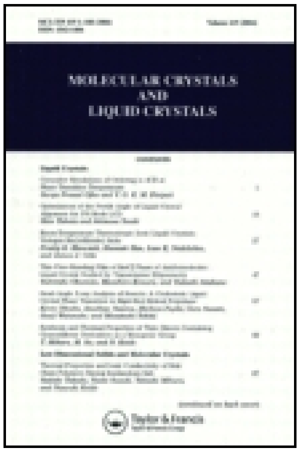

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EXPERIMENTAL DETERMINATION OF THE ELASTIC CONSTANT k_{13} OF A NEMATIC LIQUID CRYSTAL

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Abstract

The elastic constant k_{13} is the coefficient of a divergence term in the free energy density and involves the second derivative of the director field. Thus its influence is felt only at the surface of the sample. We have analysed the optical path difference of a hybrid aligned nematic liquid crystal PCH7 taken in a cell which has a weak homeotropic alignment on one glass plate and a strong homogeneous alignment on the other. We use the approximation that solutions in the class of Euler-Lagrange equations are valid up to the boundaries and extract both k_{13} and the anchoring energy at the homeotropically aligned surface. In view of the recent argument by Oldano and Barbero that the k_{13} term by itself may lead to discontinuities in the director configuration near the surfaces our measurements may be taken to yield an 'effective' value which may have contributions from other terms influencing the director configuration at the surface.

INTRODUCTION

The symmetry of the uniaixal nematic liquid crystal which is characterised by an apolar director allows for curvature elasticity of the medium[1,2]. The usual expansion for the elastic energy density consists of quadratic terms of the curvature components describing splay, bend and twist of the director field, the corresponding elastic constants being k_{11}, k_{22}, and k_{33} respectively. Terms which are linear in the second derivative of the director field are also of the same order as the above, and in particular Nehring and Saupe[3] have argued that the free energy density should contain the term k_{13} div(**n** div **n**). It is clear that such a term satisfies the Euler-Lagrange equation identically, i.e., it does not contribute to the bulk equilibrium configuration of the director. However, it does lead to a surface torque which is not important if the anchoring at the surface is strong. If it is 'weak' k_{13} does influence the director configuration and cannot be ignored. For this reason k_{13} is sometimes called 'surface-like volume elasticity'.[4,5] If we confine our attention to configurations in which the director is confined to the vertical plane, the free energy density reads as

$$F_d = \frac{1}{2}[k_{11}(\mathrm{div}\,\mathbf{n})^2 + k_{33}(\mathbf{n} \times \mathrm{curl}\,\mathbf{n})^2] + k_{13}[\mathrm{div}\,(\mathbf{n}\,\mathrm{div}\,\mathbf{n})] \qquad (1)$$

The possible consequences of the influence of k_{13} in such configurations have been discussed by some authors[6,7]. Oldano and Barbero[8] have recently argued that the variational problem in such geometries does not have a solution corresponding to the k_{13} term. Starting from the free energy density given by Eq. (1), and assuming that variation in θ and that in $d\theta/dz$ are independent variables at the boundaries, they find that θ should have discontinuities near the boundaries in order to minimise the total energy. In view of this mathematical difficulty the physical problem appears to be ill-defined. Inclusion of higher order elasticity[9] as well as other possible surface terms[10] may restore a continuous variation of θ in the sample. These new constants are unknown at present. k_{13} of course is a material parameter, dependent only on the chemical nature of the compound and the temperature, and of the same order as k_{11}, k_{22} and k_{33}. Interestingly, Faetti[11] has found that free standing MBBA films of ~50 μm thickness have a spontaneously splayed configuration. This can be understood if k_{13} has a negative value, and is sufficiently large so that the effect of k_{11} and k_{33} which would prevent any spontaneous deformation is overcome. It is of considerable interest to get an experimental estimate of k_{13}, even if it is based on a gross approximation. We have chosen to assume that the solution in the class of Euler-Lagrange equation is valid right up to the boundary. The value of θ satisfying this solution is then used in the surface energy which includes the k_{13} contribution. The surface energy is then separately minimised.[4] The k_{13} value thus obtained could be taken as an 'effective' one which may be influenced by other terms, which are necessary to fully describe the director configuration at the boundaries. There have been a couple of earlier attempts[5,12] to estimate the magnitude k_{13} in some nematics by using other approximations.

Observations on a sample taken in a capillary tube show that PCH-7 (cyanohpetylphenyl cyclohexane) can be oriented homeotropically with a relatively 'weak' anchoring on a glass surface treated with a low percentage of ODSE (octadecyl triethoxy silane) in methyl alcohol. We have used the effect of an external magnetic field on the director configuration to estimate 'k_{13}' at room temperature in this compound.

EXPERIMENTAL METHOD

The method makes use of a hybrid aligned cell. The director is parallel and strongly anchored at one of the surfaces. The other surface is treated for homeotropic alignment with weak anchoring. Consequently the director makes a small angle θ_o with the normal to the plate at the second surface (Fig. 1). An external magnetic field perpendicular to the plates is used to vary the director profile. The value of θ_o as a function of the magnetic field strength H can be determined by an optical technique and the value of k_{13} can be extracted from the surface torque balance equation.

The bulk free energy is given by

$$F = \int_0^d [k_{33}(1-\kappa\sin^2\theta)(d\theta/dz)^2/2 - \Delta\chi H^2\cos^2\theta/2]dz \qquad (2)$$

where $\kappa = (k_{33}-k_{11})/k_{33}$. $\Delta\chi$ is the anisotropy of diamagnetic susceptibility per unit volume. The k_{13} term has

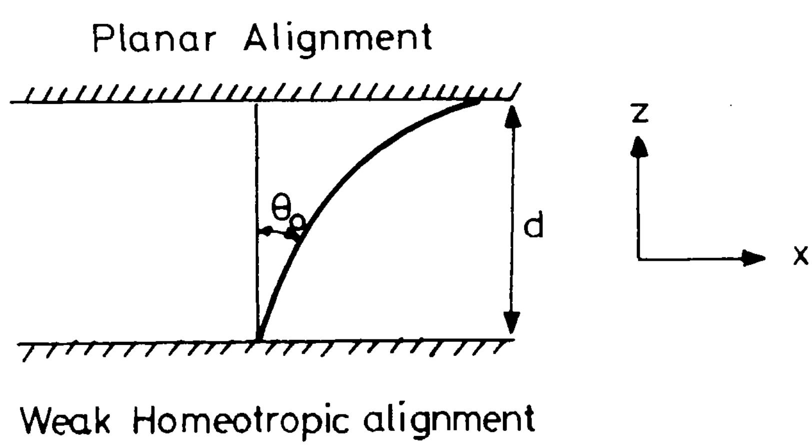

Fig. 1. Schematic drawing of the experimental geometry

been dropped since it contributes only to the surface torque.

Minimising F using the Euler-Lagrange equation we can write

$$\frac{d\theta}{dz} = \pm \left[\frac{C - \Delta\chi H^2 \cos^2\theta}{k_{33}(1 - \kappa \sin^2\theta}\right]^{1/2} \qquad (3)$$

where C is a constant of integration. As θ increrases with z the positive root is chosen. The thickness d of the sample

$$d = \int_0^d dz = \int_{\theta_0}^{\pi/2} d\theta \Big/ \left[\frac{C - \Delta\chi H^2 \cos^2\theta}{k_{33}(1 - \kappa \sin^2\theta)}\right]^{1/2} \qquad (4)$$

A measurement of the optical path difference introduced by the sample can be used to obtain the variation of θ_o with the applied magnetic field. If n_o and n_e are the ordinary and extraordinary refractive indices of the sample, the effective extraordinary index n_{eff} in the sample with a tilted director is given by

$$n_{eff} = n_e n_o / n_e (1 - R\sin^2\theta)^{1/2} \qquad (5)$$

where $R = (n_e^2 - n_o^2) / n_e^2$.

The path difference is then given by

$$\Delta\ell = \int_0^d (n_{eff} - n_o)\, dz$$

$$= n_o \int_{\theta_o}^{\pi/2} [1/(1-R\sin^2\theta)^{1/2} - 1](\frac{dz}{d\theta})\, d\theta \qquad (6)$$

Using the known values of n_e, n_o, $\Delta\chi$, k_{11}, k_{33} and our experimentally measured values of the thickness d, the path difference $\Delta\ell$ and magnetic field H, eqns. (4) and (6) can be solved by a suitable iterative procedure to obtain the values of C and θ_o. The value of θ_o thus obtained should satisfy the surface torque balance equation.

The surface anchoring energy at the weakly anchored surface, i.e., at $z = 0$ is assumed to be of the form[13] $W \sin^2 \theta_o/2$. The surface torque balance equation at $z = 0$ is given by

$$W \sin \theta_o \cos \theta_o + k_{13}(\cos^2 \theta_o - \sin^2 \theta_o)(d\theta/dz)_{z=0} + k_{13} \sin \theta_o \cos \theta_o \frac{d}{d\theta}\left(\frac{d\theta}{dz}\right)_{z=0} = k_{33}(1 - \kappa \sin^2 \theta_o)\left(\frac{d\theta}{dz}\right)_{z=0} \qquad (7)$$

The value of $(d\theta/dz)_{z=0}$ can be obtained from Eqn. (3). The path difference $\Delta\ell$ is measured both without and with an applied magnetic field H. Values of θ_o and C are obtained by the iterative procedure. These data can be used in eqn. (7) to estimate both the anchoring energy W and the elastic constant k_{13}.

The 'weak' anchoring at the homeotropic surface is not very uniform over the entire area of the sample. This results in a non-uniformity of the alignment. However, small areas with good alignment could be selected for the measurement of the path difference.

The thickness of the empty cell was measured using a double beam ultraviolet spectrophotometer (Hitachi Model U-3200). The cell was mounted between the pole-pieces of an electromagnet (Cook and Sons Ltd.). The pole pieces have holes drilled through them to allow a light beam to pass through. Optical path difference measurements were made using a (Leitz) tilting compensator. In order to increase the sensitivity of the measurements, a photo diode was used to detect the exact centre of the compensating band. The actual experimental arrangement is shown schematically in Fig. 2.

RESULTS AND DISCUSSION

As seen from eqns. 4 and 6 we need the following physical parameters for analysing the experimental data: k_{11}, k_{33} and $\Delta\chi$ which were obtained from the measurements of Schad et al.[14],. the refractive indices n_o and n_e obtained from the data of Pohl et al.[15] and d, $\Delta\ell$ and H which were experimentally measured by us as described earlier. The errors in the measurements of k_{33}, k_{11} and $\Delta\chi$ are given to be $\simeq$4%, 2% and 3% respectively. From the plots of n_o and n_e versus temperature in Ref. 15 we estimate that the error in the measurement is

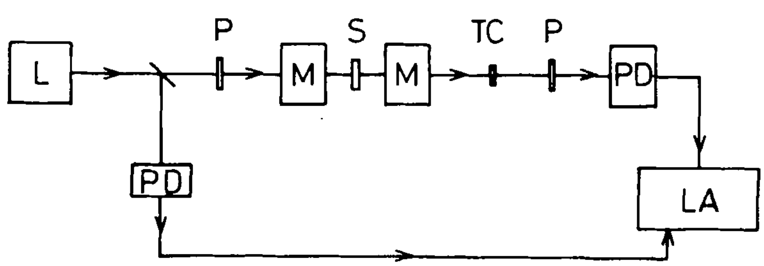

Fig. 2. Block diagram of the experimental set up. L: sodium lamp, P: Polarizer, M: Pole-piece of electromagnet, S: sample. TC: tilting compensator, PD: photo diode, LA : Lock-in-amplifier.

≃0.1%. The errors in d and $\Delta\ell$ are ≃1%. A significant change in $\Delta\ell$, and hence θ_o could be obtained only at field strengths >5000 Gauss which was also close to the highest magnetic field that could be obtained with the electromagnet used in the experiment. In this range H could be measured with an accuracy of ±25 Gauss. The alignment of the sample deteriorates as the temperature is increased. Two independent measurements were made in different cells at temperatures much below the N-I transition point. The values of k_{33}, k_{11}, n_o, n_e and $\Delta\chi$ at these temperatures are given in Table 1 and the values of k_{13} and W extracted from Eqn.(7) are given in Table 2.

Table 1

$t_r = T/T_{NI}$	k_{33} (10^{-5}) dynes	k_{11} (10^{-6}) dynes	n_o	n_e	$\Delta\chi$ (10^{-7}) CGS units
0.9088	0.171	0.99	1.485	1.599	0.346
0.9014	0.177	1.02	1.486	1.601	0.348

Table 2

$t_r = T/T_{NI}$	d (10^{-2}) cm	H Gauss	$\Delta\ell$ (10^{-4}) cm	k_{13} (10^{-7}) dynes	W (10^{-3}) ergs/cm^2
0.9088	0.1063	54*	0.795	9 ± 4	2.2 ± 0.4
		5480	0.6875		
0.9014	0.1323	54*	0.9185	14 ± 4	1.5 ± 0.4
		5450	0.753		

*residual field of the magnet

Taking into account the errors in the measurements of the various parameters that figure in the analysis one can estimate that the error in k_{13} is $\simeq 4\times10^{-7}$ dyne and that in the anchoring energy W is about 0.4×10^{-3} ergs/cm^2. The temperatures at which the two independent measurements were made differ by about 2°C. However since the temperatures are 30°C below the N-I transition point, the 2° difference cannot be expected to have a strong influence on k_{13} and the two values agree within the error limits.

The sign of k_{13} obtained from the analysis turns out to be positive. The elastic constant k_{13} is essentially the coefficient of a linear term in the second derivative of **n** and hence can be either positive or negative. The molecular model of Nehring and Saupe[16] gives the sign of k_{13} to be negative. In this theory only attractive interactions have been considered and the short range order has been ignored. Further, the shape anisotropy of the molecules has also not been taken into account. These effects can be expected to have a strong influence on k_{13}. Considering the shape factor, deviations from cylindrical symmetry should influence the sign of k_{13}. We can expect that banana shaped molecules have a positive k_{13} and pear shaped molecules have a negative k_{13}. The compound PCH-7 has the strongly polar cyano end group and hence can be expected to form antiparallel pairs. These pairs in principle can have a banana shaped conformation. This could possibly explain the positive sign of k_{13} found in this compound.

Within the accuracy of measurements the value of k_{13} turns out to be of the same order as the other elastic constants in agreement with dimensional estimates. Careful measurements are required to obtain more accurate values of 'k_{13}' and attempts are being made to improve the measurements. We are also trying to extend this method to other systems.

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