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MOLECULAR TRANSLATION — ROTATIONAL COUPLING CONTRIBUTION TO NEUTRON INCIDENT LINE BROADENING IN NEMATIC LIQUID CRYSTALS (*)

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Résumé. — On examine la contribution du couplage translation-rotation à l’élargissement du pic quasi élastique obtenu par diffusion de neutrons sur une phase nématic orientée. On suppose que les molécules, approximées par des ellipsoïdes, sont animées d’un mouvement de self-diffusion et d’un mouvement de rotation diffusionnelle autour de leur grand axe. On montre que la loi de diffusion pour le centre de masse dépend de l’amplitude du terme \( Q_4(\Delta D_{\text{body}})^2/R^2 \) où \( Q_4 \) est la composante du moment de transfert neutronique perpendiculaire à l’axe optique, \( \Delta D_{\text{body}} \) est la différence entre les coefficients de self-diffusion le long des grands et des petits axes, et \( R \) est le coefficient de diffusion rotationnelle autour du grand axe. La loi de diffusion pour le centre de masse est représentée par une seule lorentzienne ou par une somme de lorentziennes. Le premier cas, l’approximation rotation faiblement empêchée est applicable. On suggère que, pour le PAA, la dépendance avec la température des constantes de self-diffusion \( D_1 \) et \( D_2 \) (\( \parallel \) et \( \perp \) à l’axe optique) pourrait être gouvernée par la dépendance avec la température du paramètre d’ordre.

Abstract. — The component of the neutron quasi elastic line broadening in the oriented nematic phase, originating from the translation-rotational molecular coupling, is investigated. The molecules, approximated by ellipsoïdes, are assumed to undergo simple diffusion and a rotational Brownian motion along the long body axes. It is shown that in the nematic phase the translation, as modulated by the rotation, leads to the neutron scattering cross section for the center of mass motion which depends upon the relative magnitude of the term \( Q_4(\Delta D_{\text{body}})^2/R^2 \). Here, \( Q_4 \) is the component of neutron scattering vector perpendicular to the optical axis, \( \Delta D_{\text{body}} \) is the difference of molecular self diffusion constants along the short and the intermediate body axes and \( R \) is the rotational diffusion coefficient along the long molecular axis. The center of mass neutron scattering cross section is represented by a single Lorentzian or by the sum of Lorentzian terms. In the former case the weak hindering approximation is applicable in this phase. It is suggested that for PAA, the temperature dependence of the laboratory self diffusion constants \( D_1 \) and \( D_2 \) (\( \parallel \) and \( \perp \) to the optical axis) might be governed by the temperature dependence of the order parameter.

1. Introduction. — Since, when viewed on the molecular basis, the liquid crystalline properties are relatively still poorly understood, much attention has also been given to the measurements of the self diffusion coefficients in nematic systems [1] recently. Well suited for this purpose is, among the other methods, cold neutron scattering spectroscopy. In the interpretation of the experimental results, however, great care is in order as it is an established fact that they are sensitive to the various types of motion which the scatterer is undergoing, so that a high resolution experiment at small momentum transfers is to be performed [1]. The translational self diffusion constant, \( D_1 \), is traditionally evaluated from the full-width at the half height, \( \omega_{1/2} \), of the measured quasi elastic line,

\[
\omega_{1/2} = 2DQ^2
\]

where \( Q \) is the neutron scattering vector \( Q = k_0 - k \), and \( k_0(k) \) is the wave number of the ingoing (scattered)
neutrons. This is the well known Vineyard's result [2], based on the calculation of the self diffusion distribution $G_s(r, t)$ which follows the diffusion equation,

$$\frac{\partial G_s}{\partial t} = D \nabla^2 G_s,$$

(2)

hence the problem being equivalent to the study of Brownian motion of spherical particle in a fluid. $G_s(r, t)$ satisfying the conditions,

$$G_s(r, O) = \delta(r)$$

$$G_s(r, t) = G_s(r, -t)$$

(3)

is given by,

$$G_s(r, t) = \left( 4 \pi D |t| \right)^{-3/2} e^{-r^2 / 4Dt}$$

(4)

and since the double incoherent scattering cross section (limiting ourselves to protons only) is proportional to the space-time Fourier transform of $G_s$,

$$\frac{d^2 \sigma_{inc}}{d\Omega dw} \propto \hat{f}[G_s(r, t)] = \frac{2 DQ^2}{(DQ^2)^2 + \omega^2}$$

(5)

it is described by a single Lorentzian line, with the fullwidth at the half height given by the eq. (1). Here,

$$\omega = \left( k_0^2 - k^2 \right) / 2 \hbar m$$

(6)

$m$ being the neutron mass.

The eq. (5) has been originally derived for the monotonic simple liquid. Sears [3], has shown that for molecular liquids the scattering cross section can be expressed as a partial wave expansion, which involves scattering functions for both the translational and rotational motion (the spatial Fourier transform of Sears's incoherent intermediate scattering function for the translational, i.e. center of mass, motion of the molecule). The basic assumption in his derivation is a weak hindering approximation which in effect neglects the statistical correlations between the translational and the rotational motion, thus being perfectly valid only if the molecules are spherical in shape.

Perrin [4] has shown that the translational motion of a nonspherical molecule is strongly dependent on the type of a rotational motion present (the reverse is not true, however).

While it was derived under the assumption of a spherical molecule undergoing Brownian motion in an isotropic liquid, eq. (1) has been utilized also in the interpretation of data obtained from liquid crystals. These are known to be anisotropic and to consist generally of the elongated molecules of approximate length of the order of 20 Å.

In view of the observations above, it would be instructive to get the information that, given the rotation, how it will manifest itself on the translation and, therefore on the measured diffusion coefficient. Hence, what is the effect of rotation modulated translational contribution to the quasi elastic neutron broadening in nematics. In this paper an attempt to obtain a quantitative information in this direction is presented. The following treatment is applicable to the neutron scattering investigation of an oriented nematic liquid crystalline sample, however as presented, it deals with only one component of the quasi elastic line broadening. The treatment does not touch upon these contributions to the quasi elastic line which originate from various types of motion about the molecular center of mass and which are undoubtedly present therein [5]. We have calculated, assuming rigid ellipsoidal molecules, the effect of the translation-rotational coupling on the broadening of the incident neutron line in the nematic phase. It is shown that this effect, which is commonly neglected, can be indeed small under appropriate conditions. This being the case, the weak hindering approximation can be taken to be valid even for liquid crystalline molecules in the nematic phase.

Rosciszewski [6], has extended eq. (2) to include the effect of the translational anisotropy occurring in liquid crystals, neglecting the effect of the rotation upon the molecular translation.

2. Center of mass self-correlation function calculation for the nematic phase. — Perrin [4], has developed a theory of a rotational Brownian motion of an ellipsoid, which has been applied by Woessner [7] to the calculation of the nuclear spin relaxation times of two spins in an ellipsoid.

The expression for the time partial derivative of the translational probability density of the rigid ellipsoidal molecule in terms of translational diffusion coefficients in the body coordinate system (denoted by $\xi$, $\eta$, $\zeta$; $\zeta$ points along the long molecular axis) is given by,

$$\frac{\partial w}{\partial t} = D_\xi \frac{\partial^2 w}{\partial \xi^2} + D_\eta \frac{\partial^2 w}{\partial \eta^2} + D_\zeta \frac{\partial^2 w}{\partial \zeta^2}$$

(7)

$D_\xi$, $D_\eta$, $D_\zeta$ are the body translational diffusion coefficients and are inversely proportional to the coefficients of friction $f_i$ for this type of motion in the corresponding direction, i.e.,

$$D_i = \frac{k_B T}{f_i} i = \xi, \eta, \zeta$$

For an ellipsoid they have been calculated by Perrin [4].

Following Vineyard [2] the translational probability density, $w$, can be, in the first approximation, identified with the Van Hove self correlation function for the center of mass molecular motion. The quasi elastic line broadening will be calculated for the uniaxial nematic liquid crystal, considering rotationally modulated translational molecular motion. The molecules are assumed to be executing continuous small step angular diffusion around their body axes.
in such a way that \( R_1 \) and \( R_2 \) are negligible in comparison to \( R_3 \), where \( R_3 \) represents the rotation diffusion constant around the long molecular axis. It has been experimentally observed [8, 9] that the molecules in the nematic phase rotate around their long molecular axis. In what follows, the position-orientation correlations between the molecules are ignored.

Transforming the eq. (7) to the laboratory system \( x, y, z \) the corresponding diffusion equation governing the behaviour of the space-time correlation function \( G_s \) is written as

\[
\frac{\partial^2 G_s}{\partial t^2} = \sum_{i=1}^{3} \sum_{j=1}^{3} d_{ij} \frac{\partial^2 G_s}{\partial x_i \partial x_j}.
\]  

The transformation between the body and the space axes is given by Euler's angles [10] in terms of which the time dependent coefficients are given by

\[
\begin{align*}
&d_{xx} = D_x g_{11}^2 + D_y g_{12}^2 + D_z g_{13}^2 \\
&d_{yy} = D_x g_{21}^2 + D_y g_{22}^2 + D_z g_{23}^2 \\
&d_{zz} = D_x g_{31}^2 + D_y g_{32}^2 + D_z g_{33}^2 \\
&d_{yx} = D_x g_{11} g_{22} + D_y g_{12} g_{23} + D_z g_{13} g_{23} = d_{xy} \\
&d_{zx} = D_x g_{11} g_{32} + D_y g_{12} g_{33} + D_z g_{13} g_{33} = d_{xz} \\
&d_{zy} = D_x g_{11} g_{23} + D_y g_{12} g_{23} + D_z g_{13} g_{23} = d_{yz}
\end{align*}
\]  

(9)

and \( g_{ij} \) are the elements of the transformation matrix from the body to the laboratory system, i.e.,

\[
\begin{align*}
g_{11} &= \cos \psi \cos \varphi - \cos \Theta \sin \varphi \sin \psi \\
g_{12} &= - \sin \psi \cos \varphi - \cos \Theta \sin \varphi \cos \psi \\
g_{13} &= \sin \Theta \sin \varphi
\end{align*}
\]

(10)

etc.

The time dependency of the coefficients \( d_{ij} \) is caused by the rotational motion of the molecule and in order to obtain their explicit dependence on time, we assume that

\[
D_{ij}(t) \equiv \langle d_{ij} \rangle = \int d\Omega W_{rot}(\Omega, t) w_{orient}(\Theta) \ d\Omega
\]  

(11)

i.e., the time dependence of the coefficients is given by the ensemble average. Here \( w_{orient}(\Theta) \) represents the well known Maier-Saupe orientational distribution density function

\[
w_{orient}(\Theta) = \frac{\exp \left( \frac{V_0 S}{2 k_B T} (3 \cos^2 \Theta - 1) \right)}{\int_{-1}^{1} \exp \left( \frac{V_0 S}{2 k_B T} (3 \cos^2 \Theta - 1) \right) \sin \Theta \ d\Theta}
\]  

(12)

where \( S \) is the usual orientational order parameter which describes the average alignment of the molecules parallel to the preferred axis \( S = \langle \frac{1}{2} \cos^2 \Theta - \frac{1}{2} \rangle \) and is the fundamental equation of the Maier-Saupe molecular theory of the nematic phase.

\( W_{rot}(\Theta, t) \) is the orientational probability density of the molecule undergoing the Brownian rotation. For the ellipsoid it has been calculated by Perrin [4]. In the case of the rotational ellipsoid when \( R_1 = R_2 \), \( W_{rot} \) satisfies the following equation

\[
R_1 \left( \frac{\partial^2 W}{\partial \Theta^2} + \cot \Theta \frac{\partial W}{\partial \Theta} \right) + \left( R_1 \frac{1 - \cos \Theta}{1 + \cos \Theta} + R_3 \right) \times \frac{\partial^2 W}{\partial v^2} = \frac{\partial W}{\partial t}
\]  

(13)

where

\[
v = \phi + \psi.
\]

Since due to the symmetry of the problem

\[
W(\Theta, v, t) = W(\Theta, -v, t)
\]  

(14)

and with the initial condition

\[
W_{rot}(\Theta, v, 0) \sin \Theta \ d\Theta \ dv = 1
\]  

(15)

the solution of the eq. (11) is then given by [4]

\[
W_{rot}(\Theta, v, t) = \sum_{m=0}^{\infty} d_m \cos m v \cos^2 \Theta e^{-m(R_1 + mR_2) t} \times \\
\sum_{n=0}^{\infty} (2n + 2m + 1) R_{nm}(\cos \Theta) e^{-n(n+2m+1)R_1 t}
\]  

(16)

and

\[
d_0 = 1, \quad d_m = 2 \ \text{for} \ m \neq 0
\]  

(17)

where

\[
R_{nm}(u) = F \left( n + 2m + 1, -n, 1, \frac{1-u}{2} \right)
\]  

(18)

and \( F \) denotes the hypergeometric function. The following is valid (\( u = \cos \Theta \)),

\[
R_{cm}(u) = 1
\]  

(19)

\[
P_n(u) = \text{Legendre polynomial of the order } n
\]

Since the rotational motion occurs almost exclusively around the long molecular axis, the exponentials with the terms involving \( R_1 \) can be put 1. Inserting in the above sense modified eq. (16) into the eq. (11) and in view of the uniaxial symmetry of a nematic liquid crystal (the z-axis is the preferred-optical
axis) the ensemble average over the angle \( \nu \) are readily evaluated. The nonzero terms are:

\[
\langle g_{11}^2 \cos \nu \rangle = \frac{1}{4} \left(1 + \cos^2 \Theta \right) \delta_{m,0} + \delta_{m,2} \cos^2 \frac{\Theta}{2}
\]

\[
\langle g_{12}^2 \cos \nu \rangle = \frac{1}{4} \left(1 + \cos^2 \Theta \right) \delta_{m,0} - \delta_{m,2} \cos^2 \frac{\Theta}{2}
\]

\[
\langle g_{13}^2 \cos \nu \rangle = \frac{1}{2} \sin^2 \Theta \delta_{m,0}
\]

\[
\langle g_{22}^2 \cos \nu \rangle = g_{21}^2 \langle g_{12}^2 \rangle
\]

\[
\langle g_{23}^2 \cos \nu \rangle = g_{21}^2 \langle g_{13}^2 \rangle
\]

\[
\langle g_{33}^2 \cos \nu \rangle = \langle g_{31}^2 \cos \nu \rangle = \langle g_{32}^2 \cos \nu \rangle = g_{31}^2 \langle g_{13}^2 \rangle.
\]

Hence, the time dependence of the coefficients \( d_{ij} \) is given by

\[
D_{xx}(t) = A + B e^{-4R_3 t} + C,
\]

\[
D_{yy}(t) = A - B e^{-4R_3 t},
\]

\[
D_{zz}(t) = C.
\]

where

\[
A = \sum_{n=0}^{\infty} (2n+1) \left( \frac{D_{\xi} + D_{\eta}}{4} (1 + \cos^2 \Theta) + \frac{D_{z} \sin^2 \Theta}{2} \right) P_n(\cos \Theta)
\]

\[
B = \sum_{n=0}^{\infty} \frac{2n+5}{4} (D_{\xi} - D_{\eta}) \times \left( \cos^2 \frac{\Theta}{2} \cdot R_{n2}(\cos \Theta) \right)
\]

\[
C = \sum_{n=0}^{\infty} (2n+1) \left( \frac{D_{\xi} + D_{\eta}}{2} \sin^2 \Theta + \frac{D_{z} \cos^2 \Theta}{2} \right) P_n(\cos \Theta).
\]

The fundamental solution of the eq. (23) yields the central result of the calculation, which is

\[
\mathcal{J}[G_\delta(r, \theta)] = 2 e^{-r} \sum_{j=0}^{\infty} \frac{f^j}{j!} \left( \frac{A Q_1^2 + C Q_2^2 + 4 R_3 f}{(A Q_1^2 + C Q_2^2 + 4 R_3 f)^2 + \omega^2} \right) + Q_3^2 + Q_4^2.
\]

i.e., the scattering cross section is given by the sum of Lorentzian terms. Here,

\[
Q_3 = Q_x^2 + Q_y^2 + Q_z^2 = Q_1^2 + Q_2^2
\]

\( Q_3 \) and \( Q_4 \) are the components of \( Q \) parallel and perpendicular to the uniaxial nematic direction.

3. Discussion. — In order to check the result given by the eq. (25) take the spherical molecule for which \( D_{\xi} = D_{\eta} = D \). Then \( A = C = D \) and \( B = 0 \) and the eq. (25) reduces to the original Vineyard's result

\[
\mathcal{J}[G_\delta(r, \theta)] = -\frac{2 D Q_3^2}{(D Q_3^2 + \omega^2)}.
\]

For the case when the translational diffusion constants along the \( \xi \) and \( \eta \) directions are equal (prolate spheroid), \( f = 0 \), and only the first term in the expansion survives

\[
\mathcal{J}[G_\delta(r, \theta)] = \frac{2(A Q_1^2 + C Q_2^2)}{(A Q_1^2 + C Q_2^2)^2 + \omega^2}
\]

and the width of the spectra, a single Lorentzian, is independent of the rotational motion. The full-width at the half-maximum is

\[
\omega_{1/2} = 2(A Q_1^2 + C Q_2^2).
\]

Since the positional molecular distribution function in an oriented nematic liquid crystal is cylindrically symmetric, the laboratory scattering cross section is an average over the orientation of the components of the scattering vector in the \( x-y \) plane. Expanding the exponential and neglecting the terms of the second and higher orders in the expansion as well as in the sum of the eq. (25), the following is obtained:

\[
\frac{d^2 \sigma_{\text{inc}}}{d \Omega d \omega} \propto \frac{A Q_1^2 + C Q_2^2}{(A Q_1^2 + C Q_2^2)^2 + \omega^2} - \frac{Q_3^2 B^2}{32 R_3^4} \left[ \frac{A Q_1^2 + C Q_2^2 + 4 R_3^2}{(A Q_1^2 + C Q_2^2 + 4 R_3^2)^2 + \omega^2} \right] + \cdots
\]

Töpler et al. [1], have, for the nematic PAA, estimated \( R_3 \) to be of the order of \( 10^{10} \) s\(^{-1} \) and if we assume
$D_\zeta - D_\eta$ to be of the order of 10^{-6} cm²/s, then for their experiment (taking $Q_1 = 0.3 \text{ Å}^{-1}$) the expression $Q_1^2(D_\zeta - D_\eta)²/32 R_3^2 = 2.5 \times 10^{-4}$. The second term can be clearly neglected, what means that the weak hindering approximation is valid also in the present case. The width at the half maximum is given by the eq. (28). However, if we assume for the illustration purpose, $R_3 = 10^9 \text{ s}^{-1}$ and take $Q_1 = 1 \text{ Å}^{-1}$, than the above factor takes the value of 3, thus meaning that this approximation is invalid.

If the rotation does not modulate the translation to any appreciably extent ($R_3 \gg B Q_2$), then one can identify the laboratory $D_\parallel$ and $D_\perp$

$$D_\parallel = a + 2 b S$$
$$D_\perp = a - b S$$

(30)

where

$$a \equiv (D_\zeta + D_\eta + D_\varphi)/3 \quad b \equiv [D_\zeta - 2(D_\eta + D_\varphi)]/3.$$  

The condition $R_3 \gg B Q_2$ means that the rotation about the long molecular axis is greater than the contribution of the anisotropy. The above equation is also obtained if one takes the isotropic average of the coefficients $d_{ij}$, eq. (11), over the Euler’s angles $\psi$ and $\varphi$. This procedure is therefore equivalent to the averaging in the limit $R_3 \gg B Q_2$, respectively.

$D_\varphi$, $D_\eta$, and $D_\zeta$ are for an ellipsoidal molecule proportional to $T/\eta$, $\eta$ being the viscosity coefficient. For PAA it may be roughly taken to decrease linearly with temperature [11] (except at the vicinity of the transition point where it shows a discontinuity). The temperature dependence of the $D_\parallel$ and $D_\perp$ for a PAA molecule, would then be governed by the temperature variation of the order parameter $S$, and would show the opposite temperature effect. In order to test this hypothesis, a high resolution, low $Q$ experiment similar to the one performed by Töpler et al. [1] would be required.

4. Conclusions. — The neutron scattering cross section for the center of mass motion of an ellipsoidal molecule undergoing the simple translational diffusion and a rotational Brownian motion around its long axis in the nematic phase, has been calculated. The contributions to the quasi elastic peak arising from motions with respect to the molecular center of mass have not been considered. It is shown, that depending upon the relative magnitude of the term $Q_1^2(D_\zeta - D_\eta)²/32 R_3^2$ the translation may be or may not be modulated by the rotation. In the former case the scattering cross section for the center of mass motion is given by a sum of Lorentzian terms. In the latter case the weak hindering approximation is valid also for nonspherical liquid crystalline molecules in the nematic phase, i.e., the translational and the rotational motion can be taken to be effectively uncoupled in this phase.

References


