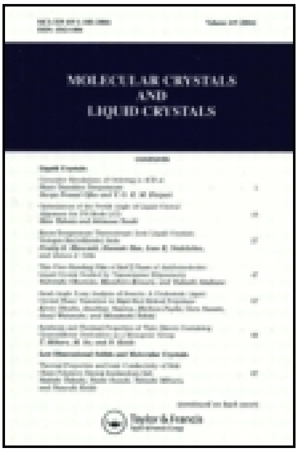

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Evidence of Alkyl Rotational Mobility from Comparison of PAA and PAP Neutron Quasielastic Scattering Data

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EVIDENCE OF ALKYL ROTATIONAL MOBILITY FROM COMPARISON OF PAA AND PAP NEUTRON QUASIELASTIC SCATTERING DATA

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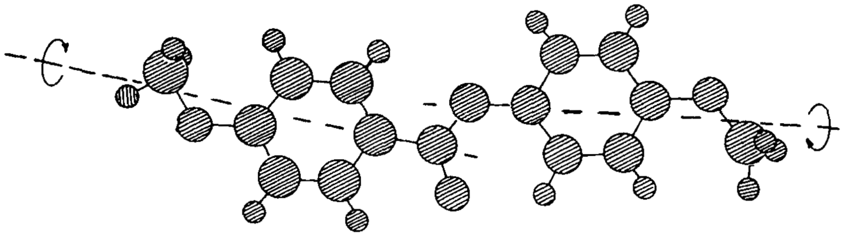
Abstract

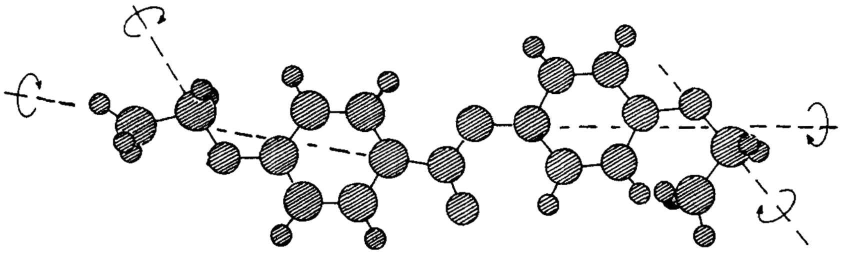
We ask whether a model assuming a rotational diffusion of two molecular "halves", consisting of rigidly coupled alkoxy groups plus benzene rings, works for interpretation of QNS data. For PAA such a model seems to work almost perfectly for both the normal and the methyl deuterated nematic substance. For PAP, however, it gives a much too intense quasielastic component in the normal nondeuterated substance indicating that there exist interconformational motions in ethoxy group which falls within the QNS observation window. When convoluting the scattering law of this motion with that of the molecular "halves" one obtains an almost perfect agreement with the QNS experimental data.

Keywords : molecular motions, neutron scattering

Among the many stochastic rotational motions which take place in nematic liquid crystals, there are some which are too slow to be detected by the neutron quasielastic experiment (QNS) carried out with a typical energy resolution of ca. 100 μeV. One such a motion is the rotation of the whole molecule around its long axis, which, although much faster than the rotation around the short axis, is still too slow for the observation window of the QNS for the above mentioned energy resolution. Indeed, for PAA and PAP the corresponding reorientational correlation times are ca. 20 and 25 ps, respectively, thus contributing very little to the quasielastic broadening [1]. Also the translatory diffusion contributes very little [2].



PAA



PAP

FIGURE 1. Schematic views of the PAA and PAP molecules. For the PAA the motion of the molecular "halves" is shown. For PAP, besides this motion, the interconformational motion in ethoxy terminals is shown.

It seems also that the alkoxy groups and the corresponding benzene rings are rather strongly coupled, since the alkyl torsion around the C(benzene)-O(alkoxy) axis occurs with rather high frequency for two molecules in question (ca. 1000 cm^{-1} [3]). Of other motions, the rotation of CH_3 terminals around their triple axes, although falling within the QNS observation window, has a too small gyration radius for H atoms to contribute significantly to the quasielastic component. Hence, if there are no interconformational jumps in the alkyls, the model assuming a rotational diffusion of two molecular "halves", consisting of alkoxy groups rigidly coupled to benzene rings, reorienting around the C(benzene)-N(central group) bond, should be adequate for interpretation of QNS data [4] (Fig.1).

This paper presents a new analysis of old QNS data reported previously in [4] and [5]. The data were obtained (for the nematic PAA and PAP) in the Institute of Energy Technology at Kjeller, Norway. The incident neutron energy was 4.64 meV. The energy resolution was 140 μeV. For PAA the temperature was 122°C and the neutron scattering angle was 30°(neutron momentum transfer 0.73 $Å^{-1}$). For PAP, the temperatures were 144°C and 154°C, and the neutron scattering angles (for both temperatures) were 30° and 40° (neutron momentum transfer 0.73 and 0.95 $Å^{-1}$). The samples were unoriented. In order to isolate the the quasielastic (plus elastic) component, the inelastic background was subtracted from the rough data.

To evaluate the adequacy of the reorientational model the following procedure was adopted : To the QNS spectrum, after conversion to energy scale, we fitted the function :

$$F(\vec{\kappa},\omega) = \sigma_{inc}\ k_f/k_i\ \exp(\hbar\omega/k_BT)[p\delta(\omega)+(1-p)S(\vec{\kappa},\omega)]\odot G(\omega)$$

where $\hbar\vec{\kappa} = \hbar(\vec{k}_f - \vec{k}_i)$ stands for the neutron momentum transfer, $\hbar\omega = E_f - E_i$ is the neutron energy transfer, $G(\omega)$ is the instrumental function, and $S(\vec{\kappa},\omega)$ is the scattering law corresponding to a reorientational model. Explicit formulas for the $S(\vec{\kappa},\omega)$ can be found, for instance, in [6]. Now, the p parameter serves for the detection of model's adequacy; if $p = 0$ the model is **formally** adequate. If $p < 0$, there is too much of the quasielastic component, hence there must be motions additional to those assumed in the model.

When this procedure (with $S(\vec{\kappa},\omega)$ corresponding to a rotational diffusion of the molecular "halves") was applied to the QNS data for nondeuterated PAA, the following results were obtained by fitting :

PAA (temp.122°C ,sc. angle 30°) $\tau_1 = 5.7$ ps $p = -0.03$

τ_1 stands here for the rotational diffusion correlation time. Fig.2 presents the model curve as fitted to the experimental points. One can see that the p value is quite close to zero, which means that the model is (at least formally) adequate. For the methyl deuterated PAA $p = +0.01$, which also indicates adequacy of the model. The rotational correlation time is typical for the observation window of the QNS method with our resolution.

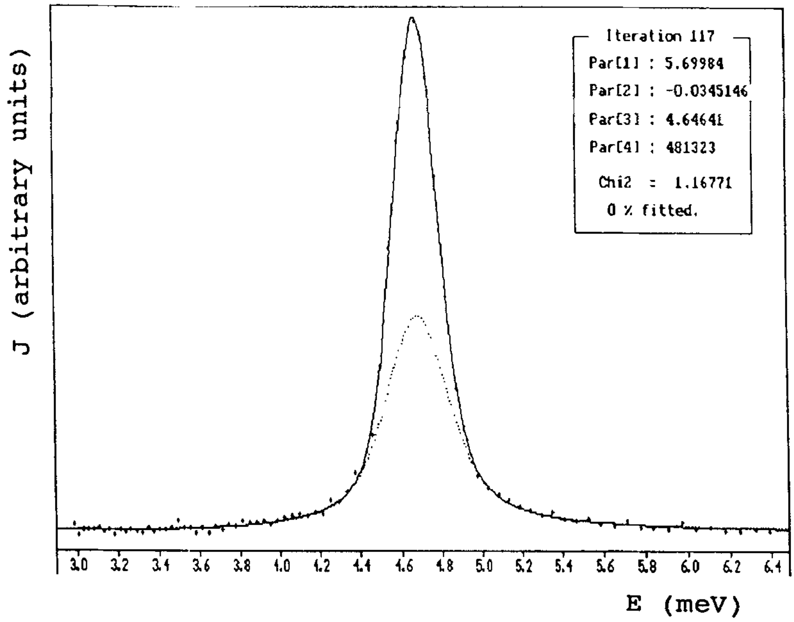


FIGURE 2. Neutron spectrum after the inelastic background subtraction for the nematic PAA. Solid line - the fitted curve. Broken line - the derived QNS component. Model (one motion only) : reorientation of the molecular "halves" .

The same procedure (again with $S(\vec{\kappa},\omega)$ corresponding to a rotational diffusion of the molecular "halves") when applied to the QNS data for the nondeuterated PAP gives :

PAP (temp.144 C ,sc. angle 30) τ_1 = 4.0 ps p = -0.39

PAP (temp.154 C ,sc. angle 30) τ_1 = 3.3 ps p = -0.44

PAP (temp.144 C ,sc. angle 40) τ_1 = 2.8 ps p = -0.30

PAP (temp.154 C ,sc. angle 40) τ_1 = 2.6 ps p = -0.35

One can now see that the p value departs significantly from zero, indicating that there must exist additional motions which were not taken into account in the model. It should be pointed out that τ_1 has no clear physical meaning, when p departs from zero so much. For the ethyl deuterated PAP p = ca. -0.08, which is much closer to zero. This, and the fact that model works for PAA, indicates that the additional motion in PAP is localized in the ethyl terminals.

Now we assume that, in addition to the rotational diffusion of the molecular "halves", there are (in the ethyl terminals) 120° - angular jumps, around the O(ethoxy)-C(ethoxy) axes. This means that for the H atoms of the ethoxy groups the scattering law has to be taken as a convolution of the scattering law of the molecular "halves" and that of the interconformational angular jumps. (In addition, this must be still convoluted with the instrumental function $G(\omega)$). The computational procedure was the following : the residence times τ_{120° for a particular conformation of the ethoxy terminals were parametrized, whereas the rotational diffusion correlation time τ_1 of the molecular "halves" and the p parameter were subjected to fitting. The results are shown in Fig.3 . One can see that for the $\tau_{120^\circ} = 5$ ps the p value is quite close to zero, which means that the model is **formally** adequate. The optimized results are :

PAP (temp.144 C ,sc. angle 30) $\tau_1 = 3.7$ ps p = -0.003

PAP (temp.154 C ,sc. angle 30) $\tau_1 = 2.9$ ps p = -0.02

PAP (temp.144 C ,sc. angle 40) $\tau_1 = 2.0$ ps p = -0.02

PAP (temp.154 C ,sc. angle 40) $\tau_1 = 1.8$ ps p = -0.05

for $\boxed{\tau_{120^\circ}}$ **equal to 5 ps.**

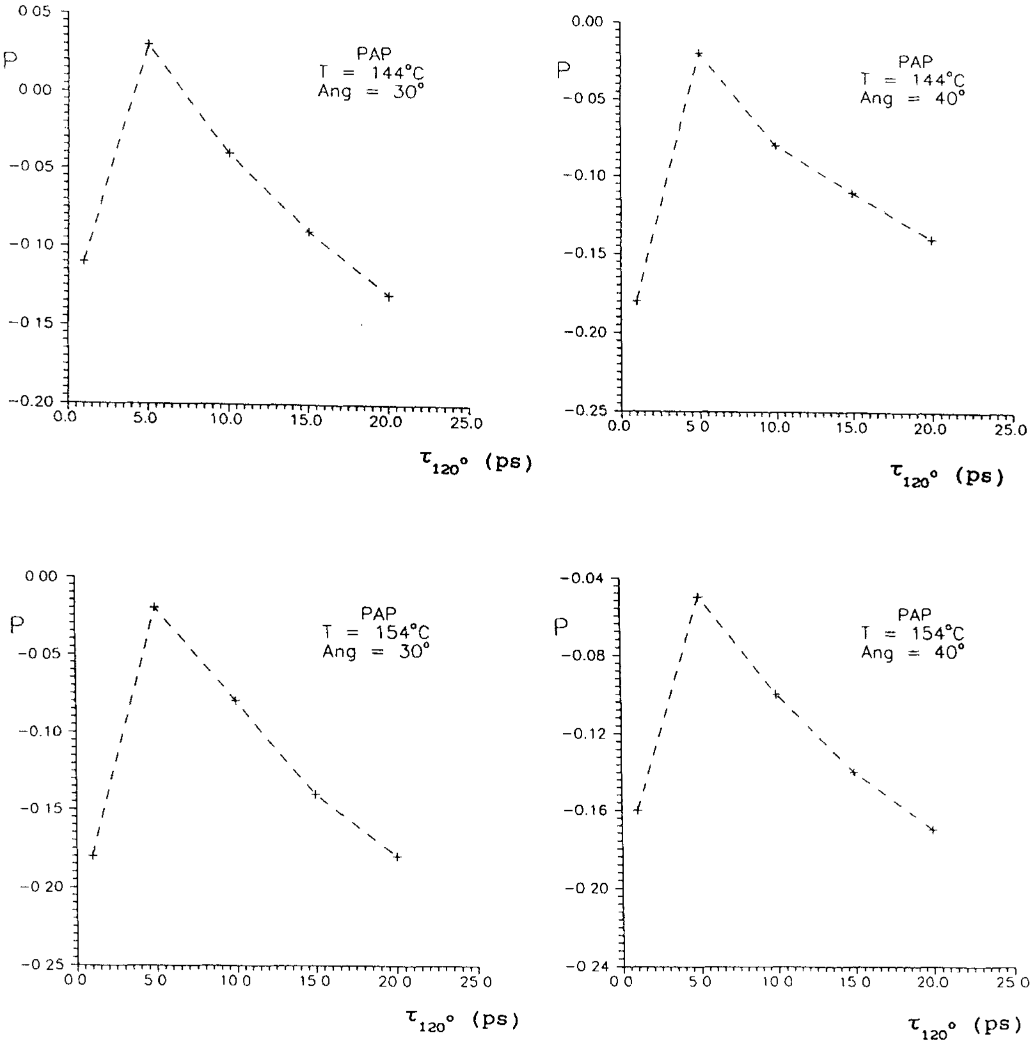


FIGURE 3. PAP : p vs. residence time of the second motion. One may see that the model which takes into account the two motions gives the best adequacy for the residence time value 5 ps, for which the p value is close to zero.

One can see that the two-motions model seems to work well for PAP. It is, however, not quite correct, since the τ_1 times show some dependence on the scattering angle. One possible explanation is that a smaller step in τ_{120° parameterization would give more accurate values for the conformation residence times, which might lead to slight corrections of the other time values. Another explanation is that in our calculation we assumed the independence of the two motions (by assuming the convolution of their scattering laws). This needs not necessarily be true.

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