INCOHERENT COLD NEUTRON SCATTERING SPECTRAL SHAPES UNDER THE INFLUENCE OF LOCALIZED STOCHASTIC MOTION OF PARALLEL MOLECULES

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Abstract

The cold neutron incoherent scattering laws for three models of localized molecular motion, applicable also to liquid crystalline phases, are compared. Two models of harmonically bound molecule yield only weekly distinguishable results for the S (Q, ω), from the one predicted by the well known uniaxial, simple rotational molecules diffusional model.

Podana je primerjava nekoherentnih sipalnih funkcij hladnih nevtronov, izračunanih za primer treh modelov lokaliziranih molekularnih gibanj, uporebnih tudi v tekoče kristalnih fazah. Rezultati izvedeni na osnovi dveh modelov harmonsko vezane molekule se le v neznatni meri razlikujejo od rezultatov kot jih podaja model enoosne enostavne rotacijske difuzije.

In the course of investigation by incoherent neutron scattering method, of rotational motion of phenyl rings of MBBA molecules in the nematic phase [1], it was conjectured that the phenyl rings are subject to two different kinds of (uniaxial) rotational dynamics: most of them, it seems, to the stochastic within two perfectly reflecting potentional barriers (on account of the steric hindrance of adjacent molecules) angular confined uniaxial librational motion (RTOM model), while the rest of them are simultaneously undergoing the uniaxial simple rotational diffusion. The calculated incoherent scattering laws for both rotational models under the assumption of the free translational diffusion of molecular center of mass, differ of course, yet the difference, when convoluted with the (broad) experimental resolution function diminishes, but for a certain particular set of parameters describing the uniaxial dynamics, disappears. The calculated unbroadened scattering low for the RTOM model exhibits the features characterized by the superposition of a narrow and a broad line. These are precisely the characteristics

which are displayed in quasielastic incoherent neutron scattering spectra for various models of damped motion of harmonically bound particle acted upon by random forces, i.e. the translational diffusion of the spherical particle in restricted geometries undergoing free rotational diffusion, as given by Nowik et al. [2].

The purpose of this note is therefore twofold. First, to investigate the spectral shape of the incoherent cold neutron scattering law for two cases of localized uniaxial rotational motion of nematic molecules subject to the free translational diffusion of the molecular center of mass and second, to exhibit the difference in spectral shapes evaluated for the case of localized uniaxial rotational dynamics (and free translational diffusion) versus localized translation of the molecular center of mass (and free rotational diffusion around it) as presented in [2].

The incoherent cold neutron scattering law, $S(Q, \omega)$, describing the in between two potentional barriers localized uniaxial stohastic libration and free translational diffusion of the molecular center of mass (c. o. m.) has been derived in [1] and reads (ν protons) for perfectly ordered molecules as,

$$S_1(Q,\omega) = 32\pi^2 \sum_{\nu} (a_{inc}^{\nu})^2 \sum_{l,s} (-1)^{s} i^{l+s} j_l(Qr_\nu)\, j_s(Qr_\nu)$$

$$\cdot \sum_{m} Y^{*}_{lm}(\Theta_Q \phi_Q)\, Y_{sm}(\Theta_\nu \phi_\nu)\, Y^{*}_{sm}(\Theta_\nu \phi_\nu) \cdot$$

$$\cdot \left\{ \frac{1-\cos(m\phi_0)}{(m\phi_0)^2} \; \frac{Q^2 D}{(Q^2 D)^2 + \omega^2} + 2 \sum_{p=1}^{\infty} \frac{(1-(-1)^{p}\cos(m\phi_0))}{\phi_0^{2}(\delta_p^{2} - m^2)^2} \; \frac{Q^2 D + \delta_p^2 R}{(Q^2 D + \delta_p^2 R)^2 + \omega^2} \right\}$$

$$\delta_p = \frac{p\pi}{\phi_0} \qquad (1)$$

where $j_1(Qr)$ is the spherical Bessel function of the order 1, $\hbar Q$ is the momentum transfer vector, $\vec{r}$ is the proton position vector as measured from c.o.m. of the molecule, Y_{1m} is spherical harmonics expressed in the body system, (θ, ϕ) are spherical components of the $\vec{r}$ or $\vec{Q}$ respectively, D is the translational diffusion constant of molecular c.o.m., ϕ_0 is the apex angle among the potential barriers, $\hbar\omega$ is the energy transfer in the scattering and R is the rate constant associated with the stochastic librational motion.

If the molecules are flat and rigid, as is this often the case with liquid crystals, and if, in analogy with Nowik et al. calculations, are subject to the along the molecule uniaxial damped torsional oscillations under the influence of stochastic torques M (t), the angular displacement φ of the plane from its rotational equilibrium direction $\varphi = 0$, is the solution of the stochastic equation $\ddot{\varphi} + \beta\varphi + \Omega^2\varphi = M(t)$, where β is associated with the frictional torques, and Ω is the frequency of harmonic torsional oscillations along the long molecular axes. Following Chandrasekhar [3], after lengthy derivation the conditional probability density in one dimensional case, $G(\varphi, \varphi_0, t)$ has been obtained and utilized for the evaluation of incoherent cold neutron intermediate scattering function which in the overdamped case reads (unlimited in space translational motion of c.o.m.) — this is the novel result —

$$I_2(Q,t) = I_t(Q,t) \cdot I_{rot}(Q,t) =$$

$$= e^{-Q^2 Dt} \cdot 16\,\Pi^2 \sum_{\nu} \nu\,(a_{inc}^{\nu})^2 \sum_{l,s} (-1)^{s_l l+s} j_l(Qr_\nu)\, j_s(Qr_\nu) \cdot$$

$$\cdot \sum_{m} Y^*_{lm}(\Theta_Q, \phi_Q)\, Y_{sm}(\Theta_Q, \phi_Q)\, Y_{lm}(\Theta_\nu \phi_\nu)\, Y^*_{sm}(\Theta_\nu \phi_\nu) \cdot$$

$$\cdot \frac{1}{\Pi} \exp\left[\frac{m^2 kT}{2J\Omega^2}\,(1 - e^{-(2\Omega^2/\beta)t})\right] \frac{\sin\left[l\Pi m(1 - e^{-(2\Omega^2/\beta)t})\right]}{m\,(1 - e^{-(\Omega^2/\beta)t})}$$

$$S_2(Q,\omega) = \frac{1}{2\Pi} \int I_2(Q,t)\, e^{-i\omega t}\, dt \qquad (2)$$

where, as before, an assembly of perfectly oriented long molecular axes of nematic molecules is assumed. J is the molecular moment of inertia evaluated with respect to the long body axis. The scattering law for this model above is obtained numericaly by FFT method.

The two model of localized uniaxial rotational diffusion do not permit the full periodic 2 Π rotations and are to be confronted with physicaly completely opposite case of a molecule being subjected to the free rotational diffusion around its center of mass, providing c.o.m. is undergoing the bound translational diffusion. For this case, Nowik et al. derived [2], (spherical molecules)

$$S_3(Q,\omega) = \frac{1}{2\Pi} \sum_{l=0}^{\infty} \sum_{r=0}^{\infty} \frac{a_{nl}(r)\,\Gamma_{nl}}{\Gamma_{nl}^2 + \omega^2} \qquad (3)$$

where

$$a_{nl}(r) = e^{-Q^2 \langle x^2 \rangle} (Q^2 \langle x^2 \rangle)^n (2l+1)\, j_l(Qr)/n!$$

$$\Gamma_{nl} = n\alpha + l\,(l+1)\,D'$$

where D' is rotational diffusion constant (uniaxial rotational motion is now discarded), α is the ratio of the harmonic and damping force constants, $\langle x^2 \rangle$ is the mean square displacement of the molecular center of mass (after a long period of time) and is given by $\langle x^2 \rangle = D'/\alpha$.

The scattering law has been evaluated for 14 protons of MBBA molecule [1], resolution broadened, and the parameters chosen in such a way that the best agreement with the experiment in $\vec{Q} \perp \vec{B}$ case has been obtained. On fig. 2 the calculated (unbroadened incoherent scattering laws for $Q = 1.287\ A^{-1}$ are presented for the values of parameters which are: $D = 2 \times 10^{-7}\ cm^2/s$, $R = 7 \times 10^9\ s^{-1}$, $\phi_0 = 53^\circ$ [1] (line 1), $D' = 10^9\ s^{-1}$, $\alpha = 10^{12}\ s^{-1}$ (line 3), $\Omega^2 = 5.39 \times 10^{24}\ s^{-2}$, $J = 2.67 \times 10^{-42}\ kgm^2$, $\beta = 9.76 \times 10^{15}\ s^{-1}$ (line 4) and also in the well known case of uniaxial along the molecular long axes sim-

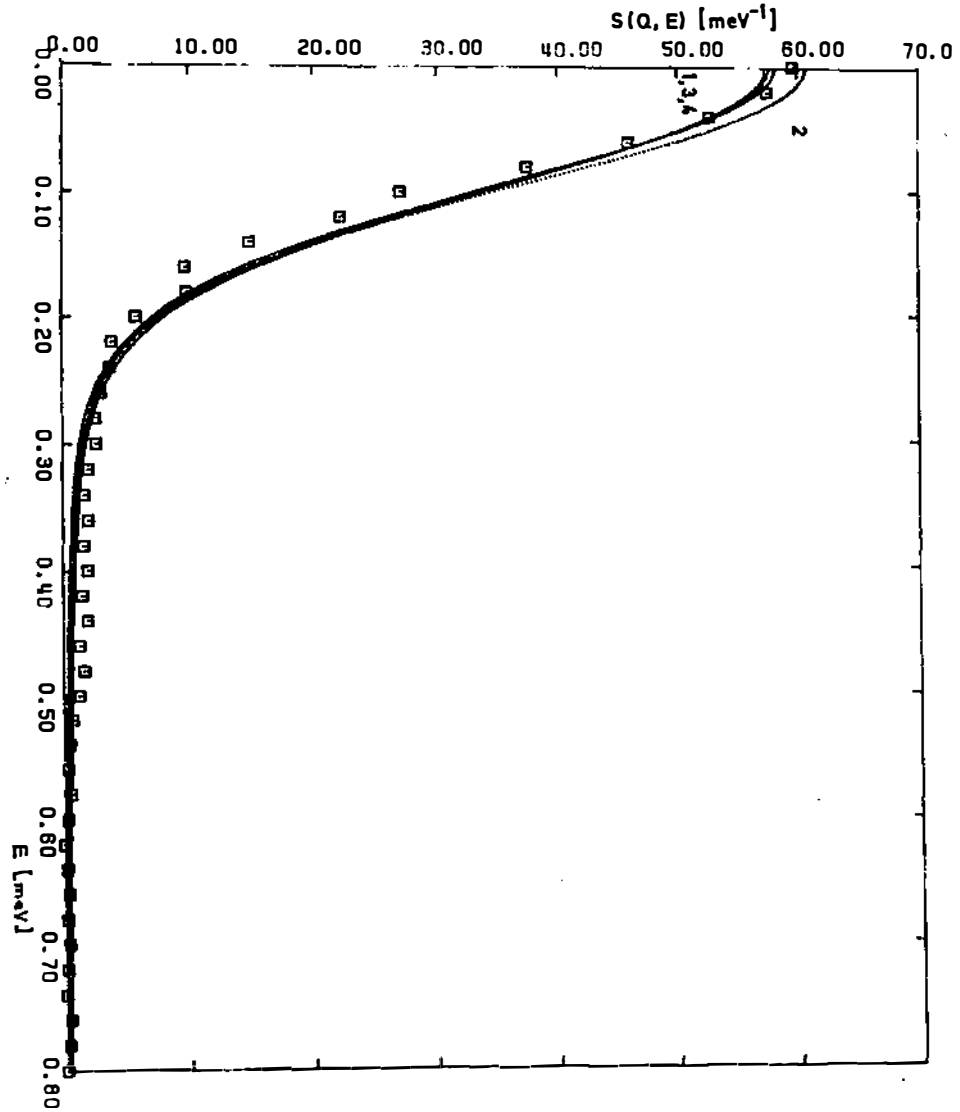

Fig. 1. The measured incoherent cold neutron scattering law normalized to one proton of MBBA molecule in nematic phase, T = 30°C, at Q = 1.287 x 10^{10} m^{-1} in $\vec{Q} \perp \vec{B}$ geometry (ref. 1) is compared to the resolution broadened calculation for the four models of molecular dynamics given in the text.

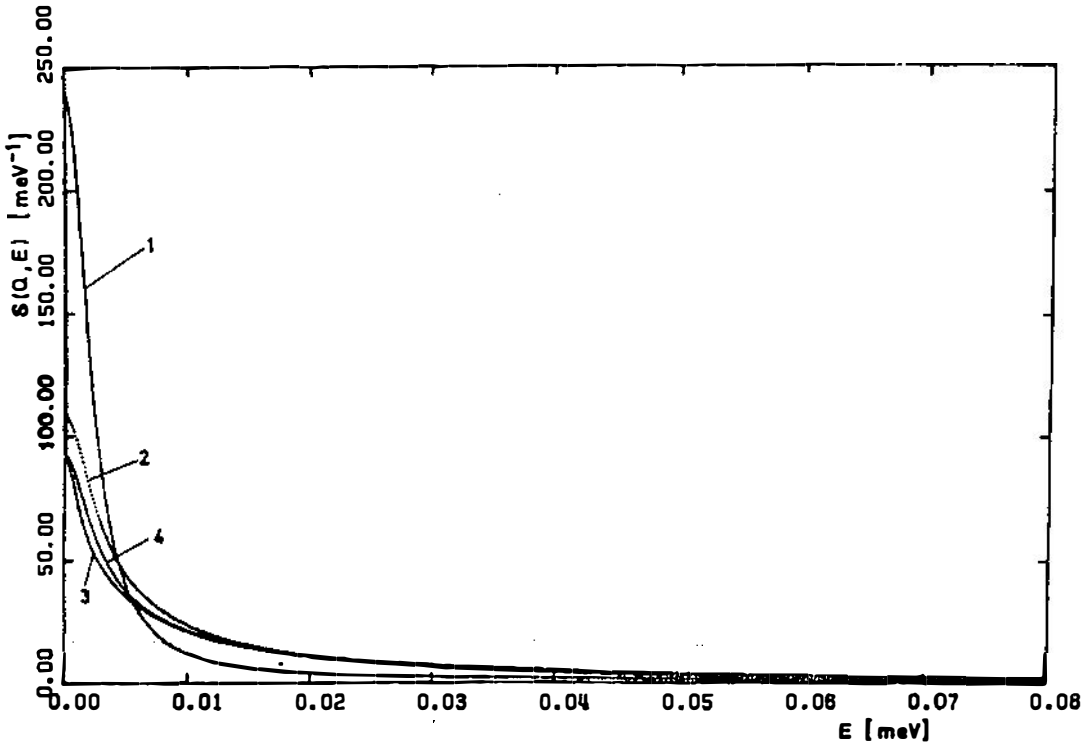

Fig. 2. The calculated unbroadened incoherent cold neutron scattering laws for the four models of molecular motion described in the text, which yield results presented on fig. 1.

ple rotational diffussion and simple translational diffusion of c.o.m. [1], $D_R = 2 \times 10^9$ s^{-1} (line 2) respectively. On fig. 3, an example of high resolution (FWHM = 0.022 meV) broadening of the four aforementioned dynamical molecular models is presented and the result if self explanatory. Even with high resolution experiments, it would be very difficult to distinguish the models of harmonically bound molecules, eq. (2) and eq. (3), as well as uniaxial simple rotational diffussion model (lines 2, 3, 4 on figures). The clear and distinct difference from this group is offered by the model of angular, between two potentional barriers localized uniaxial stochastic libration subject to simple translational difussion of c.o.m. (line 1). Hence the so often succesfull application of uniaxial simple rotational diffussion model in the QNS study of liquid crystalline molecules should now be viewed in terms of the generalization as presented above, namely that in published examples, at least in some cases, the nematic and smectic molecules might be subject to also (at least) bound harmonic uniaxial damped torsional oscillations or to some other combination of rotational, dynamics yieldig similar spectral shape as indicated above. The approximation, according to which the spectra can be resolved into the sum of broad and a narrow line, taking into account the results above, could in the same cases lead to ambiguous oversimplification of molecular dynamics.

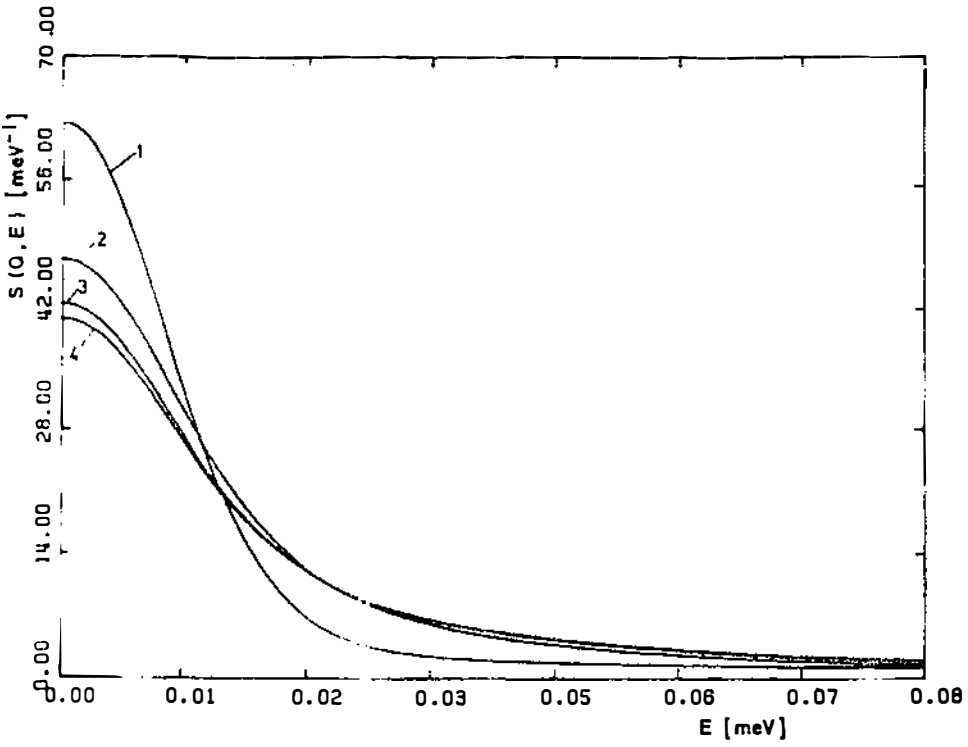

Fig. 3. The calculated incoherent cold neutron scattering laws evaluated for the four models of molecular motion described in the text are resolution broadened with ten times larger resolution then the one used on fig. 1. Even in this case the two models of harmonicaly bound molecules (lines 3 and 4) yield rather similar results as the model of uniaxial simple rotational diffussion along the long axes of long parallel molecules (line 2). Line 1 presents the incoherent cold neutron scattering law evaluated for the case of uniaxial angular between two potentional barriers stohastic molecular libration subjected to simple translational diffusion of its center of mass.

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