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The evidence for a metastable phase in norbornadiene: x-ray and quasi-elastic neutron scattering studies

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Abstract. The dynamics of the norbornadiene molecule is studied over the temperature range 190–265 K. Measurements below $T = 202$ K and above $T = 254$ K correspond to the ordered phase and to the liquid state, respectively. In the range 202–254 K, two plastic phases can exist, depending on the cooling conditions. On the timescale accessible to time-of-flight neutron spectroscopy (10^{-11} – 10^{-12} s), an elastic incoherent structure factor is extracted in the different phases. From its analysis, quasi-elastic spectra are described on the basis of a model associating 60° jump rotations with a displacement of the centre of mass of the molecules. The same model holds for the two plastic phases, no difference in the dynamics of the molecules being evident. The temperature dependence of the broadening yields a unique Arrhenius law with a rather small value of the activation energy. In the liquid state, in addition to this rotational motion, a long-range diffusion by a jump mechanism was evidenced.

1. Introduction

Among the crystals that exhibit an orientationally disordered solid phase, norbornadiene (bicyclo[2.2.1]hepta-2,5-diene), illustrated schematically in figure 1 (see also table 1), appears to be a particularly interesting candidate for molecular motion studies, because of its globular shape associated with a very low molecular symmetry. Indeed, so far, the orientationally disordered crystals that have been the most intensively investigated are those with a high molecular symmetry (T_d , C_{3v} , etc). The crystal structure of their plastic phase is usually FCC, BCC or HCP and the symmetry elements of both the molecule and the lattice are often closely related. In spite of their low molecular symmetry, norbornadiene and related compounds also exhibit plastic phases. Recently, incoherent quasi-elastic neutron scattering (IQNS) was used to study the rotational behaviour of norbornane (bicyclo[2.2.1]heptane) in its two plastic phases (Bée *et al* 1986). While norbornadiene differs from norbornane only by the existence of double bonds as indicated in figure 1, their thermodynamic properties are somewhat different (Westrum 1969, Jackson and Strange 1972). Norbornadiene is liquid at room temperature. Between $T_t = 202$ K and $T_m = 254$ K (melting, $\Delta S_m = 6.656$ J mol $^{-1}$ K $^{-1}$), it exhibits a

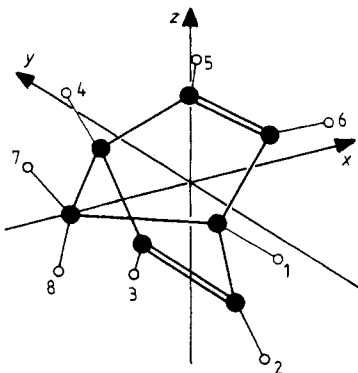


Figure 1. Sketch of the norbornadiene molecule. Carbons are in black and hydrogens in white. The axes Ox , Oy and Oz referred to in the text are indicated. Atoms are numbered according to table 1.

Table 1. Coordinates (\AA) of the atoms of the norbornadiene molecule, in the Cartesian frame ($Oxyz$) indicated in figure 1, with origin at the centre of mass. Atoms are numbered according to figure 1.

Atom	x	y	z
1	-0.690	-2.139	0.001
2	0.858	-1.763	-1.642
3	0.858	1.763	-1.642
4	-0.690	2.139	0.001
5	0.858	1.763	1.642
6	0.858	-1.763	1.642
7	-2.020	0.000	0.904
8	-2.020	0.000	0.904

plastic phase. The lattice is HCP with parameters $a = 5.89 \text{ \AA}$ and $c = 9.51 \text{ \AA}$. Below $T_t = 202 \text{ K}$ the low-temperature phase is ordered. The molecular disorder in the plastic phase was evidenced by nuclear magnetic resonance (NMR) (Folland *et al* 1973a, b, Chadwick and Forrest 1978). But it turns out that the relaxation is mainly influenced by the self-diffusion of the molecules, thus preventing precise information being obtained about their rotational dynamics.

Another important result was recently provided by x-ray scattering experiments. These latter unambiguously proved the existence of another plastic phase, with FCC structure. This phase is unstable and can be obtained by a slow cooling of the sample from the liquid state. It remains down to the temperature of transition to the low-temperature ordered phase. Its existence could be confirmed by neutron scattering experiments.

Because of its large number of hydrogen atoms, norbornadiene is well adapted to an investigation using the IQNS technique. With this method the motions of the individual hydrogen atoms within the molecule are accessible, and therefore the reorientations of the whole molecule itself are revealed. Our aim in this paper is to report on these IQNS experiments that we have performed in both the HCP and the FCC crystalline phases of norbornadiene, and to compare the dynamics of the molecules in these two plastic phases.

2. X-ray scattering experiments

The experiments were carried out using an x-ray tube with a Cu anode. The detector was a gas flow blade chamber, with a curved anode accurately located on the circle of a goniometer. The x-ray peak positions were obtained through the so-called delay line read-out method. The diffraction pattern was recorded over a 120° range in 2θ with a 4096-channel analyser providing a spatial resolution of less than 0.03 \AA . Typical diagrams are shown in figure 2, for three different temperatures: $T = 300, 200$ and 230 K . The highest temperature corresponds to the liquid phase of norbornadiene. The intense background originates from the scattering of the glass tube in which the sample had been placed. The striking feature is the presence of a broad diffuse band, which corresponds to a distance of about 4.86 \AA , thus indicating the existence of local order in this phase. The spectrum obtained at $T = 200 \text{ K}$ corresponds to the usual HCP plastic phase. In the low-Bragg-angle region it exhibits a series of three sharp reflections with lattice spacings $5.03, 4.63$ and 4.42 \AA , which can be indexed as the inter-planar distances d_{100}, d_{002} and d_{101} of the hexagonal lattice. Conversely, when the sample is slowly cooled from the liquid state, only two sharp peaks are observed at $T = 230 \text{ K}$. The lattice spacings 5.07 and 4.48 \AA are in the ratio $2 : \sqrt{3}$ characteristic of a FCC lattice.

The existence of these phases was confirmed by other methods. Therefore, we tried to get a better knowledge of them and especially of the dynamics of the molecules within them. Because of the ability of neutrons to provide both geometrical and dynamic information on molecular motions at the microscopic level, a neutron scattering experiment was performed.

3. Neutron measurements: experimental set-up and data corrections

The experiments were carried out at the Institut Laue-Langevin (Grenoble, France), using the time-focusing, time-of-flight spectrometer, IN6. The associated wavelength of the incident neutrons was 5.1 \AA , corresponding to an energy $E_0 = 3.15 \text{ meV}$, with a full width at half-maximum (FWHM) of the spectral distribution $\Delta E = 0.085 \text{ meV}$. Four series of experiments were carried out. Measurements at $T = 190$ and 265 K correspond respectively to investigations in the ordered phase and in the liquid state. A third series was performed by cooling down the sample from the liquid state into the plastic hexagonal phase. Norbornadiene was investigated at $T = 245, 235, 220$ and 210 K . Finally another series of measurements was carried out in the metastable FCC plastic phase, obtained by slow cooling from the liquid, at $T = 232, 227, 220$ and 210 K .

For each temperature of analysis, 89 spectra were recorded over the angular range $10.3\text{--}114^\circ$ (momentum transfer range $0.2\text{--}2.1 \text{ \AA}^{-1}$). Then they were added together by groups of 4–7 angles in order to improve the counting statistics of the scattered neutrons. Thus 15 spectra were finally obtained, corresponding to a resolution in momentum transfer $Q = 0.12 \text{ \AA}^{-1}$. By this method it was possible to check the actual phase of the specimen. Indeed, diffraction patterns were obtained from the variation of the integrated purely elastic intensity as a function of the scattering angle (figure 3). Furthermore, coherent scattering arising from the Bragg reflections could be avoided by eliminating the corresponding detectors in the grouping procedure for the quasi-elastic analysis.

The specimen (transmission 0.89) was held in a slab-shaped container of circular geometry ($0.3 \times 50 \text{ mm}^2$ in size) with thin walls of aluminium plates. This container was placed into a liquid-helium cryostat. In all cases, deviations in the temperature stability

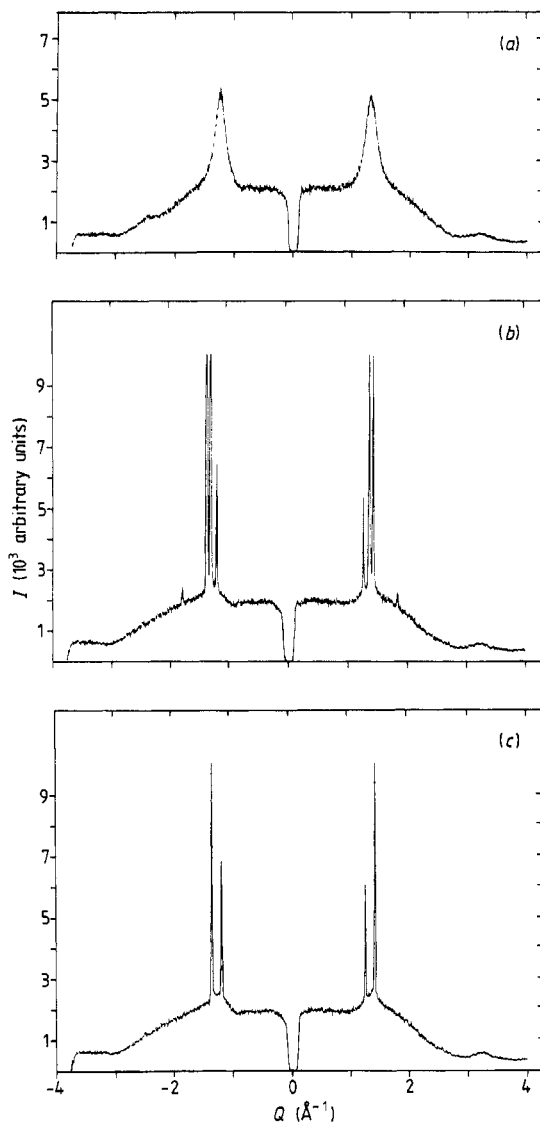


Figure 2. X-ray diffraction patterns (a) in the liquid phase ($T = 300$ K), (b) in the HCP phase ($T = 200$ K) and (c) in the FCC phase ($T = 230$ K) of norbornadiene. The raw data are not corrected for the scattering of the capillary glass tube around the sample, which is responsible for the intense background under the peaks.

were less than 0.2 K. The angle between the plane of the sample and the incoming neutron beam was 135° in all the experiments.

The time-of-flight (TOF) spectra were first corrected for absorption, self-shielding, detector efficiency and cryostat scattering using standard methods and programs. The instrument resolution was determined from a measurement with a vanadium standard, 1 mm in thickness. Then the experimental spectra were transformed into energy spectra

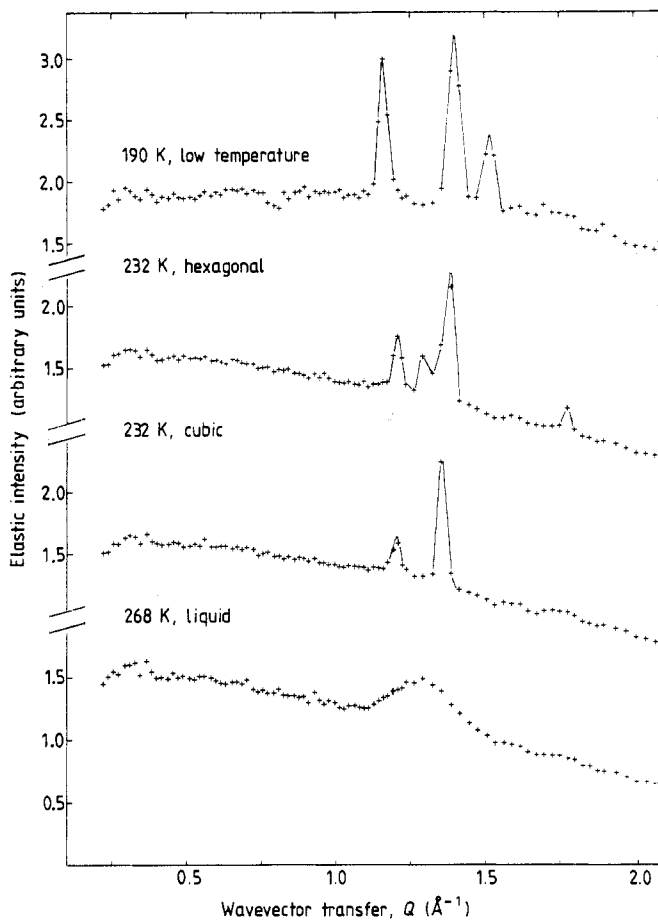


Figure 3. Neutron diffraction. Variation of the elastic intensity as a function of the wavevector transfer (\AA^{-1}) evidencing the Bragg peaks in the low-temperature phase ($T = 190$ K) and in the HCP and FCC plastic phases at the same temperature ($T = 232$ K). In the liquid phase, at $T = 268$ K a broad band appears in this Q -range.

$S(\theta, \omega)$ at constant scattering angle θ . No correction was made for multiple scattering, the thickness of the sample having been chosen as thin as possible in order to reduce these effects. (These latter were evaluated from the measured value of the transmission to be less than 4% of the total.)

Data collected at the same temperature were compared by a least-squares fit to the following scattering function (see for instance Bée 1988)

$$S_{\text{inc}}(Q, \omega) = \exp(-2W)S_{\text{inc}}^{\text{R}}(Q, \omega) + S_{\text{inc}}^{\text{I}}(Q, \omega) \quad (1)$$

folded with the instrument resolution. Here $S_{\text{inc}}^{\text{R}}(Q, \omega)$ is the rotational scattering function of the relevant model. Periodic lattice motions and intra-molecular vibrations cause an attenuation effect in the quasi-elastic region taken into account by the Debye-Waller term $\exp(-2W)$. They also introduce the inelastic term $S_{\text{inc}}^{\text{I}}(Q, \omega)$, which actually contributes only little to the scattering in this region in the form of a slowly varying function of energy.

4. Results and discussion

4.1. Inspection of the time-of-flight spectra

Before starting with the usual quantitative analysis of the energy spectra in terms of the relative amounts of their respective quasi-elastic and purely elastic parts, a simple direct inspection of the time-of-flight spectra recorded in the different phases already allows us to draw some conclusions.

The most striking feature is certainly the strong quasi-elastic broadening of the spectra corresponding to the two plastic phases (figures 4(a) and (b)). It is clear evidence of the occurrence of rapid motions of the molecules. Moreover, the relative part of the purely elastic intensity in the scattering is found to decrease strongly as a function of the momentum transfer. That reflects the existence of a large number of equilibrium positions accessible to each proton of the molecule. Another striking feature is the significant contribution in the quasi-elastic region of the part of the scattering related to the lattice vibrations. Thus the term $S_{\text{inc}}^{\text{l}}(Q, \omega)$ in (1) could not be neglected and it was taken into account in all the data analyses in the form of a $c_1 + c_2 Q^2$ term (with c_1 and c_2 adjustable constants). A point of major importance is the large similarity between the spectra (at neighbouring temperatures) obtained in the two plastic phases. Clearly, there is no direct evidence of a difference in the dynamic behaviour of the molecules in the HCP and FCC phases and the comparison requires a more quantitative analysis.

In the liquid state, we could expect to be concerned with a long-range translational diffusion of the molecules. This motion would result in the absence of any elastic intensity in the scattering, all the energy spectra being broadened according to the well known DQ^2 law. Figure 4(c) shows a crude graphical separation of the purely elastic scattering in the time-of-flight spectrum recorded at 1.63 \AA^{-1} , based on the FWHM of the instrument resolution. At this position in reciprocal space the effects of the coherent scattering (the broad band at about 1.3 \AA^{-1} in the diffraction pattern) have no influence. Clearly, the wide quasi-elastic contribution underlying the spectrum originates from the rotations of the molecules already occurring in the plastic phases. There is no drastic change in the timescale of these motions at the melting point. Especially, there is no direct evidence of a broadening of the rest of the spectrum as a result of the appearance in the liquid phase of the long-range diffusion. Actually, the spectra in the liquid state at $T = 265 \text{ K}$ look very similar to those in the plastic phases, with apparently still a noticeable amount of elastic scattering. It is well known that, strictly speaking, purely elastic scattering in liquids does not exist. However, experimentally, the distinction between 'elastic' and 'quasi-elastic' scattering is essentially governed by the instrument energy resolution. The presence of an elastic component in the IN6 spectra would simply mean that, *on the timescale* 10^{-11} – 10^{-12} s, the centres of mass of the molecules in the liquid state cannot access all the positions in space. An experiment with a better resolution in time (e.g. a high-resolution back-scattering spectrometer like IN10 (see for instance Bée 1988), which makes accessible the 10^{-9} – 10^{-10} s timescale) would resolve this scattering. Volino and Dianoux (see for instance Volino and Dianoux 1980) have shown that any restriction in the volume of space accessible to the scatterers produces an elastic contribution to the scattering. They also derived the corresponding scattering function. Such a conclusion about the limited region of space explored by the molecules within the timescale characteristic of the present experiment fully agrees with the presence of coherent scattering in the liquid state at $Q = 1.3 \text{ \AA}^{-1}$, i.e. in the region where intense Bragg peaks occur in both plastic phases, due to the persistence of a short-range order commonly observed

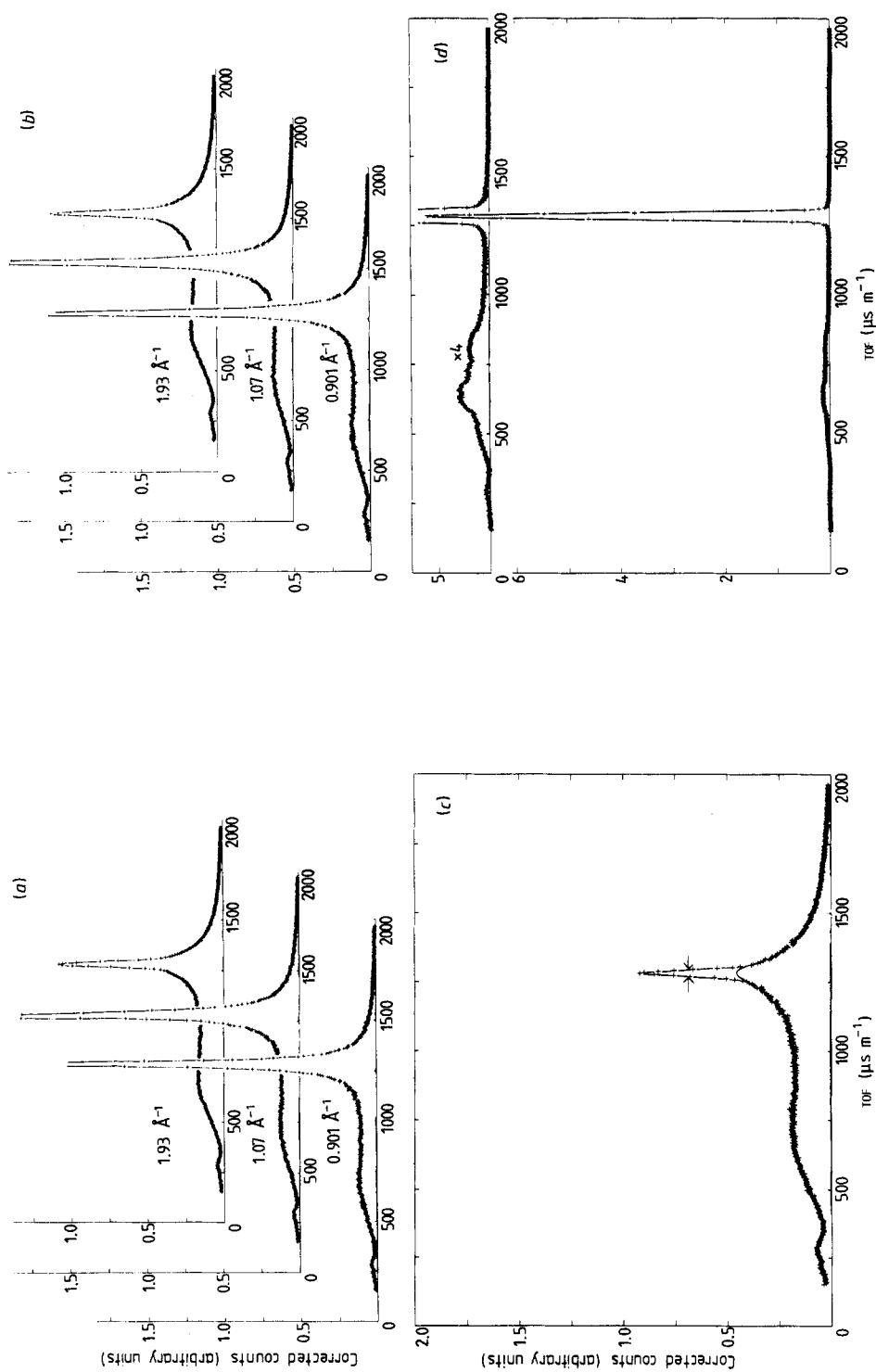


Figure 4. (a) Examples of time-of-flight (TOF) spectra recorded in the hexagonal phase of norbornadiene at $T = 232$ K. The corresponding values of the momentum transfer are 0.90 , 1.07 and 1.93 \AA^{-1} . (b) Examples of TOF spectra recorded in the cubic phase of norbornadiene at $T = 265$ K; same values of the momentum transfer as in (a). (c) Example of TOF spectrum obtained in the liquid phase of norbornadiene at $T = 265$ K. The scattering angle is $2\theta = 84.6^\circ$ corresponding to a momentum transfer $Q = 1.63 \text{ \AA}^{-1}$ (i.e. outside the region of the broad band appearing in figure 3). A rough separation of the purely elastic scattering based on the FWHM of the instrument resolution is indicated. (d) Example of TOF spectrum recorded in the low-temperature phase of norbornadiene at $T = 190$ K. The value of the momentum transfer is $Q = 1.63 \text{ \AA}^{-1}$. The scale on the upper part of the figure has been multiplied by 4.

in liquids. Actually, at this stage of our analysis and after a simple inspection of the data, it is too early to draw conclusions and to rule out the long-range diffusion motion in the liquid state. A more detailed analysis is required and will be performed later in this paper. For the moment we continue our inspection of the data in the different phases.

In the low-temperature phase ($T = 190$ K), no quasi-elastic broadening of the TOF spectra is visible (figure 4(d)). The investigation of possible motions in this phase would require a much better resolution than the IN6 one. It seemed worth comparing the spectra obtained with norbornadiene with those obtained with norbornane in the previous experiment (Bée *et al* 1986). At the highest temperature of the experiments in the temperature range $245 \text{ K} < T < 314 \text{ K}$, molecular motions in norbornane could be described as an isotropic rotational diffusion of the molecules about their centres of mass. A careful inspection showed that at larger Q -values the amount of purely elastic scattering in the TOF spectra for norbornadiene, even if it is small, is nevertheless larger than in the case of norbornane. It turns out that the motions of the norbornadiene molecules appear less isotropic.

Another difference between the behaviours of these two compounds manifests itself in the temperature evolution of the spectra. By inspection of the spectra corresponding to the same Q -value, at different temperatures, it can be noticed that the relative amount of elastic intensity in the norbornane spectra definitely increases when the temperature decreases. Conversely, there is no evidence of such a pronounced variation in the case of norbornadiene, the decrease of the temperature having more influence upon the timescale of the molecular motions (variation of the broadening) than on the geometry of these motions (figure 5).

The preliminary analysis of our data led to some conclusions that we were able to confirm by a more quantitative analysis. Especially, more information can be obtained from the determination of the so-called elastic incoherent structure factor (EISF).

4.2. Determination of the experimental EISF

A separation of the energy spectra into their elastic and quasi-elastic parts provides detailed information about the geometry of the motions responsible for the quasi-elastic broadening. To avoid the uncertainties linked to a crude graphical separation, a systematic procedure has been developed and already widely reported elsewhere (Bée *et al* 1982). It consists of a refinement of an approximate but sufficiently realistic scattering law to the experimental spectra, introducing a weight parameter controlling the respective amounts of purely elastic and quasi-elastic intensities. One of the advantages of this method is to account for the variation of the scattering vector inside the energy spectra recorded at constant scattering angle.

The lack of precise crystal structure information forbids the building of a detailed dynamic model. The same situation occurred in the case of norbornane (Bée *et al* 1986). There the strong decrease of the elastic intensity suggested the use of the so-called isotropic rotational diffusion model in the EISF extraction procedure. This description was found to agree with the experimental data at room temperature. Therefore, considering the conclusions of our TOF spectra analysis concerning the smaller isotropy of the motions in norbornadiene, this model was discarded in the present case. To get some insight about the EISF and therefrom about the region of space accessible to the protons within the molecule of norbornadiene, the quasi-elastic part of the spectra was taken into account in the computing procedure by a simple sum of two Lorentzian functions,

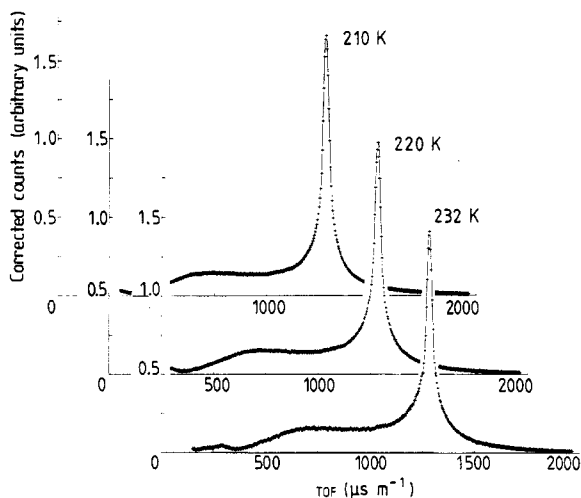


Figure 5. Temperature evolution of a TOF spectrum in the hexagonal phase of norbornadiene. The temperatures are $T = 210, 220$ and 232 K. The value of the momentum transfer is $Q = 1.63 \text{ \AA}^{-1}$.

folded with the instrument resolution. It turned out that the variation of the EISF values obtained as a function of the momentum transfer seemed in accordance with the predictions of the model based upon uniaxial rotation about the molecular twofold axis. Thus this model was introduced in the EISF extraction procedure and a new series of values was obtained. Actually these latter were only slightly different from the preceding ones. These are illustrated in figure 6, where they are compared with the theoretical predictions of this model, applied to rotations about the three axes Ox , Oy and Oz as defined in figure 1, and also of the isotropic rotational diffusion model. The radii of gyration are listed in table 2.

The points obtained at temperature $T = 265$ K correspond to the liquid phase just above the melting point ($T_m = 254$ K). Clearly at small momentum transfer, the experimental values lie below the theoretical curve related to the isotropic rotational diffusion over a sphere. This indicates that the region of space accessible to each hydrogen is larger than the simple surface of a sphere. It is well known that in the case of long-range diffusion the quasi-elastic spectra exhibit a Lorentzian shape with a broadening according to the DQ^2 law. Thus except for $Q = 0$, where the broadening vanishes, there is no purely elastic contribution to the scattered intensity. That is in contrast with the values of the experimental EISF. But it is quite possible that our results are actually an artefact of the procedure of determination of the EISF: indeed, a small broadening of the elastic part related to the rotational motion of the molecule was not taken into account in the model. On the other hand, the presence of a purely elastic component in the spectra obtained in the liquid phase is real if, on the timescale of investigation accessible to the instrument, the molecules cannot access all the positions in space and move within a restricted volume. The corresponding scattering function derived by Volino and Dianoux (1980) is composed of an elastic contribution, the amplitude of which depends on the volume dimensions, superimposed on a quasi-elastic component. The latter is essentially Lorentzian in nature. Its HWHM remains nearly constant at small Q -values and then tends asymptotically to the DQ^2 law for larger momentum transfers. In the

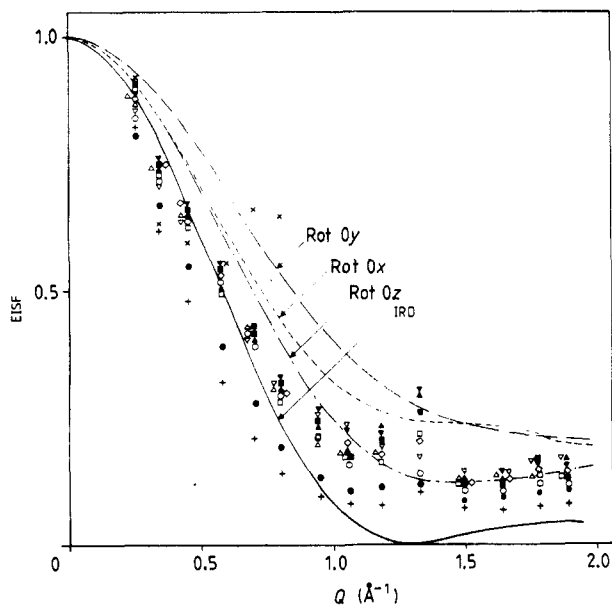


Figure 6. Determination of the experimental EISF and comparison with the uniaxial diffusion model about the three principal molecular axes and also with the isotropic rotational diffusion (IRD) model. The full symbols correspond to the HCP phase, the open symbols to the FCC phase, and the crosses refer to the liquid phase.

Table 2. Radii of gyration (\AA) of the hydrogen atoms of the norbornadiene molecule about different axes and about the centre of mass.

Atom	Radii about axes			Radius about centre of mass
	Ox	Oy	Oz	
1	2.139	0.690	2.247	2.247
2	2.408	1.854	1.963	2.545
3	2.408	1.854	1.963	2.545
4	2.139	0.690	2.247	2.247
5	2.408	1.854	1.963	2.545
6	2.408	1.854	1.963	2.545
7	0.904	2.214	2.020	2.214
8	0.904	2.214	2.020	2.214

low- Q range, it can be difficult to discriminate whether the actual shape of the spectra is the result of a small broadening of the whole spectra or of a superposition of an intense elastic part over a small amount of quasi-elastic scattering with a significant broadening. Nevertheless, the discrimination between the two hypotheses should be easier for the largest Q -values.

In the two solid phases, conversely, the experimental points definitely lie above the theoretical curve corresponding to the isotropic rotational diffusion model. The most striking feature is the failure of the models based upon uniaxial rotation about the Ox,

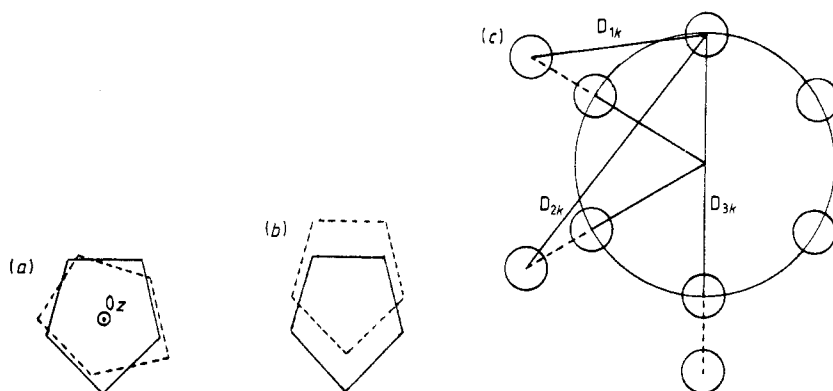


Figure 7. Illustration of the model combining a rotation and a displacement of the centre of gravity. (a) Rotation of 60° about the O_z axis. (b) Displacement of the centre of mass. (c) Combination of (a) and (b).

Oy or Oz axes (figure 6). The model corresponding to a rotation about the Oz axis is certainly the closest to the experimental points in the high- Q range. Nevertheless, the curve definitely lies above the experimental data for Q smaller than 1 \AA^{-1} . This is an indication of the possibility for the hydrogen atoms to undergo displacements larger than the maximum distances allowed in this model.

4.3. Refinements of the experimental data

It would be fruitful to have some information about the crystallographic structure of norbornadiene in its plastic phases. Especially knowledge of the equilibrium orientations of the molecules appears essential, while the determination of the thermal ellipsoids would provide some insight about the reorientations themselves.

So far, we have considered models where the reorientations of the molecules occurred about their centre of gravity or about an axis passing through their centre of gravity. All of them were unsuccessful, and, in fact, it is likely that all other attempts will also be unsuccessful, as long as only purely rotational models are considered. Clearly, the introduction of another component in the motion is required. Here it must be pointed out that the symmetry of the molecule is rather small. Given a local surrounding of the molecule, a pure rotation of less than 2π is unlikely to lead to an identical minimum of the potential energy. Conversely, close-packing considerations allow one to imagine a displacement of the centre of mass when the molecule passes from one orientation to another. This hypothesis is strengthened by the existence of a long-range self-diffusion of the molecules, evidenced by NMR (Folland *et al* 1973a, b, Chadwick and Forrest 1978). The delocalisation of the molecules could also explain the ability of norbornadiene to crystallise at the same temperature either in an HCP lattice or in an FCC lattice.

Therefore we have imagined a model combining both a rotation of the molecule about the Oz axis with a displacement of its centre of gravity perpendicular to this axis (see figure 7). The rotation was considered as a 60° rotation about the Oz axis. Indeed, it is well known that, provided that the number of jumps is sufficiently large, the EISF predicted by the jump models coincide with the EISF for a continuous uniaxial rotation.

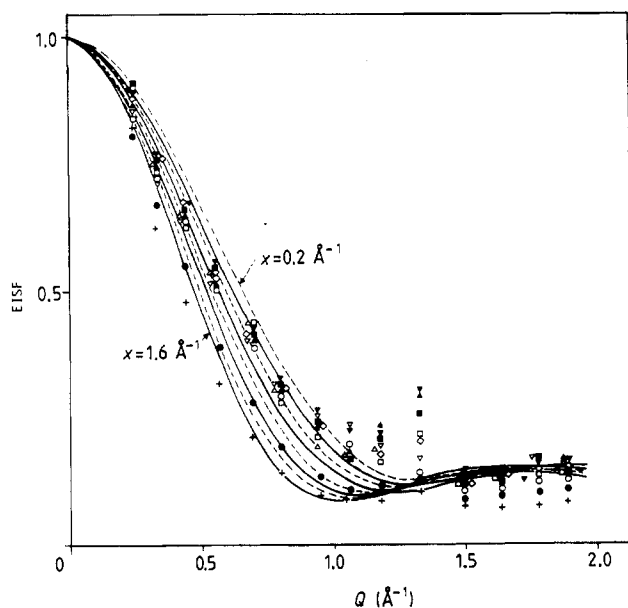


Figure 8. Comparison of the experimental values of the EISF with the model combining a rotation about Oz axis with a displacement x of the centre of mass. Symbols as in figure 6. Theoretical curves are drawn for values of x ranging from 0.2 to 1.6 \AA^{-1} (0.2, 0.4, etc). Curves are alternatively full and broken to clarify the figure.

The Oz axis was chosen because of its relatively good agreement with the experimental points at large Q . Certainly, the choice of these parameters is somewhat arbitrary, but our aim was to investigate the effects of a combination of translational and rotational motions of the molecules. The mathematical expression for the EISF is given in the appendix. In figure 8 are drawn a series of EISF curves corresponding to several values of the displacement of the centre of gravity, ranging from 0.2 to 1.6 \AA . Clearly, it turns out that a displacement of 0.6 \AA coupled with a sixfold rotation leads to a theoretical curve in better agreement with the experimental data. Similar curves were evaluated for the rotations about the two other axes. Here also, a reasonable agreement with the data could be found but for larger displacements of the centre of gravity (i.e. 0.8 \AA and 1.2 \AA for Ox and Oy axes, respectively).

For the experiments carried out in the two plastic phases, all the spectra recorded at the same temperature were fitted simultaneously on the basis of the sixfold rotation with coupled translation model. Good fits were obtained at each temperature, as illustrated in figure 9. It is worth pointing out that the refinements were carried out with a single adjustable parameter τ , the correlation time for 60° jumps. The value of the centre-of-mass displacement was determined from the EISF curves and kept *fixed* during the refinements. Several series of refinements were performed, corresponding to rotations about Ox , Oy or Oz . The differences in the final values of τ were not significant. Actually, an estimation of the maximum deviation of this parameter is provided by refining separately the spectra recorded at different scattering angles. Corresponding error bars are reported in figure 10. There is no difference for the spectra obtained in the two plastic phases. A straight line can be drawn through the experimental points, according to the Arrhenius law:

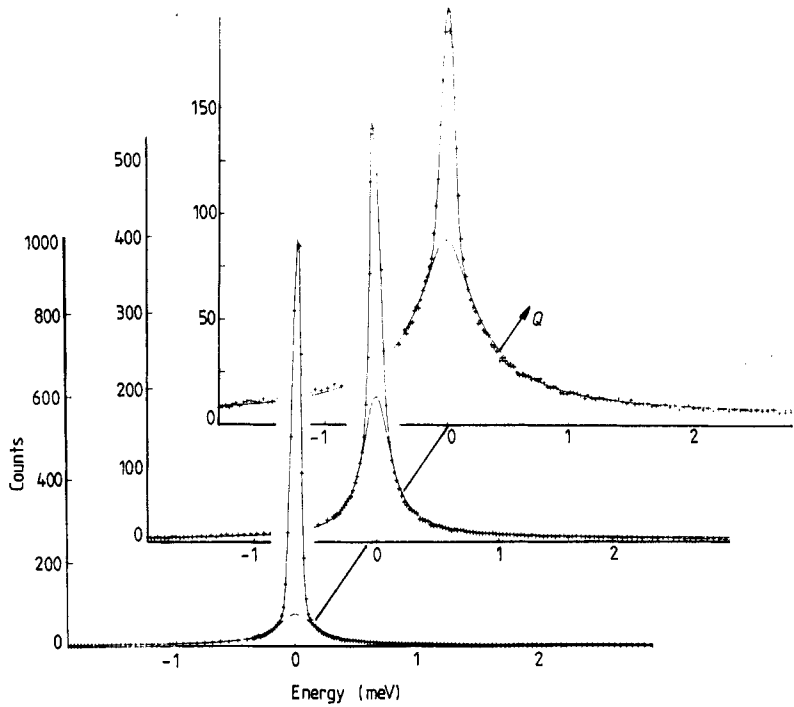


Figure 9. Examples of refinements of the energy spectra. The separation between the purely elastic scattering and the quasi-elastic part has been indicated. The spectra correspond to the plastic cubic phase at $T = 232$ K. The momentum transfer values are 0.46, 0.93 and 1.57 \AA^{-1} respectively.

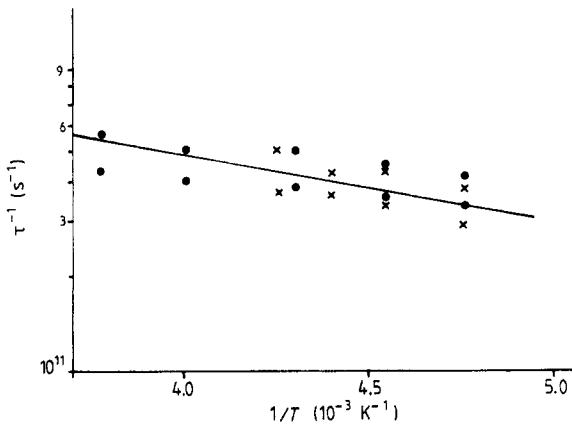


Figure 10. Evolution of the jump probability (i.e. the reciprocal of the correlation time) as a function of the reciprocal temperature).

$$\tau(s) = (2.5 + 0.1) \times 10^{-12} \exp(-\Delta H/RT)$$

with an activation energy

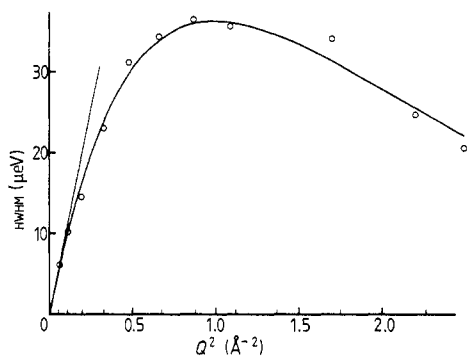


Figure 11. Half-width at half-maximum (HWHM) of the part of the scattering corresponding to long-range diffusion of the norbornadiene molecules in the liquid phase.

$$\Delta H = 4.62 + 0.15 \text{ kJ mol}^{-1}.$$

The spectra obtained in the liquid phase were refined using the same model for the rotational motions but allowing a small broadening of its 'elastic' intensity originating from a long-range diffusion of the molecules. This broadening was introduced as an adjustable parameter in the refinements. The final values for each angle of observation are plotted in figure 11. A systematic deviation from the DQ^2 law is observed at low Q -values. Then the experimental points present a maximum in the region at about $Q = 1 \text{ \AA}^{-1}$ and decrease strongly at large momentum transfer. Such behaviour is characteristic of a long-range diffusive motion by successive jumps. The model was derived by Chudley and Elliott (1961) to describe liquids assumed to have an appreciable short-range order. The scattering law has a Lorentzian shape, with the following HWHM:

$$\Delta\omega(Q) = \frac{1}{\tau} \left(1 - \frac{\sin Ql}{Ql} \right) \quad (2)$$

where l is the jump length and τ_0 is the mean time between two successive jumps ($1/\tau_0$ is the jump probability). According to this expression the HWHM exhibits a maximum at about $Ql = 3\pi/2$ and from refinement of equation (2) it is possible to derive from our data a mean jump length of about 4.57 \AA in accordance with the lattice spacings in the plastic phases. In the low- Q limit, an expansion of (2) in terms of Ql , up to third order, gives

$$\Delta\omega(Q) = Q^2 l^2 / 6\tau_0. \quad (3)$$

We obtain a DQ^2 variation, with a diffusion constant

$$D = l^2 / 6\tau_0. \quad (4)$$

The latter was found to be equal to about $1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and the characteristic time τ_0 , equal to $2.32 \times 10^{-11} \text{ s}$. Such a value is quite in accordance with the values ordinarily found in molecular liquids, i.e. cyclohexane $1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, benzene $2.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (McCall *et al* 1959).

5. Conclusions

IQNS measurements performed in three crystalline phases of norbornane have given some insight into the dynamical behaviour of the molecule. In the low-temperature

phase, there is no direct evidence of molecular reorientations. But above 202 K, the broadening of the TOF spectra indicates the occurrence of fast motions in both the HCP and the FCC plastic phases. Above all, the dynamics of the molecules is similar in the two plastic phases, with a small value of the activation energy related to the motion ($\Delta H = 4.62 \text{ kJ mol}^{-1}$), indicating a small steric hindrance. The distance between nearest neighbours being the same in both plastic phases, the molecular packing has no appreciable effect on molecule rotation. This latter appears even less hindered than in the case of norbornane, where values of the activation energy equal to 6.14 kJ mol^{-1} and 5.17 kJ mol^{-1} were found from IQNS and NMR measurements, respectively.

However, the molecular motions appear much less isotropic at the highest temperature in the plastic phases in the case of norbornadiene as compared with those observed with norbornane. Especially no isotropic rotational diffusion is observed, but the experimental EISF cannot be described on the basis of a simple uniaxial rotation about any axis. Taking into account a displacement of the centre of gravity of the molecules coupled to their reorientations yields a better agreement. In spite of the arbitrary character of the model this result can be considered as important. The case of norbornane was somewhat different. When the temperature decreases, the EISF gradually changes but does not reduce into a uniaxial rotation. A description of the data was possible only by considering that a fraction of the molecules are immobile. The hypothesis of the appearance of clusters with local arrangement was put forward, in accordance with similar pretransitional effects already observed with *p*-terphenyl (Lechner *et al* 1984) and adamantane derivatives (Bée *et al* 1987). In the case of norbornadiene, such clusters of 'immobile' molecules (on the instrument timescale) do not seem to exist, but the passage from one equilibrium orientation to another implies both a rotation of the molecule and a displacement of its centre of mass.

In the liquid phase, it was possible to evidence a slower motion of the molecules, on the 10^{-10} s timescale, corresponding to a long-range diffusion of the molecules. Analysis of the broadening of the part of the spectra sensitive to this motion yielded the conclusion that this diffusion occurs by a jump diffusion mechanism according to the Chudley-Elliott model. The jump distance was found to be consistent with the inter-molecular distances in the plastic phases and with the spacing that can be deduced from the coherent peak in the diffraction pattern. Between two successive jumps, the molecules remain in the immediate vicinity of each other, and the rotational motions, coupled with small displacements of the centres of mass, still continue as in the plastic phases. From time to time, some molecules undergo a rapid jump of mean length 4.6 \AA to other surroundings, where they stay to rotate for an average time τ_0 .

Anyway, we intend to obtain additional information about norbornadiene in this temperature range, using other experimental techniques. Simultaneously it should perhaps also be interesting to carry out additional IQNS experiments with a compound intermediate between norbornadiene and norbornane, i.e. norbornene, for which only one double bond exists. The idea is to look at the influence of molecular symmetry in the isotropy of the motions: because of the absence of molecular symmetry, it should be difficult for a group of molecules to find a very stable equilibrium configuration and the rotational motions should increase. Moreover, the coupling with a translational displacement of the centres of mass should be more important.

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Appendix. Mathematical expressions of the incoherent scattering laws for the different models

In the isotropic rotational diffusion model the molecules are assumed to have, on a time average, no preferred orientation in space and to perform more or less continuous small-angle random rotations. The rotational incoherent scattering functions, for one proton moving on a sphere of radius R , can be written (Sears 1966, 1967)

$$S(Q, \omega) = A_0(Q)\delta(\omega) + \sum_{l=1}^{\infty} A_l(Q) \frac{1}{\pi} \frac{l(l+1)D_R}{1 + \omega^2[l(l+1)D_R]^2}. \quad (\text{A1})$$

Here D_R is the isotropic diffusion constant. The elastic, $A_0(Q)$, and quasi-elastic, $A_l(Q)$, structure factors are functions of the spherical Bessel functions $j_l(QR)$:

$$A_0(Q) = j_0^2(QR) \quad (\text{A2a})$$

$$A_l(Q) = (2l+1)j_l^2(QR). \quad (\text{A2b})$$

Clearly, equation (A1) has to be evaluated for the different radii for the protons of the molecule and then expressed as a weighted sum over the various types of hydrogens. In the norbornadiene molecule, there are three kinds of hydrogen atoms. Four of them are moving over a sphere of radius $R_1 = 2.545 \text{ \AA}$, two others on a sphere of radius $R_2 = 2.305 \text{ \AA}$ and the last two on a sphere of radius $R_3 = 2.214 \text{ \AA}$.

For the uniaxial rotational diffusion model, the incoherent scattering law, for one proton moving over a circle of radius r , can be written (Dianoux *et al* 1975, Leadbetter and Lechner 1979)

$$S(Q, \omega) = A_0(Q)\delta(\omega) + \sum_{m=1}^{\infty} A_m(Q) \frac{1}{\pi} \frac{D_r m^2}{(D_r m^2)^2 + \omega^2}. \quad (\text{A3})$$

Here D_r is the uniaxial rotational diffusion constant. For a sample in powder form, the structure factors are the averages of the Bessel functions of the first kind:

$$A_0(Q) = \frac{1}{\pi} \int_0^{\pi} J_0^2(Qr \sin \beta) d\beta \quad (\text{A4a})$$

$$A_m(Q) = \frac{2}{\pi} \int_0^{\pi} J_m^2(Qr \sin \beta) d\beta \quad (\text{A4b})$$

where β is the angle between Q and the rotation axis.

The one-proton incoherent scattering function corresponding to a jump model among six positions equally spaced on a circle of radius r is given by (Dianoux *et al* 1975, Hervet *et al* 1974)

$$S(Q, \omega) = a_0(Q)\delta(\omega) + \sum_{l=1}^5 a_l(Q) \frac{1}{\pi} \frac{\tau_l}{1 + \omega^2 \tau_l^2} \quad (\text{A5})$$

with

$$a_l(Q) = \frac{1}{6} \sum_{n=1}^6 \cos\left(\frac{2\pi ln}{6}\right) j_0 \left[2Qr \sin\left(\frac{\pi n}{6}\right) \right]. \quad (\text{A6})$$

Equation (A5) holds for a polycrystalline sample. The half-widths at half maximum, τ_l^{-1} , of the Lorentzian functions are defined as

$$\frac{1}{\tau_l} = \frac{2}{\tau} \sin^2\left(\frac{\pi l}{6}\right) \quad (\text{A7})$$

where τ is the mean time between two successive jumps of the proton.

Clearly, as we have

$$1/\tau_1 = 1/\tau_5 = 0.5/\tau \quad (\text{A8a})$$

$$1/\tau_2 = 1/\tau_4 = 1.5/\tau \quad (\text{A8b})$$

$$1/\tau_3 = 2/\tau \quad (\text{A8c})$$

we are concerned with only one elastic and three quasi-elastic structure factors, namely

$$S(Q, \omega) = A_0(Q)\delta(\omega) + \sum_{l=1}^3 A_l(Q) \frac{1}{\pi} \frac{1}{1 + \omega^2 \tau_l^2} \quad (\text{A9})$$

with

$$A_0(Q) = a_0(Q) = \frac{1}{6}[1 + 2j_0(Qd_1) + 2j_0(Qd_2) + j_0(Qd_3)] \quad (\text{A10a})$$

$$A_1(Q) = a_1(Q) + a_5(Q) = \frac{1}{6}[2 + 2j_0(Qd_1) - 2j_0(Qd_2) - 2j_0(Qd_3)] \quad (\text{A10b})$$

$$A_2(Q) = a_2(Q) + a_4(Q) = \frac{1}{6}[2 - 2j_0(Qd_1) - 2j_0(Qd_2) + 2j_0(Qd_3)] \quad (\text{A10c})$$

$$A_3(Q) = a_3(Q) = \frac{1}{6}[1 - 2j_0(Qd_1) + 2j_0(Qd_2) - j_0(Qd_3)]. \quad (\text{A10d})$$

The jump distances d_1 , d_2 and d_3 are related to the radius of the circle r by

$$d_1 = r \quad (\text{A11a})$$

$$d_2 = r\sqrt{3} \quad (\text{A11b})$$

$$d_3 = 2r. \quad (\text{A11c})$$

The introduction of a centre-of-mass displacement x yields the same expression for the scattering function as given by equations (9) and (10) but the jump distances d_1 , d_2 and d_3 are now expressed by

$$d_1 = [r^2 + (r+x)^2 - r(r+x)]^{1/2} \quad (\text{A12a})$$

$$d_2 = [r^2 + (r+x)^2 + r(r+x)]^{1/2} \quad (\text{A12b})$$

$$d_3 = 2r + x. \quad (\text{A12c})$$

References

- Bée M 1988 *Quasielastic Neutron Scattering: Principles and Applications to Solid State Chemistry, Biology and Material Science* (Bristol: Adam Hilger)
- Bée M, Foulon M, Amoureux J P, Caucheteux C and Poincignon C 1987 *J. Phys. C: Solid State Phys.* **20** 337
- Bée M, Jobic H and Caucheteux C 1986 *J. Chim. Phys.* **83** 623
- Bée M, Sauvajol J L and Amoureux J P 1982 *J. Physique* **43** 1797
- Chadwick A W and Forrest J W 1978 *J. Chem. Soc., Faraday Trans. I* **74** 2560
- Chudley G T and Elliott R J 1961 *Proc. Phys. Soc.* **77** 353
- Dianoux A J, Volino F and Hervet H 1975 *Mol. Phys.* **30** 1181
- Folland R, Ross S M and Strange J H 1973a *J. Phys. Chem. Solids* **34** 1713
- 1973b *Mol. Phys.* **26** 27
- Hervet H, Volino F, Dianoux A J and Lechner R E 1974 *J. Physique Lett.* **35** 151
- Jackson R L and Strange J H 1972 *Acta Crystallogr.* **B28** 1645
- Leadbetter A J and Lechner R E 1979 *The Plastically Crystalline State* ed J N Sherwood (Chichester: Wiley)
- Lechner R E, Toudic B and Cailleau H 1984 *J. Phys. C: Solid State Phys.* **17** 405
- McCall D W, Douglass D C and Anderson E W 1959 *J. Chem. Phys.* **31** 155

1962

M Bée et al

Sears V F 1966 *Can. J. Phys.* **44** 1299

— 1967 *Can. J. Phys.* **45** 234

Volino F and Dianoux A J 1980 *Mol. Phys.* **41** 271

Westrum E F 1969 *Molecular Dynamics and Structure of Solids* ed R S Carter and J J Rush (NBS Publ. 301)
(Washington DC: National Bureau of Standards) p 459