High Precision Method for Determining Twist Elastic Constants of Nematic Liquid Crystals

I. Theory

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In a magnetic field a nematic liquid crystal may sustain a variety of twist modes. Their influence upon light propagating trough the liquid crystal can be used to evaluate the twist elastic constant from simple reflection or transmission measurements.

Introduction

The most simple elastic deformation of homogeneously oriented nematic liquid crystals, the pure twist deformation, was theoretically investigated since Ornstein [1] by several authors [2–10]. The results were given in terms of elliptic integrals or series expansions.

Of experimental papers dealing with the twist mode there existed, until recently, only one, published in 1934 by Freedericksz and Zwetkoff [11]. The method used by these authors is based on total reflection of light which is influenced by the state of deformation of the liquid crystal. This very elegant procedure, however, has fallen into oblivion. Instead of it, different methods for determining the twist elastic constant, k_{22} [6], have been proposed. Williams and Cladis [12] used Durand's [13] method by which k_{22} is determined from the cholesteric to nematic phase transition. In this case the nematic liquid crystal has to be doped with chiralic molecules in order to get the cholesteric phase.

Another procedure also using the cholesteric phase was applied by Rondolez and Hulin [14]. A magnetic field directed parallel to the helicoidal axis may produce a periodic perturbation in the liquid crystal from which k_{22} is determined.

A dynamical method proposed by De Gennes [15] was used by L. Leger [16]. Here with a rotating magnetic field 180° twist walls are produced. The value of k_{22} is calculated from their migration time. In a further publication by Leger [17] the static and dynamic properties of inversion walls are used to derive the ratio of twist to bend elastic constant k_{22}/k_{33} and twist to splay elastic constant k_{22}/k_{11}.

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Cladis [18] applied another static method. By a twist deformation a rotation of an interference pattern is caused. From the angle of rotation k_{22} may be deduced. Cladis gives the most accurate values of k_{22}.

In the most recent paper dealing with elastic constants of nematic liquid crystals [19] an electrohydrodynamic flow pattern is used for measuring k_{22}. However the precision of the values for this method is rather poor.

This paper reports a method which should allow the measurement of the ratio of twist elastic constant k_{22} and the diamagnetic anisotropy χ_a with high precision. It is a modification of the procedure proposed by Freedericksz and Zwetkoff [11]. Instead of total reflection we use a change in the optical path length caused by a deformation which creates an interference pattern with sharp maxima and minima. It is shown that these extrema in intensity are intimately related to a threshold field H_c from which k_{22}/χ_a can be directly evaluated. For this purpose we revised the theoretical background for the twist mode. It is assumed that the deformation is caused by a magnetic field. The dependence of the angle of deformation on the magnetic field and the position in the sample is derived in a closed form. These solutions of the differential equation of motion are discussed. They enable us to calculate light propagation in the deformed liquid crystal for arbitrary wavevector. By an additional simple model calculation we explain some special results from our numerical computations and give the formulae for the determination of k_{22}/χ_a.

Twist Modes

The experimental arrangement corresponding to our calculations is shown in Figure 1. The nematic liquid crystal is located between two glass plates positioned at $x=0$ and $x=x_0$. We describe the mesophase by a vector field $\boldsymbol{L}(\boldsymbol{r})$ which gives the

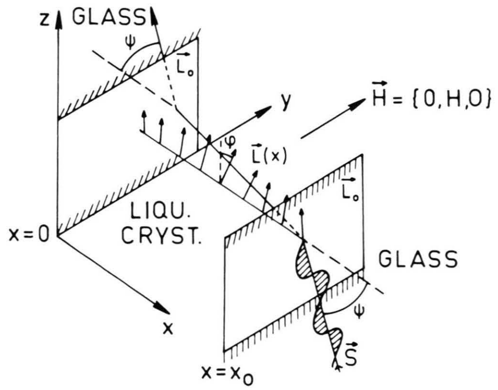

Fig. 1. The nematic liquid crystal is located between two glass plates located at $x=0$ and $x=x_0$. Its undisturbed state is characterized by $L_0=\{0, 0, L_z\}$. The deformation is introduced by a magnetic field having only a y-component. The liquid crystal is irradiated by polarized light propagating in the glass in the direction of z.

preferential direction of the molecules at the position $\boldsymbol{r}$. In the undisturbed state $\boldsymbol{L}$ is assumed to have only a z-component: $\boldsymbol{L}_0(\boldsymbol{r})=\{0,0,L_z\}$. Distortions are caused by a magnetic field $H=\{0,H_y,0\}$ so that in general $\boldsymbol{L}$ is given by

$$\boldsymbol{L}=\{0, \sin\varphi(x), \cos\varphi(x)\}.$$

The molecules on the boundaring glass plates are taken to be fixedly anchored and we adopt the boundary conditions

$$\varphi(0)=0, \quad \varphi(x_0)=0. \tag{1}$$

The configuration φ which corresponds to an extremum of the free energy satisfies the differential equation [5]

$$\mathrm{d}^2\varphi/\mathrm{d}x^2+A^2\sin\varphi\cos\varphi=0 \tag{2}$$

where

$$A=\sqrt{\chi_a/k_{22}}\,H. \tag{3}$$

k_{22} is the twist elastic constant and χ_a the anisotropy of the diamagnetic susceptibility. We suppose $\chi_a>0$. The solutions of Eq. (1) are of the form

$$\sin\varphi(x)=(a/A)\,\mathrm{sn}(A\,x\,|\,a/A). \tag{4}$$

Here a is a constant determined by the boundary condition

$$2\,n\,K(a/A)=A\,x_0 \tag{5}$$

with integer n (see Appendix). The function $\mathrm{sn}(x|k)$ is the sinus amplitudinis [20] to the modulus k. Any deformation $\varphi(x)$ of the considered system may be composed by twist modes given by Eqs. (4) and (5).

For various magnetic field strengths the first twist mode ($n=1$) is illustrated in Figure 2. The figure shows the twist angle φ as a function of the relative distance x/x_0 from one of the walls of the sample. The magnetic field is given in terms of a reduced field H/H_c or equivalently by the modulus $k=a/A$, which is equal to the sinus of the maximum angle of deformation:

$$k=\sin\varphi_{\max}. \tag{6}$$

$k=1$ corresponds to the undistorted case, $k=0$ correspond to an infinitely large field.

If $n=2,3,\ldots$ (not drawn in the figure) the curves show $1,2,\ldots$ inversion walls over the distance x_0 whose centers coincide with the zeros of the sinus amplitudinis of Equation (4). Each of the twist modes has its own threshold field. Since $K(k)\geqq\pi/2$, we deduce from Eq. (5)

$$n\,\pi\leqq A\,x_0 \quad \text{or} \quad n\,\pi=\sqrt{\chi_a/k_{22}}\,H_c\,x_0. \tag{7}$$

For $n=1$ this is the well known relation for the threshold field H_c at which the liquid crystal begins to deform [21]. From Eq. (7) we see that the higher deformations have threshold fields which are $2,3,\ldots$ times as large as for fundamental deformation ($n=1$). The higher order twist modes are energetically less favorable than the mode characterized by $n=1$, so that we can confine ourselves to this deformation only.

Optical Effects

For some samples having deformations characterized by $n=1$ we computed the transmission and reflection properties in dependence on the applied magnetic field. For the experimental arrangement cf. Figure 1. The plane of incidence of light is the x,y-plane, ψ is the angle of incidence. The liquid crystal is assumed to have positive dielectric anisotropy.

Light with the electric vector parallel or perpendicular to the x,y-plane shall be denoted as π or σ polarized light, respectively. For shortness we use symbols like $(\pi|\sigma)$ which means that the in-

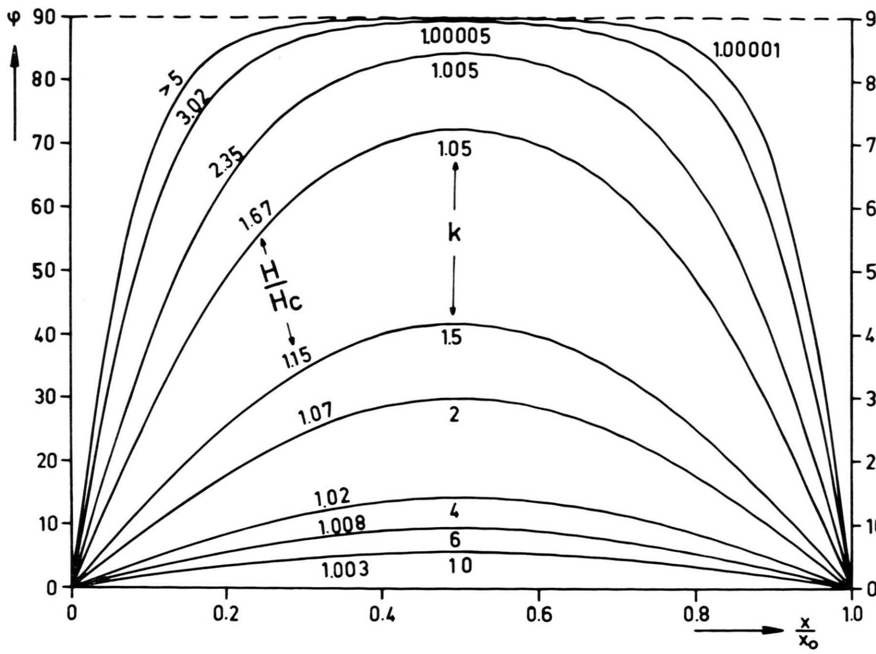

Fig. 2. Twist deformation of a homogeneously oriented liquid crystal by a magnetic field for fixed anchoring of the molecules at the walls. The Figure shows the twist angle in dependence on the reduced distance x/x_0 from the walls for various reduced magnetic fields H/H_c. The curves correspond to the lowest order deformation [$n=1$, Equation (5)]. x_0 is the sample thickness.

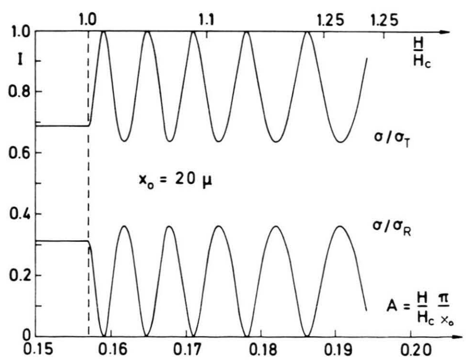

Fig. 3 a

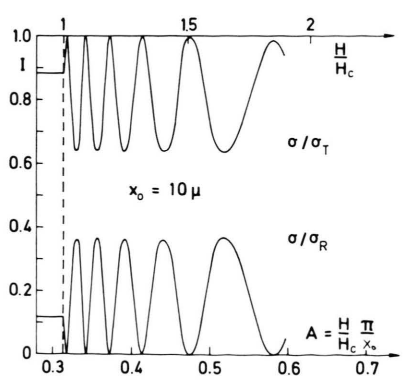

Fig. 3 b

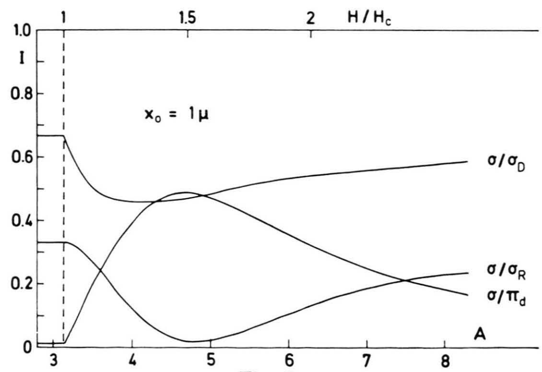

Fig. 3 c

Fig. 3. Reflected (σ/σ_r) and transmitted (σ/σ_t) intensities of light as a function of the reduced field H/H_c for various sample thicknesses; (a) $x_0=20\ \mu$, (b) $x_0=10\ \mu$, (c) $x_0=1\ \mu$. The incoming light is σ-polarized with unit intensity, the angle of incidence ψ is 67°.

going light is π polarized and the outgoing one is analized perpendicular (σ) to the plane of incidence. An index t or r at the second letter is used to indicate that either transmitted (t) or reflected (r) light is considered.

Figure 3 a shows the transmitted and reflected light intensity of a 20 μ thick sample cell in dependence of the applied reduced magnetic field H/H_c. For computation we used a propagation-matrix method described elsewhere [22].

If not stated otherwise, the intensity of the incoming light is chosen to be unity. Up to the critical field H_c there is no deformation in the liquid crystal and as usual, one part of the incoming light is reflected and the other one transmitted. Starting with the deformation the intensities are drastically changed and some sort of oscillation may be observed with increasing field. The outgoing radiation is not depolarized as can be checked by summing the reflected and transmitted intensities. The same holds for a 10 μ thick sample as indicated in Figure 3 b. Here again the polarization follows the twist [23] giving rise to the extraordinary ray only. In the case of a 1 μ thick sample (Fig. 3 c) this is no longer true because the twist occurs in a distance comparable in magnitude to the wavelength. As a consequence we get a large portion of elliptically polarized light.

From Fig. 3 we see that the threshold field H_c may in principle be determining by a simple reflection or transmission measurement. Unfortunately, our experiments showed that the theoretically predicted sharp change in intensity at H_c really occurs in a relatively broad field interval so that the threshold can only approximately be determined by this method. For higher fields, however, the oscillation in intensity with varying field can be found experimentally. The field for maximum or minimum intensity is intimately related to the threshold field so that the extrema can be used for measuring H_c. This shall now be shown.

Method for Determining k_{22}/χ_a

The oscillations are caused by interference of light at parallel plates (see Figure 4). The incident light is assumed to have σ-polarization and the liquid crystal is adopted to have uniaxial positive dielectric birefringence ($n_e > n_0$). In the unperturbed state ($H < H_c$) where the director is parallel to the z-direction, only the extraordinary ray is excited and light describes a straight line in the liquid crystal as indicated by the dashed line. If a twist deformation is introduced and the wavelength of the light is short compared to some distance where a noticeable twist occurs, the light path becomes a curved line. In consequence, the interference conditions in the outside regions (glass) are changed. In a uniaxial crystal the refractive index n for a light beam propagating in a direction $\boldsymbol{s}$ and forming an angle Θ with the optic axis $\boldsymbol{L}$ is given by (extra ordinary ray):

$$\frac{1}{n^2} = \frac{1}{n_0^2} \cos^2 \Theta + \frac{1}{n_e^2} \sin^2 \Theta .$$

n_0 and n_e are the principle refractive indices. For the nematic liquid crystal we have therefore

$$n^2 = \varepsilon_1 \varepsilon_2 / (\varepsilon_1 \cos^2 \Theta + \varepsilon_2 \sin^2 \Theta) . \quad (8)$$

In terms of the twist angle $\varphi(x)$ and the angle ϑ between $\boldsymbol{s}$ and the twist axis x, Θ is given by (see Fig. 5)

$$\cos \Theta = \sin \vartheta \sin \varphi .$$

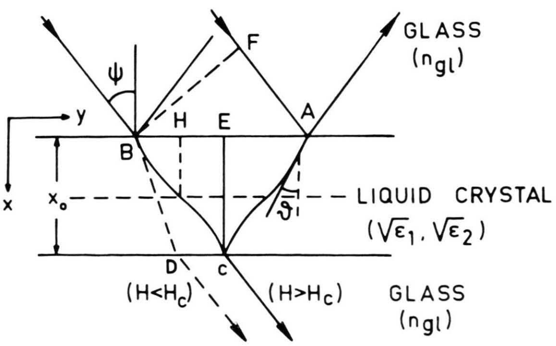

Fig. 4. The light path BD in the undistorted liquid crystal is changed into BC by introducing a deformation, thus changing the interference conditions.

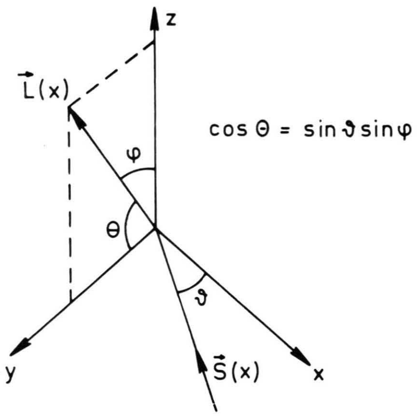

Fig. 5. Definition of some angles used in the calculations. ■ is the director of the molecules, ■ the direction of propagation of light.

Together with Snell's law

$$n(x) \sin \vartheta(x) = c = n_{gl} \sin \psi \quad (9)$$

we get

$$n^2(x) = \varepsilon_1 - (\delta/\varepsilon_2) c^2 \sin^2 \varphi(x) ; \quad \delta = \varepsilon_1 - \varepsilon_2 . \quad (10)$$

Since $\cos\vartheta = \mathrm{d}x/\mathrm{d}s$, $\mathrm{d}s$ being an element of path, from Eqs. (8) and (9) we get for the optical element of path $\mathrm{d}\sigma = n(x)\,\mathrm{d}s$

$$\mathrm{d}\sigma = \frac{\varepsilon_1 - (\delta/\varepsilon_2)\,c^2 \sin^2\varphi(x)}{\sqrt{\varepsilon_1 - c^2 - (\delta/\varepsilon_2)c^2 \sin^2\varphi(x)}}\,\mathrm{d}x\,. \qquad (11)$$

For reflected light of wavelength λ the phase difference Δ between a ray reflected at the first boundary and a ray reflected at the second boundery is given by

$$\Delta = 4\int_B^G n(x)\,\mathrm{d}s - n_{gl}\,\overline{\mathrm{FA}} - \lambda/2\,. \qquad (12)$$

With $n_{gl}\,\overline{\mathrm{FA}} = n_{gl}\sin\psi\,\overline{\mathrm{BE}} = 4\,c\int_B^H \mathrm{d}y$ and

$$\mathrm{d}y/\mathrm{d}x = c/(\sqrt{\varepsilon_1 - c^2 - c^2\sin^2\varphi}) \qquad (13)$$

we finally get

$$\Delta = 4\int_0^{x_0/2} \sqrt{\varepsilon_1 - c^2 - (\delta/\varepsilon_2)\,c^2 \sin^2\varphi(x)}\;\mathrm{d}x - \lambda/2\,. \quad (14)$$

For the deformation to be considered, $\sin\varphi(x) = k\,\mathrm{sn}(A\,x\,|\,k)$ and Eq. (14) becomes

$$\Delta = \frac{4}{A}\sqrt{\varepsilon_1 - c^2}\int_0^{Ax_0/2} \sqrt{1 - \varkappa^2 k^2 \,\mathrm{sn}^2(u\,|\,k)}\;\mathrm{d}u - \lambda/2\,;$$

$$\varkappa^2 = \frac{\delta c^2}{\varepsilon_2(\varepsilon_1 - c^2)}\,. \qquad (15)$$

If we put $x = \mathrm{sn}(u\,|\,k)$ this equation transforms into

$$\Delta = \frac{4}{A}\sqrt{\varepsilon_1 - c^2}\int_0^{sn((Ax_0/2|k)} \sqrt{\frac{1 - \varkappa^2 k^2 x^2}{(1-x^2)\,(1-k^2 x^2)}}\;\mathrm{d}x\,. \quad (16)$$

Using Eq. (5), $A\,x_0 = 2\,K(k)$, the upper limit simplifies:

$$\mathrm{sn}(A\,x_0/2\,|\,k) = \mathrm{sn}\,(K(k)\,|\,k) = 1 \qquad (17)$$

giving

$$\Delta = \frac{x_0\sqrt{\varepsilon_1 - c^2}}{K(k)}\int_0^{\pi/2} \frac{1 - \varkappa^2 k^2 \sin^2\varphi}{1 - k^2\sin^2\varphi}\,\mathrm{d}\varphi - \lambda/2 \quad (18)$$

and

$$(H/H_c)\,\pi = 2\,K(k)\,. \qquad (19)$$

The last equation is equivalent to Equation (5).

Maximum intensity should be observed for $\Delta = j\,\lambda$ with integer j, minimum intensity for $\Delta = \tfrac{1}{2}(2\,j+1)\,\lambda$. Equations (18) and (19) allow the determination of H_c from measurements of the field strengths for which extremal intensity occurs. For this the dielectric constants ε_1 and ε_2, the sample thickness x_0, the angle of incidence ψ and the wavelength λ should be known and they can all be determined with high accuracy by independent measurements.

The argument of the square root in Eq. (24) will become negative for some φ if $k > 1/\varkappa$. We interprete this as the occurence of total reflection for fields that are equal or larger than H_t

$$H_t = 2\,\frac{H_c}{\pi}\,K\left(\frac{\varepsilon_2(\varepsilon_1 - c^2)}{\delta c^2}\right). \qquad (20)$$

This relation may also be applied for determining H_c. Here the sample thickness is included implicitely.

Conclusion

By the method described above, the critical field H_c and therefore k_{22}/χ_a can be determined with high precision. Moreover it may be used for investigating experimentally the problem of fixed anchoring of the molecules of the liquid crystal at the limiting walls.

Appendix

The differential Eq. (2) has a first integral

$$\mathrm{d}\varphi/\mathrm{d}x = (a^2 - A^2\sin^2\varphi)^{1/2}\,; \qquad (21)$$

a^2 is a constant of integration. With the substitution $f = \sin\varphi$ Eq. (21) gives

$$\frac{\mathrm{d}f}{\mathrm{d}(a\,x)} = \{(1 - f^2)\,(1 - k^2 f^2)\}^{1/2} \qquad (22)$$

where $k = A/a$. Equation (22) is the differential equation for the sinus amplitudinis:

$$f = \mathrm{sn}(a\,x\,|\,k) \qquad (23)$$

$\mathrm{sn}(u\,|\,k)$ is a periodic function with the period $p = 4\,K(k)$, K being the complete elliptic integral of the first kind, and with zeros at

$$u = 2\,n\,K(k) \qquad (24)$$

$\mathrm{sn}(u\,|\,k)$ oscillates between -1 and $+1$.

From Eqs. (22) and (24) two classes of solutions meeting the boundary conditions $\varphi = 0$ for $x = 0$ and $x_0 = 0$ may be derived corresponding to $A \leqq a$ and $A \gtrless a$.

1. $A \leqq a$

$$f \equiv \sin \varphi = \mathrm{sn}(a x \mid A/a) ;$$

boundary condition:

$$x_0 = 2 n K(A/a) .$$

These solutions describe a helical structure verified in cholesteric mesophases. For $k = 0$ (no distorting field), $\varphi = a x$.

2. $A \geqq a$

With the substitution $f = (a/A) g$ Eq. (22) becomes

$$\mathrm{d}g/\mathrm{d}(A x) = \{(1 - (a^2/A^2) g^2)(1 - g^2)\}^{1/2} .$$

Hence

$$\sin \varphi = (a/A) \, \mathrm{sn}(A x \mid a/A) .$$

Boundary condition:

$$A x_0 = 2 n K(a/A) .$$

In this case $|\varphi|$ varies only from 0 to $\varphi_{\max}$ given by $a/A = \sin \varphi_{\max}$. This class of solutions describes the deformation of a homogeneously oriented nematic liquid crystal. Each n characterizes a twist mode whose energy E_n is given by

$$E_n = n^2 [(k^2 - 2) K^2(k) - 2 K(k) E(k)] .$$

$E(k)$ is the complete elliptic integral of the second kind. The modulus k is determined for a given field by $A x_0 = 2 n K(k)$. The $E_n(H)$-diagram shows that the first mode ($n = 1$) has lowest energy so that all the other modes are metastable.

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