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Anisotropy of Self-diffusion in a Liquid Crystal Studied by Neutron Quasielastic Scattering†

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Abstract—The coefficient D for self-diffusion in nematic *p*-azoxyanisole has been determined from measurements of the energy width of quasi-elastically scattered neutrons. The directional dependence of D was studied by polarizing the substance along different directions relative to the scattering vector. For an unpolarized substance we measured $D = 1.4 \times 10^{-5}$ cm^2 sec^{-1}, whereas for a polarized substance we found $D^{\parallel} = 1.8 \times 10^{-5}$ cm^2 sec^{-1} and $D^{\perp} = 1.0 \times 10^{-5}$ cm^2 sec^{-1} for diffusion parallel with and perpendicular to the optical axis, respectively. These results are in qualitative agreement with the anisotropy of the viscosity coefficient, as measured by Miesowicz (*Nature* **136**, 261 (1935); **158**, 27 (1946)).

In this paper we report what we believe is the first measurement of the anisotropy of the self-diffusion of a nematic liquid crystal. The substance investigated was *p*-azoxyanisole (PAA).

In the nematic phase, liquid crystals are known to possess anisotropic optical, electrical and magnetic properties.(1) Miesowicz(2) has measured a marked anisotropy in their viscosity, which also implies an anisotropic behaviour of the diffusion coefficient. A measurement of the diffusion coefficient in PAA by the NMR-method has earlier been reported by Blinc *et al.*(3) An approximate value of $\sim 10^{-5}$ cm^2 sec^{-1} was given for the isotropic liquid phase, but for the ordered nematic phase no value could be given.

The scattering of neutrons from PAA is almost entirely due to incoherent scattering by protons. The diffusive motion of the

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molecules is observed as a quasielastic broadening of the spectral line of the incident beam. According to the Vineyard theory,(4) this broadening (ΔE) is expressed by $\Delta E = 2\hbar DQ^2$, where D denotes the diffusion coefficient and $\mathbf{Q}$ the scattering vector. This expression results when assuming a continuous diffusion process, which also implies a Lorentzian line-shape. The actual line-shape observed is well reproduced when folding a Lorentzian with the Gaussian instrumental function, as will be shown by Fig. 3 below.

The nematic phase of PAA extends from the melting point of 119 °C to the clearing point of 135 °C. Our measurements in the nematic phase were performed in the range 123–125 °C and the temperature was in each case kept stable within 1°. Some additional measurements were made at 115° and 140 °C. The sample was contained in a flat aluminium vessel of (60 × 57) mm^2 and with a wall

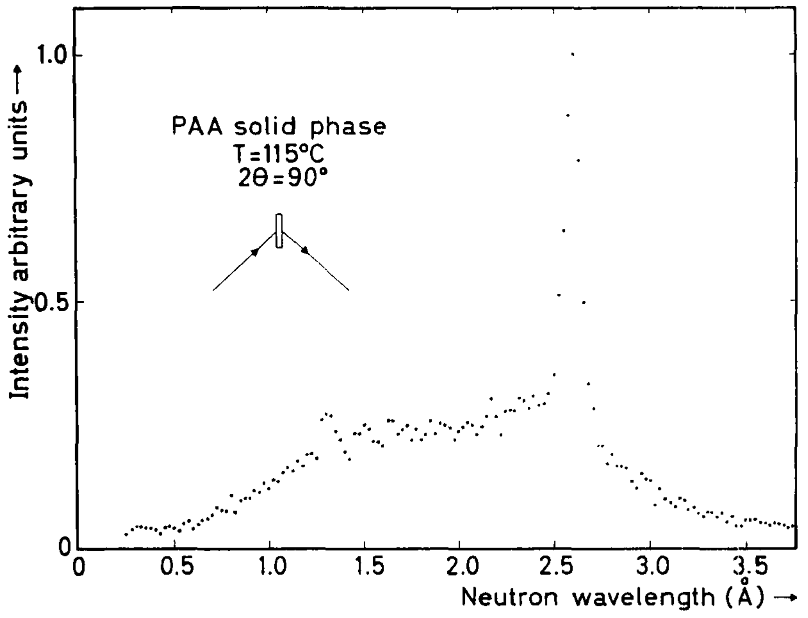

Figure 1. A recorded time-of-flight spectrum in the solid phase at a temperature of 115 °C plotted as a function of the neutron wavelength. The scattering geometery is denoted by the direction of the incoming and outgoing neutron beams, and by the position of the flat sample holder. The narrow peak at 2.61 Å is a reproduction of the incoming neutron beam folded by the Gaussian resolution function of the instrument.

distance that could be varied between 2 and 3 mm. An electrical field of 6000 V cm^{-1} could be applied along the short dimension, i.e. along the face normal.

The MISS spectrometer at the JEEP II reactor was used for the experiments. MISS is a hybrid instrument composed of a monochromator unit with a graphite crystal(5) and an analyzing part with a curved-slit mechanical rotor. The incident neutron energy used was 12.01 meV, corresponding to 2.61 Å in wavelength, and the scattering angles 2θ were 60°, 75° and 90°, corresponding to Q^2-values of 5.80, 8.59 and 11.59 $Å^{-2}$, respectively. Examples of recorded wavelength spectra in the solid and nematic phases are shown in Figs. 1 and 2, respectively. The scattering geometry is denoted in each case by the directions of the incoming and outgoing beam, by the position of the flat sample holder, and by the electrical field vectors, when applicable.

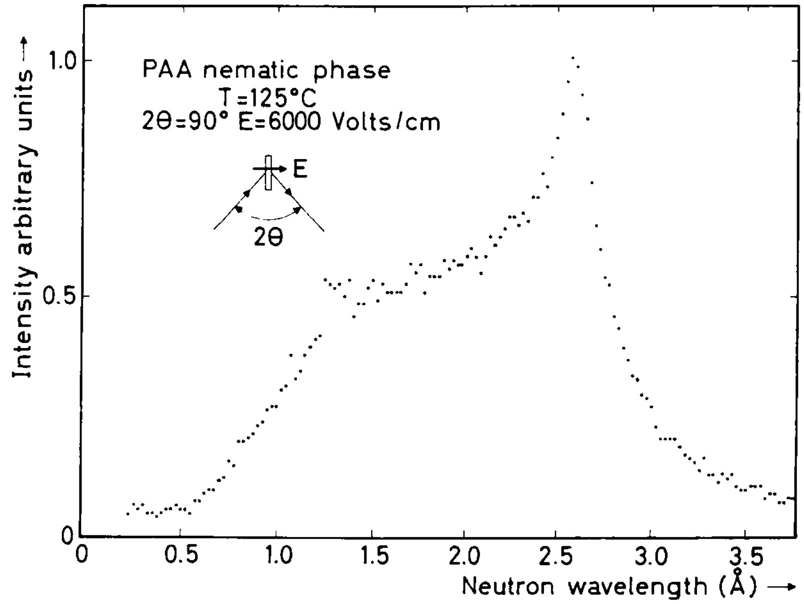

Figure 2. A recorded time-of-flight spectrum in the liquid nematic phase at a temperature of 125 °C plotted as a function of the neutron wavelength. The scattering geometry is denoted by the direction of the incoming and outgoing neutron beams and by the position of the flat sample holder. A vector **E** indicates the direction of the applied electrical field.

The sharp line at 2.61 Å in Fig. 1 is due to elastic scattering and reproduces the Gaussian form of the instrumental function. A weak $\lambda/2$ component is also visible. The rest of the scattered spectrum is due to inelastic scattering and does not change when the substance is heated to the nematic phase, as in Fig. 2. In our analysis of the diffusion type scattering in the nematic phase we are interested in the quasielastic component only. The isolation of this component was made in two steps: (1) By a subtraction of the inelastic spectrum as observed in the solid phase. (2) By a subtraction of the weak elastic component measured with an empty sample holder.

Examples of the inelastic spectra obtained in this manner are shown in Fig. 3. The smooth curves do in each case represent a convolution of the instrumental Gaussian function with a Lorentzian giving the best fit to the experimental data.

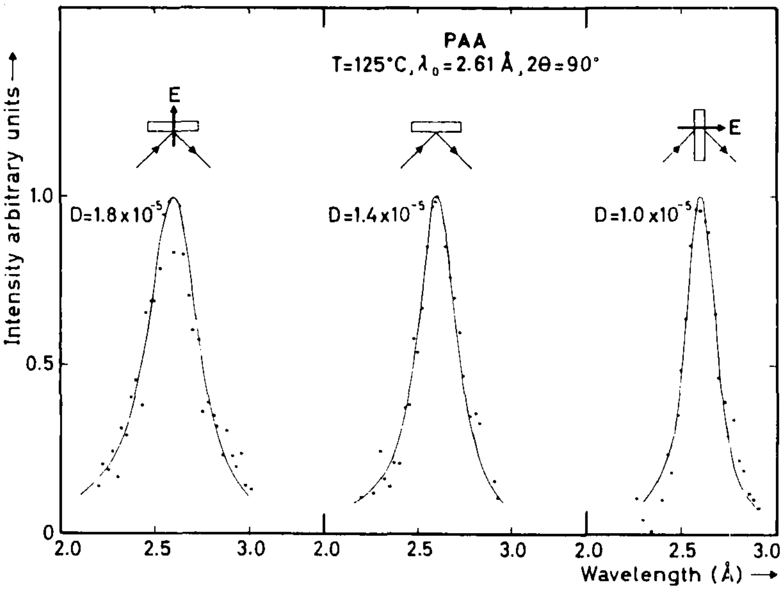

Figure 3. The dots represent the experimentally determined quasielastic peaks in the nematic phase at a temperature of 125 °C. A sketch above each peak shows the scattering geometry used. The direction of the electrical field, when applicable, is indicated by a vector. The smooth curves represent a convolution of the instrumental Gaussian function with a Lorentzian giving the best fit to the experimental data. The diffusion coefficient D is given in the unit, $\mathrm{cm}^2\ \mathrm{sec}^{-1}$.

The bulk of the data were taken in a reflection geometry, i.e. with the incoming and outgoing beam on the same side of the flat sample. Fig. 4 gives the result of the analysis for this geometry for two cases, when an electrical field was applied along the scattering vector and when no field was applied, respectively. The approximately straight lines observed in each case indicate that the self-diffusion process is a continuous one. The different slopes of the lines are interpreted as follows:

The neutron scattering cross section⁽⁶⁾ of a propagating mode of polarization vector $\boldsymbol{\xi}$ is proportional to $(\boldsymbol{\xi}\mathbf{Q})^2$, hence our neutron experiment is sensitive to diffusive modes whose polarization vectors have components along the scattering vector. When an electrical field is applied, the molecules are oriented such as to have their long axes along the field.⁽¹⁾ From this it follows that diffusion along the molecular axes is mainly seen in the experiment giving the upper curve of Fig. 4, whereas diffusion along all directions relative to the same axes is seen in the experiment giving the lower curve. Hence Fig. 4 is a direct proof of the anisotropy of the self-diffusion in nematic PAA.

Some experiments at $2\theta = 90°$ in the transmission geometry, for which the electrical field is normal to the scattering vector, enabled a study of the diffusion normal to the molecular axes. Such observations, as given by the right hand curve of Fig. 3, demonstrated that the diffusion coefficient has its minimum value along this direction.

From our measurements we arrived at the following values of the diffusion coefficients:

$$D^{\parallel} = 1.8 \times 10^{-5}\ \text{cm}^2\ \text{sec}^{-1}$$

$$D^{\perp} = 1.0 \times 10^{-5}\ \text{cm}^2\ \text{sec}^{-1}$$

$$D^{\text{average}} = 1.4 \times 10^{-5}\ \text{cm}^2\ \text{sec}^{-1}$$

for diffusion parallel with, normal to and in an arbitrary direction relative to the molecular axis, respectively. The ratio $D^{\parallel}/D^{\text{average}}$ is 1.3, which is smaller than the ratio $\eta^{\text{average}}/\eta^{\parallel} = 2$ between the corresponding viscosity coefficients, as measured by Miesowicz.⁽²⁾ It would be interesting to measure the temperature variation of D as the sample passes from the nematic to the isotropic liquid phase. This is reserved for a future work.

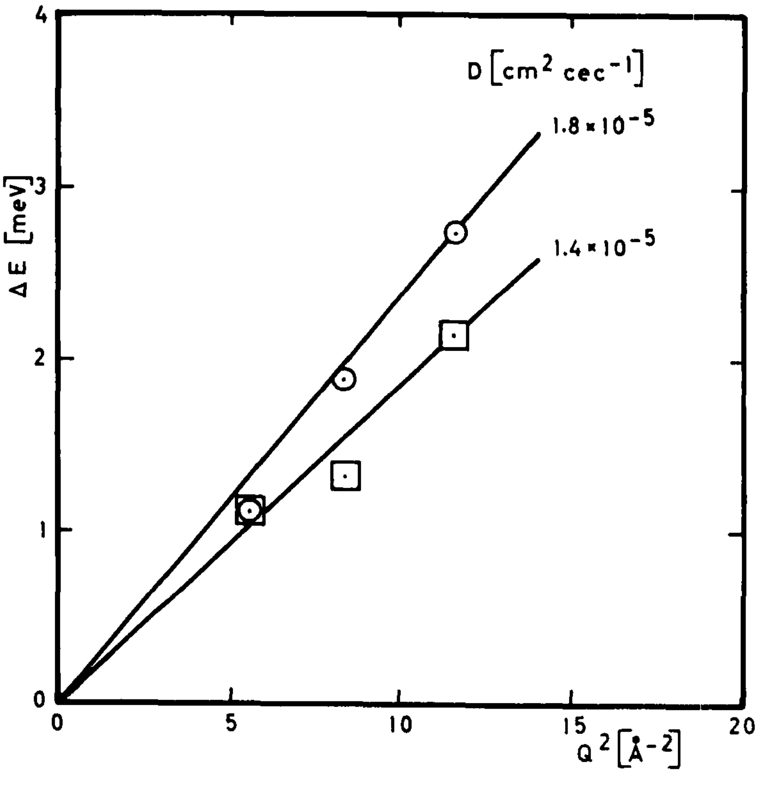

Figure 4. ΔE is plotted versus Q^2 using the relation $\Delta E = 2\hbar DQ^2$. Circles: Electrical field applied parallel to the scattering vector; Squares: No electrical field applied.

The orienting effect of the electrical field on the molecular axis was found to be absent in the isotropic liquid phase, since no difference in peak width could be seen for the cases with and without a field. In our measurements we could not detect any orienting effect of the walls of the vessel. This is inferred from the fact that D was found to be the same for the reflection and for the transmission geometry when no field was applied.

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Note added in proof

Very recently Blinc *et al.* (*Phys. Letters* **31A,** 531 (1970)) have obtained $D^{\text{average}} = (0.75 \pm 0.5) \times 10^{-5}$ cm^2/sec by neutron scattering measurements.