Vol. A54 (1978) ACTA PHYSICA POLONICA No 4

FAST STOCHASTIC REORIENTATIONS OF LIQUID CRYSTAL MOLECULES*

By J. A. Janik

Institute of Nuclear Physics, Cracow**

(Received February 1, 1978)

A critical approach to the molecular reorientation problem in methoxy deuterated PAA is presented. It is shown, how difficult it is to establish the truth about reorientations in view of various molecular responses of different methods. Four attempts, with the help of models, to explain the neutron scattering data are presented. It seems obvious that the PAA molecules reorient with the correlation time 2—4 psec, about the long axis. This correlation time does not agree with that measured by the dielectric relaxation method. Suggestions for an explanation are given.

1. Introduction

There is a lot od misunderstanding on the subject of molecular rotations in condensed matter systems. The terms: free rotation, hindered rotation etc. are very often carelessly used without a precise explanation of their meaning. Correlation times are compared carelessly although various methods lead to different kinds of the molecular response. The poor accuracy inherent in the methods of determinating the rotational parameters is too-easily forgotten. And, last but not least, one very often claims that true facts about a rotation have been established, only because a model fitting an experiment gave a good quality fit. The aim of this lecture is to show, using para-azoxyanisol as a model substance, how careful one must be in drawing such conclusions.

I must point out at this moment that in what follows I will speak only about fast reorientations of molecules, having in mind correlation times of the order of 10^{-12}—10^{-10} sec.

Now, let me remind you that there are two equivalent ways of characterizing a physical molecular system, one by the $\vec{\kappa}$, ω values and the other by the $\vec{r}$, t values ($\hbar\vec{\kappa}$ is the momen-

* Presented at the Second Liquid Crystal Conference of Socialist Countries, Sunny Beach, Bulgaria September 27–30, 1977.

** Address: Instytut Fizyki Jądrowej, Radzikowskiego 152, 31-342 Kraków, Poland.

tum, $\hbar\omega$ — the energy, $\vec{r}$ — the position and t — the time). The $\vec{\kappa}$, ω representation is obtained directly from measurements with spectrometers. For stochastic motions (e.g. reorientations), however, the use of the $\vec{r}$, t representation is much more suitable for thoretical models [1]. In the case of neutrons, the results of spectrometric measurements may be presented in the form of a scattering law $S(\vec{\kappa}, \omega)$ (i.e. a $\vec{\kappa}$, ω representation). Its correspondence to the correlation function $F(\vec{r}, t)$ (i.e. the $\vec{r}$, t representation) occurs via the Fourier transformation:

$$S(\vec{\kappa}, \omega) = \frac{1}{2\pi} \iint e^{i(\vec{\kappa} \cdot \vec{r} - \omega t)} F(\vec{r}, t) d^3\vec{r} dt.$$

2. Remarks on types of information concerning reorientations and the procedure of deriving the information

In order to obtain "monomolecular" information, i.e. that leading to a self-correlation function, one needs an additivity of the scattered intensities from all molecules and hence the incoherence of the scattering. "Polymolecular" response, on the other hand, i.e. that giving information concerning correlated reorientational motions, implies the existence of cross-terms in the expression for the scattered intensity, and hence a coherence of scattering.

For fast reorientations there exist (so far) three undoubtfully "monomolecular" methods: (a) the incoherent quasielastic neutron scattering method, (b) the IR internal vibrational bands profile method, and (c) the Raman internal vibrational bands profile method. In the incoherent QNS method (a), when applied to hydrogen containing molecules, the incoherence is due to a lack of order in the neutron–proton spin dependent part of nuclear interactions. In the IR and Raman internal band methods the incoherence is due to a lack of order between vibrations (of a given mode) of different molecules.

It should be pointed out that the dielectric relaxation method certainly does not give the "monomolecular" response, but it possesses "polymolecular" contributions which are virtually not determinable, and therefore one must be very careful, when comparing the dielectric relaxation results with those of QNS, IR or R. For the NMR relaxation method, it must be emphasized that the natural range of correlation times for this method is well above what we have called fast reorientations. In spite of that, many authors use formulas connecting the spin-lattice relaxation time T_1 with the reorientational correlation time τ_2. Their results, however, are often illusory, due to the neglection of some relaxation channels and dealing only with one mechanism of relaxation.

The most natural procedure of deriving information concerning reorientations from scattering experiments is to reproduce the experimental scattering profile from an invented model. (An obvious remark must be made here: the model profile must be convoluted with the instrumental profile when compared with the experimental one.) We must have in mind that there are often many processes by which the molecule relaxes, the reorientation being only one of them. For the neutron method, for instance, translatory diffusion is such a competing relaxational process. If it is justified to assume an independence of the trans-

lations from the rotations, the translatory diffusion profile must be convoluted with the reorientational scattering law in order to obtain the resultant profile.

The following Section shows how difficult it is to establish the truth about reorientations in view of all complications listed above.

3. *QNS results and model fitting for the methyl deuterized PAA in the nematic phase*

The results reported here are contained in two papers, [2] and [3]. It should be pointed out that the deuteration is equivalent to masking, because of the domination of the neutron scattering by protons over that by deuterons and also by other nuclei. Hence,

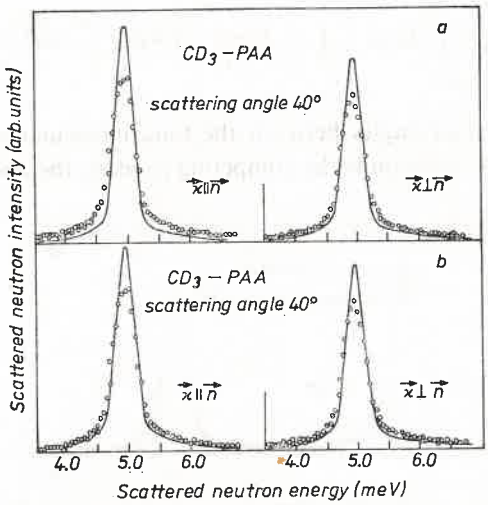

Fig. 1. A comparison of model 1 and model 2 with the QNS experiment. Details are given in the text. (a) Uniaxial rotational diffusion (translational diffusion treated approximately), sample holder contribution measured; (b) Uniaxial rotational diffusion + jumps (translational diffusion treated approximately), sample holder contribution measured

a deuteration of methoxy terminals in PAA limits information to the molecular body. We should also notice that the only fast reorientation of the molecule under discussion must be that about the long molecular axis.

Let me give you now a brief presentation of the four model attempts applied in order to reproduce the experimentally obtained QNS spectra. This presentation is given in Figs 1 and 2, for one value of the scattering angle (40°). Similar drawings could have been presented for other scattering angles: 20°, 30°, 50°, 60°. As pointed out in Figs 1 and 2, the measurements were made for two nematic orientations (in respect to the neutron momentum transfer $\vec{\kappa}$): $\vec{\kappa} \| \vec{n}$ and $\vec{\kappa} \perp \vec{n}$. As the temperature of the substance was $+125°C$, the appropriate order parameter $S = 0.6$ was used in the model calculations. The radius of proton rotation d was accepted as being equal to 2.1 Å, in accordance with the known geometry of the PAA-molecule.

In model 1 it was assumed that the molecule reorients about the long axis by small angular steps — i.e. by a rotational diffusion. The scattering law for such a model, for an oriented sample is:

$$S_{\mathrm{inc}}(\vec{\kappa}, \omega) = f_0(\vec{\kappa})\delta(\omega) + \frac{2}{\pi}\sum_{n\geqslant 1}^{\infty} f_n(\vec{\kappa})\frac{\Gamma_n}{\Gamma_n^2+(\hbar\omega)^2},$$

where $\Gamma_n = n^2\hbar/\tau_1$, τ_1 is the first of the correlation times,

$$f_n(\vec{\kappa}_{\parallel}) = \int_{-1}^{+1} J_n^2(\kappa d \sin\beta) n(\beta) d\cos\beta,$$

$$f_n(\vec{\kappa}_{\perp}) = \frac{1}{2\pi}\int_{-1}^{+1} d\cos\beta \int_0^{2\pi} d\varphi J_n^2(\kappa d\sqrt{1-\cos^2\varphi\sin^2\beta}) n(\beta),$$

and $n(\beta)$ is the distribution of angles between the long molecular axes and the nematic director. As the translatory diffusion is the competing process, the above written scattering

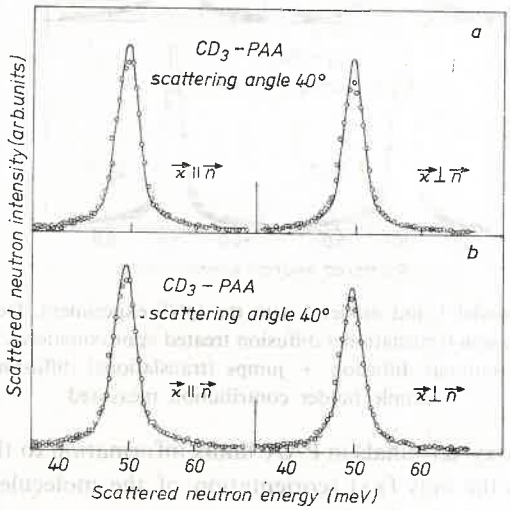

Fig. 2. A comparison of model 3 and model 4 with the QNS experiment. Details are given in the text. (a) Uniaxial rotational diffusion (translational diffusion $\sim D\kappa^2$), sample holder contribution measured; (b) Uniaxial rotational diffusion (translational diffusion $\sim D\kappa^2$), sample holder contribution fitted

law should have been convoluted by a Lorentzian, whose FWHM is $2\hbar D\kappa^2$, D being the translatory diffusion coefficient for the nematic PAA ($D_{\parallel} = 5.5\times10^{-6}$ cm^{2}s^{-1}, $D_{\perp} = 3.4\times10^{-6}$ cm^{2}s^{-1} [4]). It was felt, however, that the translatory diffusion correction is small, and hence it was not introduced by performing a convolution, but only as a peak height reducing factor, equivalent to a Debye-Waller factor. Finally, the empty sample-holder correction was introduced rigorously i.e. by using the empty sample

holder scattering data. That will be subjected to criticism in the case of model 4. Needless to say, that the scattering law for the model was convoluted by an instrumental resolution function before comparing with the experimental data.

In model 2 it was assumed that the molecule reorients as in the first model, and from time to time makes a large (180°) angular jump about the same long axis. The scattering law for such a model is a convolution of the previous scattering law and that given by the formula:

$$S_{\mathrm{inc}}(\vec{\kappa}, \omega) = \tfrac{1}{2}\,[1+f(\vec{\kappa})]\delta(\omega) + \frac{1}{2\pi}\,[1-f(\vec{\kappa})]\,\frac{\Gamma}{\Gamma^2+(\hbar\omega)^2}\,,$$

where $\Gamma = 2\hbar/\tau$, τ is the average time between instanteneous large angle (180°) jumps,

$$f(\vec{\kappa}_{\parallel}) = \int_{-1}^{+1} \frac{\sin(2\kappa d \sin\beta)}{2\kappa d \sin\beta}\,(n\beta)\,d\cos\beta, \text{ and}$$

$$f(\vec{\kappa}_{\perp}) = \frac{1}{2\pi}\int_{-1}^{+1} d\cos\beta \int_{0}^{2\pi} d\varphi\, \frac{\sin(2\kappa d\sqrt{1-\cos^2\varphi\sin^2\beta})}{2\kappa d\sqrt{1-\cos^2\varphi\sin^2\beta}}\, n(\beta).$$

The translatory diffusion correction and that of the empty sample-holder were done as in model 1.

In model 3 we return to rotational diffusion, as in model 1 (abandoning the large angle additional jumps), but the translatory diffusion was treated rigorously i.e. the convolution by a Lorentzian (FWHM $= 2\hbar D\kappa^2$ [4]) was performed. The empty sample--holder correction was done as in the models 1 and 2.

In model 4 everything was done as in model 3, except for the sample-holder correction. It must be pointed out, as a matter of fact, that the measured corrections are often illusory, as the texture of the Al-walls may cause scattering intensities very strongly dependent on small differences in angle and position reproducibilities when carrying out such empty sample-holder runs. Therefore, it was decided to treat the sample-holder correction as a free parameter contributing to the elastic peak component.

4. Discussion

It is evident that model 1 does not seem to be adequate. The statistical χ^2-test applied to the fits gives a rather large average χ^2 value equal to 73. A positive feature, on the other hand, is the τ_1 value being practically constant over the whole range of scattering angles and also being practically the same for $\vec{\kappa} \parallel \vec{n}$ and $\vec{\kappa} \perp \vec{n}$. The average τ_1 value equals 1.1 psec.

A natural temptation was to try a two-parameter version of model 2. The fits happen to be a little better — χ^2 equals 51. The τ_1 and τ parameters are sufficiently constant over the whole range of scattering angles, and also they are nearly the same for $\vec{\kappa} \parallel \vec{n}$ and $\vec{\kappa} \perp \vec{n}$. Their average values are: 1, 2 and 2.0 psec respectively.

That improvement, however, appeared to be illusory, as model 3 shows. Here the quality of the fits is much better — χ^2 equals 19. The practical equality of τ_1 parameters for $\vec{\kappa} \| \vec{n}$ and $\vec{\kappa} \perp \vec{n}$ is also observed. However, the τ_1 parameter now shows a slight dependence on the scattering angle varying from ca. 1.5 psec for the 20° angle to ca. 4 psec for the 60° angle. This is certainly a warning that something is wrong. The most probable hypothesis is that the translatory diffusion Lorentzian scattering law ($\Gamma = 2\hbar D\kappa^2$) does not hold for large κ-values; as a matter of fact the FWHM should, for the translatory diffusion, reach a saturation. Qualitatively we may say that this would work in the proper direction, diminishing the reorientational correlation times for large scattering angles. We do not know, however, where the translatory scattering law saturates. The average τ_1 value is 2.9 psec.

Finally, in model 4, χ^2 equals ca. 11. The tendency of τ_1 to increase with the scattering angle is also here observed. The average value of τ_1 is 4 psec.

If we take all these considerations into account, we feel obliged to conclude that it is impossible, as yet, to claim that an adequate reorientational model has been established, in neutron measurements performed so far for PAA. On the other hand, it seems certain that a reorientation about the long axis takes place, and that it is fast — the correlation time being 2—4 psec.

Referring to the remarks on types of response concerning reorientations, discussed in Section 2, it is worthwhile mentioning, that the dielectric relaxation time (so far attributed to a PAA rotation about the long molecular axis) equals 22 psec [5, 6] being nearly one order of magnitude larger than that obtained by the QNS. It is possible that this discrepancy is connected with the polymolecular response of the dielectric method, where as the QNS leads to the monomolecular one. On the other hand, it is not excluded that an appropriate but as yet unknown internal field correction would reduce the time value when passing from the dielectric macroscopic to the microscopic time. Finally, it is not excluded that the Cole-Cole plot established in [6] has a short relaxation time component not resolved so far, due to a lack of measurements in the high frequency region.

It is the author's opinion that a systematic study should be made in this field of a number of liquid crystals with the application of mutually complementary methods and careful analysis of their responses. The IR and Raman profile methods are here the obvious candidates as partners of the QNS method.

5. Conclusions

1. Remarks concerning various types of information obtained by various methods on reorientational motions of molecules were given.

2. Four attempts, with the help of models, to reproduce the incoherent neutron quasielastic scattering spectra for oriented and methoxy deuterized PAA were discussed. It was stressed, how careful one must be, when concluding that a true model has been established from neutron experiments.

3. From the studies under discussion, it follows that the PAA molecule performs a fast reorientation about the long axes, the correlation time being ca. 2—4 psec.

4. As the dielectric relaxation time for the same motion in PAA is 22 psec it is necessary to ask for an explanation of this discrepancy. It is suggested that it may be connected with the polymolecular response in case of the dielectric data, and the monomolecular response in the case of the QNS ones. Other possibilities are connected with an internal field correction, so far not known for such dielectrics, and/or with the existence of a fast relaxation component of the Cole-Cole diagrams, which is not yet resolved experimentally.

REFERENCES

[1] R. G. Gordon, *J. Chem. Phys.* **43**, 1307 (1965).
[2] J. A. Janik, J. M. Janik, K. Otnes, K. Rościszewski, J. Krawczyk, *Physica* **83B**, 259 (1976).
[3] J. A. Janik, J. M. Janik, K. Otnes, J. Krawczyk, to be published.
[4] J. Töpler, B. Alefeld, T. Springer, *Mol. Cryst. Liq. Cryst.* **26**, 297 (1974).
[5] A. J. Martin, G. Meier, A. Saupe, *Symp. Faraday Soc.* **5**, 119 (1971).
[6] S. Wróbel, J. A. Janik, J. K. Mościcki, S. Urban, *Acta Phys. Pol.* **A48**, 215 (1975).