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Dynamic Properties near the Nematic-Isotropic Transition of a Liquid Crystal*

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(Received 17 June 1971)

We have measured the temperature dependence of the flow birefringence in the isotropic phase of *p*-methoxybenzylidene *p*-*n*-butylaniline. We have observed a divergence as the phase transition is approached. We have determined the steady shear viscosity η_0 and the coupling coefficient μ between velocity shear and the order parameter as a function of temperature. We have also measured the real part of the shear impedance and compared the results with light-scattering data. Our results are well described by de Gennes's theory.

Recently de Gennes¹ has investigated the dynamics of fluctuations of the order parameter in the isotropic phase of a nematic liquid crystal and also discussed the flow birefringence, the spectrum of inelastically scattered light, and the attenuation of ultrasonic shear waves in terms of three viscosity coefficients η_0 , μ , and ν . In this Letter we report precise measurements of flow birefringence in the isotropic phase of *p*-methoxybenzylidene *p*-*n*-butylaniline and determination of the temperature dependence of the viscosity coefficient μ , using our flow birefringence measurements together with the magnetic birefringence data given by Stinson and Litster.² We have measured the capillary viscosity η_0 on the same sample. The real part of the high-frequency shear impedance has also been determined from a shear-wave reflectance technique, described elsewhere.³ To perform the flow birefringence experiments we used a high-sensitivity apparatus with photoelectric detection modulated by a rotating crystal. The wavelength of the light was 6328 Å. We regulated the temperature both inside and outside of the flow cell. The temperature gradient between the walls was smaller than 0.004°C. We used an internal rotor, 50 mm in diam, 70 mm in length, and with a 0.5-mm gap.

As shown earlier,^{4,5} under a velocity gradient G the isotropic phase shows a positive birefrin-

gence Δn much larger than found in normal organic liquids. Δn is a linear function of G and the extinction angle is equal to 45° for all velocity gradients. As the phase transition $T_K = 45.5^\circ\text{C}$ is approached we find a divergent behavior of $\Delta n/G$ which is related to a divergence of the fluctuations of the order.

As shown by de Gennes, the order parameter for the isotropic phase is a symmetric traceless tensor $Q_{\alpha\beta}$,⁶ proportional to the anisotropic part of the magnetic susceptibility tensor. The free-energy density may be written as

$$F = F_0 + \frac{1}{2}A Q_{\alpha\beta} Q_{\beta\alpha} + \frac{1}{3}B Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + O(Q^4) - \frac{1}{2}\chi_{\alpha\beta} Q_{\beta\alpha} H_\alpha H_\beta, \quad (1)$$

H being the magnetic field. The coefficient of the quadratic term, $A(T)$, is taken to be $A(T) = a(T - T_c^*)^\gamma$, where T_c^* is a temperature slightly below the transition point T_K , γ and a being unknown constants. One may obtain $A(T)$ from the temperature dependence of the magnetic birefringence using the equation¹

$$n_{\parallel} - n_{\perp} = MH^2 \Delta\chi / 6A\bar{n}, \quad (2)$$

where M is the proportionality coefficient between the dielectric and the order-parameter tensors and \bar{n} the mean refraction index. $\Delta\chi$ is the anisotropy of diamagnetic susceptibility in the

ordered phase. The results of Stinson and Litster show that $\gamma = 1$, $a = 0.062 \times 10^7 \text{ erg cm}^{-3} \text{ }^\circ\text{K}^{-1}$, and $T_K - T_c^* = 1.0^\circ\text{K}$.

To describe the dynamic properties, de Gennes constructed linear relations between thermodynamic fluxes and forces, the coupling factors being the three viscosity coefficients μ , ν , and η_0 . One may directly obtain μ from the flow birefringence measurements through the relationship¹

$$n_1 - n_2 = (M\mu/2\bar{n}A)G. \quad (3)$$

η_0 is obtained from capillary flow experiments. On the other hand, the frequency width of the scattered light $\Gamma(T)$ gives the value¹ of ν ,

$$\Gamma(T) = A(T)/\nu. \quad (4)$$

We may check the results obtained from light-scattering experiments by measuring the real part³ R of the shear impedance,

$$R = (\rho\omega/2)^{1/2}[\eta'' + (\eta'^2 + \eta''^2)^{1/2}]^{1/2},$$

where ρ is the density and ω the angular frequency. The relationships for η' and η'' have been given by de Gennes¹:

$$\eta' = \eta_0 - \frac{2\mu^2}{\nu[1 + \Gamma^2/\omega^2]},$$

$$\eta'' = \frac{2\mu^2\Gamma}{\nu\omega[1 + \Gamma^2/\omega^2]}.$$

We now proceed to analyze experimental data. In Fig. 1 we present our measured values of $\Delta n/G$. The variation of μ is obtained by comparing

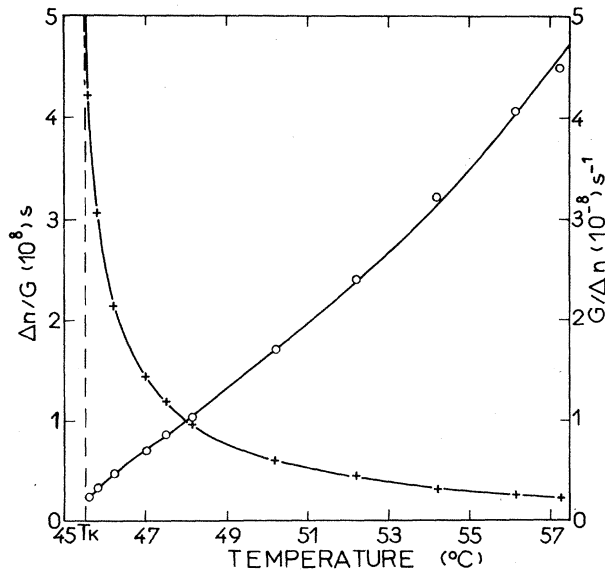


FIG. 1. The temperature dependence of the ratio of the flow birefringence to the gradient.

magnetic and flow birefringence measurements [Eqs. (2) and (3)]. Although the transition point T_K is not exactly the same for the two samples, the comparison is still possible because the magnetic birefringence shows identical behavior except for a shift in temperature scale, as reported by Stinson and Litster.

The values of μ and η_0 are reported in Fig. 2. Except at temperatures close to T_K the coefficients η_0 and μ obey the usual exponential law with the following activation energies:

$$W_{\eta_0} = 7.4 \text{ kcal/mole}, \quad W_{\mu} = 4.7 \text{ kcal/mole}.$$

On the other hand the activation energy for ν has been determined by Stinson, Litster, and Clark² from the linewidth of the spectrum of scattered light:

$$W_{\nu} = 7.1 \text{ kcal/mole}.$$

Close to the transition point where the fluctuations become very large there is an apparent departure of μ from the Arrhenius behavior (see Fig. 2). This is caused by the departure of $A(T)$ from the $(T - T_c^*)^{-1}$ dependence which was observed by Stinson and Litster and which also appears in the plot of $G/\Delta n$ versus temperature (Fig. 1).

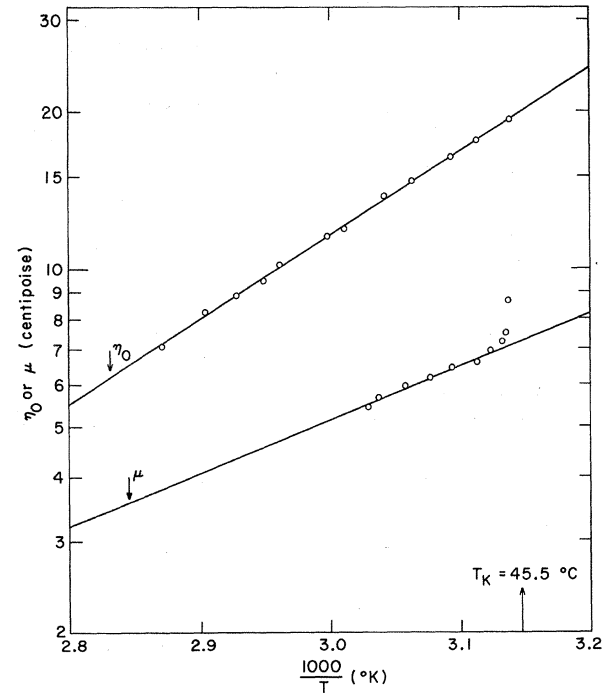


FIG. 2. The plot of the logarithm of viscosity coefficients versus $10^3/T$. The data have been obtained as described in the text: μ , from comparison of flow and magnetic birefringence measurements; η_0 , from capillary flow experiments.

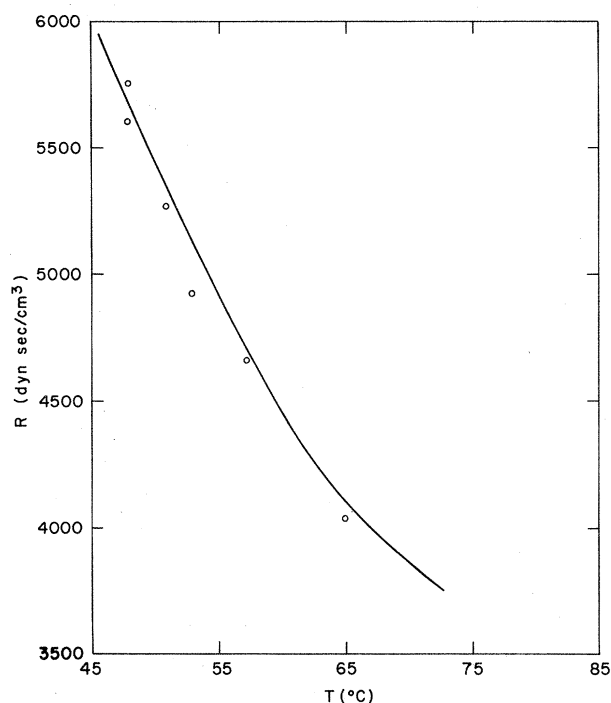


FIG. 3. The real part of the shear impedance as a function of temperature at 73 MHz. The solid line is a calculated curve. The points are experimental data.

This departure can be corrected if instead of taking the $(T - T_c^*)^{-1}$ dependence of $A(T)$ we use the experimental values. However, we do not find evidence of an anomalous increase in the 5°C above the transition temperature as observed by Stinson, Litster, and Clark.

In Fig. (3) we report experimental data measured at a frequency of 73 MHz for the real part R of the shear impedance. Also shown is the calculated curve from the best fits obtained for the coefficients μ , η_0 , and ν (Fig. 2 and Ref. 2). The agreement is good within experimental error.

*Work supported by Direction des Recherches et Moyens d'Essais, Ministère des Armées, under Contract No. 71-34-034.

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⁶ $Q_{\alpha\beta}$ is assumed dimensionless and normalized so that $Q_{zz} = 1$ in the ordered phase.

Experimental Confirmation of the Kawasaki-Einstein-Stokes Formula; Measurement of Small Correlation Lengths

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(Received 16 February 1971)

The Kawasaki formula $D = kT/6\pi\eta\xi$ is experimentally verified using the measured values in a cyclohexane-aniline critical mixture near T_c . Its application in a wide range of temperatures above T_c , where the viscosity is known, is completely verified by the measurements of the diffusion coefficient D and allows a direct determination of the correlation length ξ in a domain where no other optical method is suitable. We show that the power law $\xi = \xi(\epsilon)^\nu$ is followed up to 40° from T_c .

Kawasaki¹ has obtained a formula for the mutual diffusion coefficient D of a binary mixture in the neighborhood of the critical temperature:

$$D = kT/6\pi\eta\xi. \quad (1)$$

Here k is Boltzmann's constant, T the absolute temperature, η the viscosity, and ξ the correlation length. Equation (1) is analogous in form to the Einstein-Stokes equation $D = kT/6\pi\eta a$ for the mass diffusion coefficient for particles of radius a . The purpose of this Letter is to investigate the validity of the relation (1) close to the criti-

cal point and then to use it over a wider range of temperatures.

In the particular case of a cyclohexane-aniline critical mixture, we have all the data necessary to check this formula. Arcovito *et al.*² and Brunnett and Gubbins³ have measured the temperature dependence of the viscosity of this mixture, and D has been measured in a large number of experiments performed in this laboratory.⁴ Using these experimental values of D and η , we can deduce from formula (1) the correlation length (labeled ξ_k) at different temperatures and then com-