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CRITICAL STUDIES OF MOLECULAR REORIENTATION IN ORIENTED PAA WITH VARIOUS KINDS OF DEUTERATION

J. A. JANIK and J. KRAWCZYK

Institute of Nuclear Physics, 31-342 Kraków, Poland

J. M. JANIK

Institute of Chemistry of the Jagiellonian University, 30-060 Kraków, Poland

K. OTNES

Institutt for Atomenergi, 2007 Kjeller, Norway

Résumé. — Des mesures de diffusion quasi-élastique des neutrons ont été effectuées pour les composés nématiques PAA- d_6 et PAA- d_8 et analysés en terme de diffusion rotationnelle autour du long axe moléculaire. τ_1 , temps de corrélation rotationnel, a été estimé à 4 ps. Cette valeur n'est pas en accord avec le temps de relaxation diélectrique qui est égal à 20 ps. Une telle différence peut provenir du type de réponse mis en jeu : la méthode des neutrons conduit à une réponse mono-moléculaire alors que les mesures diélectriques reflètent des propriétés coopératives. D'un autre point de vue ce désaccord pourrait indiquer que le modèle de diffusion rotationnel est trop simple. Quelques conclusions sont données concernant la diffusion translationnelle dans le PAA et la rotation des groupes méthyles.

Abstract. — Quasielastic neutron scattering experiments carried out for nematic d_6 -PAA and d_8 -PAA were analysed by using the rotational diffusion around the long molecular axis model. The τ_1 rotational correlation time was estimated for a 4 ps. This value does not agree with the dielectric relaxation time which equals to 20 ps. Such disagreement may be a reflection of differences in the type of response : the neutron method leads to a monomolecular response, whereas dielectric measurements reflect bulk properties. On the other hand the above disagreement may be an indication that the model of rotational diffusion is too simple. A few conclusions concerning the translatory diffusion in PAA, and also the methyl groups rotation are made.

1. Introduction. — The incoherent quasi-elastic neutron scattering technique (QNS) may provide information concerning the stochastic motions of molecules if the correlation times of these motions are of the order of 10^{-11} - 10^{-12} s. The sensitivity of the QNS technique to detailed features of a stochastic motion model is, however, limited, and one must therefore be very careful when claiming that a model has been established on the basis of a model fitting procedure [1]. This paper illustrates it using the experimental data of our previously published work on methyl-deuterated PAA(d_6 -PAA) [2], as well as the newly obtained experimental data on benzene-deuterated PAA(d_8 -PAA). The experimental technique and the data processing procedure were described in paper [2].

2. Does a rotational diffusion around the long molecular axis explain the QNS spectra ? — The answer

of paper [2] to this question is no. This is depicted in figure 1, which for oriented nematic d_6 -PAA (and a scattering angle of e.g. 40°), shows a rather unsatisfactory fit of a model (a) assuming a rotational diffusion kind of reorientation, with a adjustable

FIG. 1. — Comparison of model (a) with the QNS data for nematic d_6 -PAA.

correlation time τ_1 ⁽¹⁾. As discussed in [2], the competing stochastic process, in this case the translatory diffusion, was taken into account *only* as an intensity-reducing factor of the Debye-Waller type. The amount of reduction in intensity was deduced from the Lorentzian width (FWHM) equal to $2\hbar D_{\parallel}\kappa^2$ or $2\hbar D_{\perp}\kappa^2$ for the $\kappa \parallel \mathbf{n}$ and the $\kappa \perp \mathbf{n}$ geometry, respectively. (Here $D_{\parallel} = 5.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$

and

$$D_{\perp} = 3.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$$

are the corresponding translatory diffusion coefficients [3]. $\hbar\kappa$ is the neutron momentum transfer and $\mathbf{n}$ is the nematic director.) A positive aspect of model (a) is that τ_1 is constant (within the error limits) over the whole range of scattering angles (20°-60°) studied both for $\kappa \parallel \mathbf{n}$ and $\kappa \perp \mathbf{n}$. The average value of τ_1 equals to 1.1 ps. The unsatisfactory character of model (a) is illustrated by a large value of the statistical test parameter χ^2 (73). One reason for this is certainly that the translatory diffusion has not been taken into account properly. We now try to improve the model by making a convolution of the translatory Lorentzian (FWHM equal to $2\hbar D_{\parallel}\kappa^2$ or $2\hbar D_{\perp}\kappa^2$) with the rotational diffusion scattering law (model (b)). The results for the experimental data for d_6 -PAA are presented in figures 2 and 3. The quality of the fit is now satis-

FIG. 2. — QNS data and the model fittings for d_6 -PAA in the nematic phase, $\kappa \parallel \mathbf{n}$, for the scattering angles 30, 40, 50 and 60°.

factory ($\chi^2 = 8$) but τ_1 now seems to depend both on the scattering angle, and what is worse, on whether we measure for $\kappa \parallel \mathbf{n}$ or $\kappa \perp \mathbf{n}$ (Table I). We therefore believe that a reorientation only around the long molecular axis is a too simplified picture for

FIG. 3. — Comparison of model (b) with the QNS data for nematic d_6 -PAA.

TABLE I

Values obtained for τ_1 and R using two different models ((a) and (b)) for describing the molecular reorientations in nematic d_6 -PAA. τ_1 is the rotational correlation time for the rotational diffusion around the long molecular axis of inertia (ps). R is the radius of the reorienting protons (Å)

Scattering angle (deg)	Sample orientation	Model (b) ($R = 2.1$)	Model (c) ($\tau_1 = 20.0$)
30	$\kappa \parallel \mathbf{n}$	$\tau_1 = 2.14$ $\chi^2 = 13.0$	$R = 5.89$ $\chi^2 = 5.8$
30	$\kappa \perp \mathbf{n}$	3.76	3.60
40	$\kappa \parallel \mathbf{n}$	3.13	4.84
40	$\kappa \perp \mathbf{n}$	5.1	3.8
40	$\kappa \perp \mathbf{n}$	5.3	3.8
50	$\kappa \parallel \mathbf{n}$	4.08	5.0
50	$\kappa \perp \mathbf{n}$	10.5	4.64
50	$\kappa \perp \mathbf{n}$	3.94	4.3
50	$\kappa \perp \mathbf{n}$	4.6	2.77
50	$\kappa \perp \mathbf{n}$	5.43	5.3
60	$\kappa \parallel \mathbf{n}$	10.4	4.04
60	$\kappa \parallel \mathbf{n}$	4.46	3.9
Average		$\tau_1 = 3.85$ $\chi^2 = 7.6$	$R = 4.14$ $\chi^2 = 4.6$

explaining the QNS spectra. On the other hand we want to point out the good agreement between the average value of τ_1 (3.9 ps) obtained using model (b) with that obtained in a QNS experiment with larger κ -values [4], where τ_1 amounts to 3.7 ps.

3. Can we provide any new information about the translatory diffusion? — It seems that an apparent increase of τ_1 with increasing scattering angle, as observed in model (b) (Table I), can be explained by a shortcoming of the continuous translatory diffusion scattering law for large κ -values. In fact, the width ($\Delta E = 2\hbar D\kappa^2$) of the translatory Lorentzian *can not* increase indefinitely with increasing κ -values. It must reach a *limiting value*, as for instance in the jump diffusion model [5]. If this is so, the applied $2\hbar D\kappa^2$ -correction is too large and hence the reorientational contributions are apparently too small.

⁽¹⁾ The formulae are given in paper [2].

This effect increases with increasing scattering angle. Therefore, the apparent variation of τ_1 with the scattering angle corroborates the hypothesis that the validity of the continuous translatory diffusion model in this case is dubious.

4. Are the director fluctuations affecting our QNS spectra?—The suspicion that model (b) is too simple is supported by the discrepancy between our value of τ_1 and that determined in the dielectric relaxation measurements, which gave $\tau_1 = 20$ ps for nematic PAA [6]. Of course, to a certain point, it may be due to the fact that the QNS technique gives a *single* molecular response, whereas in the dielectric measurements one measures the *bulk* properties. We feel, however, that the difference should not be so great. It is therefore tempting to keep τ_1 constant and equal to 20 ps (the dielectric value) and vary another parameter in the model. The only possibility is to vary the *radius* of the reorienting protons which in the models (a) and (b) were set equal to 2.1 Å. In these models the assumption is that the reorientation takes place around the long axis. If this radius now is adjustable (model (c)), one obtains the best fits for a value of about 4 Å. An example of such fits is shown in figure 4 ($\chi^2 = 5$) (Table I).

FIG. 4. — Comparison of model (c) with the QNS data for nematic d_6 -PAA.

This may indicate that the reorientation around the long axis is *not the only* fast motion, but that the molecules reorient with a much larger *effective* radius. A hypothetical picture could be this: the molecules, when reorienting, perform at the same time a kind of fast precession around the director $\mathbf{n}$. The two motions are strongly coupled and we can therefore speak about an effective correlation time and an effective proton radius.

If this is so, we should expect an increase of this syndrome when passing from methyl deuterated PAA to benzene deuterated PAA. In d_8 -PAA the neutron will predominantly reflect the motion of the methyl protons which are located in the terminals of the molecule. The neutron spectra will therefore mainly contain information about the fast reorientational motion. It is obvious that we should also take

into account the fast rotation of the methyl groups around their CO-axis when fitting the d_8 -PAA data. This is done in the same way as in paper [2] (see also Section 5 of this paper). Figure 5 shows (for $\mathbf{k} \parallel \mathbf{n}$)

FIG. 5. — Comparison of the model described in sec. 5 with the QNS data for d_8 -PAA in the nematic phase (τ_1 fitted).

the results of the fittings for nematic d_8 -PAA for 30° and 60° scattering angles. The trial with τ_1 and τ_{CH_3} taken as adjustable parameters and the radius of the reorienting protons fixed (2.1 Å), gives (see Table II) a τ_1 which is consistent with that for d_6 -PAA ($\tau_1 = 2$ ps). On the other hand, when the correlation time τ_1 is fixed to the dielectric value of 20 ps, the manipulation with the effective proton radius gives also good quality fits for both angles with an optimal effective radius of 6 Å (Fig. 6, Table II), i.e. larger than for d_8 -PAA. In general this is consistent with the idea that the terminals should feel the complex character of the fast reorientational motion more pronounced.

TABLE II

Values obtained for τ_1 , R and τ_{CH_3} using the model put forward in sec. 5 to describe the molecular reorientation in nematic d_8 -PAA ($\mathbf{k} \parallel \mathbf{n}$). τ_1 is the correlation time for the rotational diffusion around the long molecular axis of inertia (ps). R is the radius of the reorienting protons (Å). τ_{CH_3} is the average time between 120° jumps of the CH_3 -group (ps)

Scattering angle (deg)	$R = 2.1 \text{ Å}$ τ_1 fitted	$\tau_1 = 20 \text{ ps}$ R fitted
—	—	—
30	$\tau_1 = 1.81 \text{ ps}$ $\tau_{CH_3} = 2.37 \text{ ps}$ $\chi^2 = 5.5$	$R = 6.66 \text{ Å}$ $\tau_{CH_3} = 1.33 \text{ ps}$ $\chi^2 = 3.9$
60	$\tau_1 = 2.35 \text{ ps}$ $\tau_{CH_3} = 3.45 \text{ ps}$ $\chi^2 = 6.1$	$R = 5.82 \text{ Å}$ $\tau_{CH_3} = 3.92 \text{ ps}$ $\chi^2 = 5.3$

It should be pointed out, however, that the minima of χ^2 are rather shallow in all the fittings, and the uncertainty in the determined value of τ_1 or the radius of the reorienting protons is therefore large. It is our feeling that some of these uncertainties are

due to a possible non-applicability of the convolution approximation as the various modes of motion of the protons may not be independent [7]. The uncertainty in τ_1 may quite possibly amount to about 100 %, which makes the gap between the QNS and the dielectric relaxation data not so very drastic and the conclusions less safe.

5. Is the internal rotation of the methyl groups visible ? — It was suggested in [2] that the CH_3 -rotation can be observed by comparing the QNS results for normal PAA with those for d_6 -PAA. There we made a convolution of the experimental scattering law for d_6 -PAA with a theoretical scattering law for the internal rotation of the methyl groups where the protons made 120° jumps. In this way it was possible to obtain the time between successive jumps, τ_{CH_3} , in nematic PAA. We got $\tau_{\text{CH}_3} = 1.4$ ps.

It seems obvious that the effect of the CH_3 -rotation should be enhanced for d_8 -PAA. In the fitting procedure presented in figure 5 (see also Table II) the scattering law for each proton was a convolution of three contributions : the translatory diffusion in the continuous diffusion approximation, the rotational diffusion of the molecule (τ_1) and the CH_3 -rotation (τ_{CH_3}). The τ_{CH_3} -value obtained in this way is equal to about 3 ps, giving a rather good agreement with the result of [2].

It is worthwhile to point out that the CH_3 -rotation survives the freezing of d_8 -PAA (Fig. 7). The obtained τ_{CH_3} -value is about 7 ps. This agrees well with the previously published QNS data for solid PAA [8] where τ_{CH_3} was determined to be 9 ps, and also with the NMR relaxation data for solid PAA [9] which gave τ_{CH_3} equal to 5.1 ps.

FIG. 6. — Comparison of the model described in sec. 5 with the QNS data for d_8 -PAA in the nematic phase (R fitted).

6. Conclusions. — A critical comparison of the results obtained for d_6 -PAA and d_8 -PAA using the quasielastic neutron scattering technique leads to the following conclusions :

FIG. 7. — QNS data for d_6 -PAA and d_8 -PAA in the solid phase for a scattering angle of 60° .

1. The simple rotational diffusion around the long molecular axis is not describing the QNS spectra sufficiently well. A distinct tendency of a variation of τ_1 (reorientational correlations time) with the scattering angle, slightly different τ_1 values obtained for $\mathbf{k} \parallel \mathbf{n}$ and $\mathbf{k} \perp \mathbf{n}$ and a disagreement between the τ_1 values obtained from QNS and the dielectric relaxation measurements, are the syndrome of the above mentioned inadequacy.

2. The above mentioned variation in τ_1 with scattering angle may be removed by assuming that the translatory diffusion of the molecules is not a continuous diffusion and hence possesses a jump character.

3. If one accepts the dielectric value of τ_1 one obtains from QNS a larger effective radius of the reorienting protons which may perhaps be understood as an indication of a complex character of the reorientational motion, for instance, the reorienting molecules perform at the same time a kind of fast precession around the director $\mathbf{n}$.

4. The internal CH_3 -rotation is clearly visible in the QNS spectra for nematic d_8 -PAA and solid d_8 -PAA.

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