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INTERPRETATION OF THE QUASI-ELASTIC NEUTRON SCATTERING ON PAA BY ROTATIONAL DIFFUSION MODELS

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INTERPRETATION OF THE QUASI-ELASTIC NEUTRON SCATTERING ON PAA BY ROTATIONAL DIFFUSION MODELS

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ABSTRACT

Inelastic neutron scattering measurements were performed on PAA in liquid crystal phase. Interpretation of the quasi-elastic results was by the circular random walk model, with N=8 sites, d=4 Å diameter and $k=10^{10}$ sec^{-1} rate constant. The spherical rotational diffusion model of Sears was criticised.

АННОТАЦИЯ

Производились измерения с помощью неупругого рассеяния нейтронов на ПАА-е в жидкокристаллическом состоянии. Интерпретация квази-упругого нейтронного спектра дается с модели циркулярного стохастического гуляния. Водороды молекул вращаются по кругу, разбитому на N=8 участков, с радиусом d=4Å, с постоянной $k=10^{10}$ sec^{-1}. Указали на неточности сферической, ротационно-диффузионной модели Сирса.

KIVONAT

Rugalmatlan neutronszórás-méréseket végeztünk para-azoxy-anizolon folyadékkristály állapotban. A kvázi-rugalmas neutronspektrumokat a sztochasztikus bolyongás körpályán modellel értelmeztük. A molekula hidrogénjei N=8 helyzettel rendelkező d=4 Å sugaru körpályán mozognak $k=10^{10}$ sec^{-1} állandóval. A Sears gömbi rotációs diffuziós modell pontatlanságát mutatjuk be.

Keywords:

Nematic liquid crystals
Neutron inelastic scattering
Rotational diffusion

1. Introduction

The interpretation of the quasi-elastic scattering data measured on PAA is an old problem in neutron physics. The first interpretation was based on the simple translational diffusion model [1] or on variants of it [2] . We initially tried to interpret it on the basis of continuous rotational diffusion [3]. A similar interpretation is now given by Töpler [4] . However, we now have data for the translational diffusion [5] and can calculate its role. In this article we first collect the most important data determined by other methods for PAA, criticize the spherical rotational diffusion model of Sears [6] and compare our measurements with the circular random walk model of a simple axis rotator [7].

2. Structure and dynamics of PAA molecules

The structure of PAA in liquid crystal phase was studied by Kosterin and Chistyakov [8] by X-ray method. The probable model determined from this data for an oriented liquid-crystal PAA is shown in Fig.1.
In a non-ordered sample the molecules are similary packed together in relatively rigid groups comprising many thousand molecules.

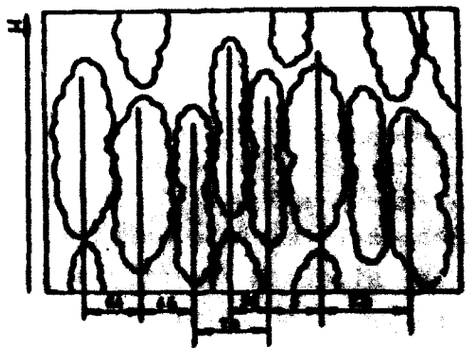
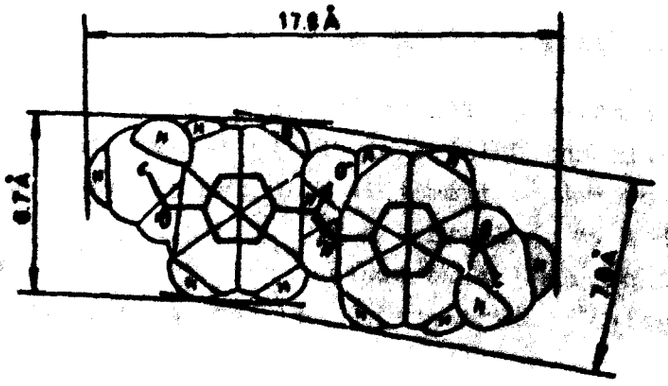


Fig.1. Probable structure of PAA in magnetic field [8]

The geometrical form, and parameters of the molecule are as follows



The N⟶O side group creates a dipole moment /μ = $2.48.10^{-18}$ CGSE, which is fixed rigidly to the molecule, and makes an angle of 58.5° with the long molecular axis. The dipoles at the two ends

of molecule probably move independently. The dipole relaxation times given by Martin, Meier and Saupe [9] have the values $\tau_1^s = 4.3.10^{-9}$ sec, $\tau_2^s = 2.5.10^{-11}$ sec, $\tau_2^a = 3.3.10^{-11}$ sec, at 125°C. The measured dielectric relaxations can be seen in Fig.2.

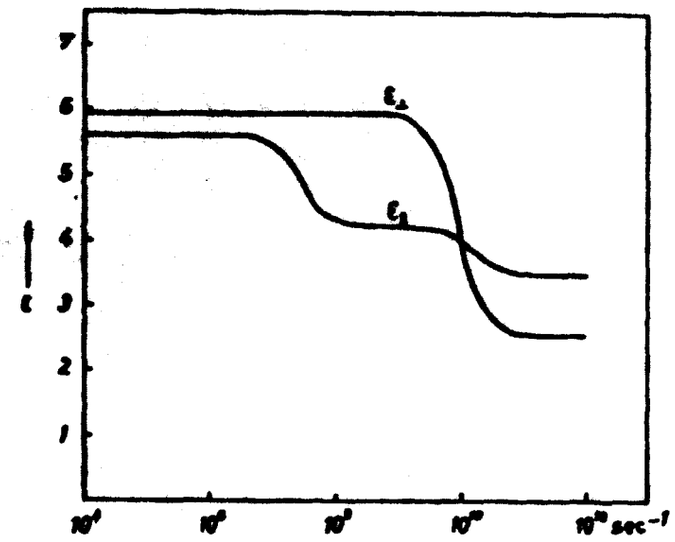


Fig.2. Frequency dependence of dielectric permittivities of PAA at 125°C.

The molecule makes a rotational oscillational motion around the nematic director /mean molecular direction/. The details of this motion can be determined by inelastic neutron scattering. At very small momentum transfer the translational diffusion constant was measured [4] and the value D = /4.1 ± 0.3/.10^{-6} cm^2/sec was found which was near to the value /3.4 ± 0.1/.10^{-6} cm^2/sec determined

by tracer method [5] . At bigger momentum transfer quasi-elastic scattering is interpreted on the basis of rotational diffusion, taking into account the smallness of translational diffusion. Two models are investigated for the interpretation: the spherical rotational diffusion /SRD/ model and the circular random walk model /CRW/.

3. Spherical rotational diffusion model of Sears.

This model is discussed in detail in [3] and relatively good agreement was found at the momentum transfers

$$Q = 1{,}17\ \text{Å}^{-1}, \quad Q = 1{,}63\ \text{Å}^{-1}$$
$$Q = 2{,}05\ \text{Å}^{-1}, \quad Q = 2{,}42\ \text{Å}^{-1}$$

Without the elastic part of the spectra, [3] the broadening of the quasi-elastic intensities is shown in Fig.3. Similar spectra were found in [3]. When $/Qd/^2 \lesssim 14$ the broadening can be approximately represented by the

$$\Delta E \simeq 0.4/Qd/^2 D_r$$

relation. The more detailed discussion shows that at certain momentum transferstne elastic part plays important role and the form of the scattering function has the appearance of that given in Fig.4. Such a type of neutron spectrum we have not been able to find, and we have concluded that the SRD model is not perfect. Therefore we have tried a new one, the CRW model.

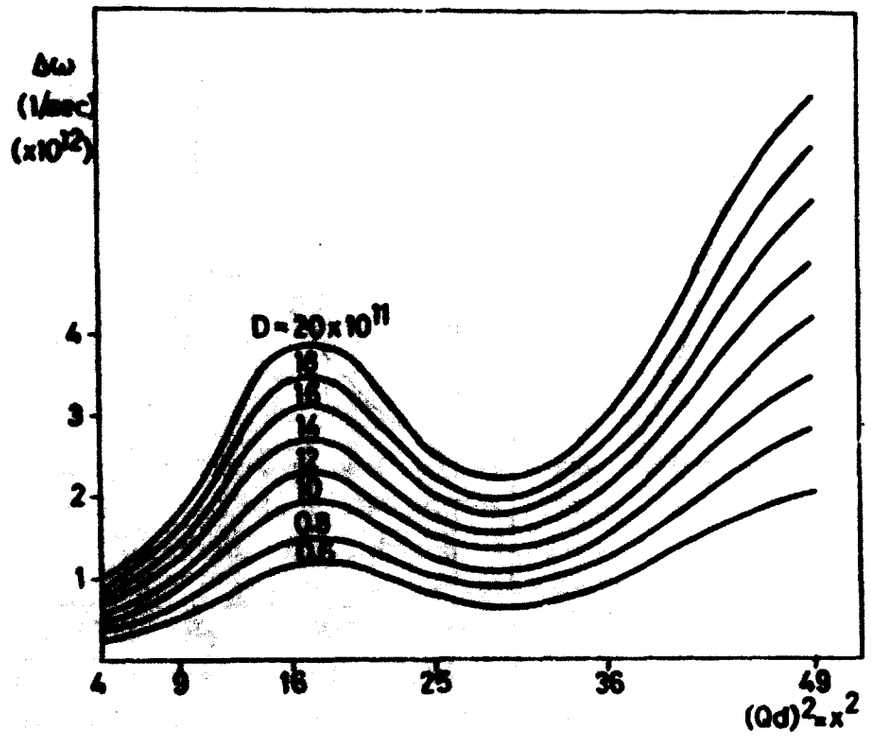


Fig.3. Calculated broadening of the spectra from spherical rotational diffusion model without the elastic term.

4. Circular random walk /CRW/ model of a single axis rotor

This model was used for the hydrocarbon chains by Barnes [7]. In this model the scattering particle /H/ is located at the i-th site of a circle on whose circumference there are N sites. The particle is allowed to perform a random walk among these N sites. The probability that it will be found on the j-th site after time /or n steps/ t is

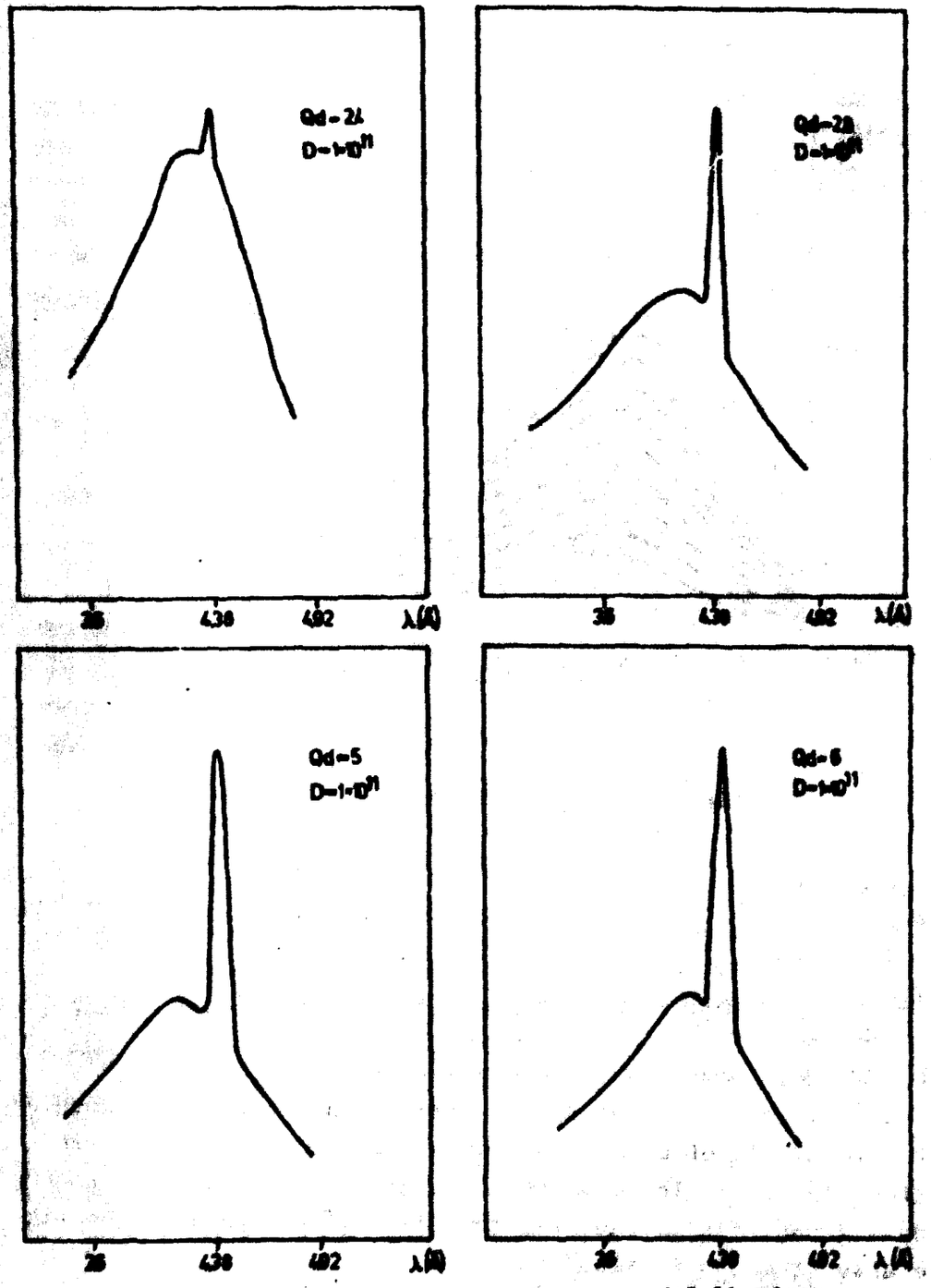


Fig.4. Calculated spectra at some special Qd values from spherical rotational diffusion model.

$$P_{ij}(t) = \frac{1}{N} \sum_{k=1}^{N} e^{-t/\tau_k} \cos \frac{2\pi k (i-j)}{N} \qquad /1/$$

where

$$\tau_k^{-1} = 4k \sin \frac{2\pi k}{N} \qquad /2/$$

K is a rate constant, τ_1 is the dipole relaxation time if the dipole is directed along the radius of the circle. We can take τ_1 from dielectric constant measurements. If the molecular motion is connected with the rotation around the long axis of the molecules $\tau_1 = \tau_\parallel$ and $\tau_1 = \tau_\perp$ in the other case. The first case is more probable, because of the nematic order. The nematic potential does not strongly hinder the rotation around the long axis nor the rotation of the methoxy group.

The scattering function is measured by the neutron inelast scattering method. From the CRW model we obtain [7]

$$S(Q,\omega) = A_N(Q)\delta(\omega) + \frac{1}{N} \sum_{l=1}^{N-1} A_l(Q) \frac{\tau_l}{1+(\omega\tau_l)^2} \qquad /3/$$

where

$$A_l(Q) = \frac{1}{N} \sum_{k=1}^{N} j_0(2Qd \sin \frac{\pi k}{N}) \cos \frac{2\pi l k}{N} \qquad /4/$$

$$j_0(x) = \frac{\sin x}{x}$$

$$\tau_l^{-1} = 4k \sin^2 \frac{\pi l}{N} \qquad /5/$$

where d is the radius of the circle.

Experimental

The experiments described below have been made on a time-of-flight facility: reactor-single crystal-stochastic--chopper-sample-detectors. The incident energy of the neutron beam was E = 4.26 meV and the resolution of the spectrometer was 0.15 meV.

The investigated material of 1 mm thickness was enclosed in a double-walled aluminium container by which the sample temperature was kept constant to within 0.1°C. The sample was not oriented by any external magnetic field and therefore the results correspond to an orientational average of the scattering over all molecular directions.

The measured quasi-elastic neutron spectra at different scattering angles are shown in Fig.5. The broadening of the calculated quasi-elastic scattering with different K values is given in Fig.6.

Discussion

From measurements of the translational diffusion constant [5] one finds that the contribution to quasi-elastic scattering is of minor importance, i.e. on the time scale of quasi-elastic cold neutron scattering, one observes predominantly the single particle motion with quasi-stationary axis. In our case this is the motion of protons relative to the rotational axis. The folded ingoing spectra with the translational diffusion process yield nearly elastic spectra.

For the comparison of the CRW model with the experiments we folded the measured elastic spectra with the scattering crossection calculated from equation /3/ .

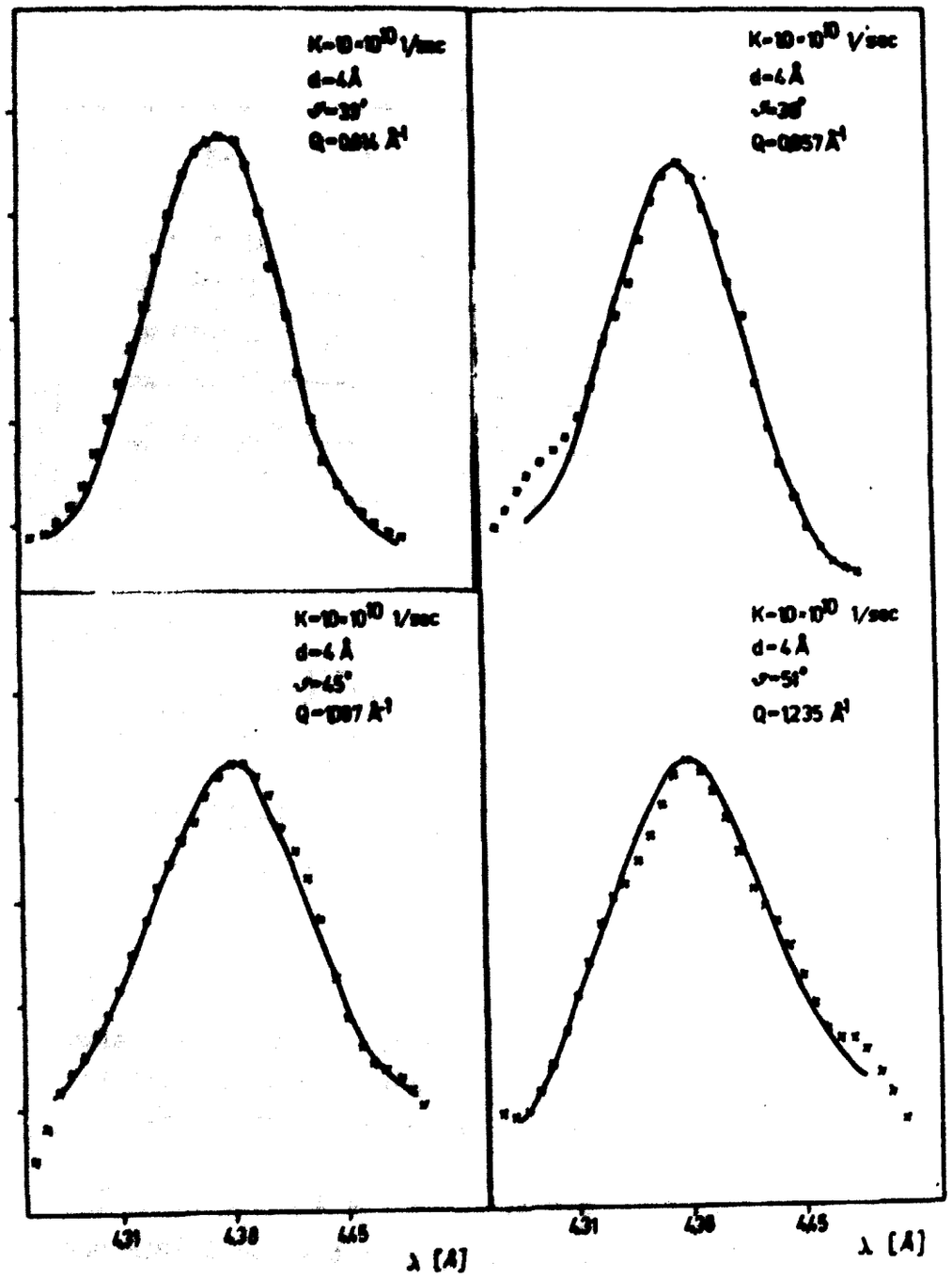


Fig.5: Quasi-elastic spectra for PAA at 121°C in liquid crystal phase. The x are the measured — calculated spectra.

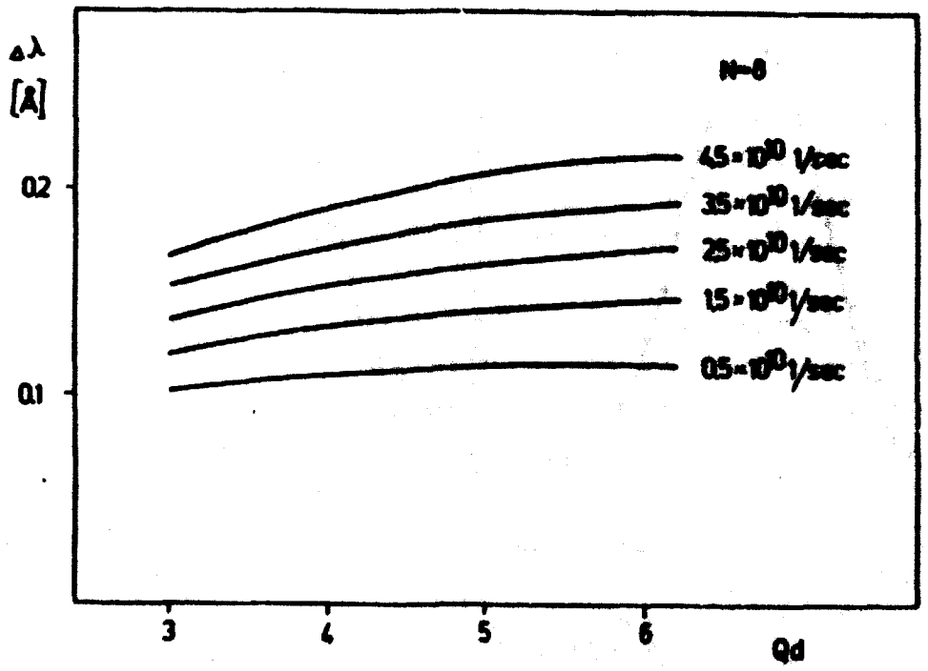


Fig.6. Broadening of the quasi-elastic spectra from CRW model at different K values.

We compared the measured spectra with the calculated one at different parameters d,K,N. The goodness of the fit to the experimental data are given in Fig.5. The best fit was found at

$$K = 1.10^{10}\,sec^{-1}, \quad N = 8, \quad d = 4\ \text{Å}$$

At this parameter the fit was not very sensitive to d /Fig.6./. With different K and N there were such spectra at some Q values at which the fit was wrong e.g. N=3, d=6; N=4, d=4; N=12, d=4; With this parameter we get for τ_i the values:

$\tau_1 = \tau_7 = 1.7.10^{-10}$ sec, $\tau_2 = \tau_6 = 5.10^{-11}$ sec

$\tau_3 = \tau_5 = 2.9.10^{-11}$ sec and $\tau_4 = 2.5.10^{-11}$ sec.

These values fit very well with dispersion of the dielectric constant /see Fig.2./.
If the angle of libration, $\theta = 40^{\circ}$ of Chandrasekhar [10] is taken, we get for the average radius for the rotations of protons around the long molecular axis the value d = 4 Å . The CH_3 groups play the most important role in this calculation. From the structure we could understand the number N = 4 with four different positions of a symmetric molecule around the nematic direction. But the two parts /benzene rings/ of the molecule from the centre are shifted from each other therefore the eight positions are understandable for unsymmetric molecule.

Conclusion

It was found that the circular random walk model fits very well with the quasi-elastic neutron scattering. The random rotation of the molecule around the nematic direction gives the important effect in quasi-elastic neutron scattering.

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