

Dynamics of liquid ammonia from cold neutron scattering

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Abstract. The scattering of 4.1 Å neutrons by liquid ammonia has been measured at 218 K in the angular range of 30-90° using the Trombay rotating crystal spectrometer. The experimental data, after correcting for multiple scattering, have been compared with model calculations, and it is shown that it is possible to get detailed information about the rotational correlation function on the basis of neutron experiments alone. The model assumes Langevin diffusion for translational motions. Rotational motions are described by means of an orientational correlation function which has a gaseous behaviour for times up to τ_0 and then changes over to a diffusive character with a rotational diffusion constant D_r . Within the framework of the model the correlation function can be described with $D_r = 0.28 \times 10^{12} \text{ sec}^{-1}$ and $\tau_0 = 0.57 \times 10^{-12} \text{ sec}$. Corrections for multiple scattering and their dependence on model parameters are discussed.

Keywords. Liquid ammonia; neutron inelastic scattering; rotational correlation function; multiple scattering.

1. Introduction

Neutron scattering cross section for molecular liquids involves rotational time dependent correlation functions which are directly determined by the dynamics of rotational motions (Steele and Pecora 1965). The analysis of neutron scattering experiments on simple molecular liquids has been performed using two approaches. The first approach demands a knowledge of first, second and higher order correlational functions (Sears 1967, Rao *et al* 1967, Venkataraman *et al* 1967). The first two functions, $F_1(t)$ and $F_2(t)$, can be obtained from optical experiments (Gordon 1965, 1968). In the second approach the use of $F_1(t)$ alone has been found to be adequate (Agrawal and Yip 1967, Agrawal *et al* 1968). Conversely using this approach one can get information about $F_1(t)$ using neutron data. Till now, however, neutron experiments have not been used to directly obtain this function. In the present paper we report neutron scattering studies on liquid ammonia (Dasannacharya *et al* 1972 *a*) and by comparison of our data with model calculations infer the characteristics of the rotational correlation function, $F_1(t)$.

Section 2 briefly gives the experimental results. The model used for calculations is described in section 3. Section 4 deals with single and multiple scattering calculations and also the discussion of our results. A summary of the paper is given in the concluding section.

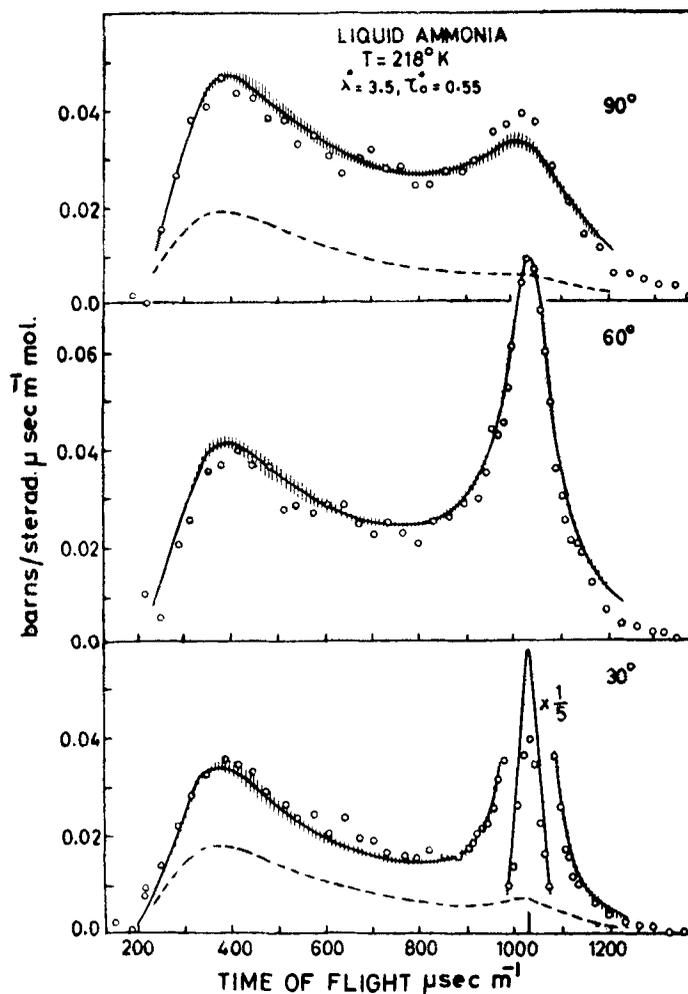


Figure 1. Scattered neutron spectra from liquid ammonia at 218 K for scattering angles of 30, 60 and 90°. (O) experimental points; — theoretical calculations with the model and parameters as discussed in the text. The hatched region corresponds to the spread in the rotational relaxation function, $F_1(t)$ shown by the hatched region in figure 4. The spectra are normalised to the differential scattering cross section, $d\sigma/d\Omega$, plus the calculated multiple scattering (dashed curves).

2. Experiments

The experiments have been performed on the Trombay rotating crystal spectrometer (Dasannacharya and Venkataraman 1967) which gives bursts of 4.1 Å neutrons. An incident energy resolution of about 0.4 meV was utilised in the present experiments. All the measurements were performed at 218 K with a flat sample of ~ 0.075 cm thickness in the transmission geometry, with the angle of incidence equal to half the scattering angle. Some typical time-of-flight distributions are shown in figure 1, after correction for the container contribution (which was small at 30° but not at 90°), air scattering and variation of detector efficiency with energy. The data are put on a cross section scale by normalizing the experimental area to the differential scattering cross section, $d\sigma/d\Omega$, plus the calculated

multiple scattering, the details of which are described in section 4. A value of 21.49 barns was used for $d\sigma/d\Omega$ (Janik *et al* 1963).

3. The model : Theory

Neutron scattering from liquid ammonia is predominantly incoherent because of the presence of the three hydrogen atoms. We shall, therefore, omit any consideration of the coherent scattering. Further, in order to proceed to calculate the cross section one has to make one more important assumption, that translational and rotational motions are not coupled. From a comparative assessment of hydrogen bonding in various liquids (Schneider 1959) it is known that liquid ammonia is much less bonded than liquid HCl. Neutron scattering data from the latter liquid have been analysed without taking any translation-rotation coupling into account and reasonable results have been obtained (Agrawal *et al* 1968). This assumption would be more appropriate in the case of liquid ammonia. We also assume that internal vibrations are not coupled to translational and rotational motions. This is a reasonable assumption (Sears 1967). Under the above assumptions the microscopic incoherent scattering cross section is given by

$$\begin{aligned} \frac{d^2\sigma}{d\Omega d\omega} &\equiv \sigma(E_0 \rightarrow E_2, \mathbf{Q}) \\ &= \frac{a_{\text{inc}}^2 k_2}{2\pi k_0} \exp\left(\frac{-\hbar\omega}{2k_B T}\right) \exp\left(\frac{-\hbar^2 Q^2}{8Mk_B T} G(T)\right) \times \\ &\quad \times \int_{-\infty}^{\infty} I_V(\mathbf{Q}, t) I_T(\mathbf{Q}, t) I_R(\mathbf{Q}, t) \cos \omega t \, dt \end{aligned} \quad (1)$$

where $I_V(\mathbf{Q}, t)$, $I_T(\mathbf{Q}, t)$ and $I_R(\mathbf{Q}, t)$ respectively denote the intermediate scattering functions for the vibrational, translational and rotational parts. Here k_0 and k_2 denote the incident and out-going wavevectors of the neutron, $\mathbf{Q} = \mathbf{k}_2 - \mathbf{k}_0$ and $\hbar\omega = \hbar^2(k_2^2 - k_0^2)/2m$; the two exponents give the detailed balance factor and the recoil terms respectively with $G(T)$ denoting the generalised frequency distribution function, T the temperature of the sample and M its molecular mass. The lowest internal vibration frequency in ammonia occurs at 1048 cm^{-1} which will make $I_V(\mathbf{Q}, t)$ at 218 K to be less than 5% different from one. This part therefore can be assumed to be unity. We now make a Gaussian approximation both for the translational and the rotational parts, that is, $I_T(\mathbf{Q}, t)$ and $I_R(\mathbf{Q}, t)$ are both assumed to be Gaussian in \mathbf{Q} . The validity of this approximation for the rotational part has been examined in some detail by Agrawal and Yip (1968) for gaseous CH_4 and similarly by Rahman (1964) for translational part for liquid argon. It seems reasonable on the basis of these studies to assume that this is a good first approximation. One then obtains,

$$\begin{aligned} \sigma(E_0 \rightarrow E_2, \mathbf{Q}) &= \frac{a_{\text{inc}}^2 k_2}{2\pi k_0} \exp\left(\frac{-\hbar\omega}{2k_B T}\right) \exp\left(\frac{-\hbar^2 Q^2}{8Mk_B T} G(T)\right) \times \\ &\quad \times \int_{-\infty}^{\infty} \exp[-Q^2\{\rho_T(t) + \rho_R(t)\}] \cos \omega t \, dt \end{aligned} \quad (2)$$

where $\rho_T(t)$ and $\rho_R(t)$ are the translational and rotational width functions*. To proceed further one has to take recourse to models for describing the width functions.

Translational width function, $\rho_T(t)$ —It is well known that for any substance $\rho_T(t)$ should show a free gas behaviour (Vineyard 1958) at very short time and should tend to the macroscopic diffusion limit for $t \rightarrow \infty$. The simplest model satisfying these conditions is the Langevin model which gives

$$\rho_T(t) = D \left[t - \frac{1 - \exp(-\eta t)}{\eta} \right] \quad (3)$$

$$\eta = k_B T / MD.$$

where

In the simple diffusion model the small time limit is not obeyed and the width function is given by

$$\rho_T(t) = Dt \quad (4)$$

We have used a value of $D = 3.0 \times 10^{-5}$ cm²/sec which fits our data (Dasannacharya *et al* 1972 *b*). All the earlier calculations (Dasannacharya *et al* 1972 *a*) were made assuming this $\rho_T(t)$. However, it is known that this model does not satisfy the small time limit and so most of the calculations reported here for comparison with experiments will be based on the Langevin diffusion model. This change in model essentially affects only the large energy transfer part of the neutron spectrum.

Rotational width function, $\rho_R(t)$.—The rotational intermediate scattering function can be described as (Agrawal and Yip 1968)

$$I_R(Q, t) = \exp[-Q^2 \rho_R(t)] \left[1 + \sum_{N=2}^{\infty} a_N(t) (Qb)^{2N} \right] \quad (5)$$

where

$$\rho_R(t) = \frac{1}{3} b^2 [1 - F_1(t)] \quad (6)$$

b being the distance between the hydrogen and the centre of mass of the molecule, and $a_N(t)$ being coefficients which depend on the higher order correlation functions, $F_2(t)$, $F_3(t)$..., as well as on $F_1(t)$. The correlation functions, therefore, are seen to be the quantities which describe the dynamics and hence the scattering cross section. In our treatment we only include the first term on the right hand side of equation (5). This amounts to making a Gaussian approximation for the rotational intermediate scattering function. The correlation functions $F_1(t)$ describes how a vector $\mathbf{u}(0)$ defined at zero time in the molecule relaxes with time. It can be shown (Gordon 1965) that the first order correlation function $F_1(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$, is just the Fourier transform of the line shape of the infrared vibration-rotation transition. For liquid ammonia the line-shape studies have not been done to our knowledge. Hence one has to resort to theoretical models or empirical descriptions of $F_1(t)$.

* The expression for $\rho_R(t)$ in the paper by Dasannacharya *et al* (1972 *a*) should read $\rho_R(t) = \frac{1}{3} b^2 [1 - F_1(t)]$.

Rotational correlation function, $F_1(t)$.—It has already been stated that $F_1(t)$ depends on the detailed rotational dynamics of the molecule in the liquid. However, certain general features of the orientational correlation function can be described without recourse to models. For example, it is well known that at sufficiently small times ($< 10^{-13}$ sec for simple liquids) $F_1(t)$ in liquids also should have the same behaviour as in the gaseous state. At intermediate times $F_1(t)$ can have, in principle, a complicated behaviour and at large times it exponentially tends to zero, so that at these times the simple rotational diffusion equation would be valid.

The correlation functions have been derived by various models (Gordon 1966, McClung 1969, 1972) and theories (St. Pierre and Steele 1969, 1972 and Fixman and Rider 1969). But all of them give complicated expressions for the correlation functions which are not very convenient for analysing the experiment. However an important feature of all these calculations is that in many cases the initial gas like behaviour of $F_1(t)$ goes over into the exponential diffusive behaviour smoothly. In view of this we have decided to use an empirical model for $F_1(t)$ which has the correct gaseous behaviour at small times, and after a time τ_0 , switches over to an exponential diffusive behaviour. The small time behaviour of $F_1(t)$ has been discussed in detail by St. Pierre and Steele (1969) who show that

$$F_1(t) = \sin^2 \theta \exp\left(-A \frac{k_B T}{I} t^2\right) + \cos^2 \theta \exp\left(-\frac{k_B t}{I} t^2\right) \quad \text{for } t \leq \tau_0 \quad (7)$$

where $A = \frac{2 + 3c + c^2}{2(1+c)}$; $c = \frac{I - I_s}{I_s}$.

For ammonia $c = -0.365$ and $\theta = 68^\circ$. After a time $t = \tau_0$ we assume that

$$F_1(t) = F_1(\tau_0) \exp\left(-\frac{(t - \tau_0)}{\lambda}\right) \quad \text{for } t \geq \tau_0 \quad (8)$$

where λ is the reciprocal of the rotational diffusion constant, D_r .

Now, combining equations (2), (3), (5) and (6) one can easily write $\sigma(E_0 \rightarrow E_2, Q)$ as

$$\begin{aligned} \sigma(E_0 \rightarrow E_2, Q) &= \frac{a_{inc}^2 k_2}{\pi k_0} \exp\left(-\frac{\hbar \omega}{2k_B T}\right) \exp\left(-\frac{\hbar^2 Q^2}{8Mk_B T} G(T)\right) \times \\ &\times \int_0^\infty \exp\left[-Q^2 \left\{D \left(t - \frac{1 - \exp(-\eta t)}{\eta}\right) + \frac{b^2}{3} [1 - F_1(t)]\right\}\right] \cos \omega t \, dt \quad (9) \end{aligned}$$

where $F_1(t)$ is given by equations (7) and (8). At large times $F_1(t) \rightarrow 0$ making $\rho_R(t) \rightarrow \frac{1}{3} b^2$ and $\rho_T(t) \rightarrow Dt + C$ where $C = -MD^2/k_B T$. Thus one can rewrite the above expression as

$$\begin{aligned} \sigma(E_0 \rightarrow E_2, Q) &= \frac{a_{inc}^2 k_2}{\pi k_0} \exp\left(-\frac{\hbar \omega}{2k_B T}\right) \exp\left(-\frac{\hbar^2 Q^2}{8Mk_B T} G(T)\right) \times \\ &\times \left\{ \int_0^t \left[\exp(-Q^2 \{\rho_T(t) + \rho_R(t)\}) - \exp(-Q^2 \{(Dt + C) + \frac{1}{3} b^2\}) \right] \right. \\ &\times \left. \cos \omega t \, dt + \exp(-Q^2 \{\frac{1}{3} b^2 + C\}) \frac{DQ^2}{(DQ^2)^2 + \omega^2} \right\} \quad (10) \end{aligned}$$

where t' is the time beyond which $\rho_R(t)$ and $\rho_T(t)$ have achieved their asymptotic forms. The integral in equation (10) gives the contributions at the larger energies whereas the second term shows clearly that the quasi-elastic part is affected by Debye-Waller type of factor which consists of a rotational ($\frac{1}{3} b^2$) as well as a translational (C) part.

In an earlier calculation (Dasannacharya *et al* 1972 *a*) we had used a simple diffusion model for describing the translations (equation 4) and the small time behaviour of $F_1(t)$ was described by that for a spherical top molecule and given by

$$F_1(t) = \frac{1}{3} \left[1 + 2 \left\{ 1 - \frac{k_B T}{I} t^2 \right\} \exp \left\{ - \frac{k_B T}{2I} t^2 \right\} \right] \quad \text{for } t \leq \tau_0 \quad (11)$$

with the moment of inertia I defined by

$$\frac{1}{I} = \frac{1}{I_x} + \frac{1}{I_y} + \frac{1}{I_z}$$

The large time part was the same as in the present description. This gives rise to a formula for cross section which is similar to equation (10) with the difference that $C=0$ and hence Debye-Waller type factor referred to earlier, now has only a rotational part.

4. Discussion

4.1 Single scattering

For a long time the customary procedure adopted for analysing the neutron scattering data from liquids was to separate the quasi-elastic and inelastic regions and discuss the two regions independently. During recent years, however, it has become more and more clear that this should be avoided as far as possible. Complete time-of-flight spectra were therefore calculated using equation (3) to describe translations and equations (7) and (8) for rotations. It is instructive to first compare the theoretical spectra, among themselves, for different values of parameters τ_0 and λ of equation (8). For convenience the spectra have been calculated for reduced parameters $\tau_0^* = \tau_0 (k_B T/I)^{\frac{1}{2}}$ and $\lambda^* = \lambda (k_B T/I)^{\frac{1}{2}}$ using this model. The results at scattering angles of 30° and 90° are shown in figure 2. The effect of increasing τ_0^* from 0.4 to 0.8 is mainly to shift the inelastic maximum to larger values of times-of-flight and increase the intensities of these maxima. This is particularly true at 30° . The effect of increasing λ^* on the other hand, is to shift the peak to somewhat smaller value of time-of-flight. However, this change is not much, especially as λ^* increases beyond 2.0. The change in the intensity of the peak is also minor for $\lambda^* \geq 1.0$. There is, however, one notable feature as one goes from $\lambda^* = 1.0$ to $\lambda^* = 2.0$, in that the curvature of the spectrum in the region of $500\text{--}700 \mu\text{sec m}^{-1}$ shows a qualitative difference both at 30° and 90° . Thus, the changes brought about in the spectra due to changes in τ_0^* and λ^* seem to be of distinctive nature and it does not seem very likely that two different pairs of τ_0^* and λ^* will give the same distribution.

Now, to make a detailed comparison between theory and experiment it is first necessary to take proper account of multiple scattering. This is considered in the following subsection.

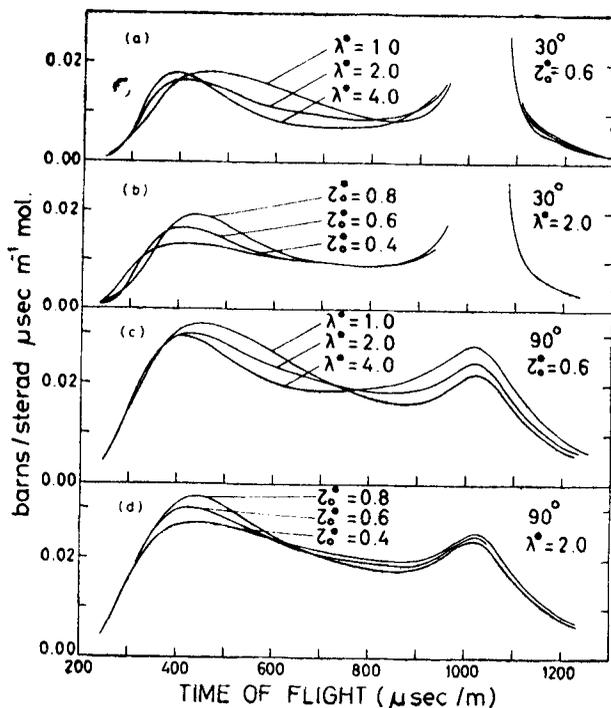


Figure 2. Calculated neutron spectra for liquid ammonia at 218 K for different values of rotational delay times τ_0^* and rotational diffusion constant $D_r^* = 1/\lambda^*$. The starred quantities are expressed in reduced units. $\lambda^* = \lambda(k_B T/I)^\dagger$, $\tau_0^* = \tau_0(k_B T/I)^\dagger$.

4.2 Multiple scattering

It is now well recognised that it is important to take multiple scattering contribution into account before making any detailed comparison between experiment and theory. If J_1 is the current due to singly scattered neutrons and J_2 that due to doubly scattered ones, the observed intensity of scattered neutrons is given by

$$\sigma(E_0 \rightarrow E_2, \mathbf{Q}) [1 + J_2/J_1]$$

assuming that higher order currents are small. Expressions for J_1 and J_2 have been derived earlier (Slaggie 1967, Rao *et al* 1971, Agrawal 1971) and the behaviour of J_2 has been examined in some detail (Dasannacharya *et al* 1972 *a*). It is also known that multiple scattering contribution depends on single scattering spectrum to some extent (Agrawal 1971, Slaggie 1967). We have investigated the dependence of doubly scattered intensity on (a) the parameters τ_0^* and λ^* of the rotational correlation function $F_1(t)$, (b) the models for translations and rotations used in the previous subsection and (c) the angle of scattering. The calculations were performed using the procedure discussed by Dasannacharya *et al* (1972 *a*)* and the results are shown in figure 3.

The changes in the calculated values of $\sigma(E_0 \rightarrow E_2, \mathbf{Q}) J_2/J_1$ at 30° for given models for translational and rotational motions when the parameters τ_0^* and λ^* are varied are represented in figure 3 *a* and 3 *b* respectively. It is seen that in the region of times-of-flight for which the experimental data can be obtained with reasonable accuracy, the calculations for $\sigma(E_0 \rightarrow E_2, \mathbf{Q}) J_2/J_1$ are not very sensitive

* The expression for J_2 in the paper by Dasannacharya *et al* (1972 *a*) has some errors. The correct expression can be found in the paper by Rao and Dasannacharya (1972).

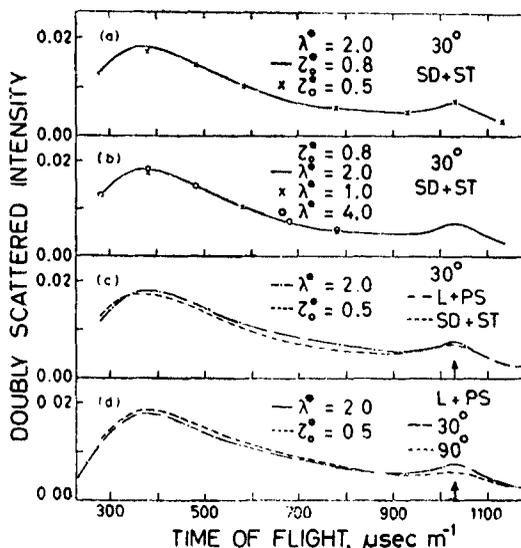


Figure 3. Doubly scattered intensity, $\sigma(E_0 \rightarrow E_2, \mathbf{Q})(J_2/J_1)$, from liquid ammonia as calculated for different models and the parameters therein. L \equiv Langevin, SD \equiv Simple diffusion, ST \equiv Spherical top, PS \equiv St. Pierre and Steele.

to the variations in these parameters. The comparison between $\sigma(E_0 \rightarrow E_2, \mathbf{Q}) J_2/J_1$ calculated on different models for translational and rotational motions and for same values of τ_0^* and λ^* is shown in figure 3 c. Considering the accuracies normally achieved in neutron experiments, it seems fair to say that the difference in multiple scattering observed for the two models cannot be considered serious. One also finds that for liquid ammonia $\sigma(E_0 \rightarrow E_2, \mathbf{Q}) J_2/J_1$ is fairly isotropic as can be seen from figure 3 d.

The comparison of spectra discussed in the following subsection is therefore based on multiple scattering calculations with $\lambda^* = 2.0$ and $\tau_0^* = 0.5$ only.

4.3 Comparison

The initial comparison was based on simple diffusion model for translation [eq. (4)], and a spherical top model for rotation [equations (11) and (8)]. Using these equations single scattering was calculated from equation (10) for several values of λ^* and τ_0^* . The experimental data were area-normalised to singly plus doubly scattered neutron intensities and the best possible agreement was obtained for $\lambda^* = 2.0$ and $\tau_0^* = 0.5$. The overall agreement was found to be fair (Dasanna-charya *et al* 1972 a). Two areas of disagreement were the region of small time-of-flight at 60° and 90° where theory gave extra intensity and the fall of quasi-elastic intensity with increase of scattering angle. The theoretical calculation predicted too sharp a fall.

One reason for this disagreement is of course the approximations involved in the theory. For example, it is known that simple diffusion gives incorrect description at small times or large energy transfers. This situation can at least partly be remedied by assuming a Langevin model for translations. Secondly, the assumption of treating the molecule as a spherical top with an effective moment of inertia again does not give the correct small time behaviour of $F_1(t)$ and hence the large energy-transfer region of the spectrum. To remove these inconsistencies the present calculations were made using Langevin model for translations [equation

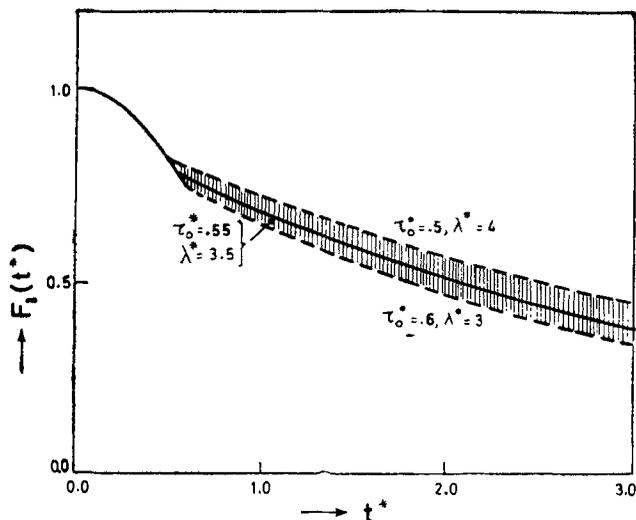


Figure 4. Rotational correlation function, $F_1(t)$, for liquid ammonia. The hatched region corresponds to the uncertainty to which this function has been determined from the present experiment in the framework of the theoretical model used.

(3)] and equations (7) and (8) for rotations. For all the calculations of multiple scattering $\lambda^* = 2.0$ and $\tau_0^* = 0.5$ was used. An extraordinarily good agreement was found between theory and experiment for $\lambda^* = 3.5$ and $\tau_0^* = 0.55$. This is shown in figure 1. The dashed region in the figure shows the variation in the spectrum when λ^* is varied between 3.0 and 4.0 and τ_0^* between 0.50 and 0.60. On the basis of this comparison we come to the conclusion that $\tau_0^* = 0.55 \pm 0.1$ ($\tau_0 = 0.57 \times 10^{-13}$ sec) and $\lambda^* = 3.5 \pm 1$ ($\lambda = 3.6 \times 10^{-13}$ sec; $D_r = 0.28 \times 10^{13}$ sec $^{-1}$) give a reasonable description of neutron spectra of liquid ammonia. The improvement in the high energy transfer region is not surprising for the reasons already described. An additional feature is a slight improvement in the description of the variation of quasi-elastic intensity with angle. The reason for this can be understood by examining figure 2 which shows that this improvement is largely because of somewhat larger λ^* value used now. The larger λ^* could not be used with earlier model since in that case the overall agreement would have become worse. The improvement can also come about because of the second term in equation (10) where one finds the Lorentzian modified by an exponential factor. For a simple diffusion model this factor depends purely on the rotational part, that is, on the distance b . In the Langevin description this factor also involves a constant C which depends on the translational dynamics. If C is negative the fall in intensity will be slower than in the simple diffusion case. In the Langevin model C (-0.0085 \AA^2) is very small compared to $\frac{1}{3}b^2$ (0.33 \AA^2), and does not affect the quasi-elastic region much. However, the fact that the theoretical intensity drops faster than the experiment suggests that in liquid ammonia the value of C in a more realistic translational model should be negative and larger than that given by Langevin diffusion model. A similar comparison of results of liquid methane shows that theoretical intensity at quasi-elastic peak position falls slower than the experimentally observed one. This would suggest a positive value of C for liquid methane.

A rotational correlation function derived on the basis of our experiments is given in figure 4. The parameters obtained with the present model may be compared with those obtained by simple diffusion plus spherical top model which gave

$\lambda^* = 2.0 \pm 0.1$, and $\tau_0^* = 0.5 \pm 0.1$. The parameters obtained now are not very different. It is pertinent to remark here that one cannot claim this to be the only function which would explain the rotations in liquid ammonia.

5. Summary

Neutron scattering data from liquid ammonia at 218 K have been presented. It is shown that it is possible to get a model-based orientational correlation function $\langle u(0) \cdot u(t) \rangle$ from neutron scattering measurements. This function has been evaluated for liquid ammonia and is shown in figure 4. This is the first attempt, as far as we are aware, at evaluating the correlation function from neutron data alone and it would be worthwhile checking this with infrared absorption measurements. A more accurate determination of the orientational correlation function from neutron scattering would require experiments which have considerably reduced multiple scattering contributions. Some information regarding the asymptotic behaviour of translatory motion has also been derived.

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