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Incoherent cold neutron scattering investigation of stochastic molecular orientational fluctuations in liquid crystals

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The model of rapid orientational fluctuations of the molecular long axis in liquid crystals, based upon the solution of the one-dimensional problem of the random walk of a particle between two perfectly reflecting barriers, is suggested and in conjunction with the translational diffusion of the molecular centre of mass and also uniaxial rotational diffusion, utilized for the evaluation of the incoherent scattering function, as well as EISF, appropriate to smectic A and nematic phases, and the comparison with measurements is made. On the basis of published measurements it is concluded that the molecules in the smectic A phase of DTBBA are subject to long axis orientational fluctuations between two potential barriers with an apex angle of about 100°.

1. Introduction

A large number of investigations of the molecular dynamics in liquid-crystalline samples by the cold neutron scattering method (QNS), have been reported. The most complete motional studies to date, based on the QNS method alone have been performed on deuteriated and undeuteriated samples of TBBA [1], EABAC [2], IBPBAC [3] and PAA [4]. On these samples in their different liquid crystal modifications, careful and thorough investigation of different aspects of the translational and rotational motion of single molecules have been performed and, in conjunction, with conclusions drawn from other techniques, such as N.M.R., N.Q.R., and dielectric relaxation spectroscopy, it has been established that the salient dynamical features of single molecule motion can be adequately described in terms of anisotropic translational motion of the molecular centre of mass, jump or continuous uniaxial rotational diffusion along the long molecular axis and in the case of TBBA [1] and IBPBAC [3], orientational fluctuations of the long molecular axes. In the course of the investigations, apart from the magnitudes of various parameters related to translational or rotational diffusion, such diverse information as the magnitude of the periodic potential barrier to translational diffusion perpendicular to the smectic layers [2, 3], the bipolar order parameter [1], the magnitude of the usual nematic order parameter as well as the average amplitude of long axis orientational fluctuations [1, 3], were obtained.

Thus, the incoherent QNS high resolution experiments have also established the importance of the contribution from molecular orientational fluctuations in order to account for the measured spectra in all mesophases, except the smectic VI phase, of TBBA [1], and the smectic A and B phases of IBPAC [3]. In the latter case it was argued that the amplitude of the orientational fluctuations and their correlation time are functions of temperature. The fact that no such contribution was observed in the investigation of EABAC [2], was explained by assuming that the axis fluctuations were too small to affect significantly the spectra [3].

Information on the orientational fluctuations of the long molecular axes is obtained indirectly (i.e. by evaluating the neutron elastic incoherent structure factor (EISF)) when no separate component in the quasi-elastic scattering is apparent, this would indicate that the correlation time for the axis fluctuations would be about the same as for uniaxial rotation ($\approx 10^{-11}$ s). In the analysis, the molecular orientational fluctuation, a dynamic process, is related to the static orientational distribution function, $f(\Theta)$, of the molecular long axes of the form (limiting ourselves to S_A and nematic phases only) [5, 6],

$$f(\Theta) \propto \exp(\delta' \cos\theta), \tag{1}$$

which is peaked at $\Theta = 0°$, where Θ is the polar angle between the molecular long axis and a macroscopic uniaxial direction of the sample. The parameter δ' is related to the width of the distribution. Richardson *et al.* [3], have remarked that the lateral displacement motion of the molecules of the order of 0.9 Å, instead of orientational fluctuations, could also explain the measured spectra, but this interpretation was discarded on account of close molecular packing in the liquid-crystalline phases investigated. In addition it was remarked, that the axis fluctuations should be largely cooperative in nature (due to the close molecular packing) and for this reason would be expected to be rather slower than the time scale ($\approx 10^{-10}$ s) of the QNS experiments. It is therefore desirable to obtain a direct approach to resolve the questions concerning

(1) the time scale of the observed molecular long axis fluctuations; and
(2) the amplitude of these fluctuations;

these could be answered if a suitable dynamical model for molecular long axis orientational fluctuations was available.

Clearly, our aim is to propose a simple model, which would help to clarify these points. In §2, such a model, based upon the solution of the problem of a (symmetric) one-dimensional random walk of a particle between two perfectly reflecting barriers is presented and the incoherent scattering function for the molecular centre of mass, uniaxial rotational motion along the long axis and its orientational fluctuations is calculated. In §4 the results of the calculations are compared with the measurements on an unoriented sample of PBH in the smectic A phase, and to the published [6] high resolution measurements of the elastic incoherent structure factor (EISF) of a powder sample of the smectic A phase deuteriated TBBA.

2. A model of molecular long axis orientational fluctuations description and calculation of the incoherent scattering function

The model of molecular long axis orientational fluctuations as proposed here, is built upon the following observations: due to thermal agitation of the molecules in the presence of long range orientational order characterizing the liquid-crystalline phases, the preferred molecular direction in space obviously exists. However, each molecule reorients in a hindered fashion about its preferred direction [7], which by itself is a function of time and position within the sample. The molecular large (20°–40°) and rapid ($\tau_c \approx 10^{-10}$ s) reorientations are due to short range interactions, while the collective fluctuations associated with the fluctuations in the preferred direction of the molecules in a certain region of space (and not the axes themselves) occur on a time scale at least two orders of magnitude longer and hence should appear static as far as the neutron scattering experiment is concerned. These collective fluctuations of the preferred molecular directions are to be associated with the usual nematic order parameter, S [7]. From the point of view of the physical picture just described, which enables the separation of slow collective orientational fluctuations from the rapid orientational fluctuations of a single molecule, the probability density given by equation (1), seems to refer to the static distribution of the angles which the molecular axes can span with respect to the local preferred direction (i.e. the local director).

The rapid long axis molecular orientational fluctuations (around their centre of mass, respectively) originate from stochastic collisions with the surroundings on account of the short and long range molecular interactions. In our view they occur around the average (which is static on our time scale) direction (the molecular preferred axis) and fluctuations are assumed symmetrical with respect to it and due to the long range orientational fources, ought to be necessarily constrained within a certain range of space, which in our simple picture will be conveniently taken to be a cone with an average apex angle, ϕ_0. The extremely large number of random collisions to which each molecule is subjected, impart to this motion a continous or diffusive character, which is two dimensional in nature. However this will be simplified by considering its one-dimensional analogue according to which the tip of the molecular long axis is constrained to move on an circular conical segment with an apex angle ϕ_0. The individual steps are small and are occurring in very rapid succession. This view allows the problem to be described in terms of the symmetric random walk of a particle moving a unit step to the right or left between two perfectly reflecting barriers, a well-known problem whose solution for the discrete case has been given by Feller [8].

In the limit of a large number of angular steps of the molecular axis, the conditional probability, $P(\varphi \mid \varphi_0 t)\, d\varphi$, that the axis will be in an angular interval $d\varphi$ at $\varphi + d\varphi$ (the angle φ is measured from one of the barriers onwards) within the apex angle ϕ_0 at time t providing it was oriented at φ_0 at $t = 0$, is given as

$$P(\varphi \mid \varphi_0 t) = \frac{1}{2\sqrt{(1/Rt)}} \sum_{k=-\infty}^{\infty} \exp\left(-\frac{(\varphi - \varphi_0 - 2k\phi_0)^2}{4Rt}\right) + \exp\left(-\frac{(\varphi + \varphi_0 - 2k\phi_0)^2}{4Rt}\right) \tag{2}$$

by the method of images (8), or as

$$P(\varphi \mid \varphi_0 t) = \frac{1}{\phi_0} + \frac{2}{\phi_0} \sum_{r=1}^{\infty} \exp\left(\frac{\pi^2 r^2 R}{\phi_0^2}\, t\right) \cos \frac{\pi r \varphi_0}{\phi_0} \cos \frac{\pi r \varphi}{\phi_0} \tag{3}$$

by the elegant method of generating functions (8); here R is the rate constant associated with the molecular orientational diffusion. It ought to be emphasized that the orientation conditional probability density $P(\varphi \mid \varphi_0 t)$, is defined in such a way that the axis never reaches its extreme positions defined by $\varphi = 0$ and $\varphi = \phi_0$, but can approach to these boundaries arbitrarily close. In addition, equations (2) and (3) are written for a symmetric case (the probability of taking a step to the right or to the left is equal), but an asymmetric model can also be easily handled [8]; in addition the case where the individual steps are not of equal length can be constructed. These models should be of interest when investigating other smectic phases.

In what follows the expression given by equation (3) is being used. For the symmetric case, assuming a uniform initial probability density, $P(\varphi_0)$ for the orientation of the axis

$$P(\varphi_0) = \frac{1}{\phi_0}, \quad 0 \leqslant \varphi_0 \leqslant \phi_0, \tag{4}$$

it can be shown, that

$$\langle \varphi \rangle = \frac{\phi_0}{2} \tag{5}$$

and so the preferred molecular axis points along the bisector of the apex ϕ_0, and is placed symmetrically with respect to the boundaries defining the position of the perfectly reflecting barriers.

The derivation of the incoherent scattering function (for a single proton) for the case of uncorrelated translational centre of mass simple molecular diffusion, uniaxial rotational diffusion along the long molecular axis and the stochastic fluctuation of the long axes between the reflecting barriers, is now described briefly. Following the general lines given by Sears [9], assuming uncorrelated motions, the incoherent scattering function is

$$S_s(Q, \omega) = \frac{1}{2\pi} \int I_s(Q, t) \exp(-i\omega t)\, dt; \tag{6}$$

$\mathbf{Q}$ is the scattering vector, $\hbar\omega$ the energy transfer and the incoherent intermediate scattering function, $I_s(Q, t)$, is [9]

$$I_s(Q, t) = \exp(-Q^2 D t) \langle \exp[-i\mathbf{Q}\mathbf{r}(0)] \exp[i\mathbf{Q}\mathbf{r}(t)] \rangle, \tag{7}$$

where D is, for the ease of computations, taken to be an average simple translational diffusion constant for the molecular centre of mass, and a gaussian approximation for this motion is assumed to be valid (thus we do not distinguish between $D_{\parallel}$ and $D_{\perp}$, see [10]), and the $\mathbf{r}(t)$ describes the instantaneous position of the proton as measured from the centre of mass. As we are concerned with smectic A and nematic phases, we choose the macroscopic uniaxial axis of the specimen to define the z axis of the laboratory coordinate system. Employing the relation

$$\exp(i\mathbf{Q}\mathbf{x}) = 4\pi \sum_{l=0}^{\infty} i^l j_l(Qx) \sum_m Y_{lm}^*(\Theta_Q \varphi_Q)\, Y_{lm}(\Theta_x \varphi_x); \tag{8}$$

that is $I_s(Q, t)$ should be invariant with respect to (a) rotation of 180° of the sample around an axis perpendicular to the uniaxial axis and (b) rotation through an arbitrary angle χ around the uniaxial axis and taking into account the uniaxial symmetry of the specimen equation (7) is written as

$$I_s(Q, t) = 16\pi^2 \exp(-Q^2 D t) \sum_{l,s} i^{l+s}(-1)^s j_l(Qr) j_s(Qr)$$
$$\times \sum_m \langle Y_{lm}(\Theta(t)\varphi(t))\, Y_{sm}^*(\Theta(0)\varphi(0)) \rangle\, Y_{lm}^*(\Theta_Q \varphi_Q)\, Y_{sm}(\Theta_Q \varphi_Q). \tag{9}$$

In this expression l and s are integers such that their sum is even, $|m| \leqslant l$ or s whichever is smaller, and Y_{lm}, the spherical harmonics are written in the laboratory frame; $j_l(Qr)$ is a spherical Bessel function of order l. We proceed by defining two new coordinate systems: $x_1 y_1 z_1$ with the z_1 axis defined along the instantaneous preferred molecular axis and the body system with the z axis pointing along the principal axis associated with the greatest component of the molecular moment of inertia tensor; this is taken simply as the long molecular axis. Let $\Omega_p(\alpha_p, \beta_p \gamma_p)$ and $\Omega(\alpha, \beta, \gamma)$ define the set of Euler angles which rotate the laboratory system into the $x_1 y_1 z_1$ system and the $x_1 y_1 z_1$ system to the body system, respectively. Employing twice the relation

$$Y_{jm'} = \sum_m D^{j*}_{m'm}(\alpha, \theta, \gamma) \tilde{Y}_{jm}, \tag{10}$$

where $D^{j*}_{m'm}$ denotes the Wigner rotation matrix of order j, and $\tilde{Y}_{jm}$ denotes the spherical harmonic expressed in the rotated coordinate system, the term to be averaged is written as

$$\begin{aligned} \langle Y_{lm}(\Theta(t), \varphi(t)) Y^*_{sm}(\Theta(0), \varphi(0)) \rangle &= \sum_{\substack{m_1 m_2 \\ m_3 m_4}} \langle D^{l*}_{mm_1}(\Omega_p) D^s_{mm_2}(\Omega_p) \rangle \\ &\times \langle D^{l*}_{m_1 m_3}(\Omega(t)) D^s_{m_2 m_4}(\Omega(0)) \rangle \bar{Y}_{lm_3}(\Theta, \varphi) \bar{Y}^*_{sm_4}(\Theta, \varphi), \end{aligned} \tag{11}$$

where due to the different time scales the averaging procedure can be performed separately. In equation (11), $\bar{Y}_{lm}$ are spherical harmonics expressed in the body coordinate system. Since

$$\begin{aligned} &\langle D^{l*}_{mm_1}(\Omega_p) D^s_{mm_2}(\Omega_p) \rangle \\ &= (-1)^{m-m_1} \sum_J C(l, s, J, -m_1, m_2) C(l, s, J, -m, m) \langle D^J_{0, m_2 - m_1}(\Omega_p) \rangle, \end{aligned} \tag{12}$$

where C is the Clebsch–Gordan [11] coefficient (note that had we not assumed at the beginning uniaxial symmetry, the first subscript in the rotation matrix would not have been zero), and averaging over uniformly distributed angles γ_p, equation (11) reduces to

$$\begin{aligned} \langle Y_{lm}(\Theta(t), \varphi(t)) Y^*_{sm}(\Theta(0), \varphi(0)) \rangle &= \sum_{\substack{m_1 m_3 \\ m_4}} \sum_J (-1)^{m-m_1} C(l, s, J, -m_1, m_1) \\ \times C(l, s, J, -m, m) \langle P_J(\cos \beta_p) \rangle &\langle D^{l*}_{m_1 m_3}(\Omega(t)) D^s_{m_1 m_4}(\Omega(0)) \rangle \bar{Y}_{lm_3}(\Theta, \varphi) \bar{Y}^*_{sm_4}(\Theta, \varphi). \end{aligned} \tag{13}$$

The uniaxial rotational and orientational fluctuational motions are built into the expression as follows:

$$\begin{aligned} \langle D^{l*}_{m_1 m_3}(\alpha, \beta, \gamma) D^s_{m_1 m_4}(\alpha_0 \beta_0 \gamma_0) \rangle &= \langle \exp(i m_1 \alpha) \exp(-i m_1 \alpha_0) \rangle \langle d^l_{m_1 m_3}(\beta) d^s_{m_1 m_4}(\beta_0) \rangle \\ &\times \langle \exp(i m_3 \gamma) \exp(-i m_4 \gamma_0) \rangle \end{aligned} \tag{14}$$

since the Euler angles are independent. We assume that the orientation of the plane within which the molecular axis fluctuates is for each individual molecule fixed in space (however, the planes are to be isotropically distributed about the uniaxial direction), i.e. $\alpha = \alpha_0$. The first term on the right side of equation (14) is then identically equal to 1. Another obvious possibility would be when α and α_0 are uniformly distributed in space. The first term in equation (14), when evaluating the average, is then equal to $\delta_{m_1, 0}$. Since the first assumption is more general, we proceed along this line. (Putting the value of $m_1 = 0$ in the final expression, equation (19), corresponds to the scattering function evaluated with the second assumption.) As shown in [10], the value of the third term with the assumption of uniaxial rotational diffusion is given by

$$\langle \exp(im_3\gamma)\exp(-im_4\gamma_0)\rangle = \exp(-D_1 m_3^2 t)\delta_{m_3,m_4}, \tag{15}$$

where D_1 is the uniaxial rotational diffusion constant. The term corresponding to the long axis orientational fluctuations

$$\langle d^l_{m_1m_3}(\beta(t))\, d^s_{m_1m_3}(\beta(0))\rangle \tag{16}$$

is evaluated by employing the equations (3) and (4). In order to do this the following transformation is required:

$$\beta = \varphi - u, \quad u = \frac{\phi_0}{2}, \tag{17}$$

as β is the instantaneous orientation of the molecular long axis as measured with respect to its preferred axis which points along the bisector of the circular segment.

Denoting

$$\left.\begin{aligned} F_1(l,s,m_1,m_3) &= \frac{1}{\phi_0^2}\int_0^{\phi_0} d^l_{m_1m_3}(\varphi - u)\,d\varphi \int_0^{\phi_0} d^s_{m_1m_3}(\varphi_0 - u)\,d\varphi_0, \\ F_2(l,s,m_1,m_3,r)& \\ &= \frac{2}{\phi_0^2}\int_0^{\phi_0} d^l_{m_1m_3}(\varphi - u)\cos\left(\frac{\pi r\varphi}{\phi_0}\right)d\varphi \int_0^{\phi_0} d^s_{m_1m_3}(\varphi_0 - u)\cos\left(\frac{\pi r\varphi_0}{\phi_0}\right)d\varphi_0 \end{aligned}\right\} \tag{18}$$

the incoherent scattering function, equation (6), for the case of uncorrelated simple translational diffusion of the molecular centre of mass, uniaxial rotational diffusion along the long molecular axis, and its stochastic orientational fluctuations between two perfectly reflecting potential barriers, for a single proton

$$\begin{aligned} S_s(Q,\omega) &= 16\pi\sum_{l,s} i^{l+s}(-1)^s j_l(Qr)\, j_s(Qr)\sum_m Y^*_{lm}(\Theta_Q\varphi_Q)\,Y_{sm}(\Theta_Q\varphi_Q) \\ &\times \sum_{m_1m_3}\sum_J (-1)^{m-m_1}\, C(l,s,J,-m_1,m_1)C(L,s,J,-m,m)\langle P_J(\cos\beta_p)\rangle \\ &\times \bar{Y}_{lm_3}(\Theta,\varphi)\,\bar{Y}^*_{sm_3}(\Theta,\varphi)\left\{F_1(l,s,m_1,m_3)\,\frac{Q^2D + D_1m_3^2}{(Q^2D + D_1m_3^2)^2 + \omega^2}\right. \\ &\left. + \sum_{r=1}^{\infty} F_2(l,s,m_1,m_3,r)\,\frac{Q^2D + D_1m_3^2 + \delta_r}{(Q^2D + D_1m_3^2 + \delta_r)^2 + \omega^2}\right\}, \end{aligned} \tag{19}$$

where $\bar{Y}_{lm}(\Theta,\varphi)$ are in the body frame, and

$$\delta_r = \frac{\pi^2 R r^2}{\phi_0^2}. \tag{20}$$

It is recalled that the sum $l + s$ is even and $|m| \leqslant l$ or s, whichever is smaller.

For an unoriented sample, this expression simplifies considerably if we consider smectic A phases where the molecules are usually pictured as pointing on average (i.e. prefered molecular direction) along the normal to the planes which in an homogeneous sample defines the axis of uniaxial symmetry. In this way $\beta_p = 0$ and $\langle P_J(\cos\beta_p) \equiv 1$ for all J. The only parameter left is now the apex angle between the barriers, ϕ_0. With an obvious change of notation we have

$$\begin{aligned} \langle S_s(Q,\omega)\rangle_{\text{av}} &= 4\sum_l j_l^2(Qr)\sum_m\sum_{m'}\left\{F_1(l,l,m',m)\,\frac{Q^2D + D_1m^2}{(Q^2D + D_1m^2)^2 + \omega^2}\right. \\ &\left. + \sum_{r=1} F_2(l,l,m',m,r)\,\frac{Q^2D + D_1m^2 + \delta_r}{(Q^2D + D_1m^2 + \delta_r)^2 + \omega^2}\right\}\bar{Y}^*_{lm}(\Theta,\varphi)\,\bar{Y}_{lm}(\Theta,\varphi), \end{aligned} \tag{21}$$

where the relation

$$\sum_J C(l,s,J,-m_1,m_1)C(l,s,J,-m,m) = \delta_{m_1,m}. \tag{22}$$

has been employed.

From equation (19) it follows, that besides the dynamic information, the incoherent scattering function contains also the static configuration of the molecular preferred axes, which enter into the expression in a rather complicated way. In the absence of orientational fluctuations (i.e. $\phi_0 \to 0$) the terms $F_2(l,s,m_1,m_3,r) \to 0$ and the terms $F_1(l,s,m_1,m_3)$ are either 1 or 0. In this case the incoherent scattering function in equation (19) depends not only on the translational and uniaxial rotational motion, but also on the linear function of unknown parameters $\langle P_J(\cos\beta_p)\rangle$. The coefficients F_1, F_2 are given to the lowest order of 1 and s in Appendix A.

The expression given by (21) can be further simplified if we assume, in equation (14), that α and α_0 are independent and can thus be averaged isotropically and separately; then in equation (21) the non-zero terms are those with $m' = 0$. In the limit of no axis fluctuation, i.e. $\phi_0 = 0$, we regain the well-known expression for the incoherent scattering function of an isotropic assembly of perfectly ordered rigid molecules subject to simple translational and also simple (uniaxial) rotational diffusion

$$\langle S_s(\Theta,\theta)\rangle_{\text{av}} = 4\sum_{l=0}^{\infty}\sum_m j_l^2(Qr)\,Y_{lm}^*(\Theta,\varphi)\,Y_{lm}(\Theta,\varphi)\,\frac{Q^2D + D_1m^2}{(Q^2D + D_1m^2)^2 + \omega^2}, \tag{23}$$

since

$$\lim_{\phi_0\to 0} F_1(l,l,m',m) = \delta_{m',m}.$$

Employing the definition of spherical harmonics,

$$Y_{lm}(\Theta,\varphi) = \sqrt{\left(\frac{2l+1}{4\pi}\,\frac{(l-m)!}{(l+m)!}\right)}\,P_l^m(\cos\Theta)\exp{(im\varphi)}, \tag{24}$$

where $P_l^m(\cos\Theta)$ are the associated Legendre polynomials, then equation (23) becomes

$$\langle S_s(Q,\omega)\rangle_{\text{av}} = \frac{1}{\pi}\sum_{l,m}(2l+1)\frac{(l-m)!}{(l+m)!}j_l^2(Qr)\,[P_l^m(\cos\Theta)]^2\,\frac{Q^2D + D_1m^2}{(Q^2D + D_1m^2)^2 + \omega^2} \tag{25}$$

and is independent of the azimuthal angle φ (in the body frame), as expected. If, for example, the proton is placed on the long body axis, $\Theta = 0$, $P_l^m(1) = \delta_{m,0}$ and

$$\langle S_s(Q,\omega)\rangle_{\text{av}} = \frac{1}{\pi}\sum_l(2l+1)j_l^2(Qr)\frac{Q^2D}{(Q^2D)^2 + \omega^2}, \tag{26}$$

which is identical to the case (see the convergence criteria given later) if, furthermore, it is placed in the origin of the body frame ($r = 0$ and $j_l(0) = \delta_{l,0}$) and so

$$\langle S_s(Q,\omega)\rangle_{\text{av}} = \frac{1}{\pi}\frac{Q^2D}{(Q^2D)^2 + \omega^2}. \tag{27}$$

This is the well-known incoherent cold neutron scattering law for isotropically diffusing particles; incidentally, the same expression is also obtained if D_1 is set equal to zero in equation (23).

If the molecular structure is not known, then setting $\Theta = \pi/2$, equation (23) can offer information on the radius of gyration for the proton.

Equation (23) is particularly suitable, on account for the problem being formulated in spherical coordinates (equation (8)), for an unoriented sample. The formulation of $\langle S(Q,\omega)\rangle_{\mathrm{av}}$ in a cylindrical frame, requires the integrals of the form [10]

$$\int_0^\pi J_n^2\,(Qr\sin\Theta\sin\vartheta)\sin\vartheta\,d\vartheta \tag{28}$$

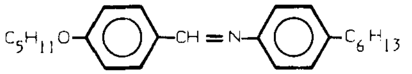
where J_n is a Bessel function of order n, to be further evaluated numerically. The direct transformation of equation (23) into the cylindrical reference of frame [10], seems to be not a trivial task. The number of terms, l, needed in an actual evaluation is determined from the convergence criterion, i.e.

$$1 = \int_{-\infty}^{\infty} \langle S_s(Q,\omega)\rangle_{\mathrm{av}}\,d\omega = \sum_l (2l+1)j_l^2(Qr), \tag{29}$$

where the addition theorem for associated Legendre functions has been utilized.

3. Measurements

The quasi-elastic neutron scattering measurements were performed on an unoriented sample of 4-*n*-pentyloxybenzylidene-4-*n*-hexylaniline (PBH), i.e.



with the rotating lead single crystal time of flight cold neutron spectrometer, using an ORTEC 7010 multichannel analyser controlled by a PDP 11/34 computer at the TRIGA Mark II reactor in Ljubljana. The incident energy of the neutron beam is 5·05 meV and the energy resolution of the spectrometer is between 0·18 and 0·20 meV. The sample was placed in a thermostatic oven with flat aluminium walls. The measurements were carried out in the solid ($T = 293$ K), smectic A ($T = 331$ K) and nematic ($T = 338$ K) phases at four different scattering angles simultaneously.

4. Model fitting

The scattering function, equation (21), has been evaluated using the crystallographic data given in [12], but for the benzene ring protons only. From equation (21) and the values of the coefficients F_2, which in the lowest order are 0, it is evident that the orientational fluctuation contribution to the incoherent scattering function is rather small. The scattering function calculated for translation and uniaxial rotation diffusion coefficients typical of a mesophase are shown in figures 1 and 2 as a function of the apex angle ϕ_0 and the rate constant, characterizing the orientational fluctuations (figure 2). The variation of ϕ_0 reflects itself in an noticeable way in the peak value of $S(Q,\omega)$, while the variation of R has somehow stronger effect on the shape of the calculated lorentzian curve. The difference in the calculated scattering function when all the motions (TRF) are present and when only the translation and fluctuation (TF) contribute, is presented in figure 3. The difference in the spectra is noted, but it is also evident that $S(Q,\omega)$ is very narrow.

The orientational fluctuation effect is visible in second order only, and this explains why the measurements could be fitted with a resolution broadened (gaussian

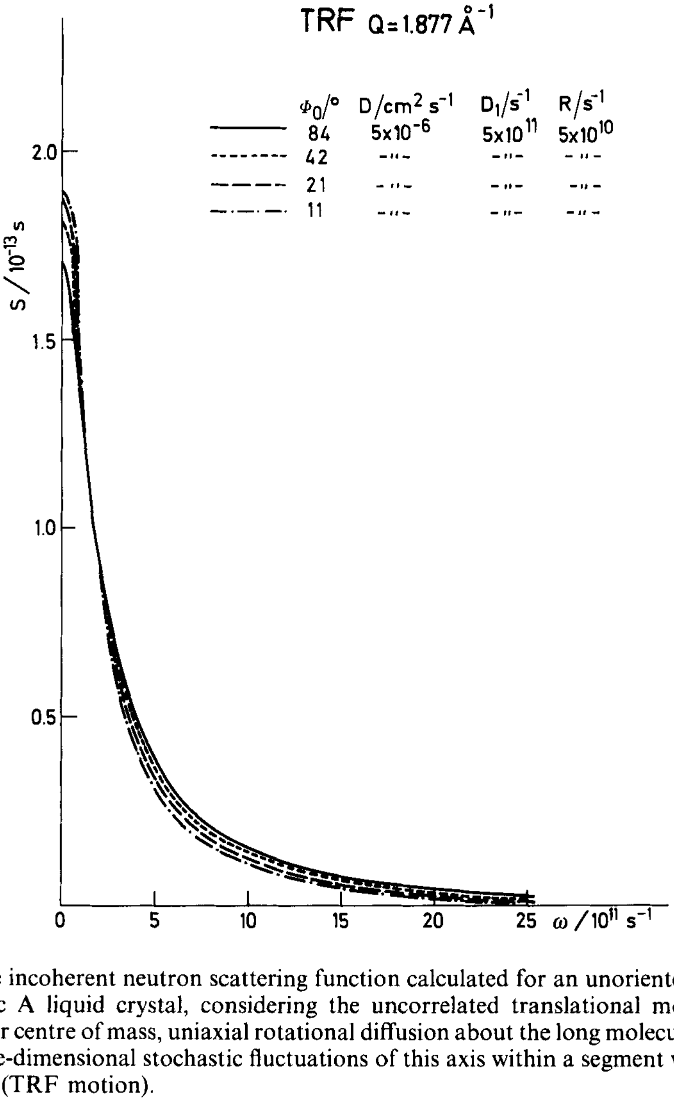


Figure 1. The incoherent neutron scattering function calculated for an unoriented sample of a smectic A liquid crystal, considering the uncorrelated translational motion of the molecular centre of mass, uniaxial rotational diffusion about the long molecular axis, and rapid one-dimensional stochastic fluctuations of this axis within a segment with an apex angle ϕ_0 (TRF motion).

function) calculated incoherent scattering function for TRF, equation (21), which is primarily dependent on the values of the translation and rotation diffusion constants, but much less so on the value of ϕ_0, and insensitive to the value of R. Although the fitting can be taken as satisfactory, (cf. figure 4) similar discrepancies between the measured and calculated peak values were obtained also at higher Q values.

The resolution of the spectrometer at our disposal is too coarse to admit the positive identification of the second order effect of long axis orientational fluctuations on the shape of the measured incoherent scattering law and in conjunction with the fact that both diffusional constants D and D_1 are unknown, the fitting ought to be viewed as a mere illustration that in the types of experiments reported here the molecular localized motion effects could perhaps be safely neglected in the first approximation.

The incoherent neutron scattering function, equation (21), has been derived on the basis of a dynamical model for the molecular orientational fluctuations, which in itself

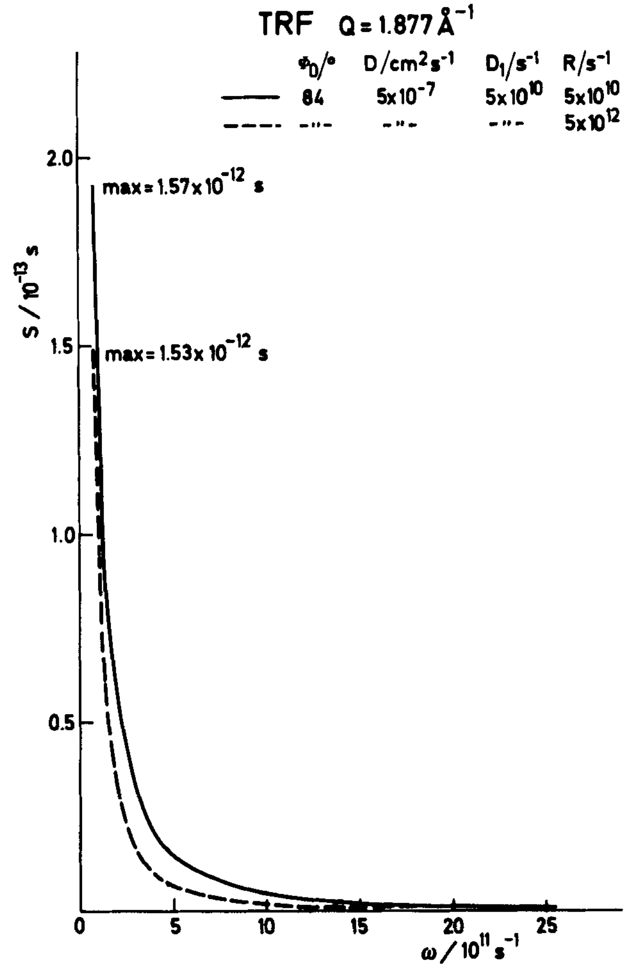


Figure 2. The incoherent neutron scattering function calculated with the TRF approximation, as a function of the rate constant associated with one-dimensional long axis stochastic orientational fluctuations about the preferred axis, taken to be represented by the bisector of a segment with an apex angle ϕ_0. This angle spans two perfectly reflecting walls which intersect in the molecular centre of mass.

is simple enough, but nevertheless differs from that currently used in the following ways:

(*a*) the time dependent behaviour of the molecular long axes orientational dynamics is considered in a way where the long range molecular orientational forces are implicitly taken into account by the existence of the constraint to molecular orientational fluctuations in the form of the apex angle ϕ_0,

(*b*) it provides the means to study, by measuring the temperature dependency of ϕ_0, the variation of the barrier to orientational fluctuations,

(*c*) it separates explicitly the low frequency collective oscillations in liquid crystals which are the dominant contribution when interpreting, for example, the light scattering and N.M.R., measurements but which appear static on the time scale of neutron scattering experiments,

(*d*) It offers the means to estimate the frequency range, through the measurements of the constant R, of the long axis orientational fluctuations.

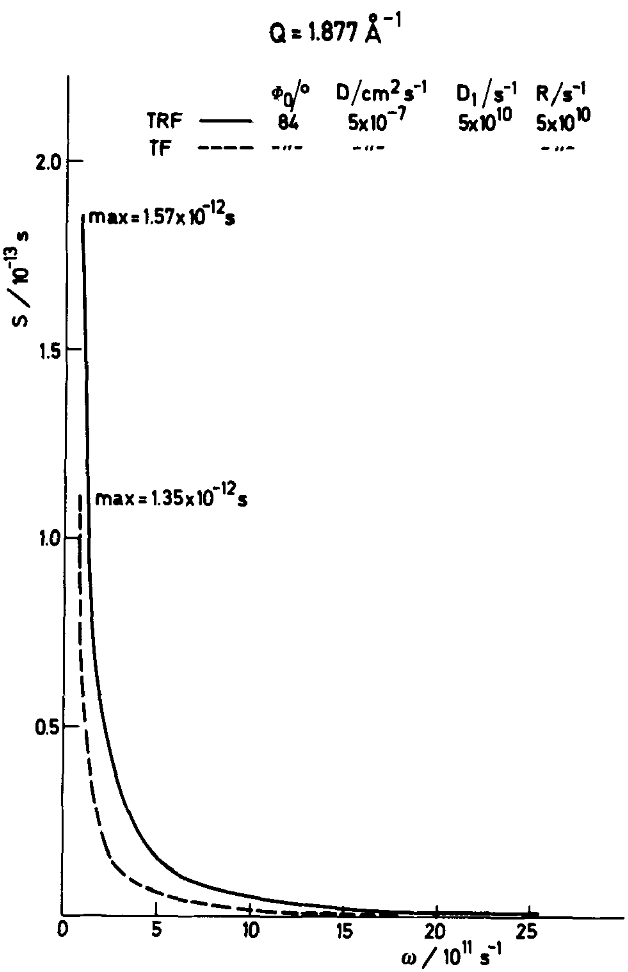


Figure 3. The TRF incoherent scattering function compared to the case when the uniaxial rotational diffusion is absent (TF motion).

It is to be recalled, (cf. equation (3)) that, due to the structure of the model conditional probability density, the orientational fluctuations are felt in two distinct ways, (cf. equation (19)): first, they appear in the coefficients $F_1(l, s, m_1, m_3)$ as a static, long time, behaviour and secondly, in the true dynamic behaviour which is hidden (admitedly in second order only) in the sum of lorentzians which are modulated by the static part of the conditional probability structure, as given by coefficients $F_2(l, s, m_1, m_3; r)$. Currently, the static features of the dynamical localized molecular motion effect as measured in high resolution quasi-elastic incoherent neutron scattering experiments in Grenoble [1–3, 5, 6, 10, 12], are obtained by investigating the elastic incoherent structure factor (EISF) [6] which is the ratio of the intensity of elastic scattering to the total intensity (i.e. elastic plus quasi-elastic). Basically, EISF offers an exceedingly sensitive means of studying the geometry of the bound motion and it is defined [6] by,

$$A_0(Q) = \langle \exp(i\mathbf{Q}\mathbf{r})\rangle\langle \exp(-i\mathbf{Q}\mathbf{r})\rangle, \tag{30}$$

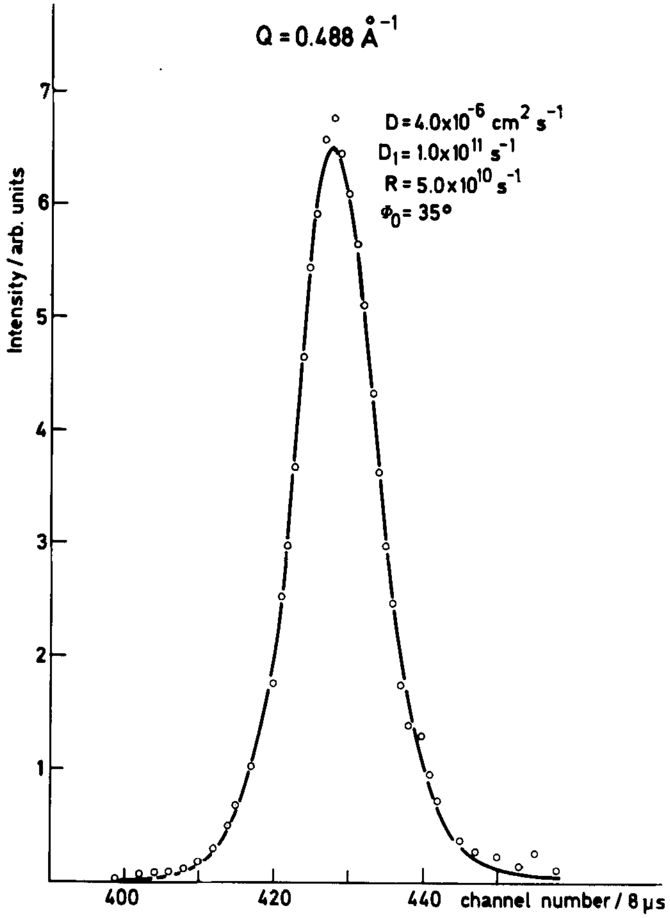


Figure 4. An example of fitting the TRF motion to the low Q measurement of incoherently scattered neutrons in the smectic A phase of an unoriented sample of PBH. The temperature of the sample is $T = 331$ K.

where **r** is the proton position vector at a given time as measured from the molecular centre of mass. On the basis of the assumptions and symmetry arguments leading to the derivation of equation (19), it can be easily shown, that equation (30) is transformed into

$$A_0(Q) = 16\pi^2 \sum_l \sum_s (-1)^s i^{1+s} j_1(Qr) j_s(Qr)\, Y_l^0(\Theta_Q \varphi_Q) Y_s^0(\Theta_Q \varphi_Q)$$
$$\times \langle P_1(\cos\beta_p)\rangle \langle P_s(\cos\beta_p)\rangle \langle P_l(\cos\beta)\rangle \langle P_s(\cos\beta)\rangle\, Y_l^0(\Theta,\varphi)\, Y_s^0(\Theta,\varphi), \quad (31)$$

where P_1 are legendre polynomials, $Y_l^0(\Theta,\varphi)$ refers to the body reference frame, $Y_l^0(\Theta_Q, \varphi_Q)$ to the laboratory frame, β_p is the angle between the preferred molecular axis and the uniaxial direction of the sample and β defines the instantaneous orientation of the molecular long axis with respect to its preferred direction (bisecting the apex angle ϕ_0), $(\Theta_Q \varphi_Q)$ are spherical coordinates of **Q** in the laboratory system and (Θ, φ) are the spherical coordinates of **r** in the body frame. As before, the sum $1 + s$ is even.

Taking the powder average of equation (31) over all orientations of the scattering vector **Q** gives

$$\overline{A_0(Q)} = \frac{1}{N} \sum_{v=0}^{N} \sum_{l=0} (2l + 1)[j_l(Qr_v) P_l(\cos\Theta_v)]^2 \langle P_l(\cos\beta_p)\rangle^2 U_l(\phi_0)^2. \quad (32)$$

where l goes over all integers, v over all N protons in the molecule, and $U_l(\phi_0)$ is defined as $(U_l(\phi_0) \equiv F_1(l, l, 0, 0)^{1/2}$, equation (18)),

$$U_l(\phi_0) = \left\langle P_l\left[\cos\left(\varphi - \frac{\phi_0}{2}\right)\right]\right\rangle. \tag{33}$$

The average is to be evaluated using the probability density function given by equation (3) for $t \to \infty$, [6], i.e.

$$P(\varphi/\varphi_0 t \to \infty) = \frac{1}{\phi_0}; \tag{34}$$

the values of the functions U_l for $l = 0$ to 10 is given Appendix B. The following is valid

$$U_l(\phi_0 = 0) \equiv 1 \tag{35}$$

for each l separately. In smectic A phases $\beta_p \equiv 0$ and so

$$\langle P_l(\cos\beta_p)\rangle \equiv 1 \tag{36}$$

but this is not necessarily true in nematic and other phases.

If there is no fluctuation of molecular long axes then $\phi_0 = 0$ and in the smectic A phase of an unoriented liquid crystal the isotropically averaged EISF is given by

$$\overline{A_0(Q)_{\mathrm{av}}} = \frac{1}{N}\sum_v \sum_l (2l+1)[j_l(Qr_v)P_l(\cos\Theta_v)]^2; \tag{37}$$

this is precisely equation (A 24) of [5], which describes the geometry of the molecular uniaxial motion only.

In figure 5 which is taken from [6], and represents the experimental EISF as a function of Q for powder DTBBA at 184°C in the smectic A phase (and using the molecular structural data given in [5]) the curve denoted a is therefore a common curve. Depending on the assumptions made in the analysis of the broadening of the sharp component of NQES spectra two sets of data for the experimental EISF are given and both are well placed along the calculated lines given by equation (32) using equation (36). For instance the circles correspond to the $\phi_0 = 96°$ and the squares to the apex angle $\phi_0 = 135°$. The fit is suprisingly good and thus the molecular long axes fluctuations in TBBA are independently confirmed with the present work.

The fact that Volino *et al.* [6] were able to analyse their EISF data with (among others) the molecular long axis orientational (static) distribution density given by equation (1), which is to be contrasted to our equation (32), is an illustration of the fact that the EISF approach offers information on the geometry of the molecular localized motion and this is, in both cases, the same. The details of the dynamical behaviour of the single molecule are obtained only when the calculated scattering law is compared to the full measured spectra but because the models usually contain a few unknown parameters this is seldom feasible.

Increasing the apex angle ϕ_0 to 180° the curve labelled b' is obtained, (cf. figure 5) and should be contrasted with b as presented in [6] and which presents the $l = 0$ term of equation (32) only (that is the EISF of a sphere). The difference in the calculated curves is marked but now the curve b' might correspond to still rapid orientational fluctuations (i.e. a large number of fast small angular steps in either

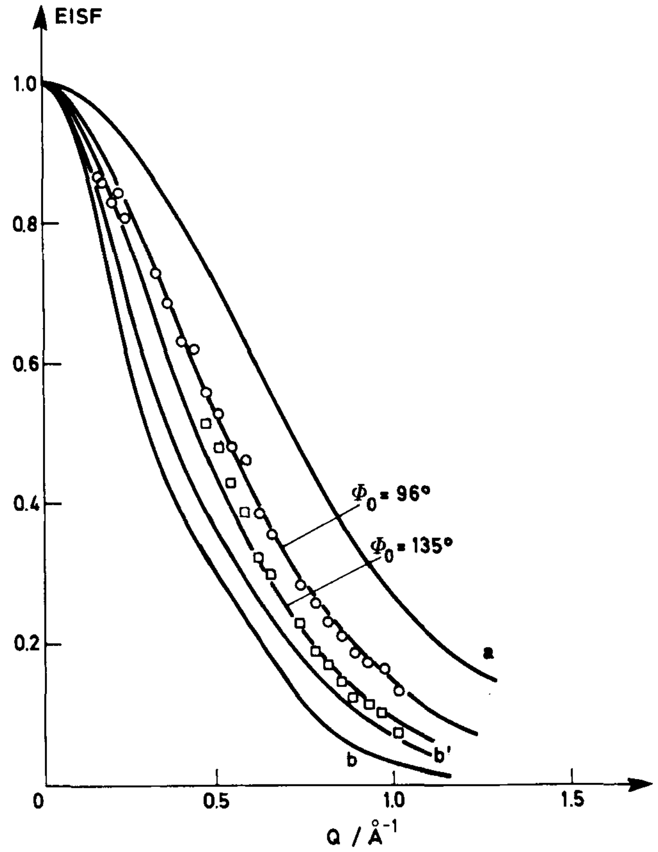


Figure 5. The experimental EISF as a function of Q for powder DTBBA at 184°C in the smectic A phase [6]. The curve labelled *a* corresponds to uniaxial rotational motion of perfectly parallel molecules in powder form, (cf. equation (37)). The lines through the experimental points [6], represent the molecular long axis small step stochastic symmetric random wall between two perfectly reflecting potential barriers with an angular apex angle $\phi_0 = 96°$ (circles) or $\phi_0 = 135°$ (squares) providing the molecular preferred axis is normal to the smectic planes of a powder sample. The line labelled *b'* corresponds to the potential barriers placed at 90° to each side of the uniaxial direction and so span an apex angle of 180°.

direction) meaning that the potential barriers are now both placed in a plane which is perpendicular to the uniaxial direction. The largest angular deviation available to a molecule (on either side) is in this case $\phi_0/2 = 90°$. Eventually, the molecule might change its orientation for π, but this is not a flipping motion.

There is also another observation worth making. No matter what the angular span, ϕ_0, available to the molecular long axis angular random motion, the frequency of this motion is related to the parameter R, (cf. equation (3)) and on the basis of the existence of molecular close packing (or not) alone, it does not necessarily follow that the axis fluctuations would expected to be slow. However, ϕ_0 is expected to be related somehow to the strength of cooperative effects, and this question is dealt with in a separate work [13]. From figure (5) it is evident, that long axis orientational fluctuations are inversly (non-linearly) related to the area under the EISF versus Q diagram, providing the molecular preferred axis remains fixed.

5. Conclusions

A stochastic model for the random walk of a particle between two perfectly reflecting barriers has served as a basis for the construction of a model of rapid, molecular orientational fluctuations in nematic and smectic A liquid crystals. The incoherent scattering functions for an unoriented specimen has been evaluated taking into account also the simple translational diffusional motion of the molecular centre of mass and the uniaxial rotational diffusion about the long axis, assuming these three motions are uncorrelated.

Calculations were fitted to the measured spectra for the smectic A phase of PBH and the predicted effect of long molecular axis orientation fluctuations, a second order effect to the incoherent scattering law, resulting from the rather coarse resolution of the spectrometer available, is not visible in the measurements.

The EISF describing the static features (i.e. geometry of the bound localized molecular motion) of the proposed dynamical model, have been utilized for the interpretation of the measured values in the smectic A phase of powder DTBBA as presented by Volino *et al.* [6] and long molecular axis stochastic orientational fluctuations between two perfectly reflecting potential barriers of the apex angle ϕ_0 of about 100° have been established independently in the smectic A phase of an unoriented DTBBA sample.

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Appendix A

The values of the coefficients $F_1(l, s, m', m_3)$ and $F_2(l, s, m', m_3; r)$, as defined by equation (18), are presented for $l = s = 0$, 1 and 2. Only independent coefficients are quoted, the rest can be obtained by utilizing the symmetry relations for the $d^l_{m'm}(\beta)$ coefficients

$$\begin{aligned} F_1(0,0,0,0) &= 1, & F_2(0,0,0,0;r) &= 0, \\ F_1(1,1,0,0) &= \frac{4\sin^2(\phi_0/2)}{\phi_0^2}, & F_2(1,1,0,0;r) &= \varepsilon^+ \frac{4\sin^2(\phi_0/2)}{\phi_0^2(1 - (\pi^2 r^2/\phi_0^2)^2}, \\ F_1(1,1,0,\pm 1) &= 0, & F_2(1,1,0,\pm 1;r) &= \varepsilon^- \frac{2\cos^2(\phi_0/2)}{\phi_0^2[1 - (\pi^2 r^2/\phi_0^2)]^2}, \end{aligned}$$

$$F_1(1,1,1,1) = \frac{[\phi_0 + 2\sin(\phi_0/2)]^2}{4\phi_0^2},$$

$$F_2(1,1,1,1;r) = \varepsilon^+ \frac{\sin^2(\phi_0/2)}{\phi_0^2[1 - (\pi^2 r^2/\phi_0^2)]^2},$$

$$F_1(2,0,0,0) = \frac{\phi_0 + 3\sin\phi_0}{4\phi_0},$$

$$F_2(2,0,0,0;r) = 0,$$

$$F_1(1,1,1,-1) = \frac{[\phi_0 - 2\sin(\phi_0/2)]^2}{4\phi_0^2},$$

$$
\begin{aligned}
F_2(1,1,1,-1;r) &= \varepsilon^+ \frac{\sin^2(\phi_0/2)}{\phi_0^2[1-(\pi^2r^2/\phi_0^2)]^2},\\
F_1(2,2,0,0) &= \frac{(\phi_0+3\sin\phi_0)^2}{16\phi_0^2},\\
F_2(2,2,0,0;r) &= \varepsilon^+ \frac{9\sin^2\phi_0}{\phi_0^2[4-(\pi^2r^2/\phi_0^2)]^2},\\
F_1(2,2,0,\pm 1) &= 0,\\
F_2(2,2,0,\pm 1;r) &= \varepsilon^- \frac{6\cos^2\phi_0}{\phi_0^2[4-(\pi^2r^2/\phi_0^2)]^2},\\
F_1(2,2,0,\pm 2) &= \frac{3(\phi_0-\sin\phi_0)^2}{32\phi_0^2},\\
F_2(2,2,0,\pm 2;r) &= \varepsilon^+ \frac{3\sin^2\phi_0}{2\phi_0^2[4-(\pi^2r^2/\phi_0^2)]^2},\\
F_1(2,2,-1,1) &= \frac{[\sin\phi_0-2\sin(\phi_0/2)]^2}{4\phi_0^2},\\
F_2(2,2,-1,1;r) &= \frac{\varepsilon^+}{\phi_0^2}\left\{\frac{\sin(\phi_0/2)}{1-(\pi^2r^2/\phi_0^2)}-\frac{2\sin\phi_0}{4-(\pi^2r^2/\phi_0^2)}\right\}^2,\\
F_1(2,2,1,2) &= 0,\\
F_2(2,2,1,2;r) &= \frac{\varepsilon^-}{\phi_0^2}\left\{\frac{\cos(\phi_0/2)}{1-(\pi^2r^2/\phi_0^2)}+\frac{\cos\phi_0}{4-(\pi^2r^2/\phi_0^2)}\right\}^2,\\
F_1(2,2,1,1) &= \frac{[\sin\phi_0+2\sin(\phi_0/2]^2}{4\phi_0^2},\\
F_2(2,2,1,1;r) &= \frac{\varepsilon^+}{\phi_0^2}\left\{\frac{\sin(\phi_0/2)}{1-(\pi^2r^2/\phi_0^2)}+\frac{2\sin\phi_0}{4-(\pi^2r^2/\phi_0^2)}\right\}^2,\\
F_1(2,2,-2,1) &= 0,\\
F_2(2,2,-2,1;r) &= \frac{\varepsilon^-}{\phi_0^2}\left\{\frac{\cos(\phi_0/2)}{1-(\pi^2r^2/\phi_0^2)}-\frac{\cos\phi_0}{4-(\pi^2r^2/\phi_0^2)}\right\}^2,\\
F_1(2,2,2,2) &= \frac{[\frac{3}{2}\phi_0+\frac{1}{2}\sin\phi_0+4\sin[\phi_0/2)]^2}{16\phi_0^2},\\
F_2(2,2,2,2;r) &= \frac{\varepsilon^+}{4\phi_0^2}\left\{\frac{2\sin(\phi_0/2)}{1-(\pi^2r^2/\phi_0^2)}+\frac{\sin\phi_0}{4-(\pi^2r^2/\phi_0^2)}\right\}^2,\\
F_1(2,2,2,-2) &= \frac{[\frac{3}{2}\phi_0+\frac{1}{2}\sin\phi_0-4\sin(\phi_0/2)]^2}{16\phi_0^2},\\
F_2(2,2,2,-2;r) &= \frac{\varepsilon^+}{4\phi_0^2}\left\{\frac{2\sin(\phi_0/2)}{1-(\pi^2r^2/\phi_0^2)}-\frac{\sin\phi_0}{4-(\pi^2r^2/\phi_0^2)}\right\}^2,
\end{aligned}
$$

where

$$\varepsilon^\pm = 1 \pm (-1)^r.$$

Appendix B

Denoting $\phi_0/2$ by u the functions

$$U_l(u) = \frac{1}{2u}\int_0^{2u} P_l[\cos(\varphi - u)]\, d\varphi,$$

are given by ($U_l(u) \equiv F_l(l, l, 0, 0)^{1/2}$)

$$\begin{aligned}
U_0(u) &= 1,\\
U_1(u) &= j_0(u),\\
U_2(u) &= \tfrac{3}{4}[j_0(2u) + \tfrac{1}{3}],\\
U_3(u) &= \tfrac{5}{8}[j_0(3u) + \tfrac{3}{5}j_0(u)],\\
U_4(u) &= \tfrac{35}{64}[j_0(4u) + \tfrac{4}{7}j_0(2u) + \tfrac{9}{35}],\\
U_5(u) &= \tfrac{63}{128}[j_0(5u) + \tfrac{5}{9}j_0(3u) + \tfrac{10}{21}j_0(u)],\\
U_6(u) &= \tfrac{231}{512}[j_0(6u) + \tfrac{6}{11}j_0(4u) + \tfrac{5}{11}j_0(2u) + \tfrac{50}{231}],\\
U_7(u) &= \tfrac{429}{1024}[j_0(7u) + \tfrac{7}{13}j_0(5u) + \tfrac{63}{143}(3u) + \tfrac{175}{429}j_0(u)],\\
U_8(u) &= \tfrac{6435}{16384}[j_0(8u) + \tfrac{8}{15}j_0(6u) + \tfrac{28}{65}j_0(4u) + \tfrac{56}{143}j_0(2u) + \tfrac{245}{1287}],\\
U_9(u) &= \tfrac{12155}{32768}[j_0(9u) + \tfrac{9}{17}j_0(7u) + \tfrac{36}{85}j_0(5u) + \tfrac{84}{221}j_0(3u) + \tfrac{882}{2431}j_0(u)],\\
U_{10}(u) &= \tfrac{692835}{1966080}[j_0(10u) + \tfrac{10}{19}j_0(8u) + \tfrac{135}{323}j_0(6u) + \tfrac{120}{323}j_0(4u) + \tfrac{1470}{4199}j_0(2u) + \tfrac{23814}{138567}]
\end{aligned}$$

and $j_0(x)$, the spherical Bessel function of the order 0, is defined by

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

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