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Viscosity Measurements by Quasi Elastic Light Scattering in *p*-Azoxyanisol†‡

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Abstract—We discuss some difficulties inherent to the light scattering measurement of the viscosity coefficients in paraazoxyanisol. In contrast with a previous report, we present a unique set for these quantities, in reasonable agreement with the conventional determination by Miesowicz.

In recent publications^(1,2) we have reported on the observation of thermally excited fluctuations of orientation in *p*-azoxyanisol (PAA). From these observations we deduced values for the Ericksen-Leslie viscosity coefficients α_i.^(3) In fact, these values did not agree satisfactorily with the classical measurements of Miesowicz.^(4) In this paper, we explain this discrepancy in term of two difficulties: the presence of multiple scattering, and a recent recalibration of the indices of refraction for pure PAA.^(5) Using a recalibration of our previous observations, we present new data, with a unique determination of viscosity coefficients that we compare to the classical measurements.

As stated above, the first difficulty comes from the very high value of the Rayleigh number ($\sim 10^2$) for light scattered by angular fluctuations in a nematic, which appears as opalescent as a fluid near its critical point. In the geometry of Ref. (1),§ the mode 2 cross section is two orders of magnitude larger than the cross section for mode 1. So, the mode 1 observation (($\mathbf{k}_e \mathbf{k}'_e$) configuration) is masked by double scattering from mode 2, which changes successively the light polarization, and then the wave vector from $\mathbf{k}_e$ to $\mathbf{k}''_0$, and from

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‡ Presented at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.

§ In this paper, we use the notations of Ref. (1).

$\mathbf{k}_0''$ to $\mathbf{k}_e'$. ($\mathbf{k}_0''$ is a wave vector in an arbitrary direction, and with ordinary polarization). The double scattering intensity goes like e^2, (e is the sample thickness), compared to e for the simple scattering. To prevent multiple scattering, we would then have to restrict to use samples with thickness of order of a few microns, but in these conditions the fluctuations of orientation would be quenched by the walls, and would no more be characteristic of the bulk modes. So, the geometry of Ref. (1) can only be used for mode 2 observations.

To observe the mode 1 we use now the homeotropic geometry, where the director **n**, normal to the plates, is parallel to the incoming beam wave vector $\mathbf{k}_0$. The scattering plane ($\mathbf{k}_0, \mathbf{k}_0'$) contains the incoming and the scattered directions of polarization. The homeotropic geometry allows also the observation of mode 2, when one chooses the incoming polarization normal to the scattering plane ($\mathbf{k}_0\,\mathbf{k}_0'$), and the outgoing polarization in this plane. In this geometry, the cross sections are comparable for the two modes. Their values is two orders of magnitude lower than for the mode 2 in the geometry of Ref. (1), so that double scattering is negligible.

We first checked our previous determination of γ_1 by observing the angular dependence of the scattered light half width u_2 which should vary as $K_{22}q^2/2\pi\gamma_1$ in forward scattering. We do find a quadratic dependence in q, but the value of γ_1 ($6.3\ 10^{-2}$ in CGS units) was very different from our value of ref. (1) ($\gamma_1 = 9.1\ 10^{-2}$). This discrepancy vanishes when we use the new refractive index data from Châtelain and Mme Brunet,⁽⁵⁾ for pure PAA. A new analysis of our results using these indices leads to $\gamma_1 = 5.8\ 10^{-2} \pm 0.25$ from the data of Ref. (1) and $\gamma_1 = 5.9\ 10^{-2} \pm 0.3$ from the present data, giving now a reasonable internal check. The other coefficients, always from data of Ref. (1), become $\alpha_v' = 21 \pm 3$ and $\alpha_4' = 10 \pm 1.5$.

Our observation of the mode 1 width u_1, in the homeotropic geometry, gives an angular dependence almost quadratic, as expected, for small scattering angle ψ. A difficulty arises from the fact that one goes continuously from an heterodyne regime for small $\psi (\psi < 2°)$ to a mixture of homodyne and heterodyne for larger ψ. In the small angle region, the curvature of $u_1(q)$ leads to a splay viscosity $\eta_s = (4.8 \pm 1)10^{-2}$ CGS units. For large values of ψ, we have tried to fit the spectrum with superpositions of two lorentzian curves of width u_1 (heterodyne) and $2u_1$ (homodyne). Our results are then consistent with a value of $\eta_s = (6 \pm 0.5)10^{-2}$ CGS. Further experiments are necessary to improve our present accuracy. A reasonable compromise for η_s is $\eta_s = 5.6\ 10^{-2}$ CGS. With this value we can compute(7) four out of the five Ericksen-Leslie coefficients(8) (i.e. α_2, α_3, α_4, α_5 in notations of ref. 3) by resolving second degree equations. The tentative values of these quantities are listed in Table 1.†

Table 1

	α_2	α_3	α_4	α_5	γ_1	γ_2
set 1	$-5.4\ 10^{-2}$	$+0.5\ 10^{-2}$	$5.9\ 10^{-2}$	$0.7\ 10^{-2}$	$5.8\ 10^{-2}$	$-4.9\ 10^{-2}$
set 2	$-6.4\ 10^{-2}$	$-0.6\ 10^{-2}$	$8.3\ 10^{-2}$	$2.5\ 10^{-2}$	$5.8\ 10^{-2}$	$-7\ 10^{-2}$

A useful way to compare these results with those of Miesowicz is to calculate η_1, η_2 and η_3 from our values of α_1.(9) This is done in Table 2.

Table 2

	t °C	η_1	η_2	η_3
Miesowicz	122°	$2.4\ 10^{-2}$	$9.2\ 10^{-2}$	$3.4\ 10^{-2}$
Set 1	125°	$1.1\ 10^{-2}$	$6.1\ 10^{-2}$	$3\ 10^{-2}$
Set 2	125°	$1.5\ 10^{-2}$	$8.6\ 10^{-2}$	$4.1\ 10^{-2}$

Note that $|\alpha_3|$ is in both cases rather weak compared to $|\alpha_2|$, as predicted by Helfrich;(10) as seen on Table 2, the agreement with the results of Miesowicz is reasonable for both sets. Let us show how we can distinguish between them.

The two quantities $\gamma_1 + \gamma_2 = 2\alpha_3$ and $\gamma_1 - \gamma_2 = -2\alpha_2$ characterize the torque exerted by the fluid on one molecule when its axis is, respectively, parallel to the flow and normal to the velocity gradient or normal to the flow and parallel to the velocity gradient. The important difference between the two sets is the change of sign of α_3

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† We have to thank Dr. Pershan and Dr. Martin for noticing a computation error in the first draft of this paper, which masked the change of sign of α_3.

positive for the set 1 and negative for the set 2. It has been shown by Leslie⁽³⁾ that a negative value of α_3 is required if the director alignment is to be stable in a stationary velocity gradient, close to the direction of the flow. This situation is indeed observed in usual nematics.† On this argument, we can choose the set 2 as giving our present tentative values for the viscosity coefficients in PAA at 125 °C.

At this point it is important to check if the change of sign of α_3 between the two sets is stable or not compare to a small change in the experimentally measured quantities γ_1, $\eta_s = \gamma_1 - (2\alpha_3^2/\alpha_s)$ and $\eta_b = \gamma_1 - (1/\alpha_v')$ which are respectively the " twist ", " splay ", and " bending " viscosities. A small algebra shows that the product of the two values of α_3 in set 1 and 2 is equal to: $\alpha_3^{(1)}\alpha_3^{(2)} = -\gamma_1(\gamma_1 - \eta_s)/((\eta_s/\eta_b) - 1)$ i.e. is negative when the inequality $\gamma_1 > \eta_s > \eta_b$ is fulfilled.‡ This is indeed always verified: from our measurements, we can estimate the following inequalities:

$$5.6\ 10^{-2} < \gamma_1 < 6.\ \ 10^{-2}$$

$$3.8\ 10^{-2} < \eta_s < 6.5\ 10^{-2}$$

$$0.2\ 10^{-2} < \eta_b < 1.8\ 10^{-2}$$

Whatever may be the uncertainty on η_s, its value is found always larger than η_b. Now, in spite of the small possible overlap between γ_1 and η_s, their difference should remain positive because it can be written as: $\gamma_1 - \eta_s = \alpha_3^2/\eta_1$. There is then just one set of viscosity coefficients compatible with the stability condition of Leslie.

To conclude, we can say that our present data are not incompatible with the measurements of Miesowicz nor with the Helfrich model. Presently, we believe that our value of the " twist " viscosity γ_1 is rather well established. The " splay " and " bending " viscosities η_s and η_b are also determined with a reasonably accuracy, but the larger possible variations in the difference between these quantities make difficult, at the present time, a more accurate determination of the other viscosity coefficients. However, the inequality $\gamma_1 > \eta_s > \eta_b$ is experimentally well established. This result

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† See for instance the papers describing the alignment induced by the electrodynamical instabilities, in the same Conference.

‡ Note that, conversely, $\eta_s > \eta_b$ implies that the set with the positive α_3 root corresponds always to an unstable (and not observed) type of flow.

coupled with the flow stability condition of Leslie allows a non-ambiguous determination of the viscosity coefficients. Our experimental accuracy should obviously be improved to obtain with the light scattering method the same reliability than with the direct measurement of Miesowicz.

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