_a} D \qquad (4)$$

DISCUSSION

In comparison to the expression originally derived by Maier and Saupe[7], each of the Eqs. (1) to (4) comprises an additional term depending on D which accounts for the assumed biaxiality of the molecules. For real nematogens this term will generally be different from zero. The polarizabilities are derived from the related refractive indices, which are subject to S and D as well.

From either the polarizabilities or the diamagnetic susceptibilities, S or D cannot be determined seperately. When the results from Eqs. (2) and (4) are identified with S alone, as it was done up to now, discrepancies occur provided the factors α_f/α_a and χ_f/χ_a are different. Theoretically they are bounded to the interval {-1, +1}, in practice the range will be much smaller. Hence, in general it will be difficult to derive reliable results on D from the comparison of these two experiments or with others. Additionally, D will be about one order of magnitude smaller than S, provided the result from NMR measurements[4] can be taken to be representative. This is supported by the fact, that for nematogenic compounds not as low values for S or S+D (what might be obtained from linear dichroism measurements[6]) have been reported as would be expected in the accessible temperature range from theory[4] for considerably larger ratios of D/S.

The components α_i (with i = x',y',z') which α_a and α_f are composed of must be determined from the crystalline state, where the geometry of the molecules might differ from the one in the nematic phase. Apart from this well known problem - which exists for the diamagnetic susceptibility as well - another difficulty arises from the fact that due to the assumed biaxiality all the three α_i are different; therefore, each of them must be derived from the related refractive index by considering the internal field[8] for which the correction is not known precisely.

The order parameter S of cylindrically symmetric molecules can conveniently and precisely be determined from refractive index measurements. However, when the deviation from this symmetry cannot be neglected, the disadvantages mentioned above come into play. At least for the determination of D linear dichroism (in the ultraviolet and probably even more in the infrared region[6]) and NMR measurements seem to offer better chances.

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