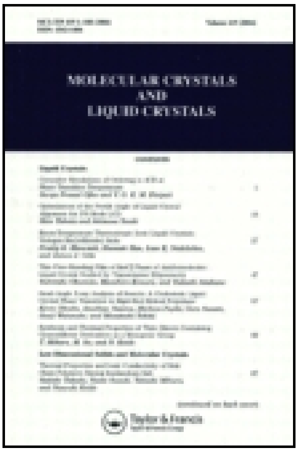

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Properties of Nematics Studied by Four Wave Mixing

Irena Drevensek [a] & Martin Čopič [a]

[a] Dept. of Physics, Institute J. Stefan University of Ljubljana, Ljubljana, Yugoslavia

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Properties of nematics studied by four wave mixing

Irena Drevenšek and Martin Čopič
Institute J.Stefan and Dept. of Physics, University of Ljubljana, Ljubljana, Yugoslavia

Abstract

Diffraction efficiency and time dependence of optically induced diffraction grating in the nematic phase of a commercial mixture ZLI 1738 was measured with a separate probe beam. From the data, using the known values of the indices of refraction, bend and splay orientational elastic constants and effective viscosities were calculated.

1 INTRODUCTION

Liquid crystals, especially nematic ones, have remarkable nonlinear optical properties due to reorientation of the molecular director in the optical field. The light induced changes in the refractive index are large because of the large optical anisotropy, which makes the coupling between the director and light field strong and causes even small reorientation of the director to change the index of refraction appreciably. Also, the elastic restoring stress in liquid crystals is weak. Orientational optical nonlinearity manifests itself in several interesting effects, like self-focusing, optical wavefront conjugation, infrared-to-visible image conversion or self-diffraction of crossing light beams [1, 2, 3, 4, 5]. Due to the low necessary optical power density, all these effects have attracted considerable attention, mainly because of possible use in optical devices.

Self-diffraction of two crossed laser beams, a degenerate four wave mixing experiment, was also successfully used to study the orientational elastic constants and viscosity coefficients of a nematic sample [6]. In the geometry of that experiment the authors were able to obtain the twist and bend elastic constants. In a recent paper, the ratio of two orientational elastic constants was measured[7]. In this report we want to describe a similar four wave mixing experiment in an arrangement which gave us the values of the splay and bend constants and the associated viscosities.

To measure the elastic and viscous properties of nematics by optical four wave mixing, one needs to measure the build-up or decay time of the induced optical grating as the crossed pump beams are turned on and off, and the total stationary

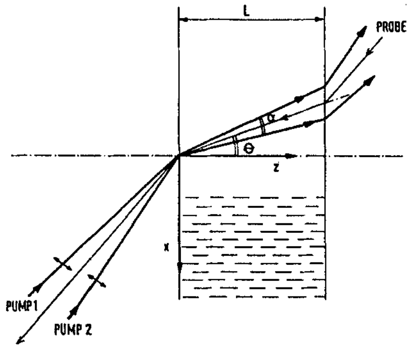

Figure 1: The geometry of the experiment

diffraction efficiency. The advantage of the method is that the only other relevant material parameters besides elastic constants and viscosities are the indices of refraction, the difference of which determines the strength of the coupling between the light field and the director.

Instead of looking at self-diffraction of one of the pump beams, as is customary, we used a different beam to probe the induced diffraction grating. This gave us greater experimental flexibility, allowing us for example to change the incoming angle or polarization of the probe beam. The other advantage is a somewhat better signal as one can reject with a color filter the unwanted background of the pump beams. The disadvantage is that it is necessary to precisely align the probe beam on the crossing region of the pump beams in order to measure the amplitude of the induced grating.

2 GRATING FORMATION AND DIFFRACTION EFFICIENCY

The distortion of an aligned nematic liquid crystal sample in the electric field of two crossed coherent light beams can be analyzed in the framework of the continuum elastic theory of nematics. The starting point is the elastic free energy of the system

$$f = \frac{1}{2}K_1(\nabla \cdot \vec{n})^2 + \frac{1}{2}K_2(\vec{n} \cdot \nabla \times \vec{n})^2 + \frac{1}{2}K_3(\vec{n} \times \nabla \times \vec{n})^2 - \frac{1}{2}\epsilon_0\epsilon_a(\vec{E} \cdot \vec{n})^2 \ . \quad (1)$$

Here K_1, K_2 and K_3 are the splay, twist and bend orientational elastic constants and $\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp}$, with $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ being the components of the dielectric tensor parallel and perpendicular to the director $\vec{n}$.

Let us choose the geometry of the experiment as shown in Fig. 1. The sample is homeotropically aligned and tilted by a bias angle θ with respect to the line bisecting the angle between the two laser beams. Let us choose the normal to the sample as the z axis. The two laser beams are polarized as extraordinary waves, that is in the xz plane, and intersect at a small angle α. In the crossing region, the coupling term between the director and light field is given by

$$(\vec{E}\cdot\vec{n})^2 = 2E_0^2(n_1\cos\theta_R + n_3\sin\theta_R)^2[\cos(\vec{q}\cdot\vec{r})+1] \tag{2}$$

where

$$\vec{q} = \alpha k(\cos\theta, 0, \sin\theta) = (q_1, 0, q_3)\ .$$

θ_R is the ray direction, which is because of birefringence not equal to the direction of $\vec{k}$. θ_R and θ are connected by

$$\epsilon_{\parallel}\tan\theta = \epsilon_{\perp}\tan\theta_R\ . \tag{3}$$

The coupling to light field causes a small deformation in the x component of the director field n_1, which can be most conveniently obtained by taking an ansatz of the form[6]

$$n_1 = \sin\frac{\pi}{L}z(u_0 + u_1\cos\vec{q}\cdot\vec{r})\ . \tag{4}$$

Strong anchoring is assumed, so that at $z = 0$ and $z = L$ n_1 must be 0. Putting (3) into the free energy and maximizing with respect to u_0 and u_1 we obtain

$$u_0 = \frac{4\epsilon_0\epsilon_a E_0^2\sin 2\theta_R L^2}{\pi^2 K_3}$$

$$u_1 = \frac{2\epsilon_0\epsilon_a E_0^2\sin 2\theta_R}{\pi\{K_1q_1^2 + K_3[q_3^2 + (\frac{\pi}{L})^2]\}}\ . \tag{5}$$

Reorientation of the director causes also a change in the index of refraction of the extraordinary ray of given direction. The periodic part of this change represents a diffraction grating on which a light beam of extraordinary polarization can be diffracted.

The diffraction efficiency is usually [6, 7] computed by first calculating the change in the index of refraction, which is due to the local rotation of the optical indicatrix, then integrating over the path of the probing beam the total phase shift and finally using the formula for the diffraction efficiency of a thin phase grating. When the sample is thick compared to the wavelenght of light, such an approach is not completely justified even though the total phase shift is small. It is better to use the coupled wave theory[8], which turns out to be also computationally simpler.

In such an approach, one starts from the wave equation in an anisotropic medium

$$\nabla\times(\nabla\times\vec{E}) = k_0^2(\underline{\epsilon} + \delta\underline{\epsilon})\vec{E}\ , \tag{6}$$

where $\delta\underline{\epsilon}$ is the induced periodic perturbation of the medium. In our case it has, to first order in n_1, the form

$$\delta\underline{\epsilon} \simeq \epsilon_a \begin{bmatrix} 0 & 0 & n_1 \\ 0 & 0 & 0 \\ n_1 & 0 & 0 \end{bmatrix} \tag{7}$$

The electric field of the probe beam can be decomposed into transverse spatial Fourier components

$$\vec{E} = \sum_l \psi_l(z)\vec{e_l} \exp i(\beta_l z + lq_1 x) \tag{8}$$

where the amplitudes ψ_l are only slowly changing with z. $\vec{e_l}$ is the polarization direction of the extraordinary wave. Also, since the medium is uniaxial, the longitudinal propagation constant β_l is connected to the transverse wavenumber lq_1 by

$$\frac{\beta_l^2}{n_o^2} + \frac{l^2 q_1^2}{n_e^2} = k_0^2 \; . \tag{9}$$

We put (8) into (6), neglect the second derivatives of ψ_l and take on both sides of the resulting equations only the projections on the polarization direction $\vec{e_l}$, and we obtain a set of coupled equations

$$2i\beta_{l+1}\frac{d\psi_{l+1}}{dz} = -\frac{1}{2}k_0^2\epsilon_a \sin 2\varphi_R \sin\frac{\pi}{L}z \exp[i(\beta_l - \beta_{l+1} + q_3)z]\psi_l \; . \tag{10}$$

Here φ_R is the ray direction of the probe beam in the sample. Let also φ be the direction of the corresponding wave normal. The incoming beam contains just one Fourier component ψ_0 with $q_0 = nk_0 \sin\varphi$. To get the amplitude of the first diffracted beam ψ_1, we assume that it is weak so that ψ_0 is approximately constant. After a simple integration we obtain for the diffraction efficiency

$$\left|\frac{\psi_1(L)}{\psi_0}\right| = \frac{\pi\epsilon_a k_0 \sin 2\varphi_R}{2n\cos\varphi}\left|\frac{\cos(\beta_0 - \beta_1 + q_3)\frac{L}{2}}{(\beta_0 - \beta_1 + q_3)^2 L^2 - \pi^2}\right| Lu_1 \; . \tag{11}$$

The difference between the propagation constants $\beta_0 - \beta_1$ must be computed from relation (9).

In the above derivation of eq. (11) all the spatial phase factors are kept and so the obtained formula is valid also when the incoming probe beam satisfies the Bragg condition, that is when the denominator of the factor within absolute value signs is zero. The diffracted intensity must of course be small so that the probe beam is not depleted. By including more equations from the infinite chain (10) one can also compute the higher diffraction orders if necessary. It is worthwhile to note that the often used thin grating approximation or Raman-Nath[9] approximation do not give a maximum in the diffraction efficiency when the Bragg condition is satisfied and are therefore useful only well away from the Bragg angle of incidence, as is the case in self-diffraction experiments.

The time dependence of the periodic reorientation of the medium as the pump beams are switched on and off is obtained from the linearised equations of nematodynamics. In our chosen geometry with homeotropic alignment, the periodic deformation is of bend-splay type and it's relaxation is a simple exponential with a relaxation frequency

$$\frac{1}{\tau_\perp} = \frac{1}{\eta_\perp}[K_1 q_1^2 + K_3(q_3^2 + \frac{\pi^2}{L^2})] \ . \tag{12}$$

In case of homogeneous alignement of the sample all the above formulas remain valid if one exchanges K_1 and K_3 in formulas (5) and (12) and $\epsilon_\perp$ and $\epsilon_\parallel$ in (9). In particular, for the relaxation time of the homogeneously aligned sample one has

$$\frac{1}{\tau_\parallel} = \frac{1}{\eta_\parallel}[K_3 q_1^2 + K_1(q_3^2 + \frac{\pi^2}{L^2})] \ . \tag{13}$$

In (12) and (13) the effective viscosity is a function of the direction of $\vec{q}$[10]. Equation (11), together with the expression for the amplitude of the periodic deformation, contains known geometrical factors, both indices of refraction which are also known, and in u_1 the orientational elastic constants. So (11) allows one to determine the elastic constants from the measurements of the diffraction efficiency at different orientations and magnitudes of $\vec{q}$. Measurements of the rise and decay time of the diffracted probe beam provides, through (12) and (13), also the value of the viscosity at different $\vec{q}$.

3 EXPERIMENT

Our experimental arrangement is shown in Fig. 2. A polarizing beam-splitter is used so that a polarization rotator is necessary in one arm. The nearly counter-propagating probe beam is separated from the pump beams by a dichroic mirror.

The focal length of the lens LN1 is 63 cm and of LN2 31 cm, so that the size of the pump beams in the crossing region is 0.1 mm and that of the probe beam 0.05. The probe beam was adjusted to the center of the crossing region by maximizing the diffracted signal. Pump power was adjusted so that there was no observable single beam self-focusing distortion. With the chosen focusing lens this power was around 70 mW at the sample. Probe beam from a He-Ne laser had a power of 0.4 mW.

To study the turn-on and decay time of the induced grating, a mechanical shutter was inserted in one arm of the setup. Alternatively we used an electrooptic modulator before the beamsplitter, which allowed us to vary the phase difference between the vertically and horizontally polarized waves. The modulator was driven with an AC voltage with frequency 10 kHz which was switched on and off. A phase difference between the pump beams brings about a shift of the induced grating. At high frequencies the nematic director can not follow this shifting and so only sees an average over one period of modulation. If the amplitude of the phase difference is

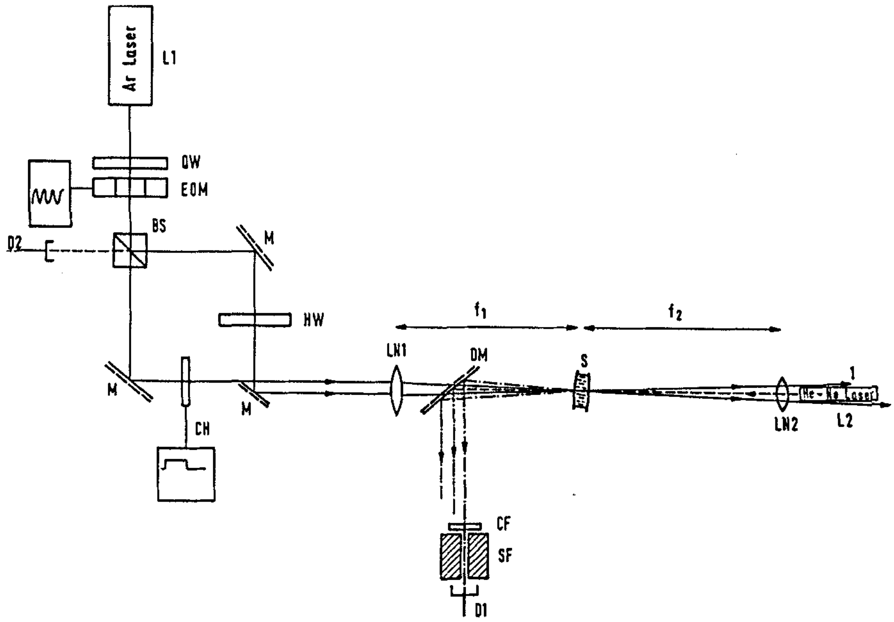

Figure 2: Experimental setup

equal to the first zero of the Bessel function J_0, the average of the induced grating is zero. This second method of modulation of the grating has an additional advantage: it allows us to ascertain that there is no measurable distortion due to heating of the sample. Thermal relaxation time is sufficiently shorter then orientational one that the thermal grating, if present, would follow the 10 kHz modulation. As we observed no diffraction with the modulation on, we concluded that the thermal grating is negligible. The measurements were performed in the commercial nematic mixture ZLI 1738 of Merck company. We used both homeotropic and homogeneous alignement obtained by surface treatment of glass plates. The sample thickness was 50 μm in the homeotropic case and 75 μm in homogeneous case. All the measurements were done at room temperature, that is at 22^o C.

The producer of ZLI 1738 specifies the indices of refraction to be $n_o = 1.517$ and $n_e = 1.705$. An average flow viscosity at room temperature is about 0.3 P.

4 RESULTS AND DISCUSSION

To obtain the orientational elastic constants K_1 and K_3 we measured the scattering efficiency as a fuction of the magnitude of the grating wavevector q at several angles θ between q and n. Fig. 3 shows this dependence. The probe beam was incident at an angle equal to θ and propagating in the counter direction, as shown in Fig. 2. The electric field inside the sample was computed from the measured light

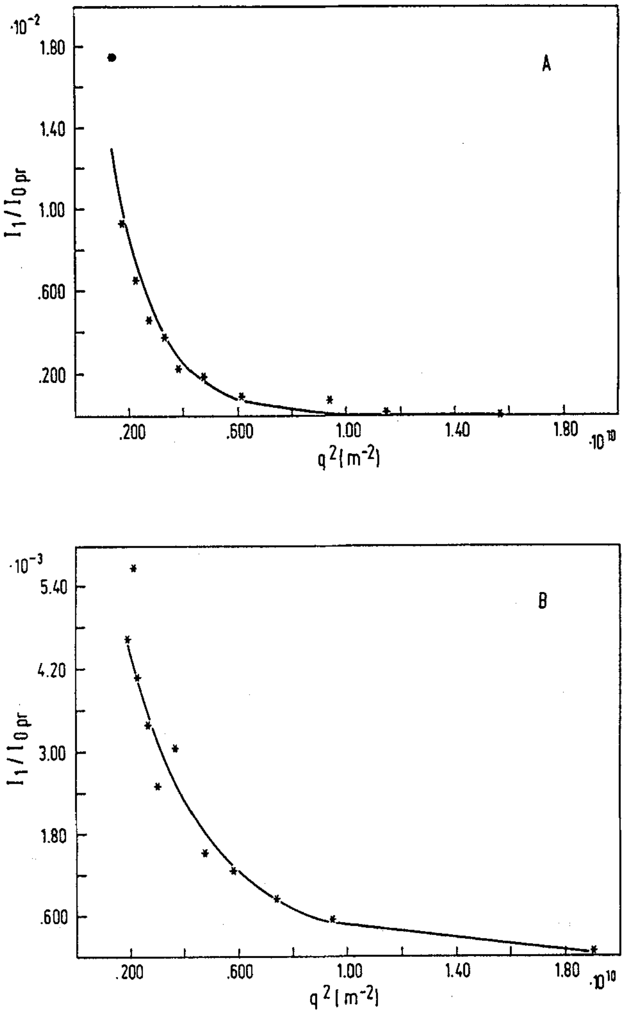

Figure 3: The dependence of the scattering efficiency as a function of the square of the grating wavevector. a) Homogeneous alignment, $\theta = 32^o$, $\varphi = 32^o$. b) Homeotropic alignment, $\theta = 29^o$, $\varphi = 29^o$. Full line shows the wieghted best fit with respect to K_1 and K_3 to expression (11).

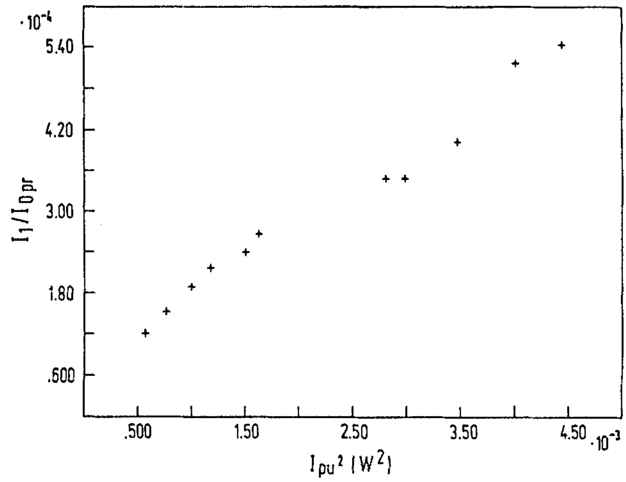

Figure 4: The diffraction efficiency as a function of the square of the pumping power. Homogeneous alignment, grating period 50 μm.

intensity falling on the sample, which was corrected for reflection at the sample boundary. The solid line in Fig. 3 shows the best fit of expression (11) to the data. In obtaining the fit only K_1 and K_3 were taken as fitting parameters. From these data we obtained for the elastic constants the values $K_1 = 3.9 \times 10^{-11}$ N (1 ± 0.4) and $K_3 = 2.9 \times 10^{-11}$ N (1 ± 0.4). The ratio of these two values is consistent with what Merck specifies for some similar mixtures.

In order to check that our measurements are not affected by single pump beam distortions we measured the dependence of the diffraction efficiency on the square of the pump power. This is shown in Fig. 4. The obtained dependence is approximately linear. The data at small powers is not very reliable due to the necessary subtraction of the background of spontaneous scattering which is quite strong at low angles.

Both the build-up and the decay of the diffraction grating amplitude, as the pumping is modulated in either of the ways descirbed above, can be described by a single exponential relaxation. The relaxation frequency is a quadratic function of the grating wavevector, as is evident from Fig. 5. From the best fit to these data and from the previously obtained values of the elastic constants we get the two viscosities: $\eta_\perp = 1.0$ P(1 ± 0.3) and $\eta_\| = 0.21$ P(1 ± 0.3). The two effective viscosities correspond to two different directions of q, the first one about 20^o and the second around 60^o away from the director. The average capillary flow viscosity of the material, as specified by the producer, is 0.3 P at room temperature, so the values that we found are quite reasonable. Large anisotropy of the effective viscosity was observed also in other nematic materials[11].

The measurements of the decay time of the grating are quite reliable and reproducible, so the relatively large errors in the results come from the measurements

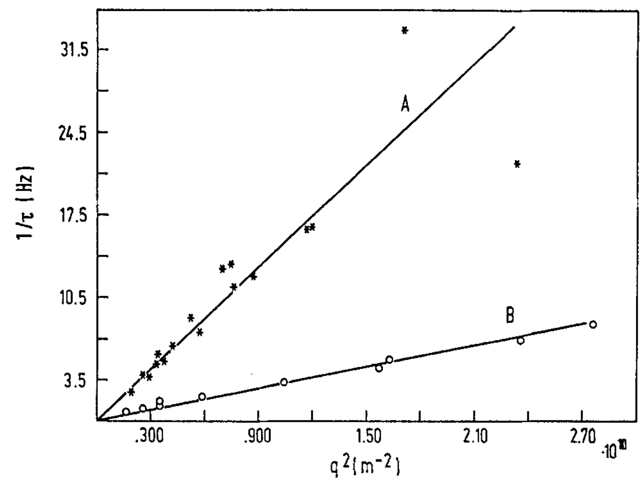

Figure 5: The dependence of the relaxation frequency as a function of the square of the wavevector. * - homogeneous alignment, $\theta = 23^o$, o - homeotropic alignment, $\theta = 33^o$.

of the diffraction efficiency as it is quite difficult to keep the whole system well calibrated for intensity measurements. As these problems are to a certain degree smaller with self-diffraction arrangement, and other advantages of a separate probe beam, like being able to select the incoming angle, do not seem to help in getting better accuracy, we conclude that it is better to look at self-diffraction to get the amplitude of the induced distortion.

In any case, although by choosing proper experimental geometry all three orientational elastic constants and the wavevector dependent viscosities can be determined by four wave mixing experiments, the results can not be expected to be more precise than those obtained by other methods. So we think that the main application of the method in the study of the properties of liquid crystals is in exploring the dynamics of these systems in a very wide range of timescales.

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