

# Cold-Neutron Incoherent Scattering by Homogeneously Oriented Nematic Liquid Crystals

BY ALFREDO OLIVEI

Laboratorio Circuiti e Memorie, Olivetti S.p.A., 10015-Ivrea, Italy

(Received 9 April 1973; accepted 21 May 1973)

A study is made of the incoherent scattering of cold neutrons by a homogeneously oriented nematic liquid crystal composed of anisotropic molecules which show fluctuations in orientation and are so distributed that the medium possesses a unique isotropic axis. It is believed that the main features of several scattering experiments on homogeneously oriented nematic liquid crystals may be understood on the basis of the formulae presented, whose usefulness is discussed in terms of both bad and good-resolution measurements.

## 1. Introduction

A theoretical study is made of the incoherent scattering of cold neutrons by a liquid composed of anisotropic particles which show fluctuations in orientation and are so distributed that the medium possesses a unique isotropic axis. This scheme applies to homogeneously oriented nematic liquid crystals. In practice nematic liquids can readily be homogeneously oriented. Thin films between glass plates can be oriented by boundary effects, without external magnetic or electric fields. By suitable surface treatment (Chatelain, 1943), it is possible to obtain two different homogeneous orientations. Rubbing of the surface of the glass in a given direction leads to 'planar layers' in which the optical axis lies in the plane of the film and parallel to the rubbing direction; 'erected layers' in which the optical axis is perpendicular to the plane of the film, are obtained by careful cleaning of the surfaces, e.g. with sulphuric acid/bichromate. The study of the behaviour of thin sheets of homogeneously oriented nematic liquid crystals sandwiched between glass plates, in the absence of any external magnetic or electric field, is very important from many theoretical and practical standpoints.

From a general point of view, the radiation scattering offers the most direct determination of both the static and the dynamic structure of liquids. In liquid crystals the radiation, considered as a probe, should be able to couple to motion of molecules directly or indirectly. Both X-rays and light interact with electrons. In a nematic liquid crystal, which is an insulating liquid, electrons can be regarded as firmly attached to individual atoms so that the electromagnetic wave couples to motions of atoms indirectly *via* atomic electrons. On the other hand, neutrons interact primarily with the nucleus of an atom and thus are able to couple to the atomic or molecular motion directly.

In order to understand what types of fluctuations a given radiation can effectively measure let us assess briefly the main attributes of X-ray, light and neutron-scattering methods in nematic liquid crystals.

In a radiation-scattering process there are two basic parameters: the momentum transfer  $\hbar\mathbf{q}$  and the energy transfer  $\hbar\omega$  to the system. We have:

$$\mathbf{q} = \mathbf{K}_i - \mathbf{K}_s \quad (1)$$

$$\hbar\omega = E_i - E_s \quad (2)$$

where the wave-vector and the energies of the incident and scattered waves are indicated respectively by  $(\mathbf{K}_i, E_i)$  and  $(\mathbf{K}_s, E_s)$ .

For electromagnetic waves the energy and the wave vector are related by:

$$E = i\hbar K \quad (3)$$

and for neutrons:

$$E = \hbar^2 K^2 / 2m. \quad (4)$$

Because of relationships (3) and (4), the momentum transfer  $\hbar\mathbf{q}$  and the energy transfer  $\hbar\omega$  in (3) and (4) are related.

Now for electromagnetic waves, the magnitude of the momentum transfer vector  $\mathbf{q}$  [equation (1)] usually reduces to:

$$\mathbf{q} = 2n\mathbf{K}_i \sin \varphi / 2 \quad (5)$$

where  $\varphi$  is the scattering angle and  $n$  the index of refraction of the medium.

Equation (2) can be rewritten as:

$$q^2 = \frac{2m}{\hbar^2} (K_i^2 + K_s^2 - 2K_i K_s \cos \varphi). \quad (6)$$

Equation (5) shows that measurement at a constant angle does give a constant  $q$  measurement. The scattered intensity at constant momentum transfer  $q$  gives the  $q$ th Fourier component of the spatial correlation between atoms in the system. Such measurements are useful in obtaining the static structure factor of a nematic liquid crystal. This is an advantage of X-ray and light scattering over neutrons. In effect equation (6), valid for neutron scattering, shows that if one fixes the scattering angle  $\varphi$  and measures the energy distribution, then different energy transfer  $\hbar\omega$  would correspond to different momentum transfer  $\hbar\mathbf{q}$ . If one were

able to analyze the energy distribution at a constant  $q$ , the intensity at a particular energy transfer  $\hbar\omega$  gives the  $\omega$ th Fourier component of the time correlation for the fluctuation with wave vector  $q$ . This latter quantity is useful for the dynamic structure-factor determination. Anyhow Brockhouse (1958) has demonstrated the possibility of programming the neutron spectrometer in such a way as to obtain a constant  $q$ , so that one can obtain a neutron intensity distribution at different  $\hbar\omega$  for a fixed  $q$ .

Then the difference between neutrons, X-ray and light probing methods of nematic liquid crystals reduces essentially to the different range of probing distances within the liquid crystal and the different range of time intervals of probing.

Neutrons are capable of probing the liquid crystal structure within a distance of  $q^{-1} \sim 10^{-8}$  cm and within a time intervals of  $\omega^{-1} \sim 10^{-13}$  s. Then cold-neutron scattering provides a direct mean of studying the dynamic behaviour of a single molecule in a homogeneously oriented nematic liquid crystal showing orientational fluctuations.

For X-rays,  $q^{-1}$  is again of the order of  $10^{-8}$  cm, but the energy exchanged with the liquid-crystal molecules during scattering is negligible. Therefore X-ray studies of homogeneously oriented nematic liquid crystals yield no precise information about the librational and rotational motions of molecules. However structure-factor measurements can be made by measuring the integrated intensity at constant  $q$ .

Light, for example a red light from a helium-neon gas laser, is capable of probing the liquid-crystal structure within a distance of  $q^{-1} \sim 5 \cdot 10^{-6}$  cm and within a time interval of  $\omega^{-1} \sim 2 \cdot 10^{-15}$  s. Then light scattering is only suited for the study of long-range fluctuations in nematic liquid crystals.

In conclusion, neutron scattering in homogeneously oriented nematic liquid crystals is suited for the study of short-range fluctuations and single-molecule behaviour, while both X-ray and light scattering from a homogeneously oriented nematic liquid crystal contain only the coherent scattering and therefore do not give information on the single-particle motion.

## 2. Structure of the scattering medium

We study the behaviour of thin sheets of homogeneously oriented nematic liquid crystals in the absence of any external magnetic or electric field.

The ordering effect is exclusively due to boundary effects of the glass plates sandwiching the nematic liquid crystal. The homogeneously oriented nematic liquid crystal is composed of anisotropic particles which show fluctuations in orientation and are so distributed that the medium possesses a unique isotropic axis. Each molecule is visualized as a line with protons hooked on at selected positions.

We contemplate the case in which the orientational fluctuations are far larger than density fluctuations so

that density fluctuations can be completely neglected. According to this assumption, a volume  $V$  will contain  $N$  molecules regularly spaced with the centre of mass stationary and unchanged in position with time so that the centre of mass of the molecules can be thought of as placed in a three-dimensional Bravais lattice. The position vector of each centre of mass is given with respect to some reference axes.

The molecules assume a needle-stacked arrangement so that the molecular axes tend to be aligned parallel to one another, owing to boundary effects, along the unique isotropic axis labelled by the unit vector  $\mathbf{n}_0$ . However there exist thermal orientational fluctuations of the molecular axes about the unique isotropic axis  $\mathbf{n}_0$ . Each molecule is supposed to be able to perform a motion relative to its centre of mass, namely, librational motion for a time  $\tau_0$  during which its average angular orientation does not change, followed by rotational motion for a time  $\tau_1$  during which its angular orientation changes.

In all subsequent formulae the orientation  $\mathbf{n}_i$  of a molecule, whose long axis has unit direction  $\mathbf{n}_i^*$  in space at time  $t$ , will be defined with respect to the unit direction,  $\mathbf{n}_0$ , of the isotropic axis as:

$$\mathbf{n}_i = r_d \mathbf{n}_i^* - \mathbf{n}_0 \quad (7)$$

where  $r_d$  is the scalar distance of the scattering nucleus from the centre of mass, Fig. 1.

Let  $\mathbf{n}_i(0)$ , ( $i=1, 2, \dots$ ), denote the orientation of a particle at some initial time and  $\mathbf{n}_i(t)$  the orientation at some other time.

Should the molecule contain several incoherently scattering nuclei at the same or at different distances from the centre of mass, a summation over all the scatterers in the molecule should be made to obtain the cross section per molecule.

## 3. Correlation function, structure factor and scattering cross section

A general theory of neutron scattering by an arbitrary system of particles has been given by Van Hove (1954). In this theory, the differential scattering cross section is expressed as a four-dimensional Fourier transform of the generalized distribution function, usually denoted as  $G(\mathbf{r}, t)$ . In the classical limit, the interpretation of this function is that given an atom at the origin at time  $t=0$ , it defines the probability of finding an atom within a unit volume at the point  $\mathbf{r}$ , and at time  $t$ . The atom at the position  $(\mathbf{r}, t)$  may be the same as was at the origin at time  $t=0$ , or may be another atom.

The total scattering can be divided into a coherent part and an incoherent part; the former is given by the Fourier transform of  $G(\mathbf{r}, t)$  and the latter by the Fourier transform of the self-correlation function  $G_s(\mathbf{r}, t)$ .

In other words, the incoherent scattering probes the single-particle motion and the coherent scattering the collective motion of atoms. Since we are essentially

interested in the single-particle motion, we will use a self-correlation function  $\Gamma_s(\mathbf{n}, t)$  depending on the orientation vector  $\mathbf{n}$  defined by equation (7) and a time interval  $t$  for describing the behaviour of a given molecule, whose centre of mass is stationary, in a liquid composed of anisotropic particles which show fluctuations in orientation and are so distributed that the medium possesses a unique isotropic axis. In other words for describing the correlation between orientations of one and the same particle at different times we consider the function:

$$\Gamma_s(\mathbf{n}, t) = N^{-1} \left\langle \sum_{i=1}^N \int d\mathbf{n}' \delta(\mathbf{n} + \mathbf{n}_i(0) - \mathbf{n}') \cdot \delta(\mathbf{n}' - \mathbf{n}_i(t)) \right\rangle \quad (8)$$

where  $\mathbf{n}_i(0)$  and  $\mathbf{n}_i(t)$  are orientation vectors, considered as Heisenberg observables, of the  $i$ th molecule at time zero and at time  $t$ .

The thermal average of an operator  $U$  is defined as:

$$\langle U \rangle = \text{Tr} \{ U \exp(-\beta H) \} / \text{Tr} \{ \exp(-\beta H) \}. \quad (9)$$

The function  $\Gamma_s(\mathbf{n}, t)$  as defined in (8) can be called the self-orientation-time correlation function and is in general a complex function:

$$[\Gamma_s(\mathbf{n}, t)]^* = \Gamma_s(-\mathbf{n}, -t) \neq \Gamma_s(\mathbf{n}, t). \quad (10)$$

In effect  $\mathbf{n}_i(0)$  and  $\mathbf{n}_i(t)$  regarded as Heisenberg operators do not in general commute and therefore the order of the two delta functions in (8) has to be maintained.

Nematic liquid crystals may be considered classical as long as the thermal de Broglie wavelength  $\lambda = h/(2\pi MK_B T)^{1/2}$  is smaller than the interparticle distance; then for times  $t$  larger than the Debye relaxation time, the function  $\Gamma_s(\mathbf{n}, t)$  is real, positive and even in  $t$ .

The remaining part of this section is organized around measurements of the dependence upon wave vector  $\mathbf{q}$  and frequency  $\omega$  of the self-orientational structure factor  $S_s(\mathbf{q}, \omega)$  for the reasons that: (i)  $S_s(\mathbf{q}, \omega)$  is directly obtainable from scattering experiments, and (ii) since  $S_s(\mathbf{q}, \omega)$  is defined as the Fourier transform of the orientation-and-time-dependent function  $\Gamma_s(\mathbf{n}, t)$  describing the correlation of a particle with itself, its measurement provides one with a great deal of useful information about the microscopic properties of a molecule of a homogeneously oriented nematic liquid crystal.

In effect it is useful to define the following two Fourier transforms of the orientation-time self-correlation function  $\Gamma_s(\mathbf{n}, t)$ :

$$\begin{aligned} I_s(\mathbf{q}, t) &= \int \exp(i\mathbf{q} \cdot \mathbf{n}) \Gamma_s(\mathbf{n}, t) d\mathbf{n} \\ &= \frac{1}{N} \sum_{i=1}^N \langle \exp[-i\mathbf{q} \cdot \mathbf{n}_i(0)] \exp[i\mathbf{q} \cdot \mathbf{n}_i(t)] \rangle \end{aligned} \quad (11)$$

$$S_s(\mathbf{q}, t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp(-i\omega t) I_s(\mathbf{q}, t) dt. \quad (12)$$

$I_s(\mathbf{q}, t)$  is called the 'intermediate scattering function', a name derived from its appearance in the scattering cross section. The second line of (11) follows from using definition (8) for  $\Gamma_s(\mathbf{n}, t)$ . The physical meaning of  $I_s(\mathbf{q}, t)$  is that it describes the time behaviour of a single-particle orientation oscillation of wave vector  $\mathbf{q}$  in an  $N$ -particle system.  $S_s(\mathbf{q}, t)$  is then the spectral density of the orientation oscillation of this single particle.

From the definition of  $S_s(\mathbf{q}, t)$  and as a consequence of the fact that the system is in thermal equilibrium it can be shown that one important property of  $S_s(\mathbf{q}, t)$  is the so-called detail balance condition:

$$S_s(-\mathbf{q}, -\omega) = \exp(-\hbar\omega/K_B T) S_s(\mathbf{q}, \omega). \quad (13)$$

In the classical limit when  $\Gamma_s(\mathbf{n}, t)$  is an even function of  $t$ ,  $S_s(\mathbf{q}, \omega)$  becomes even in  $\omega$ . From equation (13) it is seen that the classical limit corresponds to the high-temperature limit  $K_B T \gg \hbar\omega$ , when the exponential factor in the right-hand side of (13) approaches unity.

We have:

$$\int_{-\infty}^{+\infty} S_s(\mathbf{q}, \omega) d\omega = I_s(\mathbf{q}, 0) = 1. \quad (14)$$

Now consider a neutron beam focused upon a macroscopically small volume  $V$ . We can consider each of the individual particles in the volume  $V$  to be the source of a spherical 'scattered wave'. Although the amplitude of the scattered wave originating at a specific particle will be proportional to the sum of the amplitudes of the original incident wave plus that of the waves scattered from other particles, we can neglect the latter since it is small compared to the incident field. Neglecting this multiple scattering is equivalent to making the Born approximation. If the dimensions of the illuminated volume  $V$  are small compared to the distance  $\mathbf{r}$  to the observation point, then the position vectors of the particles are negligible with respect to  $\mathbf{r}$ . Furthermore we suppose that the isotopic states are randomly distributed among atoms at various positions.

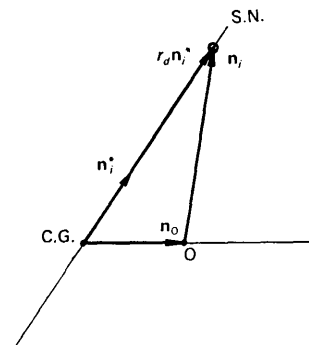


Fig. 1. Illustration of a scattering nucleus (S.N.), sitting at a distance  $r_d$  from the centre of gravity (C.G.) of the molecule, relative to the origin  $O$ . The origin  $O$  is placed at a unit distance ( $|n_0| = 1$ ) from C.G. on a straight line passing through C.G.

Then we have the following time-dependent incoherent-scattering amplitude:

$$f(\mathbf{q}, t) = - \sum_{i=1}^N \alpha_{\text{incoh}} \exp [i\mathbf{q} \cdot \mathbf{n}_i(t)] \quad (15)$$

and the incoherent scattered wave at the detector is thus:

$$\psi(\mathbf{n}, t) = f(\mathbf{q}, t) \exp [i(\mathbf{K}_s \cdot \mathbf{r} - \omega_s t)]/r \quad (16)$$

where  $\alpha_{\text{incoh}}$  is the bound-atom incoherent-scattering length of the nucleus.

If we now perform an energy analysis of the incoherent scattering wave, we should be extracting one of the Fourier components:

$$\psi(\mathbf{n}, t)_{\omega_s} = f(\mathbf{q}, \omega_p) \exp [i(\mathbf{K}_s \cdot \mathbf{r} - \omega_s t)]/r \quad (17)$$

where we first decompose

$$\left. \begin{aligned} f(\mathbf{q}, t) &= \sum_p f(\mathbf{q}, \omega_p) \exp (i\omega_p t) \\ \omega_p &= \frac{2\pi}{\tau} p, \quad p = \text{integer} \end{aligned} \right\} \quad (18)$$

and obtain:

$$f(\mathbf{q}, \omega_p) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_{-t/2}^{+t/2} f(\mathbf{q}, t) \exp (-i\omega_p t) dt. \quad (19)$$

Using (18) in (16) and comparing with (17) we obtain:

$$\omega_p = \omega_i - \omega_s \quad (20)$$

which in the limit  $\tau \rightarrow \infty$  tends to the  $\omega$  defined in (2).

Since we are performing an energy analysis, let us define the double differential cross section per unit solid angle, per unit outgoing energy, namely:

$$\frac{d^2\sigma_{\text{incoh}}}{dE d\omega} = \frac{K_i}{K_s} \left[ \frac{\langle f^*(\mathbf{q}, \omega_p) f(\mathbf{q}, \omega_p) \rangle}{\hbar(2\pi/\tau)} \right]_{\tau=\infty}. \quad (21)$$

Using (19) and the stationarity of the time correlation function, it is easily shown that:

$$\langle f^*(\mathbf{q}, \omega_p) f(\mathbf{q}, \omega_p) \rangle_{\tau=\infty} = \frac{1}{\tau} \int_{-t/2}^{+t/2} \langle f^*(\mathbf{q}, t) f(\mathbf{q}, t) \rangle \times \exp (-i\omega_p t) dt. \quad (22)$$

Then equation (21) becomes:

$$\begin{aligned} \frac{d^2\sigma_{\text{incoh}}}{dE d\omega} &= \frac{K_s}{K_i} \\ &\times \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \langle f^*(\mathbf{q}, t) \overline{f(\mathbf{q}, t)} \rangle \exp (-i\omega_p t) dt \\ &= \frac{K_s}{K_i} \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \left\langle \sum_{i=1}^N a_{\text{incoh}}^2 \exp [-i\mathbf{q} \cdot \mathbf{n}_i(0)] \right. \\ &\times \exp [i\mathbf{q} \cdot \mathbf{n}_i(t)] \rangle \exp (-i\omega t) dt \\ &= Na_{\text{incoh}}^2 \frac{K_s}{K_i \hbar} \left( \frac{1}{2\pi} \int_{-\infty}^{+\infty} (1/N) \right. \\ &\times \sum_{i=1}^N \langle \exp [-i\mathbf{q} \cdot \mathbf{n}_i(0)] \exp [i\mathbf{q} \cdot \mathbf{n}_i(t)] \rangle \\ &\times \exp (-i\omega t) dt \left. \right) = Na_{\text{incoh}}^2 \frac{K_s}{K_i \hbar} S_s(\mathbf{q}, \omega), \quad (23) \end{aligned}$$

where definitions (11) and (12) have been used in the last line. Now the main problem is to calculate an explicit expression for  $\Gamma_s(\mathbf{n}, t)$  or its Fourier transform  $S_s(\mathbf{q}, \omega)$ .

#### 4. Explicit expressions for the structure factor and the scattering cross section

The centre of mass of each molecule remains fixed with time. The molecule is supposed to be able to perform a motion relative to its centre of mass, namely, a librational motion for a time  $\tau_0$  during which its average angular orientation does not change, followed by a rotational motion for a time  $\tau_1$  during which its angular orientation changes, and then repeats this sort of motion.

We shall first define the following quantities: (a)  $g(\mathbf{n}, t)$  is the probability of finding a molecule having the orientation  $\mathbf{n}$  at time  $t$  when it is performing a librational motion about an equilibrium position, starting from an orientation parallel to the isotropic axis at time  $t=0$ ; (b) starting from a librational motion at time  $t=0$ ,  $p(t)$  gives the probability that the particle remains in the same librational state at a later time; (c)  $h(\mathbf{n}, t)$  is the probability of finding a molecule with an orientation  $\mathbf{n}$  at time  $t$  when it is performing a friction-damped rotation between two equilibrium positions starting from an orientation parallel to the isotropic axis a time  $t=0$ ; (d) starting from a state of rotational motion at time  $t=0$ ,  $q(t)$  gives the probability that the molecule remains in the same state of rotational motion at a later time  $t$ ; (e)  $p(t) - p(t+dt) = -p'(t)dt$  gives the probability that the molecule has left its librational state during the time interval  $t$  and  $t+dt$ , and has gone into the rotational state; and (f)  $q(t) - q(t+dt) = -q'(t)dt$  gives the probability that the molecule has left its rotational state during the time interval  $t$  and  $t+dt$ , and has gone into the librational state.

In order to obtain  $\Gamma_s(\mathbf{n}, t)$  and  $S_s(\mathbf{q}, t)$  let us divide the motion into steps numbering  $0, 1, 2, \dots, 2N, \dots$ . Starting from an orientation parallel to the isotropic axis where we assume that the molecule is making a librational motion, it could have arrived at the orientation  $\mathbf{n}$  in time  $t$  after making  $0, 1, 2, \dots$  steps. The zeroth step corresponds to the librational motion, step 1 to the succeeding rotational motion, step 2 again to librational motion, step 3 to the rotational motion and so on. Then  $\Gamma_s(\mathbf{n}, t)$  is given by

$$\Gamma_s(\mathbf{n}, t) = \sum_i F_i(\mathbf{n}, t) \quad t > 0, \quad (24)$$

where the various  $F_i$ 's are given by:

Step 0,

$$F_0(\mathbf{n}, t) = g(\mathbf{n}, t)p(t) \quad (25)$$

Step 1,

$$F_1(\mathbf{n}, t) = - \int_0^t dt_1 \int d\mathbf{n}_1 q(t-t_1) \times h(\mathbf{n} - \mathbf{n}_1, t-t_1)p'(t_1) \cdot g(\mathbf{n}_1, t_1)$$

Step 2,

$$F_2(\mathbf{n}, t) = (-1)^2 \int_0^t dt_2 \int_0^{t_2} dt_1 \int d\mathbf{n}_2 d\mathbf{n}_1 p(t-t_2) \\ \times g(\mathbf{n}-\mathbf{n}_2, t-t_2) q'(t_2-t_1) h(\mathbf{n}_2-\mathbf{n}_1, t_2-t_1) \\ \times p'(t_1) g(\mathbf{n}_1, t_1)$$

Step  $2N$ ,

$$F_{2N}(\mathbf{n}, t) = (-1)^{2N} \int_0^t dt_{2N} \int_0^{t_{2N}} dt_{2N-1} \dots \\ \times \int_0^{t_2} dt_1 \int \dots \int d\mathbf{n}_{2N} d\mathbf{n}_{2N-1} \dots d\mathbf{n}_1 \\ \times p(t-t_{2N}) g(\mathbf{n}-\mathbf{n}_{2N}, t-t_{2N}) q'(t_{2N}-t_{2N-1}) \\ \times h(\mathbf{n}_{2N}-\mathbf{n}_{2N-1}, t_{2N}-t_{2N-1}) \\ \dots p'(t_1) g(\mathbf{n}_1, t_1).$$

In writing expression (25) it has been supposed that when the particle makes a transition from one step into the other, say from a librational motion into a rotational motion or *vice versa*, there is no correlation between the motions in the two steps. By substituting (25) in (24), it is possible in principle to calculate  $F_s(\mathbf{n}, t)$ . However we are interested in  $S_s(\mathbf{q}, t)$ , to say the Fourier transform of the  $F_i$ 's. Write the integral:

$$\int_0^\infty dt \int d\mathbf{n} F_{2N}(\mathbf{n}, t) \exp [i(\mathbf{q} \cdot \mathbf{n} - \omega t)] \quad (26)$$

as

$$\int_0^\infty d\tau_{2N+1} \int_0^\infty d\tau_{2N} \dots \int_0^\infty d\tau_1 \int d\xi_{2N+1} \int d\xi_{2N} \dots \int d\xi_1 \\ \times p(\tau_{2N+1}) g(\xi_{2N+1}, \tau_{2N+1}) \\ \times q'(\tau_{2N}) h(\xi_{2N}, \tau_{2N}) \dots \\ \times p'(\tau_1) g(\xi_1, \tau_1) \exp [i(\mathbf{q} \cdot \mathbf{n} - \omega t)], \quad (27)$$

where the following change of variable for the time integrals has been made:

$$t - t_{2N} = \tau_{2N+1}, \\ t_{2N} - t_{2N-1} = \tau_{2N} \dots t_2 - t_1 = \tau_2, \\ t_1 = \tau_1. \quad (28)$$

A similar change of variables for the orientation integrals has also been made. Hence

$$\int_0^\infty dt \int d\mathbf{n} \exp [i(\mathbf{q} \cdot \mathbf{n} - \omega t)] F_{2N}(\mathbf{n}, t) \\ = \int_0^\infty d\tau \int d\xi \exp [i(\mathbf{q} \cdot \xi - \omega\tau)] p(\tau) g(\xi, \tau) \\ \times \left\{ - \int_0^\infty d\tau' \int d\xi' \exp [i(\mathbf{q} \cdot \xi' - \omega\tau')] p'(\tau') \right. \\ \times g(\xi', \tau') \left. \right\}^N \cdot \left\{ - \int_0^\infty d\tau'' \int d\xi'' \\ \times \exp [i(\mathbf{q} \cdot \xi'' - \omega\tau'')] q'(\tau'') h(\xi'', \tau'') \right\}^N \\ = AC^N D^N \quad (29)$$

and similarly it can be shown that:

$$\int_0^\infty dt \int d\mathbf{n} \exp [i(\mathbf{q} \cdot \mathbf{n} - \omega t)] F_{2N+1}(\mathbf{n}, t) \\ = BC^{N+1} D^N \quad (30)$$

where

$$A = \int_0^\infty dt \int d\mathbf{n} \exp [i(\mathbf{q} \cdot \mathbf{n} - \omega t)] p(t) g(\mathbf{n}, t) \\ B = \int_0^\infty dt \int d\mathbf{n} \exp [i(\mathbf{q} \cdot \mathbf{n} - \omega t)] q(t) h(\mathbf{n}, t) \\ C = - \int_0^\infty dt \int d\mathbf{n} \exp [i(\mathbf{q} \cdot \mathbf{n} - \omega t)] p'(t) g(\mathbf{n}, t) \\ D = - \int_0^\infty dt \int d\mathbf{n} \exp [i(\mathbf{q} \cdot \mathbf{n} - \omega t)] q'(t) h(\mathbf{n}, t). \quad (31)$$

Finally

$$\int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} d\mathbf{n} \exp [i(\mathbf{q} \cdot \mathbf{n} - \omega t)] \sum_{N=0}^{\infty} F_N(\mathbf{n}, t) \\ = A \sum_{N=0}^{\infty} (CD)^N + BC \sum_{N=0}^{\infty} (CD)^N + \text{c.c.} = \frac{A+BC}{1-CD} + \text{c.c.} \quad (32)$$

where c.c. means the complex conjugate term. In deriving equation (32) use of identity (10) has been made. In deriving (32) it has been assumed tacitly that at time  $t=0$ , all particles start with a librational motion. This is not true in general and some of the particles will start with rotational motion. In this case, following the same procedure as above, it can be shown that the corresponding expression to (32) is  $(B+AD)/(1-CD) + \text{c.c.}$ . Hence the self-structure factor  $S_s(\mathbf{q}, t)$  is given by:

$$S_s(\mathbf{q}, t) = \frac{\tau_0}{\tau_0 + \tau_1} \frac{A+BC}{1-CD} + \frac{\tau_1}{\tau_0 + \tau_1} \frac{B+AD}{1-CD} + \text{c.c.} \quad (33)$$

In (33),  $\tau_0/(\tau_0 + \tau_1)$  gives the fraction of particles performing a librational motion, and  $\tau_1/(\tau_0 + \tau_1)$  gives the fraction of particles performing a rotational motion at time  $t=0$ . We shall now assume the following forms for the various functions occurring in (31):

$$p(t) = \exp(-t/\tau_0), \quad (34)$$

$$q(t) = \exp(-t/\tau_1) \quad (35)$$

then

$$C = \left( \frac{1}{\tau_0} \right) A, \quad (36)$$

$$D = \left( \frac{1}{\tau_1} \right) B. \quad (37)$$

Now  $A$  and  $B$  can be written in the following form:

$$A = \int_0^\infty dt \exp(-i\omega t - t/\tau_0) \int d\mathbf{n} g(\mathbf{n}, t) \exp i\mathbf{q} \cdot \mathbf{n} \\ = \int_0^\infty dt \exp(-i\omega t - t/\tau_0) \chi_V(\mathbf{q}, t) \quad (38)$$

$$B = \int_0^\infty dt \exp(-i\omega t - t/\tau_1) \int d\mathbf{n} h(\mathbf{n}, t) \exp i\mathbf{q} \cdot \mathbf{n}$$

$$= \int_0^\infty dt \exp(-i\omega t - t/\tau_1) \chi_R(\mathbf{q}, t).$$

If we suppose that the librational motion during the time  $\tau_0$ , when the molecule performs rotational oscillations around an equilibrium direction, is very similar to what occurs for an atom in a solid, then the intermediate scattering function,  $\chi_\nu(\mathbf{q}, t)$ , during  $\tau_0$  assumes the following expression:

$$\chi_\nu(\mathbf{q}, t) = \exp\{-q^2[\gamma(0)_\nu - \gamma(t)_\nu]\} \quad (40)$$

where

$$\gamma(t)_\nu = (\hbar/2M_\nu) \int_0^\infty (\coth \beta \xi \cos \xi t + i \sin \xi t) \cdot f(\xi)_\nu / \xi d\xi. \quad (41)$$

$M_\nu$  is the rotational mass,  $f(\xi)_\nu$  is the frequency distribution of rotational oscillations (librational motion) and  $\beta = \hbar/2K_B T$ . The Debye-Waller factor usually denoted by  $2W_\nu$  is defined for librational motion by the equation:

$$2W_\nu = q^2 \gamma(0)_\nu \quad (42)$$

and has a form similar to that encountered for solids.

Explicit expressions for the effective rotational mass  $M_\nu$  have been discussed for linear and other molecules (Sears, 1966a, 1967). In the case of linear molecules we have:

$$M_\nu = Iq^2 \left\{ \sum_{l=1}^\infty l(l+1)(2l+1) j_l(qr_d)^2 \right\}^{-1} \quad qr_d \ll 1 \quad \frac{3I}{2r_d^2} \quad (43)$$

where  $I$  is the moment of inertia of the molecule,  $j_l(qr_d)$  is a spherical Bessel function of the first kind and of order  $l$  and  $r_d$  is the distance of the scattering nucleus from the centre of mass of the molecule.

An expansion of (40) gives:

$$\chi_\nu(\mathbf{q}, t) = \exp(-2W_\nu) \times \{1 + 2W_\nu[\gamma(t)_\nu/\gamma(0)_\nu] + \dots\}. \quad (44)$$

The hindered rotational motion during  $\tau_1$  when the molecule changes its direction in space is described by the general formalism developed by Sears (1966b) which is valid if there is no statistical correlation between librational motion and hindered rotational motion and if the isotropic forces acting on a molecule are much stronger than the anisotropic ones. We have:

$$\chi_R(\mathbf{q}, t) = \sum_{l=0}^\infty (2l+1) j_l(qr_d)^2 F_l(t), \quad (45)$$

where the mechanism of the rotational motion is hidden in the rotational relaxation functions  $F_l(t)$ . Explicit forms for  $F_l(t)$  can be calculated in a rigorous

way for the limiting cases (i) free rotation  $F_{IRD}$  and (ii) rotational diffusion,  $F_{IRF}$ . Components of both these modes of rotational motion probably exist in a real nematic liquid crystal. Both these rotational motions can be taken into account by assuming that during the time  $\tau_1$ , the rotational intermediate scattering function  $\chi_R(\mathbf{q}, t)$  is the result of the contribution of both rotational diffusion and free rotation. Accordingly we write:

$$F(l) = \alpha F_{IRD} + \beta F_{IRF} \quad (46)$$

where  $\alpha$  and  $\beta$  are two parameters determined so that:

$$0 < \alpha < 1 \quad \text{and} \quad 0 < \beta < 1. \quad (47)$$

Moreover we must require that when  $\alpha=0$  then  $\beta=1$  and when  $\alpha=1$  then  $\beta=0$ . Therefore the two parameters,  $\alpha$  and  $\beta$ , can be reduced to only one,  $y$ , by putting:

$$\alpha = y \quad \text{and} \quad \beta = 1 - y \quad (48)$$

with

$$0 < y < 1.$$

Equation (46) becomes:

$$F(l) = y F_{IRD} + (1 - y) F_{IRF}. \quad (49)$$

This procedure introduces the parameter  $y$ , which should be determined by studying experimentally the rotational relaxation functions  $F_l(t)$  which contain components of both kinds.

For free rotation the actual form of  $F_{IRF}$  is:

$$F_{IRF} = \frac{1}{\pi} \frac{\Gamma[\frac{1}{2}(l+1)]}{(\frac{1}{2}l)!} + \frac{2}{\pi} \sum_{m=1}^l \frac{\Gamma[\frac{1}{2}(l-m+1)] \Gamma[\frac{1}{2}(l+m+1)]}{[\frac{1}{2}(l-m)]! [\frac{1}{2}(l+m)]!} \times \exp(-\frac{1}{2}m^2 t^{*2}) M(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}m^2 t^{*2}) \quad (50)$$

where  $t^* = t(K_B T/I)^{1/2}$  and  $M(a, b, x)$  is Kummer's confluent hypergeometric function (Abramowitz & Stegun, 1965), and  $E_l = 0$  and  $1$  for  $l$  odd and even respectively.

For the case of rotational diffusion, when the rotational autocorrelation function obeys a simple diffusion equation, the form of  $F_{IRD}(t)$  is

$$F_{IRD}(t) = \exp[-l(l+1)D_r t] \quad (51)$$

where  $D_r$  is a rotational diffusion constant. As seen from equation (50), the constant terms in  $F_{IRF}$  lead to functions  $\psi(qr_d)$  which are:

$$\psi(qr_d) = \frac{1}{\pi} \sum_{l=0}^\infty (2l+1) j_l(qr_d)^2 \frac{\Gamma[\frac{1}{2}(l+1)]}{(\frac{1}{2}l)!} E_l \quad (52)$$

with

$$\sum_{l=0}^\infty j_l(qr_d)^2 = \frac{\text{Si}(2qr_d)}{2qr_d}. \quad (53)$$

$\text{Si}(2qr_d)$  is the sine integral function.

The two constituents of  $S_s(\mathbf{q}, t)$ ,  $A$  and  $B$  are given by:

$$A = \exp(-2W_\nu) \int_0^\infty dt \times \exp(-i\omega t - t/\tau_0) [1 + q^2 \gamma(t)_\nu + \dots]. \quad (54)$$

Higher terms are not included in the expansion because they do not add to the physical clarity of the resulting formulas. We have:

$$\begin{aligned} A &= \exp(-2W_\nu) \int_0^\infty dt \exp(-i\omega t - t/\tau_0) \\ &+ q^2 \exp(-2W_\nu) \int_0^\infty dt \exp(-i\omega t - t/\tau_0) \gamma(t)_\nu \\ &= \exp(-2W_\nu) \frac{\tau_0}{1+i\omega\tau_0} + q^2 \exp(-2W_\nu) \frac{\hbar}{2M} \int_0^\infty dt \\ &\times \exp(-i\omega t - t/\tau_0) \int_0^\infty d\xi [f(\xi)/\xi] \cdot [\coth \beta\xi \cos \beta t \\ &\quad + i \sin \xi t] \\ &= \exp(-2W_\nu) \frac{\tau_0}{1+i\omega\tau_0} \\ &+ q^2 \exp(-2W_\nu) \frac{\hbar}{2M} \frac{1}{2} \int_0^\infty d\xi [f(\xi)/\xi] \\ &\times \int_0^\infty dt \{ \coth \beta\xi [\exp(i\xi t) + \exp(-i\xi t)] \\ &+ [\exp(i\xi t) - \exp(-i\xi t)] \} \exp(-i\omega t - t/\tau_0) \\ &= \exp(-2W_\nu) \frac{\tau_0}{1+i\omega\tau_0} \\ &+ q^2 \exp(-2W_\nu) \frac{\hbar}{2M} \frac{\tau_0}{2} \int_0^\infty d\xi [f(\xi)/\xi] \\ &\times \left[ \frac{\coth \beta\xi + 1}{1+i(\omega-\xi)\tau_0} + \frac{\coth \beta\xi - 1}{1+i(\omega+\xi)\tau_0} \right] \\ &= \exp(-2W_\nu) \frac{\tau_0}{1+i\omega\tau_0} + q^2 \exp(-2W_\nu) \\ &\times \frac{\hbar}{2M} \left\{ \int_0^\infty d(-\xi) \frac{f(-\xi)}{-\xi} \frac{-1}{\exp(2\beta\xi) - 1} \frac{\tau_0}{1+i(\omega+\xi)\tau_0} \right. \\ &\left. + \int_0^\infty d\xi \frac{f(\xi)}{\xi} \frac{1}{\exp(2\beta\xi) - 1} \frac{\tau_0}{1+i(\omega-\xi)\tau_0} \right\} \\ &= \exp(-2W_\nu) \frac{\tau_0}{1+i\omega\tau_0} \\ &+ q^2 \exp(-2W_\nu) \frac{\hbar}{2M} (I_0 + iI_1) \end{aligned} \quad (55)$$

with

$$I_0 = \tau_0 \int_{-\infty}^{+\infty} d\xi \frac{f(\xi)}{\xi} \frac{1}{\exp(2\beta\xi) - 1} \frac{1}{1+(\omega+\xi)^2\tau_0^2} \quad (56)$$

$$I_1 = -\tau_0 \int_{-\infty}^{+\infty} d\xi \frac{f(\xi)}{\xi} \frac{1}{\exp(2\beta\xi) - 1} \frac{(\omega+\xi)\tau_0}{1+(\omega+\xi)^2\tau_0^2}. \quad (57)$$

It is seen that if the Lorentz function in  $I_0$  and  $I_1$  is small compared with the width of  $f(\xi)$ , and if  $f(\xi)$  does not vary too rapidly within a range of  $\xi$  values corresponding to the width of the Lorentz function, we find

$I_1 \ll I_0$  and we may in a first approximation neglect the imaginary part  $I_1$ . The term  $I_0$  is dominated by the frequency distribution  $f(\xi)$ . If a well defined and narrow quasi-elastic peak is observed, then  $I_0$  may be approximated by the expression:

$$\frac{\tau_0}{\tau_0 + \tau_1} \frac{f(\omega) \exp(-\beta\omega)}{\omega \sin \beta\omega} \quad (58)$$

which is the 'one-phonon' librational term.

The constituent  $B$  is given by:

$$\begin{aligned} B &= \psi(qn) \frac{(1-y)\tau_1}{1+i\omega\tau_1} \\ &+ y\tau_1 \sum_{l=1}^{\infty} (2l+1) j_l(qr_a)^2 \frac{1+\tau_1 l(l+1)D_r - i\omega\tau_1}{[1+\tau_1 l(l+1)D_r]^2 + \omega^2\tau_1^2} \\ &+ \frac{(1-y)}{\pi} \sum_{l=1}^{\infty} (2l+1) j_l(qr_a)^2 \\ &\times \sum_{m=1}^l \frac{\Gamma[\frac{1}{2}(l-m+1)] \Gamma[\frac{1}{2}(l+m+1)]}{[\frac{1}{2}(l-m)]! [\frac{1}{2}(l+m)]!} \\ &\times 2 \int_0^\infty M \left( -\frac{1}{2}, \frac{1}{2}, \frac{1}{2} m^2 \frac{K_B T}{I} t^2 \right) \\ &\times \exp \left( -\frac{1}{2} m^2 \frac{K_B T}{I} t^2 - t/\tau_1 - i\omega t \right) dt. \end{aligned} \quad (59)$$

After some manipulations on the integral of the last term of the preceding equation, that term reduces to:

$$\begin{aligned} &(1-f) \sum_{l=1}^{\infty} (2l+1) j_l(qr)^2 \sum_m \frac{\Gamma[\frac{1}{2}(l-m+1)] \Gamma[\frac{1}{2}(l+m+1)]}{[\frac{1}{2}(l-m)]! [\frac{1}{2}(l+m)]!} \\ &\times \int_{-\infty}^{+\infty} \frac{I}{m^2 k_B T} |\omega'| \exp \left[ -\frac{I}{2m^2 K_B T} (\omega')^2 \right] \\ &\times \frac{\tau_1}{1+(\omega'-\omega)^2\tau_1^2} d\omega' \end{aligned} \quad (60)$$

The prime over the second summation means sum over all odd  $m$ 's, when  $l$  is odd, and over all even  $m$ 's (starting with 2), when  $l$  is even.

Then the self-structure factor assumes the following form:

$$\begin{aligned} S_s(\mathbf{q}, t) &= \frac{\tau_0}{\tau_0 + \tau_1} A \frac{1+B/\tau_0}{1-AB/\tau_0\tau_1} \\ &+ \frac{\tau_1}{\tau_1 + \tau_0} B \frac{1+A/\tau_1}{1-AB/\tau_0\tau_1} + \text{c.c.} \\ &= \frac{1}{1-AB/\tau_0\tau_1} \left\{ \frac{\tau_0}{\tau_0 + \tau_1} A(1+B/\tau_0) \right. \\ &\left. + \frac{\tau_1}{\tau_1 + \tau_0} B(1+A/\tau_1) \right\} + \text{c.c.} \\ &= \frac{1}{1-AB/\tau_0\tau_1} \left\{ \frac{\tau_0}{\tau_0 + \tau_1} A + \frac{\tau_1}{\tau_0 + \tau_1} B \right. \\ &\left. + \frac{2AB}{\tau_0 + \tau_1} \right\} + \text{c.c.} \end{aligned} \quad (61)$$

The term in brackets of the preceding equation shows that the true physical situation can be described by a mixture of the extreme cases occurring when either

$\tau_0 \gg \tau_1$  or  $\tau_1 \gg \tau_0$ . The transition terms between the two phases of motion are represented by the third term in brackets and by the factor before the brackets.

The doubly differential cross section assumes the following form:

$$\frac{d^2\sigma_{\text{incoh}}}{dEd\omega} = Na_{\text{incoh}} \frac{K_s}{K_i\hbar} \frac{1}{1 - AB/\tau_0\tau_1} \left\{ \frac{\tau_0}{\tau_0 + \tau_1} A + \frac{\tau_1}{\tau_0 + \tau_1} B + \frac{2AB}{\tau_0 + \tau_1} \right\} + \text{c.c.} \quad (62)$$

The results obtained for the doubly differential cross section after substitution of the explicit values of  $A$  and  $B$ , is extremely complex and the chance of obtaining a result of some physical transparency is small. The cross section so obtained contains all the basic components in the scattered-neutron spectrum of a homogeneously oriented nematic liquid crystal presenting orientational fluctuations but not density fluctuations (the centre of mass of each molecule of the liquid crystal is stationary), and in absence of any external magnetic or electric field. The cross section (62) involves the basic idea that during the time  $\tau_0$  the molecule performs librations around a fixed direction, and during  $\tau_1$  it performs both rotational diffusion and free rotation, while the centre of mass of each molecule remains stationary.

When explicit expressions (55) and (59) for  $A$  and  $B$  respectively are substituted in equation (62), the terms of (62) can be grouped essentially in four terms after some quite elementary, even if lengthy, calculations:

$$\frac{d^2\sigma_{\text{incoh}}}{dEd\omega} = Na_{\text{incoh}} \frac{K_s}{K_i\hbar} \left\{ \Delta_1(y, f, \omega, \tau_0, \tau_1, q, n) + \Delta_2(y, f, \omega, \tau_0, \tau_1, q, n) + \Delta_3(y, f, \omega, \tau_0, \tau_1, q, n) + \Delta_4(y, f, \omega, \tau_0, \tau_1, q, n) \right\} \quad (63)$$

The term  $\Delta_1$  predicts a quasi-elastic peak of non-Lorentzian shape while the remaining terms predict an inelastic part determined essentially by three components: the librational term  $\Delta_2$  due to molecular motion during  $\tau_0$ , the free rotational term  $\Delta_3$  due to the molecular motion occurring during  $\tau_1$  and the rotational diffusion term  $\Delta_4$  due to the molecular motion occurring during  $\tau_1$ . The near-elastic scattering is characterized by a sharp central peak, the width of which is determined by a lifetime effect, while the inelastic contribution is concentrated quite close to the sharper quasielastic peak.

In order to simplify expression (63) and bring out the basic physics, we will discuss simplifications of (63) from the point of view of 'good' and 'bad' resolution measurements.

### 5. Good and bad-resolution measurements of cross sections and linewidths

The near-elastic scattering is characterized by a sharp central peak, the width of which is determined by a

lifetime effect. The rotational motion produces an inelastic contribution, which may be concentrated quite close to the sharper quasi-elastic peak, as seen on an energy scale, a time-of-flight scale or an angular scale.

The estimated width of the inelastic rotational spectra is, say, of the order of  $10^{12} \text{ s}^{-1}$  or about 1 meV and the width of the central quasi-elastic peak of the order of  $10^{11} \text{ s}^{-1}$  or about 0.1 meV, for a MBBA homogeneously oriented liquid crystal.

For free rotation as well as for rotational diffusion, the corresponding inelastic-scattering term consists of a series of terms beginning with  $l=1$ , as shown by equations (50)–(60). For bad-resolution measurements, terms with  $l \geq 2$  may influence the width of the central quasi-elastic peak, so that the inelastic and quasi-elastic peaks are not separated. Only one broadened peak is observed, whose width is determined by a weighted sum of the narrow quasielastic peak and the broader inelastic rotational spectrum. The importance of good resolution in experiments aiming at a study of the rotational effects in homogeneously oriented nematic liquid crystals is obvious.

Useful quantities, which may be tested experimentally are the angular variation of the intensity of the quasi-elastic and inelastic peaks. The  $\omega$  integration of the quasi-elastic peak, term  $\Delta_1$  of equation (63), and the inelastic peak, terms  $\Delta_2$ ,  $\Delta_3$  and  $\Delta_4$  of equation (63), according to equation (63) may be carried out in closed form and are given by:

$$I(q)_{\text{q.el.}} = a_{\text{incoh}}^2 \frac{\tau_0 \exp(-2W_\nu) + \tau_1 [y\psi(qr_d) + (1-y)j_0(qr_d)^2]}{\tau_0 + \tau_1} \quad (64)$$

for the quasi-elastic peak, and

$$I(q)_{\text{inel.}} = a_{\text{incoh}}^2 \frac{\tau_1 \exp(-2W_\nu) [1 - y\psi(qr_d) - (1-y)j_0(qr_d)^2]}{\tau_0 + \tau_1} \quad (65)$$

for the inelastic peak.

Formula (64) predicts that, if the libration is dominating, *i.e.*  $\tau_0 \gg \tau_1$ , the intensity is given by:

$$I(q)_{\text{q.el.}} = a_{\text{incoh}}^2 \exp(-2W_\nu) \quad (66)$$

whereas, if the rotation is dominating, *i.e.*  $\tau_1 \gg \tau_0$ , it is given by:

$$I(q)_{\text{q.el.}} = a_{\text{incoh}}^2 [y\psi(qr_d) + (1-y)j_0(qr_d)^2] \quad (67)$$

As the variation of  $I(q)_{\text{q.el.}}$  is quite different in the two cases, these formulae can be compared with experiments without difficulty. Up to now very few cold-neutron-scattering experiments on liquid crystals have been performed. However some comparisons of the theoretical results with experiments can be done. In effect, recalling equation (42), we have for  $W_\nu$ :

$$2W_\nu = q^2\gamma(0)_\nu = \frac{1}{2}q^2\langle r_\nu^2 \rangle \quad (68)$$



which follows from an analogy with solids;  $\langle r_v^2 \rangle$  is the mean-square radius of the fully developed thermal cloud in the librational motion. Now it has been experimentally found by Dimic, Barbic & Blinc (1972) that the intensity of the quasi-elastic peak at different scattering angles for cold-neutron scattering in a MBBA liquid crystal is governed by a single exponential:

$$I(q)_{q.e.l.} = A \exp\left(\frac{q^2 \langle r_v^2 \rangle}{6}\right). \quad (69)$$

Substituting equation (68) in equation (66) leads to

$$I(q)_{q.e.l.} = a_{\text{incoh}}^2 \exp - \frac{q^2 \langle r_v^2 \rangle}{6}. \quad (70)$$

Comparing equations (70) and (69), we can conclude that in the experiments performed by Dimic, Barbic & Blinc (1972) the libration dominates. In this limit, *i.e.*  $\tau_0 \gg \tau_1$ , the quasi-elastic peak reduces to:

$$\left[ \frac{d^2\sigma}{dEd\omega} \right]_{q.e.l.} = \frac{a_{\text{incoh}}^2 K_s}{\pi K_i} \tau_0 \exp(-2W_\nu) \times \frac{1 - \psi(qr_d) \exp(-2W_\nu)}{[1 - \psi(qr_d) \exp(-2W_\nu)]^2 + \omega^2 \tau_0^2}. \quad (71)$$

This cross section is of Lorentzian shape and the full width at half maximum is defined by:

$$\Delta\omega = \frac{2}{\tau_0} [1 - \psi(qr_d) \exp(-2W_\nu)]. \quad (72)$$

The limiting behaviour at small and large  $q$  values is:

$$\Delta\omega \xrightarrow{q \rightarrow 0} \frac{\langle r_v^2 \rangle + 2r_d^2}{3\tau_0} q^2 \quad (73)$$

$$\Delta\omega \xrightarrow{q \rightarrow \infty} \frac{2}{\tau_0}. \quad (74)$$

On the other hand, if rotations dominate, *i.e.*  $\tau_1 \gg \tau_0$ , the quasi-elastic peak reduces to

$$\left[ \frac{d^2\sigma}{dEd\omega} \right]_{q.e.l.} = \frac{a_{\text{incoh}}^2 K_s}{\pi K_i} \tau_1 \exp(-2W_\nu) \times \frac{1 - [y\psi(qr_d) + (1-y)j_0(qr_d)^2] \exp(-2W_\nu)}{\{1 - [y\psi(qr_d) + (1-y)j_0(qr_d)^2] \exp(-2W_\nu)\}^2 + \omega^2 \tau_1^2}. \quad (75)$$

The inelastic contribution is due to the contribution of the free rotation as well as of the rotational diffusion and the corresponding inelastic scattering term consists of a series of terms beginning with  $l=1$ . If we consider only the term  $l=1$  and neglect the other higher terms (this neglect is legitimate in the case of good-resolution measurements) the inelastic peak, which may be concentrated quite close to the sharper

quasi-elastic peak, reduces to:

$$\left[ \frac{d^2\sigma}{dEd\omega} \right]_{\text{inel}} = \frac{a_{\text{incoh}}^2 K_s}{\pi K_i} \times \exp(-2W_\nu) \left[ \frac{(1-y)\tau_1}{\tau_0 + \tau_1} \frac{3j_1(qr_d)^2}{\pi} \int_{-\infty}^{+\infty} \frac{I\omega'}{2K_B T} \times \exp(-i\omega'^2/2K_B T) \frac{\tau_1 d\omega'}{1 + (\omega' - \omega)^2 \tau_1^2} + \frac{y\tau_1}{\tau_0 + \tau_1} \frac{3j_1(qr_d)^2}{\pi} \frac{(1 + 2D_r \tau_1) \tau_1}{(1 + 2D_r \tau_1)^2 + \omega^2 \tau_1^2} \right]. \quad (76)$$

The first term of equation (76), which can be easily integrated if the quasi-elastic central peak may be approximated by a  $\delta$  function, describes a Maxwellian type distribution on each side of  $\omega=0$ , the separation of maxima being:

$$2\Omega = 2(K_B T/I)^{1/2}. \quad (77)$$

The second term describes a Lorentzian distribution of width:

$$\Delta\omega = 2(1/\tau_1 + 2D_r). \quad (78)$$

Once again it results quite clearly that line-width studies carried out in various cold-neutron-diffraction observations on homogeneously oriented nematic li-

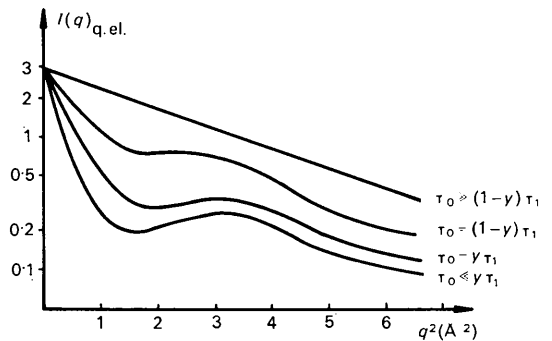


Fig. 2. Intensity,  $I(q)_{q.e.l.}$ , of the quasi-elastic peak *vs.*  $q^2$  for various ratios  $\tau_0/\tau_1$  and for  $y=0.9$ . Libration is supposed to occur during  $\tau_0$ , free rotation during  $y\tau_1$  and diffusive rotation during  $(1-y)\tau_1$ .

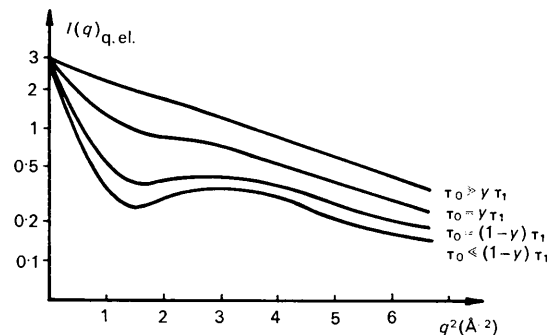


Fig. 3. Intensity  $I(q)_{q.e.l.}$  of the quasi-elastic peak *vs.*  $q^2$  for various ratios  $\tau_0/\tau_1$  and for  $y=0.1$ . Libration is supposed to occur during  $\tau_0$ , free rotation during  $y\tau_1$  and diffusive rotation during  $(1-y)\tau_1$ .

quid crystals may have different meanings depending on the relative values of  $\tau_0$ ,  $\tau_1$ ,  $D$ , and  $\Omega$ . The relative values of  $\tau_0$  and  $\tau_1$  in a homogeneously oriented nematic liquid crystal depend upon the shape of the molecules and the nature of the intermolecular forces. It is to be expected that  $\tau_1 < \tau_0$  for long molecules sensitive to anisotropic forces or for strongly bound molecules, that  $\tau_1 \sim \tau_0$  for molecules of intermediate length or more loosely bound molecules, and that  $\tau_1 > \tau_0$  for spherical molecules or weakly bound molecules.

If  $\tau_1$  were of the same order of magnitude as  $D\tau_1^{-1}$  or  $\Omega^{-1}$ , the quasi-elastic peak would be determined by the relative magnitude of  $\tau_0$  and  $\tau_1$ . If  $\tau_1 \geq \tau_0$  the width of the quasi-elastic peak would be of the order of  $1/\tau_1$  ( $\sim D$ , or  $\Omega$ ), and therefore it would be so wide that it could not be separated from the broader inelastic rotational spectrum, regardless of whether the rotation is free or diffusive. If  $\tau_0 \gg \tau_1$  the width of the quasi-elastic peak would be determined by  $\tau_0^{-1}$ , and the broader rotational inelastic spectrum would not be observed because its area is determined by the ratio  $\tau_1/\tau_0$ .

If  $\log I(q)_{q,el.}$  is plotted as a function of  $q^2$  assuming a case described by equation (64):

$$I(q)_{q,el.} = a_{incoh}^2 \frac{\tau_0 \exp(-2W_V) + \tau_1 [y\psi(qr_d) + (1-y)j_0(qr_d)^2]}{\tau_0 + \tau_1},$$

a set of curves as given in Figs. 2 and 3 is obtained when the ratio  $\tau_0/\tau_1$  is varied between the limits 0 and  $\infty$ , for fixed values of  $y$ . It is also assumed that  $2W_V = u^2 q^2$  with  $u^2 = 0.5 \text{ \AA}^2$  and  $r_d = 3 \text{ \AA}$ . It was assumed that only one distance  $r_d$  of the scattering nucleus from the molecular centre of mass exists in order to bring out clearly the basic physics. In most nematic liquid crystals several values of  $r_d$  are involved, which means that the general tendency of  $I(q)_{q,el.}$ , as shown in Figs. 2 and 3, will remain even if its marked structure is lost upon summation of several terms.

The slope of the curves  $I(q)_{q,el.}$  of Figs. 2 and 3 at the origin is obtained from a series expansion of equation (64):

$$I(q)_{q,el.} = a_{incoh}^2 \left( 1 - \frac{\tau_0 u^2 + \tau_1 y r_d^2 / 3 + (1-y) \tau_1 r_d^4 q^2 / 36}{\tau_0 + \tau_1} q^2 \right) \quad \text{as } q \rightarrow 0. \quad (79)$$

We will remark that the slope of the curves  $I(q)$  at the origin does not depend on the contribution of the term  $(1-y)j_0(qr_d)^2$ . The slope varies from  $-u^2$ , if  $\tau_0 \gg \tau_1 y$  to  $-r_d^2/3$ , if  $\tau_1 y \gg \tau_0$ .

If  $\tau_0$  and  $\tau_1$  interchange their roles over the meso-phase range, a characteristic variation of this slope as

a function of the temperature is expected. The expected magnitude of the slope for a MBBA liquid crystal molecules in the nematic-liquid phase varies from 0.06 to 0.2  $\text{\AA}^2$  to about 2.5  $\sim$  3  $\text{\AA}^2$  in the isotropic-liquid phase. The physical meaning of these findings is clear: in the nematic-liquid phase the homogeneously oriented molecules perform librations; the amplitude of these librations increases steadily over the whole nematic-liquid range, and near the isotropic-liquid phase the molecules have great probability of rotating freely. It is of particular interest in this connexion to study the slope of the curves of  $\log I(q)$  vs.  $q^2$  for small  $q$  values according to equation (79) for a MBBA liquid crystal homogeneously oriented. The variation of the intensity of the elastic peak is completely dominated by the motion of alkyl end chains. Equation (79) predicts that this slope varies from very small values of about 0.06  $\text{\AA}^2$  in the nematic-liquid range just below the solid phase to values of about 0.2  $\text{\AA}^2$  just above the isotropic-liquid phase. The alkyl end chains are thus bound and perform librations just below the solid phase, whereas the probability of rotational motion increases when the isotropic-liquid phase is reached.

## 6. Conclusion

We have presented a rather general formulation of the cold-neutron incoherent scattering by a homogeneously oriented nematic liquid crystal, showing fluctuations in orientation, allowing various models for molecular librational motion, as well as rotational motion (free and diffusive rotation) to be tested against experimental facts. In this paper the rotational motion has been assumed to be composed of both rotational diffusion and free rotation.

It is believed that the main features of several scattering experiments on homogeneously oriented nematic liquid crystals may be understood on the basis of the formulae presented, whose usefulness has been discussed also from the standpoint of bad and good-resolution measurements.

## References

- ABRAMOWITZ, M. & STEGUN, I. A. (1965). *Handbook of Mathematical Functions*, p. 504. New York: Dover Press.
- BROCKHOUSE, B. N. (1958). *Nuovo Cim.* **9**, 45-71.
- CHATELIN, P. (1943). *Bull. Soc. Fr. Minér. Crist.* **66**, 105-130.
- DIMIC, V., BARBIC, L. & BLINC, R. (1972). *Phys. Stat. Sol.* (b), **54**, 121-124.
- SEARS, V. F. (1966a). *Canad. J. Phys.* **44**, 1279-1297.
- SEARS, V. F. (1966b). *Canad. J. Phys.* **44**, 1299-1311.
- SEARS, V. F. (1967). *Canad. J. Phys.* **45**, 237-254.
- VAN HOVE, L. (1954). *Phys. Rev.* **95**, 249-262.