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LIGHT SCATTERING FROM THE FREE SURFACE OF A NEMATIC LIQUID CRYSTAL

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Résumé. — Nous avons étudié le spectre de la lumière diffusée par les ondes de surface excitées thermiquement à la surface libre d'un cristal liquide nématique dans un champ magnétique, pour plusieurs angles de diffusion. Nous avons dépouillé les résultats expérimentaux à l'aide du spectre théorique, que nous avons calculé en utilisant le théorème de fluctuation-dissipation et la théorie hydrodynamique de Eriksen et Leslie. Dans le domaine de fréquences et de vecteurs d'onde que l'on étudie, la partie antisymétrique du tenseur des contraintes est négligeable. Le problème hydrodynamique ne dépend que de 3 coefficients de viscosité cinétique, comme tout système incompressible uniaxe. La forme spectrale fait intervenir un 4^e paramètre, la tension superficielle σ , que nous supposons isotrope. Le spectre théorique dépend de l'orientation des molécules par rapport au vecteur d'onde $\mathbf{q}$ des fluctuations, ainsi que nous l'avons observé.

Nous présentons des résultats obtenus pour deux cristaux liquides : P. A. A. à 122 °C et M. B. B. A., dans la zone de température allant de 35° à 52 °C (la température de transition t_c étant 45 °C). Nos résultats pour le P. A. A. sont en accord avec des résultats antérieurs obtenus avec des techniques conventionnelles. Nos mesures sur le M. B. B. A. donnent la valeur de la tension superficielle et des 3 viscosités en fonction de la température. La tension superficielle est discontinue à la transition. Les résultats des mesures de viscosité sont comparés à ceux obtenus par viscosimétrie ou absorption ultrasonore.

Abstract. — We have measured the spectrum of light scattered by surface waves thermally excited on the free surface of a nematic liquid crystal in a magnetic field at several scattering angles. We have fitted the data by the theoretical spectrum that we have derived using the fluctuation-dissipation theorem and the Eriksen-Leslie hydrodynamic theory. For the range of frequencies and scattering angles of interest, the asymmetric part of the Leslie viscous stress tensor is shown to be negligible : one is left with 3 independent shear viscosities as for any uniaxial incompressible system. A fourth parameter affecting the spectral shape is the surface tension σ which is supposed isotropic. The theoretical spectrum depends on the orientation of the molecules with respect to the wave vector $\mathbf{q}$ of the fluctuations, as we have observed.

We present the results obtained for two liquid-crystals : P. A. A. at 122 °C and M. B. B. A. in the temperature range 35° to 52 °C (the transition temperature t_c being 45 °C). Our results for P. A. A. are consistent with those obtained previously with more conventional techniques. Our measurements for M. B. B. A. yield the value of the surface tension and of the three viscosities versus temperature. σ exhibits a discontinuity at t_c . The viscosity data are compared to those deduced from viscosimetry or ultrasonic methods.

On a liquid interface, thermal motion produces small asperities, about ten angstroms high. The liquid interface is submitted to a capillary restoring force, its motion is damped by viscosity. The evolution of the fluctuations can be described by the laws of hydrodynamics on a macroscopic scale of time and space. Using a laser and heterodyne beating spectroscopy [1], we have investigated the spectrum of light scattered from the fluctuations on the free surface of a nematic liquid in a magnetic field.

Let us consider a surface vibration mode or surface phonon, with a given wave vector $\mathbf{q}$. The scattering process is simply :

incident photon + surface phonon $\rightarrow$ scattered photon

or

incident photon $\rightarrow$ surface phonon + scattered photon

It is for surface fluctuations the analog of Brillouin scattering for density fluctuations in the bulk. Scattered light is concentrated in a well defined direction, simply related to $\mathbf{q}$ by expressing momentum conservation in the surface plane during the scattering process. Experimentally we select with a diaphragm, light scattered by fluctuations having a wave vector well defined both in direction, and modulus. A photomultiplier receives light inelastically scattered by the fluctuations and light elastically scattered by the windows of the liquid container. In such conditions, it can be shown that the photocurrent power spectrum reflects exactly the power spectrum for the fluctuations of the vertical displacement of the free surface. We perform, then, the frequency analysis of the photocurrent power spectrum.

For an ordinary liquid, the spectrum is isotropic, it only depends on the modulus of $\mathbf{q}$. For a nematic liquid crystal, as shown in the following, it is aniso-

tropic, it depends on the relative orientation of $\mathbf{q}$ with respect to the mean orientation of the molecules $\mathbf{n}_0$. In our experiments we have fixed $\mathbf{n}_0$ by applying to the sample a magnetic field of two to three thousand gauss.

I) THEORETICAL RESULTS. — To perform a detailed interpretation of experimental data, it is necessary to derive the theoretical power spectrum of surface fluctuations. We have done this by using the hydrodynamic theory of Eriksen and Leslie [2] and by applying the fluctuation-dissipation theorem.

In the range of wave-vectors and frequencies of interest it can be shown [3] that the elastic part of the stress tensor is entirely negligible. The stress tensor can be written with the help of only three viscosity coefficients, as for any incompressible uniaxial system :

$$\sigma_{ij} = \eta_3 n_i n_j A_{kp} n_k n_p + 2\eta_2 A_{ij} + 2(\eta_1 - \eta_2)(n_i n_k A_{kj} + n_j n_k A_{ki}) - p\delta_{ij}.$$

σ_{ij} depends on the molecular orientation $\mathbf{n}$ and on the velocity gradients :

$$A_{ij} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right).$$

For an ordinary liquid $\eta_3 = 0$, and $\eta_1 = \eta_2 = \eta$ is the usual shear viscosity.

The three viscosity coefficients can be related to the Leslie parameters as follows :

$$\eta_3 = \alpha_1 + \frac{(\alpha_2 + \alpha_3)^2}{\alpha_3 - \alpha_2},$$

$$\eta_2 = \frac{\alpha_4}{2},$$

$$\eta_1 = \frac{\alpha_4 + \alpha_6}{2} - \frac{\alpha_3 (\alpha_2 + \alpha_3)}{2(\alpha_3 - \alpha_2)}.$$

This form of the stress tensor can also be obtained very easily by using the Harvard [4] new hydrodynamic theory for nematic liquid crystals.

The theoretical spectrum can be derived for different relative orientations of $\mathbf{q}$ and $\mathbf{n}_0$ [3]. In particular we have to take into account that the free surface imposes a preferential orientation to the molecules at the free surface. Let us suppose first that this orientation is horizontal. If the applied magnetic field is also horizontal, $\mathbf{n}_0$ will be parallel to $\mathbf{H}$ in the whole sample. So the spectrum becomes easy to calculate. If $\mathbf{q}$ is parallel to $\mathbf{H}$, one finds that the spectrum depends on three parameters, σ the surface tension (that will be supposed isotropic), η_1 and η_3 . If $\mathbf{q}$ is perpendicular to $\mathbf{H}$, it depends on two parameters, σ and η_2 . In this last case it is identical to the spectrum of an ordinary liquid having a viscosity η_2 . This arises from a complete decoupling between the molecular orientation and the flow.

$$\begin{aligned} \mathbf{q} \parallel \mathbf{H} P_1(v) &= \frac{kT}{2\pi^2 v} \frac{\tau_1^2 q}{\rho} \operatorname{Im} \left\{ \frac{1}{y_1 + \frac{S^2 + [S^2 + (2 + A/2)S] \varepsilon \sqrt{2S+1}}{\sqrt{2S+2+A+2\varepsilon\sqrt{2S+1}}}} \right\}_{S=-2i\pi v\tau_1} \\ \varepsilon &= \operatorname{sign} \operatorname{Re} \left\{ \sqrt{2S+2+A+2\sqrt{2S+1}} - \sqrt{2S+2+A-2\sqrt{2S+1}} \right\}_{S=-2i\pi v\tau_1} \\ \mathbf{q} \perp \mathbf{H} P_2(v) &= \frac{kT}{2\pi^2 v} \frac{\tau_2^2 q}{\rho} \operatorname{Im} \left\{ \frac{1}{y_2 + (1+S)^2 - \sqrt{1+2S}} \right\}_{S=-2i\pi v\tau_2} \end{aligned}$$

with the following parameters :

$$y_1 = \frac{\sigma\rho}{4\eta_1^2 q}, \quad y_2 = \frac{\sigma\rho}{4\eta_2^2 q}, \quad \tau_1 = \frac{\rho}{2\eta_1 q^2},$$

$$\tau_2 = \frac{\rho}{2\eta_2 q^2}, \quad A = \frac{\eta_3}{\eta_1}.$$

$\sqrt{}$ is the square root determination having a positive real part, and ρ represents the liquid density.

When the liquid viscosity is very low, the spectra given above become very simple : they are centered at the frequency

$$v_q = \frac{1}{2\pi} \sqrt{\frac{\sigma q^3}{\rho}},$$

and they are lorentzian with half-width :

$$\Delta v_1 = \frac{\eta_1 + \eta_3/8}{\pi} \frac{q^2}{\rho} \quad \text{for } \mathbf{q} \parallel \mathbf{H},$$

$$\Delta v_2 = \frac{\eta_2 q^2}{\pi\rho} \quad \text{for } \mathbf{q} \perp \mathbf{H}.$$

When the liquid viscosity is very high, the spectrum is a Lorentzian curve centered at zero frequency and having for half-width :

$$\Delta v_1 = \frac{\sigma q}{4\pi\eta_1 \sqrt{1 + \frac{\eta_3}{4\eta_1}}} \quad \text{for } \mathbf{q} \parallel \mathbf{H},$$

$$\Delta v_2 = \frac{\sigma\rho}{4\pi\eta_2} \quad \text{for } \mathbf{q} \perp \mathbf{H}.$$

In the intermediate case the spectrum is more interesting because it yields in principle the value of the three viscosity coefficients and of the surface tension. In particular the spectrum $P_1(\nu)$ is very sensitive to the value of $A = \eta_3/\eta_1$. Figure 1 shows two spectra corresponding to $A = 0$ and $A = 4$, and to the same values of γ_1 and τ_1 , i. e. of σ and η_1 . The first one, $A = 0$, is identical to the spectrum of an ordinary liquid having a viscosity η_1 . These two spectra are quite different: η_3 , equal to $4\eta_1$, produces a large increase of the wave damping.

FIG. 1. — Theoretical spectra $P_1(\nu)$ for $A = 0$ (full line curve) and $A = 4$ (dashed line curve), and for the same γ_1 value, $\gamma_1 = 1$.

Let us now suppose that the orientation of the molecules at the free surface is vertical. It is then shown that the spectrum in a vertical magnetic field is identical to $P_1(\nu)$ obtained previously for $\mathbf{H} \parallel \mathbf{q} \parallel \mathbf{n}_0$. If the field is horizontal, its effect on the orientation competes against that of the free surface. As a result, there is a distortion in the orientation [5] in the vicinity of the free surface, over a thickness

$$\xi = \sqrt{\frac{K}{\chi_a}} \frac{1}{H}.$$

If the condition $q\xi \lesssim 0.1$ is fulfilled, this does not modify the spectrum and everything holds as if the molecules were parallel to the surface.

II. Experimental results. — We have studied two different liquid crystals.

1. PARA-AZOXYANISOLE. — We have first done some preliminary measurements on para-azoxyanisole (P. A. A.), which is nematic in the temperature range 118° to 135°. The P. A. A. molecules lie parallel to the surface. We have studied this liquid at a single temperature 122° with an horizontal magnetic field. The liquid viscosity is relatively low, so the expressions found for $\gamma \gg 1$ are valid. Thus one can only deduce from the spectra σ and two viscosity coefficients $\eta_1 + \eta_3/8$ and η_2 . The lack of anisotropy observed

experimentally on the spectrum proves on another hand that these two viscosity coefficients are very similar and confirms that the surface tension is isotropic. Figure 2 shows a typical experimental spectrum for a wave vector $q = 400 \text{ cm}^{-1}$. The full line curve is the theoretical Lorentzian.

FIG. 2. — Spectrum of light scattered by the free surface of PAA at 122 °C corresponding to a wave vector $q = 400 \text{ cm}^{-1}$.

The results of the measurements of peak-frequencies and half-widths as functions of q in the range $167 < q < 1000 \text{ cm}^{-1}$ give :

$$\sigma = (38 \pm 4) \text{ dynes/cm},$$

$$\eta_2 = \eta_1 + \eta_3/8 = (3.6 \pm 0.4) \text{ cp}.$$

These value of σ and η_2 agree well with those obtained previously by more conventional techniques [6], [7]. If we use the Miesowicz's [7] value for η_1 we obtain $\eta_3/\eta_1 = 4$, which is close to the corresponding ratio that we have been able to measure on MBBA.

2. METHOXY-BENZILIDÈNE-BUTYL-ANILINE. — We have done a more detailed study of methoxy-benzilidene-butyl-aniline (M. B. B. A.) which is nematic in the temperature range 20° to 45 °C.

The M. B. B. A. molecules are tilted at an angle $\theta \sim 75^\circ$ from the surface, which depends on temperature [8]. So it exists a distortion in the vicinity of the surface when an horizontal or a vertical magnetic field is applied. But as $q\xi$ is of the order of 0.1 the effect of the distortion on the spectrum is negligible.

The experimental data have been fitted by the theoretical spectrum using a program on a computer to minimize the mean square distance between experimental and theoretical spectra, with the assumption that the surface tension is isotropic.

Figure 3 shows a typical experimental spectrum corresponding to the wave vector $q = 263 \text{ cm}^{-1}$, $t_c - t = 3^\circ$ (t_c being the transition temperature nematic $\rightleftharpoons$ isotropic) and an horizontal magnetic field $\mathbf{H} \parallel \mathbf{q}$. The full line curve is theoretical. Figure 4 shows the same spectrum with $\mathbf{q} \perp \mathbf{H}$. The anisotropy is quite noticeable. We have done a systematic study of the

FIG. 3. — Spectrum of light scattered by the free surface of MBBA in an horizontal magnetic field $H \parallel q$, for $t_c - t = 3^\circ$ and $q = 263 \text{ cm}^{-1}$.

FIG. 4. — Spectrum of light scattered by the free surface of MBBA in an horizontal magnetic field $H \perp q$ for $t_c - t = 3^\circ$ and $q = 263 \text{ cm}^{-1}$.

spectrum as a function q , for $138 < q < 509 \text{ cm}^{-1}$, and temperature, in the range $-10 < t - t_c < 7^\circ$.

The results are plotted in figure 5. When t goes to t_c , η_3 goes to 0, η_2 becomes equal to η_1 and to the viscosity η of the isotropic phase. The surface tension decreases by an amount of 4 dynes/cm at the transition.

FIG. 5. — Results of measurements of surface tension and viscosities for MBBA.

We note that the values of η_1 measured in a magnetic field vertical or horizontal parallel to q , are the same within the uncertainty of measurements. This confirms the isotropy of the surface tension. Our measurements of η_1 agree with existing measurements done by capillary viscosimetry [9], [10]. On the other hand measurements of η_1 and η_2 by ultrasonic absorption [10], present marked differences with ours. As we work in a low frequency range ($\nu < 20 \text{ kHz}$) it does not seem unreasonable to ascribe these differences to relaxation phenomena, occurring between 20 kHz and ultrasonic frequencies ($\nu > 10 \text{ MHz}$).

A more detailed description of the experiments summarized in this paper will be presented elsewhere [11].

References

- [1] For a description of the experimental set-up see for instance : BOUCHIAT (M. A.), MEUNIER (J.), *C. R. Acad. Sci. Paris*, 1968, **266**, Série B 255 et 301.
- [2] See for instance : LESLIE (F. M.), *Quart. J. Mech. Appl. Math.*, 1966, **19**, 357.
- [3] LANGEVIN (D.), BOUCHIAT (M. A.), *J. Physique*, to be published.
- [4] FORSTER (D.), LUBENSKI (T. C.), MARTIN (P. C.), SWIFT (J.), PERSHAN (P. S.), *Phys. Rev. Letters*, 1971, **26**, 1016.
- [5] DE GENNES (P. G.), *C. R. Acad. Sci. Paris*, 1968, **266**, Série B 15.
- [6] See for instance : CHYSTYAKOV (I. B.), *Soviet Physics Uspekhi*, 1967, **9**, 551.
- [7] MIESOWICZ (M.), *Nature*, 1946, **158**, 27.
- [8] BOUCHIAT (M. A.), LANGEVIN (D.), *Phys. Letters*, 1971, **34**, 331.
- [9] BERCHET (D.), HOCHAPPEL (A.), VIOVY (R.), *C. R. Acad. Sci. Paris*, 1970, **270**, Série C, 1065.
- [10] MARTINOTY (P.), CANDAU (S.), *Proc. of the third Int. Conf. on Liq. Cryst.*, to be published.
- [11] LANGEVIN (D.), *J. Physique*, to be published.