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Investigation of the Circular Random Walk Motion in Nematic Material

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Quasi-elastic neutron spectra measured on an aligned sample are compared with those calculated from the circular random walk model of a single axis rotor, i.e. the random walk on a circle. The difference between the spectra is discussed and a new model—the random walk on a sphere with parallel circles on the surface—is worked out taking into account the possibility of jumps from one circle to the other. The non-equivalence of hydrogen atoms in the molecule is shown.

1 INTRODUCTION

In the past few years considerable attention has been paid to the study of the molecular dynamics of liquid crystalline mesophase. NMR,[1] dielectric[2] and inelastic light scattering[3] measurements have been successfully used. Inelastic neutron scattering measurements can, in principle, give more detailed information by determining the space–time correlation function $G(r, t)$.

At low energies (quasi-elastic scattering with $E_0 \approx 5$ meV) and momentum transfer ($Q < 0.3$ Å^{-1}) the long time limit form of the self-correlation function can be determined. This is partly connected with the translational diffusion motion. The components $D_{\parallel}$ and $D_{\perp}$ of the diffusion tensor are determined by the trace method.[4] $D_{\parallel}$ and $D_{\perp}$ are the diffusion coefficients parallel and perpendicular to the director, respectively.

At higher momentum transfers the measured spectra are determined by other types of motion. Our measurements[5] on a non-aligned sample were successfully interpreted by the circular random walk model of a single axis rotor in which the molecule was considered to move as a whole in the same way as one of its hydrogen atoms. (Hydrogen atoms were supposed as being equivalent.)

We present here measurements on an aligned sample which proved to be sufficiently sensitive for the investigation of further details of the molecular dynamics. From dielectric relaxation measurements[6] the motion around the short axis is known; from our neutron measurements the motion around the director can be determined. In the new model describing the rotational motion on a sphere with two relaxation times, these motions are coupled. On this basis of this model our measurements are interpreted and the non-equivalence of the hydrogen atoms is shown.

2 THEORETICAL

The rotational motion of the molecule as a whole around the director (which may coincide with the long axis) is characterized by circular random walk motion on a circle on which there are N equidistant sites. This motion can be studied by inelastic incoherent scattering, when the scattering function is the measured quantity which, according to Barnes,[7] has the following form:

$$S(Q, \omega) = A_0(QR \sin \beta)\delta(\omega) + \sum_{n=1}^{N-1} A_n(QR \sin \beta) \frac{\tau_n}{1 + (\omega\tau_n)^2} \tag{1}$$

with

$$A_n(x) = \frac{1}{N} \sum_{l=1}^{N} J_0\left(2x \sin \frac{\pi l}{N}\right) \cos \frac{2\pi l n}{N} \tag{2}$$

and

$$\tau_n^{-1} = 4K_1 \sin^2 \frac{\pi n}{N}, \quad \tau = \frac{1}{2K_1} \tag{3}$$

where J_0 is a Bessel function of the first kind of order 0, and β is the angle between the momentum transfer $\bar{Q}$ and director $\bar{n}$.

In a real system the molecular axes are generally tilted from the director by an angle ϑ, which varies due to thermal motion to molecular rotation around the short axis. Dianoux *et al.*[8] took this fact into account by averaging over ϑ using the Maier–Saupe distribution function. However this averaging neglects that the molecular rotation around the short axes is a relaxation process. We shall take this into account by allowing the molecule to jump from one circle to another on a sphere. Only the rotational motion of the molecules will be investigated therefore the centre of mass motion will not be considered. The motion of the hydrogen atoms will be approximated by a random walk on the surface of a sphere with radius R.

As the preferred direction of the molecules is the z axis, let $P(\vartheta)$ be the probability of finding a molecule tilted from that direction by angle ϑ.

$P(\vartheta)$ can be approximated, for example, by the Maier–Saupe distribution function. At a given value of ϑ a hydrogen atom of the molecule can move on a circle. Let us assume that there are M parallel circles on the sphere; these can be characterized by discrete values of ϑ, i.e.

$$\vartheta_l = \frac{\pi(l + \frac{1}{2})}{M}, \quad 0 \leq l \leq M - 1 \tag{4}$$

Each circle has N sites. As illustrated in Figure 1, the sites on a circle are given by the angle

$$\varphi = \frac{2\pi i}{N}, \quad 0 \leq i \leq N - 1 \tag{5}$$

The probability that the molecule jumps from one site to one of the neighbouring sites on the same circle is $P_1 = K_1 \Delta t$, and that it jumps to one of the neighbouring circles is $P_2 = K_2 \Delta t$, where K_1 and K_2 are the rate constants and Δt is the required time per step.

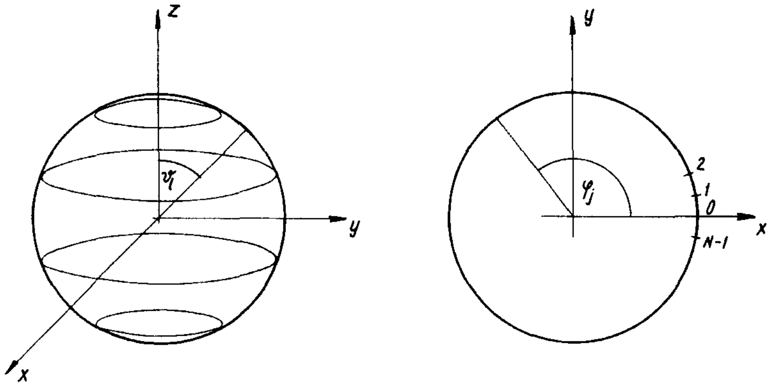


FIGURE 1

The probability of moving from the i-th site of the μ-th circle to the j-th site of the ν-th circle during time t is given by

$$P_{ij}^{\mu\nu}(t) = \frac{1}{NM} \sum_{k=0}^{N-1} \sum_{l=0}^{M-1} \cos\frac{2\pi k(i-j)}{N} \cos\frac{2\pi l(\mu-\nu)}{M} e^{-t/\tau_{kl}} \tag{6}$$

where

$$\tau_{kl}^{-1} = 4K_1 \sin^2\frac{\pi k}{N} + 4K_2 \sin^2\frac{\pi l}{M} \tag{7}$$

(For $K_2 = 0$ or $M = 1$ the Barnes result is obtained.) The scattering function is:

$$S(\bar{Q}, t) = \langle e^{i\bar{Q}[\bar{r}(0) - \bar{r}(t)]} \rangle \tag{8}$$

Let us introduce the following notations

$$\begin{aligned} q_{\parallel} &= 2QR \cos \beta \\ q_{\perp} &= 2QR \sin \beta \end{aligned} \tag{9}$$

After some algebra, the Fourier transform of $S(Q, \omega)$ is obtained as

$$S(Q, \omega) = \sum_{k=0}^{N-1} \sum_{r=0}^{M-1} L_{kr}(\omega) B_{kr} \tag{10}$$

$$L_{kr}(\omega) = \frac{1}{\pi} \frac{\tau_{kr}}{1 + (\omega\tau_{kr})^2} \tag{11}$$

and

$$\begin{aligned} B_{kr} = \frac{1}{NM} \sum_{l=0}^{M-1} P(\vartheta_l) \sum_{j=0}^{N-1} \cos \frac{2\pi kj}{N} \sum_{l'=0}^{M-1} J_0(q_\perp d^j_{ll'}) \cos \frac{2\pi r(l - l')}{M} \\ \cdot \cos\left\{ q_{\parallel} \sin \frac{\pi(l + l' + 1)}{2M} \sin \frac{\pi(l - l')}{2M} \right\} \end{aligned} \tag{12}$$

where

$$d^j_{ll'} = \left[\sin^2 \frac{\pi(l - l')}{2M} \cos^2 \frac{\pi(l + l' + 1)}{2M} + \sin \frac{\pi(l + \frac{1}{2})}{M} \sin \frac{\pi(l' + \frac{1}{2})}{M} \sin^2 \frac{\pi j}{N} \right]^{1/2} \tag{13}$$

J_0 is the Bessel function of zeroth order.

If $K_1 \gg K_2$, as is generally the case, we can simplify the above expression of $S(Q, \omega)$. In this limit we may use the approximation

$$\begin{aligned} \tau_{kl} \approx \tau_{k0} &= \left(4K_1 \sin^2 \frac{\pi k}{N} \right)^{-1} \qquad \text{if} \quad k \neq 0 \\ \approx \tau_{0l} &= \left(4K_2 \sin^2 \frac{\pi l}{M} \right)^{-1} \qquad k = 0 \end{aligned} \tag{14}$$

and we get

$$S(Q, \omega) = \sum_{r=0}^{M-1} L_{0r}(\omega) A_1(r) + \sum_{k=1}^{N-1} L_{k0} A_2(k) \tag{15}$$

where

$$A_1(r) = \frac{1}{M} \sum_{l=0}^{M-1} P(\vartheta_l) \sum_{l'=0}^{N-1} J_0(q_\perp d^0_{ll'}) \cos \frac{2\pi r(l - l')}{M} \tag{16}$$

$$d^0_{ll'} = \sin \frac{\pi(l - l')}{2M} \cos \frac{\pi(l + l' + 1)}{2M} \tag{17}$$

$$A_2(k) = \frac{1}{N} \sum_{l=0}^{M-1} p(\vartheta_l) \sum_{j=0}^{N-1} J_0\left(q_\perp \sin \vartheta_l \sin \frac{\pi j}{N}\right) \cos \frac{2\pi kj}{N} \tag{18}$$

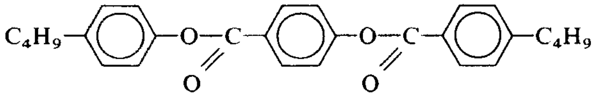
The first term of Eq. (15) representing the contribution from the rotation of molecule around the short axis appears as a narrower peak. The second term, which describes a contribution from the rotation of the molecule around the z axis (director), is the sum of much broader Lorentz type curves.

In the opposite, i.e. $K_1 \ll K_2$, case we have a similar expression for $S(Q, \omega)$ but the narrower spectrum is due to the rotation of the molecule around the preferred direction.

If the two rate constants K_1 and K_2 have the same order, our model will correspond to the simple jump rotational motion weighted with the probability of the occurrence of the tilted angles.

3 EXPERIMENTAL

We have chosen for investigation the di-butyl derivative of phenyl-benzoyl azoxy-benzoate, i.e.



This molecule has positive dielectric anisotropy, similar end groups and nematic mesophase in a broad temperature interval, i.e.

$$\mathrm{Cr} \underset{74\text{-}85^\circ\mathrm{C}}{\overset{85^\circ\mathrm{C}}{\longleftrightarrow}} \mathrm{N} \xleftrightarrow{183^\circ\mathrm{C}} \mathrm{I}$$

The quasi-elastic neutron scattering measurements were performed at different temperatures on a stochastic time-of-flight spectrometer: reactor-single crystal—stochastic chopper—sample-detectors. The incident energy of the neutron beam was 4.26 ± 0.07 meV. The investigated material of 1 mm thickness was enclosed in a double-walled aluminium container. The temperature was kept constant to within 0.1°C. The molecules were oriented by an alternating electric field. The quasi-elastic spectra measured at four scattering angles at three temperatures are shown in Figure 2. The full lines are the

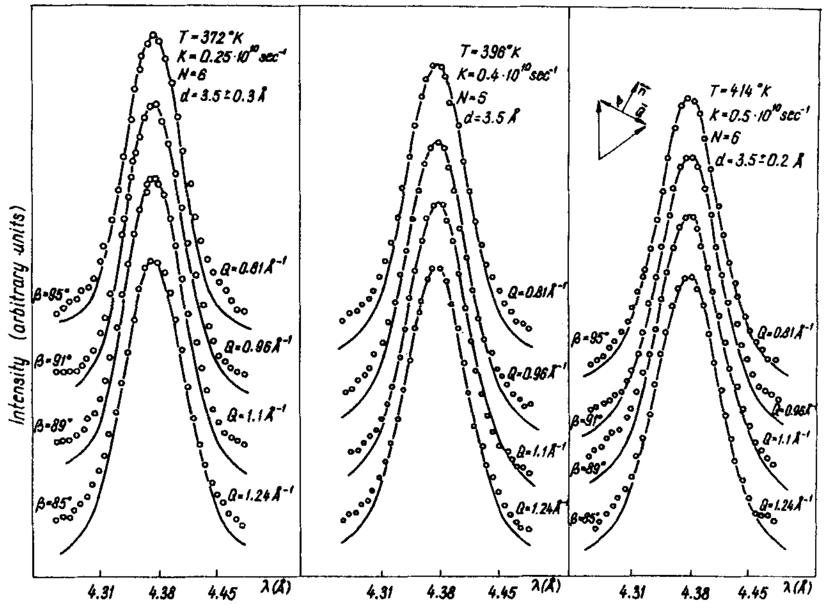


FIGURE 2 Quasi-elastic spectra for di-butylderivative of phenyl-benzoyloxybenzoate in ordered state at three temperatures. Measured spectra are represented by o, calculated by Barnes model by ———.

spectra calculated from Eq. (1). Only a slightly better fit can be obtained by averaging with the Maier–Saupe distribution function as done by Dianoux *et al.*[8] The parameters determined from fitting agree with those already published.[5] The relaxation times are given in the figure; the activation energy of the relaxation times connected with the circular random walk on the circle was found to be $W = 0.2$ eV. The average radius of the rotational motion is $R = 3.5$ Å.

4 DISCUSSION

If we take, in accordance with the dielectric relaxation measurements,[6] the value $K_2 \sim 10^8\ \mathrm{s}^{-1}$ for the relaxation time around the short axis, and the τ values given in the figure for the motion around the director, $K_1 \ll K_2$ holds and a greater discrepancy appears at the tails between the calculated and the measured spectra.

In this model we considered the motion of one of the hydrogen atoms characterizing the motion of the molecule as a whole. All the hydrogen atoms in the molecule contribute to the neutron spectra; when averaging over R we have to divide them into two parts: one part performing the motion described above and the other which moves faster. Probably the end groups of the molecule, the butyls, perform the faster motion and the motion of the core is described by the model presented here. (The averaging over R for the core does not change the calculated spectra, R being the distance between the centre of mass of the molecule and a given hydrogen atom.)

Two relaxation processes are coupled by the model without introducing any arbitrary parameter so the contribution of the end groups in the measured spectra can be separated. The relaxation time corresponding to this faster process is only approximately determined here and has a value of $\sim 10^{-11}$ s. The contribution of the butyls can be more precisely determined by other measurements using the material DCI–PBB, i.e. the material where the butyls are substituted by chlorine.[6]

5 CONCLUSION

The circular random walk motion on a sphere model with two relaxation times, one characterizing the molecular motion around their short axes and the other that around the director, describes the motion of the molecule as a whole. Some parts of the molecule (probably the butyls) perform an additional motion with the shorter relaxation time.

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