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Ivan Haller [a], H. A. Huggins [a] & M. J. Freiser [a]
[a] IBM Thomas J. Watson Research [Cgrave]enter, Yorktown Heights, New York, 10598
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On the Measurement of Indices of Refraction of Nematic Liquids

IVAN HALLER, H. A. HUGGINS and M. J. FREISER

IBM Thomas J. Watson Research Center
Yorktown Heights
New York 10598

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We wish to report on a simple method for measuring the birefringence and indices of refraction of nematic liquids with an accuracy comparable with or superior to previously reported means.[1-3] The method is exemplified in measurement of the temperature dependences of the indices of refraction of *p*-methoxybenzylidene *p*-butylaniline (MBBA) at two wavelengths.

The index of refraction of an isotropic fluid is most conveniently (and accurately) determined with an Abbe refractometer. The functioning of this instrument is based on internal reflection of light at the interface between the liquid and the surface of an optically dense glass prism. The maximum measurable index of refraction is therefore that of the glass. The index of refraction of the extraordinary ray in nematic liquids can be larger than that of the glass in the refractometer. A further difficulty precluding the use of the refractometer for the measurement of n_e is the problem of aligning the liquid on the surfaces of the illuminating prism, which are not polished. The ordinary index of refraction poses no such problems. Indeed, if a nematic liquid is used in an Abbe refractometer a sharp line is observed corresponding to n_0 in the absence of alignment or of polarization of the light, although contrast and intensity are influenced by these factors, since the light will, in general, contain an ordinary component suffering internal reflection at the appropriate angle of incidence.[4] The instrument is therefore entirely suitable for the determination of n_0 which, combined with an independent measurement of $\Delta n = n_e - n_0$, yields n_e.

For both fundamental and applicational reasons it is desirable to have an accurate and direct measurement of Δn. An extraordinarily simple and accurate means of measuring Δn is available.

Consider a wedge of uniaxial liquid, enclosed by flat transparent plates, with the optic axis (Z) perpendicular to the wedge angle, as shown in Fig. 1. Let the wedge be illuminated by parallel light propagating in the Y direction with polarization direction 45° from

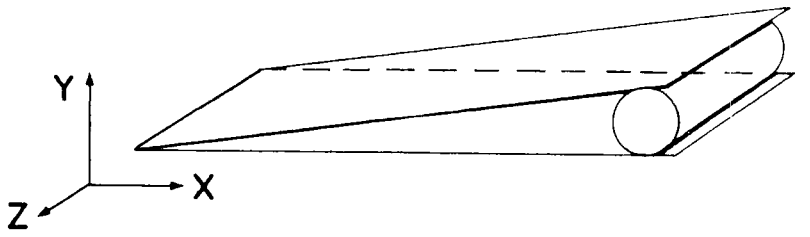

Figure 1. Sample geometry for birefringence measurement.

X. The phase angle between the ordinary and extraordinary wave (retardation) is given by:

$$\phi = (2\pi/\lambda)\Delta n\, l, \tag{1}$$

where λ is the wavelength of light in vacuum,

$$\Delta n = n_e - n_0,$$
$$l = xd/x_0$$

is the thickness of the sample at distance x from the apex, and d is the thickness of the spacer located at distance x_0 from the apex.

If the structure is viewed through an analyzer either parallel or perpendicular to the polarizer, a series of uniformly spaced fringes appear whose separation, Δx, can be measured. As successive fringes correspond to a phase difference of 2π,

$$\Delta n = \lambda x_0/\Delta x d. \tag{2}$$

We have used this method to determine the indices of refraction as functions of temperature, of MBBA at two wavelengths. The wedge of MBBA was prepared by enclosing it between two optically flat quartz slides, $25 \times 25 \times 1.5$ mm, in contact along one edge and separated along another by a molybdenum wire of 0.750 mm diameter. The optic axis was established by rubbing the slides,[5] prior to assembly, along the contact edge. In order to confirm that the desired alignment of the liquid by surface forces was adequate for the measurements, a magnetic field of 8 kOe was applied in the rubbing direction with no observable change in the fringe spacing. The

structure was held rigidly by finger springs in a microscope hot stage whose temperature was controlled to $\pm 0.1\,^{\circ}C$. The temperature was measured with a copper–constantan thermocouple located near the sample. The fringe pattern was observed and photographed on a Leitz Ortholux polarizing microscope; fringe separations were calibrated with a stage micrometer.

The refractive index of the ordinary wave was measured on a Zeiss Model A Abbe refractometer. The temperature of the measuring block was maintained to better than $0.1\,^{\circ}C$ by a circulating water bath and was measured by a copper–constantan thermocouple. The refractometer was calibrated with Phillips Research Grade benzene.[6]

The light sources in both measurements were an Optics Technology Model 170 helium–neon laser, diffused with a rotating translucent disc, and a General Electric Na-1 sodium arc.

The MBBA sample, when prepared, had a nematic–isotropic transition temperature of $47\,^{\circ}C$. It deteriorated rapidly,[7] however, during measurement, while in contact with air; the transition temperature was therefore checked frequently, and the data are presented in terms of reduced temperature, $\tau = (T - T_{NI})/T_{NI}$.

The measured birefringences of MBBA at 589.3 nm and 632.8 nm are presented in Fig. 2. The corresponding indices of refraction for the ordinary wave are shown in Fig. 3.

A test of consistency is provided by the Lorentz–Lorenz relation:

$$(\bar{n}^2 - 1)/(\bar{n}^2 + 2) = 4/3 \cdot \pi N \bar{\alpha}, \tag{3}$$

where $\bar{\alpha}$ is the mean polarizability, N the number of molecules per unit volume, and in the nematic liquid $\bar{n}^2 = (n_e^2 + 2n_0^2)/3$.[8] In the isotropic phase $\bar{n} = n_i$, the measured refractive index, which within experimental error is given by $n_i\ (\lambda_1) = 1.6117 - 0.125\ \tau$ and $n_i\ (\lambda_2) = 1.6048 - 0.136\ \tau$ at $\lambda_1 = 589.3$ and $\lambda_2 = 632.8$ nm. Since the mean polarizability is independent of temperature and state of matter, a plot of the left-hand side of Eq. (3) as a function of temperature should, if the formula is applicable, reflect the temperature variation of density only. As seen from Fig. 4, the data taken at the two wavelengths are consistent, significant deviations being observable only near the transition temperature where errors in temperature measurement are important. Least square fitting results in slopes (for the nematic phase) of 0.67×10^{-3} and

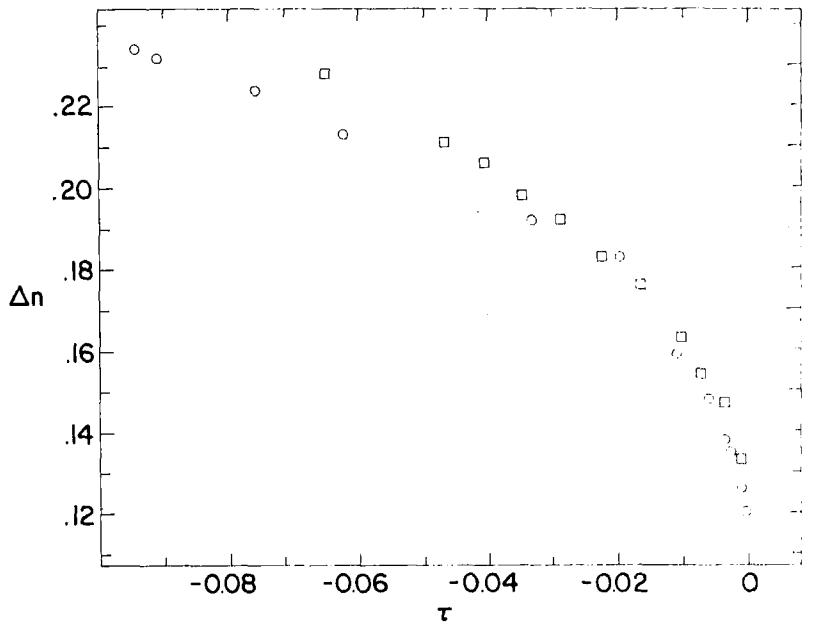

Figure 2. Birefringence of MBBA vs reduced temperature, $\tau = (T - T_{NI})/T_{NI}$, at 589.3 nm (squares) and 632.8 nm (circles). A least square fit for 589.3 nm and $1.2 \times 10^{-3} < |\tau| < 0.065$ yields $\Delta n = 0.117 + 0.456\ |\tau|^{0.5} - 0.01\ |\tau|$ and for 632.8 nm and $5.3 \times 10^{-4} < |\tau| < 0.094$ gives $\Delta n = 0.107 + 0.574\ |\tau|^{0.5} - 0.53\ |\tau|$.

$0.74 \times 10^{-3}\ °C^{-1}$ at 632.8 and 589.3 nm, respectively, in fair agreement with the reported[9] volume expansion coefficient of $0.807 \times 10^{-3}\ °C^{-1}$. Assumption of the applicability of Eq. (3) and extrapolation of the fitted lines to the transition temperature, indicates the fractional volume expansion associated with the nematic–isotropic transition to be 5.8×10^{-3} or 5.4×10^{-3} from the two sets of data. Using a specific gravity of 1.088 for MBBA at 25 °C, the mean polarizability is calculated as $\alpha_D = 347 \times 10^{-25}$ ml.

Near the transition temperature, the dominant error in our measurements results from the temperature determination. This is particularly serious in the case of MBBA, whose transition temperature is very sensitive[7] to minor decomposition products. The width of the nematic–isotropic transition, even in well-controlled samples, amounts to at least 0.1 °C.

In a temperature regime sufficiently distant from the transition temperature, the accuracy of the birefringence data are determined

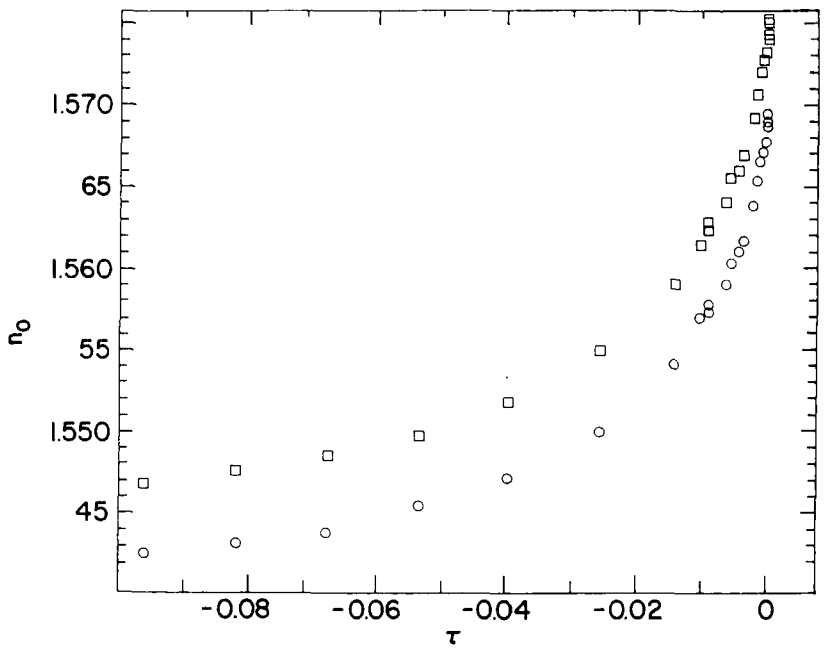

Figure 3. Ordinary index of refraction of MBBA in the nematic phase vs reduced temperature, at 589.3 nm (squares) and 632.8 nm (circles). A least squares fit to these data in the range $2 \times 10^{-4} < |\tau| < 10^{-1}$ yields

$$n_0 = 1.5765 - 0.1740\,|\tau|^{0.5} + 0.253\,|\tau|$$

for 589.3 nm and $n_0 = 1.5708 - 0.1643\,|\tau|^{0.5} + 0.236\,|\tau|$ for 632.8 nm.

by the errors of angle or distance measurements. Specifically, from Eq. (2),

$$\delta(\Delta n)/\Delta n = \left|\,\delta(x_0/d)/(x_0/d)\,\right| + \left|\,\delta(\Delta x)/\Delta x\,\right|.$$

In our application of the method, the wedge angle, x_0/d, was easily measured with the use of a micrometer and a caliper, with an estimated error of 1%. Twenty fringes were used for the determination of the fringe spacing, Δx, contributing an error which we estimate to be about 0.5% since the fringe center can be located to within one-tenth of a fringe. For comparison, the Chatelain prism method[3] involves the measurement of the prism angle, θ, and the angle of deviation, D. One then finds, for small prism angles,

$$\delta n/(n-1) = \left|\,\delta\theta/\theta\,\right| + \left|\,\delta D/D\,\right|.$$

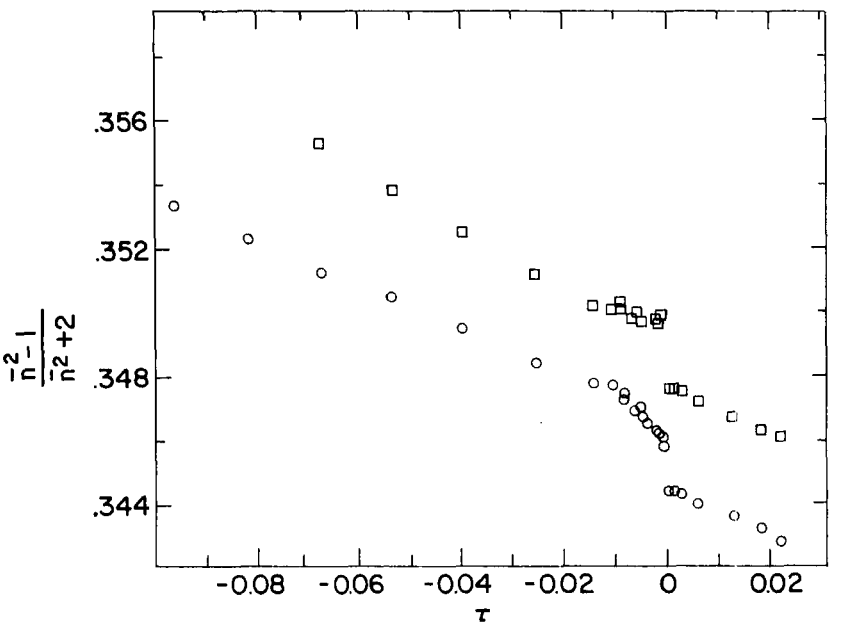

Figure 4. Temperature dependence of $(\bar{n}^2-1)/(\bar{n}^2+2)$ in the nematic and isotropic phases, at 589.3 nm (squares) and 632.8 nm (circles).

Thus, for the same accuracy in angle measurement, the Chatelain method yields about the same fractional error in $n-1$ as we attain for Δn. The consequent error in n_e is therefore almost an order of magnitude greater in the Chatelain method then here. In order to achieve the same accuracy in the prism method, far greater care is required in the angle measurement than in the method described here.

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