

INCOHERENT CROSS-SECTION FOR NEUTRON QUASI-ELASTIC SCATTERING IN A LIQUID CRYSTAL

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(Received July 23, 1971; Revised paper received November 11, 1971)

The incoherent cross-section for neutron quasi-elastic scattering in a liquid crystal is calculated. The cross-section depends on the orientation of the momentum transfer vector with respect to the nematic axis. The models used correspond in the case of isotropy to the diffusion model of Vineyard and to the Singwi-Sjölander model developed by Larsson *et al.*

1. Introduction

There are many approaches to the theory of neutron scattering by atomic or molecular liquids. One of them is to formulate a precise quantum theory, based on the formalism of the correlation functions which in turn are calculated from basic principles [4].

Another approach is a more phenomenological one. A number of such models exist. The simplest one is the Vineyard's model [6]. Another model, a more sophisticated one, is Singwi-Sjölander model [5]. The Singwi-Sjölander theory has been applied to the liquids composed of simple and small molecules (for example H_2O). A generalization to all other isotropic molecular liquids was made by Larsson and Bergstedt [2] and Larsson *et al.* [3].

The present paper deals with the case of anisotropy in liquids. A few months ago the first neutron measurement of anisotropy of the self-diffusion in paraazoxyanisol (PAA) was performed by Janik *et al.* [1]. The aim of this work is to describe and explain the results of measurements of the anisotropic self-diffusion coefficient.

2. The generalized Vineyard model

Van Hove has shown that the incoherent differential scattering cross-section per atom per unit solid angle Ω and per unit energy $\hbar\omega$ is given by the self-correlation function:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{a^2}{2\pi} \frac{k}{k_0} \iint \exp i(\mathbf{kr} - \omega t) G_s(\mathbf{r}, t) d\mathbf{r} dt \quad (1)$$

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where $\hbar\kappa$ is the momentum transferred to the scatterer by neutrons and a the incoherent scattering length for protons in the molecule. Other atoms may be neglected.

The self-correlation function G_s is defined as follows:

$$G_s(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i|1}^N \int d\mathbf{r}' \delta(\mathbf{r} + \mathbf{r}_i - \mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}_i(t)) \right\rangle \quad (2)$$

where $\mathbf{r}_i(t)$ is position of the i -th proton.

Vineyard suggested the computation of G_s for isotropic liquid with the aid of the diffusion equation:

$$D\nabla^2 G_s(\mathbf{r}, t) = - \frac{\partial}{\partial t} G_s(\mathbf{r}, t) \quad (3)$$

where D is the self-diffusion coefficient. Equation (3) may be written in the alternative form:

$$\oint\!\!\!\int D\nabla G_s dS = - \frac{\partial}{\partial t} \int G_s dV. \quad (4)$$

The current of G_s is $\mathbf{J} = D\nabla G_s$.

In the case of anisotropic diffusion occurring in liquid crystals, we assume that the current takes the form:

$$\mathbf{J}^\alpha = D^{\alpha\beta} \partial_\beta G_s. \quad (5)$$

We use the tensor notation but do not distinguish between contra and covariant tensors. The symmetry of the liquid crystal requires certain conditions to be satisfied. Let us assume that the nematic axis is parallel to the z axis. Then the z component of current \mathbf{J} is described by the parallel component of the diffusion coefficient:

$$J^z = D_{||} \partial_z G_s. \quad (6)$$

The x and y components of \mathbf{J} are described by the normal component of the diffusion coefficient:

$$J^x = D_{\perp} \partial_x G_s; \quad J^y = D_{\perp} \partial_y G_s. \quad (7)$$

In a chosen coordinate system the tensor $D^{\alpha\beta}$ is diagonal:

$$[D^{\alpha\beta}] = \begin{bmatrix} D_{\perp} & 0 \\ 0 & D_{||} \end{bmatrix}. \quad (8)$$

In other coordinate systems the following relations are fulfilled:

$$|\mathbf{J} \cdot \mathbf{n}| = \left| D_{||} \frac{\partial G_s}{\partial \mathbf{n}} \right|; \quad |\mathbf{J} \cdot \mathbf{m}| = \left| D_{\perp} \frac{\partial G_s}{\partial \mathbf{m}} \right| \quad (9)$$

where \mathbf{n} is a unit vector parallel to the nematic axis and \mathbf{m} is a unit vector normal to the nematic axis (this axis is present in the crystal in the presence of a strong electric or magnetic field).

In the lowest approximation $D^{\alpha\beta}$ is independent of κ and ω . Now we obtain the equation of the anisotropic diffusion and the initial condition which follows from (2):

$$D^{\alpha\beta} \partial_\alpha \partial_\beta G_s = - \frac{\partial}{\partial t} G_s; \quad G_s(\mathbf{r}, 0) = \delta(\mathbf{r}). \quad (10)$$

We define the function:

$$F_s(\kappa, t) = \int d\mathbf{r} \exp(i\kappa\mathbf{r}) G_s(\mathbf{r}, t). \quad (11)$$

and the self-correlation function of Van Hove:

$$S_s(\kappa, \omega) = (2\pi)^{-1} \int dt \exp(-i\omega t) F_s(\kappa, t). \quad (12)$$

Equation (10) may be written in the form:

$$\frac{\partial}{\partial t} F_s = D^{\alpha\beta} \kappa_\alpha \kappa_\beta F_s. \quad (13)$$

The solution is given by:

$$F_s(\kappa, t) = \exp\{-D^{\alpha\beta} \kappa_\alpha \kappa_\beta |t|\} \\ S_s(\kappa, \omega) = \frac{1}{\pi} \frac{D^{\alpha\beta} \kappa_\alpha \kappa_\beta}{(D^{\alpha\beta} \kappa_\alpha \kappa_\beta)^2 + \omega^2}. \quad (14)$$

In the case of isotropic liquid $D_{||} = D_{\perp} = D$ and expressions (14) take the form of Vineyard [6]:

$$S_s(\kappa, \omega)_{iz} = \frac{1}{\pi} \frac{D\kappa^2}{(D\kappa^2)^2 + \omega^2}. \quad (14')$$

It follows from the investigation of scattering with the momentum transfer vector parallel to the z axis (the nematic axis) that:

$$S_s(\kappa_z, \omega) = \frac{1}{\pi} \frac{D_{||}\kappa_z^2}{(D_{||}\kappa_z^2)^2 + \omega^2} = \frac{1}{\pi} \frac{D_{||}\kappa^2}{(D_{||}\kappa^2)^2 + \omega^2}. \quad (15)$$

For the momentum transfer vector normal to the z axis we obtain:

$$S_s((\kappa_x, \kappa_y, 0), \omega) = \frac{1}{\pi} \frac{D_{\perp}\kappa^2}{(D_{\perp}\kappa^2)^2 + \omega^2}. \quad (16)$$

Let us consider the case without any field orienting the nematic axis. The liquid crystal is then divided into small domains with the nematic axis randomly oriented in space. The incoherent cross-section is described by the function \bar{S}_s ; i.e. the mean value

of S_s with respect to the orientation of κ . Introducing the spherical coordinate system in κ space we obtain the expression for \bar{S}_s :

$$\bar{S}_s(\kappa, \omega) = \pi^{-1} \int \frac{\kappa^2 \{D_{||} \cos^2 \vartheta + D_{\perp} \sin^2 \vartheta\}}{\kappa^4 \{D_{||} \cos^2 \vartheta + D_{\perp} \sin^2 \vartheta\}^2 + \omega^2} \times \frac{d(\cos \vartheta) d\varphi}{4\pi} \quad (17)$$

where

$$D^{\alpha\beta} \kappa_\alpha \kappa_\beta = \kappa^2 \{D_{||} \cos^2 \vartheta + D_{\perp} \sin^2 \vartheta\}; \quad \begin{cases} \kappa_x = \kappa \cos \varphi \sin \vartheta \\ \kappa_y = \kappa \sin \varphi \sin \vartheta \\ \kappa_z = \kappa \cos \vartheta \end{cases} \quad (18)$$

The integral (17) can be calculated exactly, but the resulting expression is too complicated. For this reason we shall fit the shape of \bar{S}_s by means of a Vineyard-like curve. Thus in order to obtain certain results the approximation should be used as follows: the solution of the equation of isotropic diffusion is taken and for $\omega = 0$, D is computed from the comparison of S_s and \bar{S}_s

$$S_s(\kappa, 0)_{iz} = \bar{S}_s(\kappa, 0). \quad (19)$$

It is simple to solve the integral (17) if $\omega = 0$ and the parameter D is obtained in the following form:

$$D = \sqrt{AD \times D_{\perp}} / \arctan \sqrt{\frac{AD}{D_{\perp}}}; \quad AD = D_{||} - D_{\perp}. \quad (20)$$

Naturally the quasi-elastic broadening of the spectral line of the incident beam $-\Delta E$ is:

$$\Delta E = 2\hbar \kappa^2 D. \quad (21)$$

It should be noted here that the expression for D is rather complicated. By using approximation (19) — D is not computed exactly, however it is clear that the expression used up to now:

$$D = \frac{1}{3} D_{||} + \frac{2}{3} D_{\perp} \quad (22)$$

is incorrect. It is easy to explain that fact. Expression (22) is obtained from averaging $D^{\alpha\beta}$. It is not allowed. Incoherent cross-section should instead be averaged, which leads to formula (20).

However in the case of weak anisotropy both expressions (20) and (22) are close enough, within experimental error limits.

It is worthwhile noting that the Vineyard model is a primitive one and cannot explain the microscopic properties of liquid crystals. Its only advantage is its mathematical simplicity. However in the limit $\kappa \rightarrow 0$ the model is correct. All other models should take the Vineyard form in this limit.

3. The self-correlation function

In this Chapter the results of the work [2] are collected. These results are correct for isotropic liquids only.

Now we shall generalize them to be correct in both cases of isotropy and anisotropy.

Let us consider the molecule composed of protons and other atoms. We assume the following motion of protons:

A. Within the molecule (see Fig. 1)

In positions 1 and 2 the protonic motion is described with the aid of functions g_i and p_i . The functions h_i , q_i describe the motion between these positions.

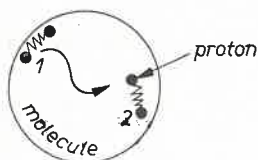


Fig. 1. Protonic motion within the molecule. At positions 1 and 2 the proton vibrates. Between those positions a large and quick rotational jump takes place

$g_i(\mathbf{r}, t)$ is the probability of finding the proton vibrating at the position \mathbf{r} within the molecule at the time t if it starts at the origin at the time $t = 0$.

$p_i(t)$ is the probability that the proton remains in the vibrating state at the time t if it starts at $t = 0$.

In an analogous way $h_i(\mathbf{r}, t)$ is the probability of finding the proton jumping, at the position \mathbf{r} at the time t . This jump is equivalent to a rotation of the molecule.

$q_i(t)$ is the probability that the proton remains in the rotating state at the time t .

Of course the functions g_i , h_i are applicable for pure cases of vibration and rotation respectively. The possibility of the transition vibration-rotation is not taken into account. These transitions may be described with the aid of the functions p'_i and q'_i .

B. External protonic motion generated by the motion of the centre of gravity of the molecule (see Fig. 2)

In positions 1' and 2' the motion of the centre of gravity of the molecule is described by functions g_e and p_e . The functions h_e and q_e describe the diffusive jump.

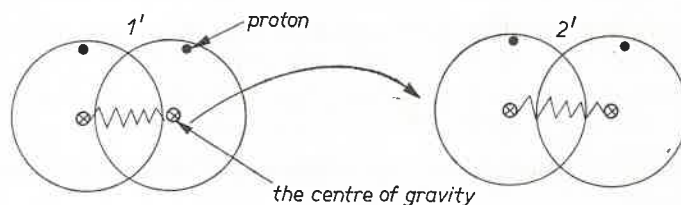


Fig. 2. Protonic motion generated by the motion of the centre of gravity. In positions 1' and 2' the centre of gravity vibrates. There is a long diffusive jump between them

$g_e(\mathbf{r}, t)$ is the probability of finding the centre of gravity vibrating stationarily at the position \mathbf{r} at the time t if it starts at the origin at the time $t = 0$. Thus only pure vibrations

are considered without taking into account the possibility of the transition between the vibration and the diffusive jump.

$p_e(t)$ is the probability that the centre of gravity remains in the vibrating state at the time t if it starts at $t = 0$.

$h_e(r, t)$ is the probability of finding the centre of gravity jumping (jumping diffusion), at the position r at the time t if it starts at the origin at $t = 0$.

$q_e(t)$ is the probability that in the time t the centre of gravity remains in the diffusive state, if it starts at $t = 0$.

We divide the molecular motion into steps numbered 0, 1, 2, ... Then:

$$H_0(r, t) = \int g_e(r', t) p_e(t) \sum_{n|0}^{\infty} F_n(r-r', t) dr' \quad (23)$$

describes the probability of finding the proton at r and at the time t if the centre of gravity of the molecule remains all the time in the vibrating state. F_n describes the probability of finding the proton within the molecule. This proton performs the motion in n steps; vibration follows rotation and rotation follows vibration. Here the unprimed quantities describe the coordinates of the proton and primed quantities describe the coordinates of the centre of gravity.

The situation is the following: between $t = 0$ and t the centre of gravity vibrates and at the same time the protons within the molecule vibrate and rotate.

Then:

$$H_1(r, t) = - \int_0^t dt_1 \int dr_1 q_e(t-t_1) \int dr' h_e(r'-r'_1, t-t_1) \times \\ \times \sum_{n|0}^{\infty} F_n(r-r_1-r'_1+r', t-t_1) \times \int g_e(r'_1, t_1) p'_e(t_1) \sum_{n|0}^{\infty} F_n(r_1-r'_1, t_1) dr'_1 \quad (23')$$

describes the protonic motion if the centre of gravity at first vibrates and next performs the diffusive jump.

In expression (23') functions of the type p'_e are present. For example the term $-p'_e(t)dt$ gives the probability that an internal vibrating state of the proton is left between t and $t+dt$.

In an analogous way we define H_m . If we sum all steps H_m we find:

$$G_s = \sum_{m|0}^{\infty} (H_{2m} + H_{2m+1}); \quad t \geq 0. \quad (24)$$

Instead of trying calculate G_s we will calculate its Fourier transform.

Now we obtain:

$$\int_0^{\infty} dt \int dr \exp i(\kappa r - \omega t) H_{2m} = AC^m G^m \quad (25)$$

$$\int_0^{\infty} dt \int dr \exp i(\kappa r - \omega t) H_{2m+1} = BC^{m+1} G^m. \quad (26)$$

The values A, B, C, G are defined by:

$$\begin{aligned}
 A &= \int_0^{\infty} dt \int dr \exp i(\kappa r - \omega t) p_e(t) \int g_e(r', t) \sum_{n|0}^{\infty} F_n(r-r', t) dr' \\
 B &= \int_0^{\infty} dt \int dr \exp i(\kappa r - \omega t) q_e(t) \int h_e(r', t) \sum_{n|0}^{\infty} F_n(r-r', t) dr' \\
 -C &= \int_0^{\infty} dt \int dr \exp i(\kappa r - \omega t) p'_e(t) \int g_e(r', t) \sum_{n|0}^{\infty} F_n(r-r', t) dr' \\
 -G &= \int_0^{\infty} dt \int dr \exp i(\kappa r - \omega t) q'_e(t) \int h_e(r', t) \sum_{n|0}^{\infty} F_n(r-r', t) dr'. \quad (27)
 \end{aligned}$$

With the aid of this expressions one obtains:

$$\int dt \int dr \exp i(\kappa r - \omega t) \sum_m H_m = (A+BC)/(1-CG) + c.c \quad (28)$$

where use has been made of the fact that $G_s(r, t) = G_s^*(-r, -t)$ (the appearance of c.c).

Expression (28) is not the Van Hove self-correlation function because in (23)–(28) the use has been made of the following assumption: the centre of gravity begins its motion from vibration. However, there is the possibility of starting the motion of the centre of gravity from the diffusive jump. The probabilities of first and second possibility are equal to $\tau'_0/(\tau'_0 + \tau'_1)$ and $\tau'_1/(\tau'_0 + \tau'_1)$ respectively.

We have introduced the characteristic times τ'_0, τ'_1 i.e. the life times of the states of vibrational motion and diffusive motion respectively (for the centre of gravity of the molecule). After performing the calculations in an analogous way, we obtain:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{a^2}{2\pi} \frac{k}{k_0} \left\{ \frac{\tau'_0}{\tau'_0 + \tau'_1} \frac{A+BC}{1-CG} + \frac{\tau'_1}{\tau'_0 + \tau'_1} \frac{B+AG}{1-CG} + c.c \right\}. \quad (29)$$

Then the problem to solve, is the evaluation of ΣF_n . For example:

$$\begin{aligned}
 F_{2m}(r, t) &= (-1)^{2m} \int_0^t dt_{2m} \int_0^{t_{2m}} dt_{2m-1} \dots \int dr_{2m} \dots dr_1 p_i(\tau_{2m+1}) \times \\
 &\quad \times q'_i(\tau_{2m}) \dots p'_i(\tau_1) g_i(\eta_{2m+1}, \tau_{2m+1}) h_i(\dots) \dots g_i(\eta_1, \tau_1) \\
 \tau_{2m+1} &= t - t_{2m}, \quad r - r_{2m} = \eta_{2m+1}, \dots \quad (30)
 \end{aligned}$$

Assuming for simplicity that the Fourier transforms of functions h_e, g_e fulfil relations (in κ space):

$$\begin{aligned}
 g_e(\kappa, t) &= \prod_{n|1}^{2m+1} g_e(\kappa, \tau_n) \\
 h_e(\kappa, t) &= \prod_{n|1}^{2m+1} h_e(\kappa, \tau_n) \quad (31)
 \end{aligned}$$

we obtain:

$$\int_0^{\infty} dt e^{-i\omega t} p_e(t) \int e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \int g_e(\mathbf{r}', t) F_{2m}(\mathbf{r}-\mathbf{r}', t) d\mathbf{r}' = a_A c_A^m g_A^m$$

$$\int_0^{\infty} dt e^{-i\omega t} p_e(t) \int e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \int g_e(\mathbf{r}', t) F_{2m+1}(\mathbf{r}-\mathbf{r}', t) d\mathbf{r}' = b_A c_A^{m+1} g_A^m. \quad (32)$$

From these relations the other expressions follow:

$$A = \frac{\tau_0}{\tau_0 + \tau_1} \frac{a_A + b_A c_A}{1 - c_A g_A} + \frac{\tau_1}{\tau_0 + \tau_1} \frac{b_A + a_A g_A}{1 - c_A g_A}$$

$$B = \frac{\tau_0}{\tau_0 + \tau_1} \frac{a_B + b_B c_B}{1 - c_B g_B} + \frac{\tau_1}{\tau_0 + \tau_1} \frac{b_B + a_B g_B}{1 - c_B g_B} \quad (33)$$

where τ_0 and τ_1 are proton life times within the molecule, in vibrating and rotating state respectively and where

$$a_A = \int_0^{\infty} dt e^{-i\omega t} p_e(t) p_i(t) g_i(\mathbf{\kappa}, t) g_e(\mathbf{\kappa}, t)$$

$$b_A = \int_0^{\infty} dt e^{-i\omega t} p_e(t) q_i(t) h_i(\mathbf{\kappa}, t) g_e(\mathbf{\kappa}, t)$$

$$c_A = \int_0^{\infty} dt e^{-i\omega t} p_e(t) p_i'(t) g_i(\mathbf{\kappa}, t) g_e(\mathbf{\kappa}, t)$$

$$g_A = \int_0^{\infty} dt e^{-i\omega t} p_e(t) q_i'(t) h_i(\mathbf{\kappa}, t) g_e(\mathbf{\kappa}, t)$$

$$a_B = \int_0^{\infty} dt e^{-i\omega t} q_e(t) p_i(t) g_i(\mathbf{\kappa}, t) h_e(\mathbf{\kappa}, t)$$

$$b_B = \int_0^{\infty} dt e^{-i\omega t} q_e(t) q_i(t) h_i(\mathbf{\kappa}, t) h_e(\mathbf{\kappa}, t)$$

$$c_B = \int_0^{\infty} dt e^{-i\omega t} q_e(t) p_i'(t) g_i(\mathbf{\kappa}, t) h_e(\mathbf{\kappa}, t)$$

$$g_B = \int_0^{\infty} dt e^{-i\omega t} q_e(t) q_i'(t) h_i(\mathbf{\kappa}, t) h_e(\mathbf{\kappa}, t). \quad (34)$$

If the simple model is used: $p_e = \exp(-t/\tau'_0)$; $q_e = \exp(-t/\tau'_1)$ then

$$-C = A/\tau'_0; \quad -G = B/\tau'_1. \quad (35)$$

Thus we have presented the Larsson theory without assuming the isotropy of the liquid. From this, it follows that this theory is applicable to anisotropic liquids in spite of its raw form.

4. The anisotropic liquids

4.1.

We shall describe the motion of the centre of gravity of the molecule as follows:
The life time of vibrating state is τ'_0

The life time of diffusive jump is τ'_1 .

p_e and q_e describe the probability that the centre of gravity remains in these states.
The Fourier transforms in κ space of functions g_e, h_e are:

$$g_e(\kappa, t) = \exp -\kappa^\alpha \kappa^\beta \gamma_{\alpha\beta}^{(e)}(t) \approx \exp -\kappa^\alpha \kappa^\beta \gamma_{\alpha\beta}^{(e)}(\infty)$$

$$h_e(\kappa, t) = \exp -\kappa^\alpha \kappa^\beta D_{\alpha\beta}^{(e)} |t|. \quad (36)$$

For diagonal tensors $\gamma_{\alpha\beta}^{(e)}, D_{\alpha\beta}^{(e)}$ with the parallel components equal to the normal ones, we obtain isotropic expressions. The formulas (36) are the simplest generalization of the isotropic ones.

If the nematic axis is parallel to the z axis then:

$$\begin{aligned} \kappa^\alpha \kappa^\beta \gamma_{\alpha\beta}^{(e)} &= \kappa_\perp^2 \gamma_\perp^{(e)} + \kappa_\parallel^2 \gamma_\parallel^{(e)} \\ \kappa^\alpha \kappa^\beta D_{\alpha\beta}^{(e)} &= \kappa_\perp^2 D_\perp^{(e)} + \kappa_\parallel^2 D_\parallel^{(e)}. \end{aligned} \quad (37)$$

The subscripts \perp and \parallel denote the normal and parallel components with respect to the nematic axis.

4.2.

It is more difficult to describe the protonic motion within the molecule.

τ_0 is the protonic life time in the vibrating state. The probability of remaining in this state is $p_i = \exp(-t/\tau_0)$.

The Fourier transform of g_i in κ space is:

$$g_i(\kappa, t) \approx \exp -\kappa^\alpha \kappa^\beta \gamma_{\alpha\beta}^{(i)}(\infty). \quad (38)$$

The approximations in (36) and (38) are good enough because the γ -functions depend on t only at times of the order of 10^{-14} s, hence the neutrons see only the clouds set up by the protons.

The rotational jump follows the vibrations. We will divide all jumps into groups a), b) and c) (see Fig. 3).

During the time τ_a the proton jumps once, which is equivalent to a small rotation of the molecule. The mean-square displacement vector of protons is $(l_{a\perp}^2, l_{a\parallel}^2)$. In the nematic crystal the relation $l_{a\perp}^2 \gg l_{a\parallel}^2$ is valid. In the PAA molecule it is a small rotation around the nematic axis. The rotational jumps will occur only by very small angles.

During the time τ_b the proton jumps once, which is equivalent to a large rotation of the molecule around the nematic axis. It may be rotation of some molecular atomic groups too. The mean-square displacement vector of protons is $(l_{b\perp}^2, 0)$. In the PAA molecule,

inversional jumps of the benzene rings, of the CH_3 groups and of the N_2O groups correspond to this rotation.

During the time τ_c there occur single reorientational jump of some molecular atomic groups, but not around the nematic axis. The mean-square displacement vector of protons

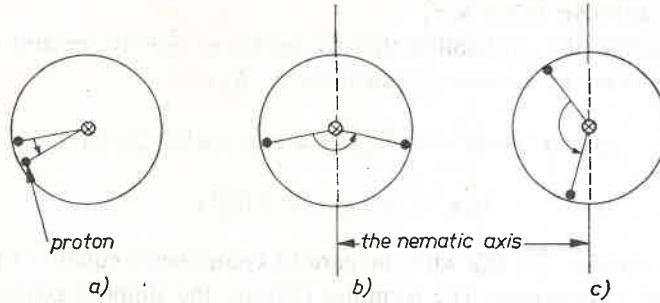


Fig. 3. Jump of type a): a small rotation of molecule, jump of type b): a large rotation of molecule or molecular atomic groups, around the nematic axis, jump of type c): a large rotation of atomic groups, but not around the nematic axis

is $(l_{c\perp}^2, l_{c\parallel}^2)$. In the PAA molecule a rotation of the CH_3 groups around their three-fold symmetry axis corresponds to these jumps.

The characteristic times follow the relation:

$$\frac{1}{\tau_0} = \frac{1}{\tau_a} + \frac{1}{\tau_b} + \frac{1}{\tau_c} \quad (39)$$

The rotational jumps occur rapidly. Their life time is $\tau_{1(j)}$ where $j = a, b, c$ (j describes the type of the motion).

Let us assume:

$$q_{i(j)} = \theta(t + \tau_{1(j)}) - \theta(t - \tau_{1(j)}); \quad \tau_{1(j)} \approx 0 \quad (40)$$

where θ is the Heavieside function.

The function $q_{i(j)}$ is the same as the function q_i , but it corresponds to the rotation of the type j only.

The form of h_i in the system where the nematic axis is parallel to the z axis is:

$$h_i(\mathbf{r}, 0) \approx \sum_{(j)} \frac{l_{j\parallel}}{\pi} \frac{\tau_j}{\tau_0} \delta(x^2 + y^2 - l_{j\perp}^2) \delta(z^2 - l_{j\parallel}^2) \quad (41)$$

Here use has been made of the fact that $\tau_{1(j)} \approx 0$. It is possible to write the Fourier transform:

$$h_i(\boldsymbol{\kappa}, 0) = h_i(\boldsymbol{\kappa}) = \sum_{(j)} \frac{\tau_j}{2\pi\tau_0} \cos \kappa_{\parallel} l_{j\parallel} \times \int_0^{2\pi} e^{i\boldsymbol{\kappa}_{\perp} l_{j\perp} \cos\varphi} d\varphi. \quad (42)$$

For $\kappa \approx 0$ we have the simple expression:

$$h_i(\kappa) \approx \sum_{(j)} \frac{\tau_j}{\tau_0} \left(1 - \frac{1}{2} \kappa_{\parallel}^2 l_{j\parallel}^2 - \frac{1}{4} \kappa_{\perp}^2 l_{j\perp}^2 \right). \quad (43)$$

The factor $l_{j\parallel}/\pi$ is the normalization factor.

Computing values a_A, b_A, \dots in the limit $\tau_{1(j)} = 0$ we obtain:

$$\begin{aligned} a_A &= \frac{\tau_{00}}{1 + i\tau_{00}\omega} \exp -\kappa^\alpha \kappa^\beta (\gamma^{(e)} + \gamma^{(i)})_{\alpha\beta} \\ \frac{1}{\tau_{00}} &= \frac{1}{\tau_0} + \frac{1}{\tau'_0} \\ b_A &= b_B = 0 \\ c_A &= -a_A/\tau_0 \\ c_B &= -a_B/\tau_0 \\ a_B &= \frac{\tau_{01}}{1 + \tau_{01}\{\kappa^\alpha \kappa^\beta D_{\alpha\beta}^{(e)} + i\omega\}} \exp -\kappa^\alpha \kappa^\beta \gamma_{\alpha\beta}^{(i)} \\ \frac{1}{\tau_{01}} &= \frac{1}{\tau_0} + \frac{1}{\tau'_1} \\ g_B &= -h_i(\kappa) \end{aligned} \quad (44)$$

Now it is easy to write the correlation function S_s . If we assume: $\tau_{1(j)} \approx 0$; τ_0 and $\tau'_0 \gg \tau'_1$ then

$$S_s(\kappa, \omega) = \frac{2\tau'_1 A_1 B_2 (A_2 B_2 - A_1 B_1)}{(A_2 B_2 - A_1 B_1)^2 + \omega^2 A_3 B_2} \quad (45)$$

where:

$$\begin{aligned} A &= \tau'_1 A_1 / (A_2 + i\omega A_3) \\ B &= \tau'_0 B_1 / (B_2 + i\omega B_3). \end{aligned} \quad (45')$$

The expressions (45') define the values A_i, B_i with the aid of the values A and B (see expressions (33); $i = 1, 2, 3$).

The quasi-elastic broadening ΔE is given by the expression:

$$\begin{aligned} \frac{\Delta E}{2\hbar} &= \frac{1}{\tau_{00}} \left\{ 1 - \frac{h_i(\kappa) \times \exp -\kappa^\alpha \kappa^\beta (\gamma^{(e)} + 2\gamma^{(i)})_{\alpha\beta}}{\tau_0/\tau_{00}} - \right. \\ &\quad \left. - \frac{\tau_{00}}{\tau'_0} \frac{\exp -\kappa^\alpha \kappa^\beta (\gamma^{(e)} + 2\gamma^{(i)})_{\alpha\beta}}{1 + \tau_{01} \kappa^\alpha \kappa^\beta D_{\alpha\beta}^{(e)}} \right\}. \end{aligned} \quad (46)$$

For $\kappa \rightarrow 0$ we obtain:

$$\begin{aligned} \frac{\Delta E}{2\hbar} = & \left\{ \frac{1}{\tau_{00}} (\gamma^{(e)} + 2\gamma^{(i)})_{\parallel} + D_{\parallel} + \frac{1}{\tau_0} \sum_{(j)} \frac{\tau_j}{2\tau_0} l_{j\parallel}^2 \right\} \kappa_{\parallel}^2 + \\ & + \left\{ \frac{1}{\tau_{00}} (\gamma^{(e)} + 2\gamma^{(i)})_{\perp} + D_{\perp} + \frac{1}{\tau_0} \sum_{(j)} \frac{\tau_j}{4\tau_0} l_{j\perp}^2 \right\} \kappa_{\perp}^2 \end{aligned} \quad (47)$$

where

$$D_{\alpha\beta} = \tau_1' D_{\alpha\beta}^{(e)} / \tau_0'$$

For $0 \ll \kappa \ll \infty$ we obtain:

$$\frac{\Delta E}{2\hbar} = \frac{1}{\tau_{00}} + \frac{1}{\tau_0} \frac{h_i(\kappa)}{\kappa^\alpha \kappa^\beta (\gamma^{(e)} + 2\gamma^{(i)})_{\alpha\beta}} \quad (48)$$

Here the second term is anisotropic.

Finally, in the limit $\kappa \rightarrow \infty$ we obtain the expression without anisotropy [2]:

$$\frac{\Delta E}{2\hbar} = \frac{1}{\tau_{00}} \quad (49)$$

The problem of the correctness of formula (49) should be resolved by an appropriate future experiment.

A remark is needed that the expression $\kappa^\alpha \kappa^\beta \gamma_{\alpha\beta}$ is the generalization of the Debye-Waller factor. Usually for the isotropic case $\gamma^{(i)}(\infty) = \frac{1}{6} \langle r_i^2 \rangle$ where $\langle r_i^2 \rangle$ is the mean-square radius of the thermal cloud set up by the proton.

In an analogous way $\gamma^{(e)} = \frac{1}{6} \langle r_e^2 \rangle$. Here $\langle r_e^2 \rangle$ is the mean-square radius of the thermal cloud set up by the centre of gravity of the molecule.

In the case of isotropy:

$$\kappa^\alpha \kappa^\beta \gamma_{\alpha\beta}^{(i,e)} \rightarrow \kappa^2 \gamma^{(i,e)} = 2W_{(i,e)} \quad (50)$$

where W is the Debye-Waller factor.

If anisotropy is present and the nematic axis is parallel to the z axis, we obtain:

$$\kappa^\alpha \kappa^\beta \gamma_{\alpha\beta}^{(i,e)}(\infty) = \frac{1}{2} \kappa_{\parallel}^2 \langle r_{\parallel(i,e)}^2 \rangle + \frac{1}{4} \kappa_{\perp}^2 \langle r_{\perp(i,e)}^2 \rangle \quad (51)$$

This expression is valid in both cases of isotropy and anisotropy. In an isotropic system $\kappa^\alpha \kappa^\beta \gamma_{\alpha\beta}$ is equal to $2W$ as before.

In an intuitive way we assume that $\sum l_j^2 \gg \langle r_{i,e}^2 \rangle$. With the aid of this inequality, the quasi-elastic broadening may be written, in the limit $\kappa \rightarrow 0$, in a very short form:

$$\begin{aligned} \frac{\Delta E}{2\hbar} = & \kappa_{\parallel}^2 \left(D_{\parallel} + \frac{1}{\tau_0} \sum_{(j)} \frac{\tau_j}{2\tau_0} l_{j\parallel}^2 \right) + \\ & + \kappa_{\perp}^2 \left(D_{\perp} + \frac{1}{\tau_0} \sum_{(j)} \frac{\tau_j}{4\tau_0} l_{j\perp}^2 \right) \end{aligned} \quad (52)$$

5. Conclusions

The Larsson-Bergstedt formalism permits the incoherent cross-section for the nematic liquids to be found. From this cross-section the quasi-elastic broadening of the spectral line of the incident beam is obtained.

In the case of small momentum transfer vector, the expression for this broadening takes the Vineyard form. There is a strong anisotropy of the self-diffusion coefficient. This anisotropy depends on the orientation of the vector κ with respect to the nematic axis.

For κ increasing the anisotropy decreases. In the limit $\kappa \rightarrow \infty$ there is no anisotropy.

The author would like to express his gratitude to Professor J. A. Janik for suggesting this work, for reading the manuscript and for many helpful suggestions.

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