

NEUTRON INCOHERENT SCATTERING OF ROTATIONAL AND TRANSITIONAL DYNAMICS IN ANISOTROPIC SYSTEMS – A NEW THEORETICAL APPROACH

N. Kirov, J. Jordanova^{a*}, G. B. Hadjichristov

Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

^aInstitute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

The rotational and translational contributions for the elastic incoherent structure factor (EISF) of neutron scattering in anisotropic systems are considered. New approaches are proposed, taking into account the molecular biaxiality and the steric hindrance of reorientational processes. The numerical data for EISF and intermediate scattering functions are in good agreement with the existing experimental data for aligned liquid crystals. The proposed new theoretical models are applicable to all kinds of anisotropic materials with rotational and translational degrees of freedom.

(Received December 9, 2004; accepted January 26, 2005)

Keywords: Neutron incoherent scattering, Rotational dynamics, Transitional dynamics, Computer simulation

1. Introduction

Neutron scattering spectroscopy is an important tool for the investigation of the molecular dynamics in systems with partial rotational and translational order. The quasielastic incoherent scattering $S_{\text{inc}}(Q, \omega)$ contains rich information about individual motions (both translational and rotational) of the molecules, and about the orientational order. However, the separation of the translational and rotational contributions to the scattering is a very difficult task. Thus, a very important characteristic of the spectra is the elastic incoherent structure factor (EISF), defined as the relative intensity of the purely elastic part of the quasielastic scattering [1 - 8]:

$$EISF = I_{el} / (I_{el} + I_{qe}) \quad (1)$$

where I_{el} and I_{qe} are the integral intensities of the purely elastic and the quasielastic contributions to the spectra. The EISF does not depend on the mechanisms of the different molecular motions, but only on their geometry and time scale. It provides an easy way for separating the transitional and rotational parts of the neutron scattering spectra. In fact, any motion which is not restricted in space leads only to a small broadening of both the elastic and the quasielastic parts of the spectra, and thus does not change the structure factor. In contrast, in the process of the molecular reorientation, the proton never leaves some limited volume around its initial position and the EISF becomes very sensitive to the time scale and the geometry of the rotation.

In this paper, we present new theoretical models and numerical calculations of the rotational and transitional contributions to EISF of neutron scattering in anisotropic systems. To ascertain the

* Corresponding author: jordanaj@inrne.bas.bg

validity of the proposed models for the influence of molecular dynamics on neutron scattering, we selected aligned liquid crystals and, for simplicity, those for which the mesomorphic phase is uniaxial (e.g. nematic or smectic A phase). Our approach is easily generalized for any less symmetric phase with rotational and transitional degrees of freedom.

2. Theoretical models

Let us consider the rotational contribution of one proton to the scattering law $S_{\text{inc}}^R(Q, \omega)$. The time-dependent intermediate scattering function (i.e. the Fourier transform of $S_{\text{inc}}^R(Q, \omega)$) is [7-9]:

$$I(Q, t) = \int d\Omega_0 \int d\Omega P(\Omega_0, \Omega, t) \exp\{i\vec{Q} \cdot [\vec{R}(t) - \vec{R}(t=0)]\} \quad (2)$$

where \vec{Q} is the scattering vector, \vec{R} the radius-vector of the proton in the center of the mass reference frame, Ω_0 and Ω are the sets of Euler angles defining the molecular orientation in the laboratory frame at times $t = 0$ and t , respectively, and $P(\Omega_0, \Omega, t)$ is the joint probability density for molecular orientation at Ω_0 and Ω . Expanding the exponential in a spherical harmonic series, we have:

$$\begin{aligned} \exp(i\vec{Q} \cdot \vec{R}) &= 4\pi \sum_{\lambda, m} (i)^\lambda j_\lambda(QR) Y_{\lambda m}^*(\Omega_Q^L) Y_{\lambda m}(\Omega_R^L) = \\ &= \sum_{\lambda, m, n} (2\lambda + 1) (i)^\lambda j_\lambda(QR) D_{-m0}^\lambda(\Omega_Q^L) D_{0-n}^\lambda(\Omega_R^M) D_{mn}^{\lambda*}(\Omega) \end{aligned} \quad (3)$$

where $Q = |\vec{Q}|$; $R = |\vec{R}|$; Ω_Q^L and Ω_R^L are the sets of polar angles of \vec{Q} and \vec{R} in the laboratory frame; Ω_R^M are the polar angles of \vec{R} in the molecular frame; $j_\lambda(QR)$ are the Bessel's spherical functions; and $D_{mn}^\lambda(\Omega)$ are the Wigner's matrices.

At this stage we assume, as usual, that the orientational interaction tensor of the molecule has an effective cylindrical symmetry. The equilibrium orientational distribution function is [10]:

$$f(\Omega) = \frac{1}{8\pi^2} \sum_s (2s + 1) \langle P_s \rangle D_{00}^s(\Omega) \quad (4)$$

where

$$\langle P_s \rangle = \langle D_{00}^s \rangle = \int d\Omega D_{00}^s(\Omega) f(\Omega) \quad (5)$$

are the usual orientational order parameters [10].

The dynamical information is contained in the orientational correlation functions $G_{mmnn}^{\lambda k}(0)$, and their values do not depend on the reorientation model [11, 12]. Substituting Eq. (3) into Eq. (2), we obtain:

$$I(Q, t) = \sum_{\lambda=0}^{\infty} \sum_{\substack{k=\lambda \\ (\lambda+k) \text{ even}}}^{\infty} \sum_{n=0}^{\lambda} \sum_{m=0}^{\lambda} F_{mn}^{\lambda k}(\theta_Q, \theta_R, QR) G_{mmnn}^{\lambda k}(t) \quad (6)$$

with

$$F_{mn}^{\lambda k}(\theta_Q, \theta_R, QR) = (2 - \delta_{\lambda k})(2 - \delta_{n0})(2 - \delta_{m0})(-1)^{\lambda/2 - k/2}(2\lambda + 1) \times$$

$$\times (2k + 1) j_\lambda(QR) j_k(QR) d_{n0}^\lambda(\theta_R) d_{n0}^k(\theta_R) d_{m0}^\lambda(\theta_Q) d_{m0}^k(\theta_Q) \quad (7)$$

where θ_Q is the angle between \bar{Q} and the symmetry axis (the director) of the phase, θ_R is the angle between \bar{R} and the symmetry axis (the long axis) of the molecule, and $d_{n0}^k(\theta)$ are the reduced Wigner's matrices.

From Eq. (2), for the structure factor we obtain:

$$EISF = \lim_{t \rightarrow \tau_\infty} I(Q, t) \quad (8)$$

where τ_∞ depends on the resolution of the experiment and is the longest time for which the quasielastic component can be still distinguished from the elastic one. In very high-resolution backscattering experiments [13-15] the halfwidth $\Delta\Gamma$ of the resolution function is about 1 μeV and τ_∞ is of the order of 10^{-8} s [9]. In these experiments, however, the available Q-range is very small and there is no quasielastic contribution to the spectra but only a small broadening of the elastic part due to the translational diffusion [7]. In the rest of the existing experiments, $\Delta\Gamma \sim 20 - 30 \mu\text{eV}$ and $\tau_\infty \sim 10^{-9} - 10^{-10}$ s.

The reorientation of the highly anisotropic molecules is a very complicated process. There are at least two different rotational motions with different time-scales. In fact, the reorientation around the long molecular axis (spinning motion) is fast since both the moment of inertia and steric hindrances are small. Several experimental techniques give for spinning correlation time τ_s values of the order of 10^{-11} s [16, 17]. On the other hand, the reorientation of the long axis itself (tumbling motion) is much slower, since the moment of inertia and the steric hindrance are about an order of magnitude higher. The experimental studies give tumbling correlation time τ_t values of the order of $10^{-8} - 10^{-9}$ s [18 - 20]. The tumbling motion is very sensitive to the molecular orientational order, and τ_t varies substantially with the order parameters and with the rank (λ , k) of the correlation function [11].

Assuming that one or more of the possible rotational motions of the molecule relax to equilibrium at $t = \tau_\infty$, we obtain different models for calculation of the EISF.

Model 1: Let us suppose that $\tau_\infty \gg \tau_t > \tau_s$, i.e. that all the rotational motions are fast compared to the experimental time scale. In this case:

$$EISF_{(1)} = \lim_{t \rightarrow \infty} I(Q, t) = \sum_{\substack{\lambda=0 \\ \text{even}}}^{\infty} \sum_{\substack{k=\lambda \\ \text{even}}}^{\infty} F_{00}^{\lambda k}(\theta_Q, \theta_R, QR) \langle P_\lambda \rangle \langle P_k \rangle =$$

$$= \left[\sum_{\substack{\lambda=0 \\ \text{even}}}^{\infty} (-1)^\lambda (2\lambda + 1) j_\lambda(QR) d_{00}^\lambda(\theta_Q) d_{00}^\lambda(\theta_R) \langle P_\lambda \rangle \right]^2 \quad (9)$$

This result is not very useful for experimental data treatment since $\tau_\infty \gg \tau_t$ is satisfied only for very high resolution experiments for which $QR \ll 1$ and the rotational contribution to the spectra is negligible.

Model 2: Let us now suppose $\tau_t \gg \tau_\infty \gg \tau_s$, which is more realistic. In this case, at $t \rightarrow \infty$ all terms in Eq. (6) with $n \neq 0$ vanish due to the fast spinning relaxation and:

$$EISF_{(2)} = \sum_{\substack{\lambda=0 \\ (\lambda+k) \text{ even}}}^{\infty} \sum_{k=\lambda}^{\infty} \sum_{m=0}^{\lambda} F_{m0}^{\lambda k}(\theta_Q, \theta_R, QR) G_{m0m0}^{\lambda k}(0) \quad (10)$$

This result corresponds to uniaxial rotation – the spinning motion relaxes but the tumbling is “frozen out” on the experimental time-scale. It is equivalent to the formula derived in [4, 7, 9] but is much simpler to deal with and, moreover, it might be simplified further. Let us present \vec{R} as: $\vec{R} = \vec{R}_{||} + \vec{R}_{\perp}$ where $R_{||}$ and R_{\perp} are the components of \vec{R} parallel and perpendicular to the molecular long axis, respectively. For uniaxial rotation, only the component R_{\perp} changes with time, thus:

$$EISF_{(2)} = \sum_{\substack{\lambda=0 \\ \text{even}}}^{\infty} \sum_{\substack{k=\lambda \\ \text{even}}}^{\infty} \sum_{m=0}^{\lambda} F_{m0}^{\lambda k}(\theta_Q, \frac{\pi}{2}, QR_{\perp}) G_{m0m0}^{\lambda k}(0) \quad (11)$$

In Eq. (11), there are no terms with odd λ and/or k . More importantly, R_{\perp} (usually 2 Å) is smaller than R (R can be as high as 10 Å) and the series (11) converges much faster than Eq. (10), since $j_{\lambda}(QR_{\perp}) < j_{\lambda}(QR)$ at high λ . That is why, for computational purposes, Eq. (11) is more convenient than Eq. (10).

Model 3: Till now, we have assumed that the tumbling relaxation is, compared to the experimental time-window, either too fast (model 1) or too slow (model 2). Both these assumptions are not very realistic. In fact, the reorientation of the long molecular axis in anisotropic systems is a very complicated process. The tumbling relaxation times might be quite different for the different correlation functions. In particular, it is well known [11] that for odd λ the functions $G_{mmmm}^{\lambda\lambda}(t)$ relax much more slowly than for even λ . In order to understand the physical basis of this feature, let us suppose that the orientational order is very high ($1 - \langle P_2 \rangle \ll 1$). Then the distribution function has two high (δ - function like) peaks around $\beta = 0$ and $\beta = \pi/2$. For even λ the correlation function $G_{mmmm}^{\lambda\lambda}(t)$ relaxes to its equilibrium value $\langle P_1 \rangle^2$ after time τ_{t1} , characterizing the small-angle orientations inside the peak. For odd λ , however, the equilibrium value is $G_{mmmm}^{\lambda\lambda}(\infty) = 0$ and the relaxation takes place after time τ_{t2} , characterizing the reorientations of the long molecular axis at an angle $\beta - \beta_0 \sim \pi$ (from one peak to the other). The π -jumps are strongly hindered by the mean field potential and by steric factors – usually $\tau_{t2} \gg \tau_{t1}$.

Let us now suppose that the spinning motion and the tumbling at small angles (inside the peak) relax fast on the time-scale of experiment, but that π -jumps are negligibly rare. From Eqs. (6) and (8) we have:

$$EISF_{(3)} = \sum_{\substack{\lambda=0 \\ (\lambda+k) \text{ even}}}^{\infty} \sum_{k=\lambda}^{\infty} F_{00}^{\lambda k}(\theta_Q, \theta_R, QR) \langle P_{\lambda} \rangle \langle P_k \rangle \quad (12)$$

This equation differs from Eq. (11) by the assumption that the odd order parameters are non-vanishing. Physically, $\langle P_{\lambda} \rangle$ in Eq. (12) are not the usual equilibrium order parameters given by Eq. (5) but the quasi-equilibrium values at $\tau_{t2} > t > \tau_{t1}$. They can be calculated using the single-peaked quasi-equilibrium distribution function [6]:

$$f(\beta) = \frac{\delta}{2 \sinh \delta} \exp(\delta \cos \beta) \quad (13)$$

Model 4: The π -jumps of the long molecular axis are hindered by both the mean field potential and steric factors. In model 3, however, the steric hindrance is not taken into account. In

fact, for an orientational order parameter $\langle P_2 \rangle \rightarrow 0$ (e.g. the isotropic liquid phase) the peaks of the distribution function $f(\beta)$ (one or two) become flat and there is no difference between the reorientation inside the peaks or between them, i.e. the prohibition for π -jumps disappears! In reality, however, even in the isotropic phase the long mesomorphic molecule can hardly reorient through a π -jump due to the high steric hindrance.

On the other hand, at moderate $\langle P_2 \rangle$ values ($\langle P_2 \rangle \sim 0.5$) (typical for the nematic phase), the peaks of $f(\beta)$ are wide and the probability of finding the molecule with $\beta \sim \pi/2$ is not negligible. In the spirit of model 3, if the molecule has $\beta_0 = 0.49\pi$, the probability to find it after moderately long times ($\tau_{i2} \gg t \gg \tau_{i1}$) in the peak around $\beta = 0$ is much higher than to find it around $\beta \sim \pi$. This feature of model 3 is obviously quite unrealistic – it might be expected that $P(0.49\pi, 0, t) \equiv P(0.49\pi, \pi, t)$ at $\tau_{i2} \gg t \gg \tau_{i1}$. That is why model 3 is physically acceptable only for high $\langle P_2 \rangle$ values (but in that limit it is very close to model 2).

In order to take into account the steric hindrance for the large angle tumbling, we will use the two-stage reorientational relaxation model [21]. For the usual order parameters

$$\langle P_s \rangle = \langle \tilde{P}_s \rangle \langle P_s \rangle \quad (14)$$

$\langle \tilde{P}_s \rangle$ can be non-zero for an odd s -a π -jump of the molecule strongly hindered by the static environment.

For $\tau_{i2} \gg t \gg \tau_{i1}$

$$EISF_{(4)} = \sum_{\substack{\lambda=0 \\ (\ell+k) \text{ even}}}^{\infty} \sum_{\substack{k=\lambda \\ m=0}}^{\infty} F_{m0}^{\lambda k}(\theta_Q, \theta_R, QR) g_{m0m0}^{\lambda k}(0) \langle \tilde{P}_\lambda \rangle \langle \tilde{P}_k \rangle \quad (15)$$

where $g_{m0m0}^{\lambda k}(t)$ are the reorientational correlation functions for the slow Σ -relaxation.

Model 5: Up to now we have assumed that the mesogen molecule has $D_{\infty h}$ (cylindrical) symmetry. This is a useful first approximation which is widely employed in studies of the reorientational dynamics in anisotropic systems. In reality, however, the symmetry of the mesogen molecule is never so high, and this can seriously influence the static and dynamic properties of the phase [22]. Let us now assume that the molecule is biaxial and its orientational interaction tensor has D_{2h} symmetry. The rotational correlation functions are given in [12]. If both tumbling and spinning relaxations are fast on the experimental time-scale, we obtain ($\tau_\infty \gg \tau_t \gg \tau_s$):

$$EISF_{(5)} = \left[\sum_{\substack{\lambda=0 \\ \text{even}}}^{\infty} \sum_{\substack{n=0 \\ \text{even}}}^{\lambda} (2\lambda+1)(-1)^{\lambda/2} j_\lambda(QR) d_{00}^\lambda(\theta_Q) (2-\delta_{n0}) \times \right. \\ \left. \times d_{0n}^\lambda(\theta_R) \cos(n\phi_R) \langle D_{0n}^\lambda \rangle \right]^2 \quad (16)$$

where the azimuth is chosen in such a way that $\phi_R = 0$ corresponds to a proton lying in the plane containing the two major components of the molecular orientational interaction tensor (e.g. if the benzene rings of the mesogen are coplanar, $\phi_R = 0$ corresponds to a proton lying in the same plane).

Model 6: Let us now assume that the molecule is biaxial but the tumbling motion is slow on the experimental time-scale, i.e. $\tau_t \gg \tau_\infty \gg \tau_s$. Then, as in model 2, only the R_\perp component relaxes. Taking into account that $\langle D_{02}^2 \rangle \ll \langle P_2 \rangle$ [22], neglecting all quadratic or higher order terms

in $\langle D_{02}^2 \rangle$, and assuming that tumbling and spinning relaxations are fast on the experimental time-scale ($\tau_\infty \gg \tau_t \gg \tau_s$), we have

$$EISF_{(6)} = \sum_{\substack{\lambda=0 \\ \text{even}}}^{\infty} \sum_{\substack{k=0 \\ \text{even}}}^{\infty} \sum_m (-1)^{\lambda/2-k/2} (2\lambda+1)(2k+1)(2-\delta_{m0}) d_{m0}^\lambda(\theta_Q) d_{m0}^k(\theta_Q) j_\lambda(QR_\perp) j_k(QR_\perp) + \quad (17)$$

$$+ \left[d_{00}^\lambda(\pi/2) d_{00}^k(\pi/2) G_{m0m0}^{\lambda k}(0) + 2d_{00}^\lambda(\pi/2) d_{02}^k G_{m0m0}^{\lambda k}(0) \cos(2\phi_R) + \right.$$

$$\left. + 2d_{02}^\lambda(\pi/2) d_{00}^k G_{m2m0}^{\lambda k}(0) \cos(2\phi_R) \right]$$

The translational motion is considered as a two-stage-process: fast bound translation of the molecule in the stochastic “cage”, superposed on slow free diffusion of the cage itself. The “cage” has an average symmetry of an ellipsoid of rotation, with the main axis parallel to the molecular long axis \vec{I} . The halfwidths $a_{||}$ and a_{\perp} are parallel and perpendicular to \vec{I} , respectively.

Considering the cylindrical symmetry of the molecule, we obtain the structure factor [23]:

$$EISF_{(6)} = \sum_{\substack{\lambda \\ \text{even}}} \sum_{\substack{m \\ \text{even}}} (-1)^{(m-1)/2} (2\lambda+1)(2m+1) j_\lambda(Qr_\perp) j_m(Qr_\perp) \quad (18)$$

$$\times \sum_{\substack{\lambda', m'}} d_{\lambda'}^\lambda(\theta_Q) d_{m'0}^m(\theta_Q) d_{00}^\lambda(\pi/2) d_{00}^m(\pi/2)$$

$$\times \int d\Sigma f(D_{\lambda'0}^{\lambda*}(\Sigma)) D_{m'0}^m(\Sigma) \exp[-a_\perp^2 Q^2 - (a_{||}^2 - a_\perp^2) Q_{||}^2]$$

where j_λ are the Bessel’s spherical functions, and $D_{\lambda'\lambda''}^\lambda(\Omega)$ and $d_{\lambda'0}^\lambda(\theta)$ are respectively the usual and reduced Wigner’s matrices.

3. Results and discussion

The computed simulations based on the models given above are presented in Fig. 1. The numbers on the curves correspond to the rotational theoretical model used in their calculation. In most cases, the predictions of models 1 and 5 ($\tau_\infty \gg \tau_t$, cylindrical or biaxial molecule respectively) differ substantially from those of the other models. The disagreement of these predictions with the experimental data reported in the literature [3, 5, 6, 9] confirms the conclusion [3,9] that on the time-scale of neutron scattering experiments the relaxation of the tumbling motion is not complete (if any). The consideration of the molecular biaxiality (model 5) does not change this conclusion. For model 4, $\langle \tilde{p}_2 \rangle = 0.8$ (4a) or $\langle \tilde{p}_2 \rangle = 0.45$ (4b).

The choice between the rest of the models is much more difficult. The experimental data for the isotropic phase [2,4] disagree with model 3, but are qualitatively (and semi-quantitatively) compatible with models 2, 4 and 6. In fact, at $\langle P_2 \rangle = 0$, the predictions of model 3 coincide with those of model 1 and $EISF_{(3)}$ for our “average” proton is much smaller than the experimental one [4]. On the other hand, the experimental data for powder samples [5, 6] are in better agreement with model 3 (or 4) than with model 2 (or 6) (pure uniaxial rotation). The most stringent test of the theoretical models is obviously their comparison with the experimental data obtained in aligned samples [4, 9]. In such studies, a striking result has been obtained – the structure factors measured with $Q_{||}$ and Q_{\perp} are very close to one another, in disagreement with models 2 or 3. A possible explanation of this feature is the translational contribution to the EISF due to the restricted motion normal to the layers in the smectic phases [9,13,14] or to a possible rotational-translational

correlation in the nematic state [1]. Models 4 and 6 are in better agreement with the experimental EISF in the nematic phase than models 2 and 3. We see from Fig. 1 (b, c) that the angular dependence of curves 4 and 6 is less strong than for curves 2 and 3. A model, taking into account both the steric hindrance and the molecular biaxiality, might be expected to give a quantitative agreement with the experimental data in aligned samples. Unfortunately, such a model will be too complicated and will have too many phenomenological parameters.

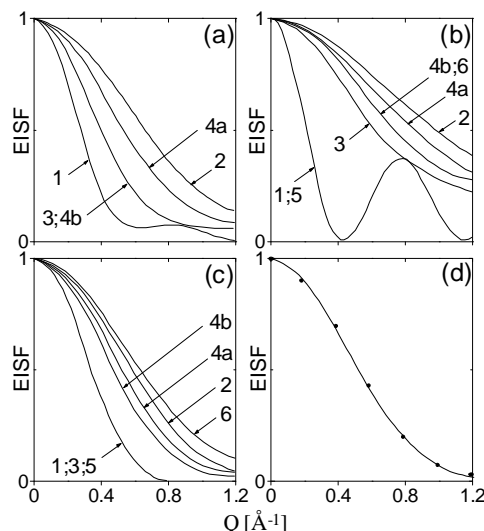


Fig. 1. EISF calculated by different theoretical models in an anisotropic system.

Rotational dynamics contributions for: (a) a non-aligned sample for $\theta_Q = 0$; (b) an aligned sample for $\theta_Q = 0$; (c) an aligned sample for $\theta_Q = 90^\circ$. In all cases, $\langle P_2 \rangle = 0.45$. (d) - EISF for translational diffusion: $\langle P_2 \rangle = 0.55$, $\theta_Q = 0$ (solid line) and $\theta_Q = 90^\circ$ (experimental points from [3]) for $a_{||} = 1.6 \text{ \AA}$.

Fig. 1(d) presents numerical results for the translational contribution to EISF, calculated from Eq. (18). For this value of $a_{||}$, the curves for both geometries are almost identical, in good agreement with the experimental data from [3].

In our opinion, the physical basis of our approach for the translational contribution to EISF is more convincing than that of the “inclined rotation” models [2 - 7]. However, for the time being, the experimental data are too scarce and not precise enough to prove or reject unambiguously which one of the models (if any) corresponds to the real mechanism of the bound translational motions in anisotropic systems.

An unequivocal choice between the theoretical models for the rotational and translational contributions to EISF presented in this paper is difficult on the basis of the experimental data reported in the literature. However, we can propose some experiments, which have not been exploited so far and which can clarify the mechanism of reorientation. For example, a good test for our model 4 will be the measurement of the EISF for the isotropic liquid phase of long, hard and symmetric molecules, similar to the hard-core of the mesomorphic compounds. A good candidate for such a study is the tolane molecule. For this, most of the difficulties discussed at the beginning of this section are absent, but the steric hindrance for the tumbling motion is qualitatively the same as for the mesogens. The same experiment can also test model 2 versus models 1 or 3. Partial deuteration of the molecule can give very valuable proton-by-proton information about the reorientation. Moreover, a comparison between the structure factors of different protons will contribute to the study of the translational motion if the steric hindrance or other factors restrict it in the space.

4. Conclusions

Many new materials are being explored as possible candidates for incorporation in molecular electronic systems. Their electronic parameters (carrier mobility, lifetime, conductivity, etc.) and their stability/reproducibility at an operational level are very dependent on molecular orientation and molecular diffusion in the system. The rotational and translational dynamics is an important and complicated problem, and a lot of techniques should be used for complete elucidation of relaxation processes in anisotropic systems. Depending on the frequency 'windows' of the respective spectroscopic techniques, two types of reorientational process can be studied. Vibrational spectroscopy and neutron scattering give information on the reorientation of the molecules in the time domain 1-100 ps. The fluorescence experiment and electron paramagnetic resonance (EPR) in the frequency range 1 to 100 ns deal with the influence of the local structure on the preorientation of the individual molecule, i.e. these two spectral techniques reveal the collective nature of the reorientational processes. Relaxation of the individual molecule and of local molecular clusters depend differently on temperature. Obviously, more studies are needed for complete clarification of the dynamic picture in anisotropic systems.

References

- [1] F. Volino, A. J. Dianoux, H. Hervet, *Sol. State Commun.* **18**, 453 (1976).
- [2] A. J. Leadbetter, R. M. Richardson, C. J. Carlile, *J. Physique Colloq.* **37**, C3-65 (1976).
- [3] D. H. Bonsor, A. J. Leadbetter, F. P. Temme, *Molec. Phys.* **36**, 1805 (1978).
- [4] H. Hervet, F. Volino, A. J. Dianoux, R. E. Lechner, *J. Physique Lett.* **35**, L-151 (1974).
- [5] F. Volino, A. J. Dianoux, H. Hervet, *Mol. Cryst. Liq. Cryst.* **38**, 125 (1977).
- [6] F. Volino, A. J. Dianoux, H. Hervet, *J. Physique Colloq.* **37**, C3-55 (1976).
- [7] A. J. Leadbetter, R. M. Richardson, *The Molecular Physics of Liquid Crystals*, Ed. G. R. Luckhurst, G. W. Gray, Academic Press, New York, 1979, Ch. 20.
- [8] A. J. Leadbetter, R. M. Richardson, J. C. Frost, *J. Physique Colloq.* **40**, C3-125 (1979).
- [9] A. J. Leadbetter, R. M. Richardson, *Molec. Phys.* **35**, 1191 (1978).
- [10] S. Jen, N. A. Clark, P. S. Pershan, E. B. Priestley, *J. Chem. Phys.* **66**, 4635 (1977).
- [11] P. L. Nordio, U. Segre, *The Molecular Physics of Liquid Crystals*, Ed. G. R. Luckhurst and G. W. Gray, Academic Press, New York, 1979, Ch. 18.
- [12] I. Dozov, N. Kirov, B. Petroff, *Phys. Rev. A* **36**, 2870 (1987).
- [13] F. Volino, A. J. Dianoux, A. Heidemann, *J. Physique Lett.* **40**, L-583 (1979).
- [14] A. J. Dianoux, A. Heidemann, F. Volino, H. Hervet, *Molec. Phys.* **32**, 1521 (1976).
- [15] J. Töpler, B. Alefeld, T. Springer, *Mol. Cryst. Liq. Cryst.* **26**, 297 (1973).
- [16] J. A. Janik, *Advances in Liquid Crystals*, Academic Press, New York, 1982, p. 215.
- [17] I. Dozov, N. Kirov, M.P. Fontana, *J. Chem. Phys.* **81**, 2585 (1984).
- [18] M. P. Fontana, B. Rosi, N. Kirov, I. Dozov, *Phys. Rev. A* **33**, 4132 (1985).
- [19] G. R. Luckhurst, R.N. Yeates, *J. Chem. Soc. Faraday Trans., II* **72**, 996 (1976).
- [20] A. Arcioni, F. Bertinelli, R. Tarroni, C. Zannoni, *Molec. Phys.* **61**, 1161 (1987).
- [21] I. Dozov, S. Temkin, N. Kirov, *Liq. Cryst.* **8**, 727 (1990).
- [22] G. R. Luckhurst, C. Zannoni, P. L. Nordio, U. Segre, *Molec. Phys.* **30**, 1345 (1975).
- [23] I. Dozov, N. Kirov, S. Temkin, *J. Mol. Liquids* **51**, 1 (1992).