

MOLECULAR DYNAMICS CALCULATION OF NEUTRON INELASTIC SCATTERING FROM WATER*

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Abstract. The data generated by a molecular dynamics calculation on liquid water at 1 gm cm^{-3} and 10°C have been used to simulate a neutron inelastic scattering experiment on water. It is shown that already at $\kappa \sim 1 \text{ \AA}^{-1}$ the function $\omega^2 S_{\text{inc}}(\kappa, \omega)/\kappa^2$ is a good replica of the spectrum of proton velocity autocorrelation. It is emphasized that the separation of $S_{\text{inc}}(\kappa, \omega)$ into quasielastic and inelastic parts or the use of a phonon expansion in analyzing the data are both invalid procedures.

Résumé. La diffusion inélastique des neutrons par l'eau est simulée, utilisant des trajectoires produites par un calcul de dynamique moléculaire sur l'eau de densité 1 gm cm^{-3} et à une température 10°C . On a trouvé qu'une valeur de $\kappa \sim 1 \text{ \AA}^{-1}$ est déjà suffisamment petite pour que $\omega^2 S_{\text{inc}}(\kappa, \omega)/\kappa^2$ soit une bonne représentation du spectre de corrélation des vitesses de protons. On constate que (i) la séparation de $S_{\text{inc}}(\kappa, \omega)$ en une partie quasiélastique et une partie inélastique et (ii) l'usage d'une expansion phononique pour l'analyse des données d'une expérience de cette sorte sont, tous les deux, des procédés non-valables.

1. Introduction

In recent years computer simulation of liquids has led to an increasing degree of insight into the structural and kinetic properties of liquids at the molecular level [1]. Firstly, by solving a classical N -body problem under completely well defined mathematical conditions one can provide data for the development of the theory of liquids; the best example of this is the creation of the perturbation theory of monatomic liquids which would have been impossible otherwise [2]. Secondly, by drawing attention to rather unexpected aspects of the structure and kinetics of liquids, molecular dynamics data is able to provide guidelines for the analysis of data obtained on real materials in the laboratory [3]; it is worth recalling that the quasi-crystalline model for the analysis of liquid state properties has been abandoned almost universally because of the overwhelming evidence from molecular dynamics that such a model is quite inappropriate. Thirdly, by comparing experimental and molecular dynamics data of comparable accuracy, it has become possible to throw light on various interparticle interactions that are considered appropriate in certain liquids; a beginning in this direction has been made by studying liquid alkali metals experimentally and by molecular dynamics [4]. The recent work on water also falls into this category [5, 6].

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It is the purpose of the following contribution to give an example of the second feature of molecular dynamics mentioned above. We have shown that valuable insight into the structural and kinetic properties of liquid water can be obtained by making molecular dynamics calculation on water. On the other hand neutron inelastic scattering is a valuable tool for the study of proton motions in water (in fact in any hydrogenous material). In this paper we shall present a mock-up of a neutron experiment using the trajectories of the protons generated in a molecular dynamics calculation on water.

In section 2 we give a short summary of the various ingredients which make up the molecular dynamics project on water which has been underway now for about three years. In Section 3 we present the results from one such molecular dynamics run; keeping in view the theme of this paper, only those aspects of the results are presented which are germane to the theme, namely the time behavior of proton trajectories; the detailed presentation of the results in their totality will be made elsewhere [6]. Section 4 describes the manner in which neutron inelastic scattering would analyze the motion of protons generated in the molecular dynamics calculation. In Section 5 the results are presented; where appropriate an effort is made to contrast the conclusions one can draw from these results with the manner in which neutron data has been analyzed and interpreted in the literature. In the final Section 6 a short discussion is given for the manner in which questions of a quantum mechanical nature related to our problem might be resolved. The difficulties of correcting neutron inelastic scattering data for multiple scattering are also mentioned there. Lastly, brief remarks regarding the vibratory modes of the molecules have been made in that section.

2. Molecular Dynamics Model for Water

The total potential energy used in the calculation being reported here consists of a sum of effective pair potentials. The present version of this effective pair potential uses a four-point-charge model for each molecule; the molecule itself is considered to be a rigid structure. Specifically

$$V(1, 2) = V_{LJ}(r_{12}) + S(r_{12}) V_{el}(1, 2), \quad (2.1)$$

where r_{12} is the separation between oxygen nuclei. V_{LJ} is a central interaction of the Lennard-Jones type:

$$V_{LJ}(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6], \quad (2.2)$$

with $\epsilon = 5.2605 \times 10^{-15}$ erg and $\sigma = 3.1$ Å. The four point charges, two $+q$ and two $-q$ on each molecule, contribute sixteen Coulombic interactions gathered in V_{el} . The charges have magnitudes $0.2357 e$ or 1.13194×10^{-10} esu. The two $+q$'s are at 1 Å distance from the oxygen nucleus at the positions occupied by the protons. The $-q$'s are 0.8 Å distance from the oxygen nucleus. The four lines joining the oxygen to these

charges form precise tetrahedral angles ($109^\circ 28'$) with one another. Finally

$$\begin{aligned} S(r) &= 0 & 0 \leq r < R_L, \\ &= \frac{(r - R_L)^2 (3R_U - R_L - 2r)}{(R_U - R_L)^3} & R_L \leq r < R_U, \\ &= 1 & R_U \leq r, \end{aligned}$$

with $R_L = 2.0160 \text{ \AA}$ and $R_U = 3.1287 \text{ \AA}$.

The molecular dynamics run was made with 216 water molecules at a density 1 g cm^{-3} and $T = 10^\circ\text{C}$. The total run time was $38100 \Delta t$; the integration step, Δt , was $10^{-4} \tau$ where $\tau = (M\sigma^2/\epsilon)^{1/2} = 2.126 \times 10^{-12} \text{ s}$, M being the mass of the molecule.

This potential seems to give a moderately good account of the properties of liquid water. In particular the constant of self-diffusion is found to be $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Details will be published elsewhere [6].

3. Characteristics of Proton Motions

Each proton participates in the translational motion of the center of mass of the parent molecule and in the rotational motion of the molecule around the center of mass. We will be interested in studying the details of this motion for microscopic times of the order of 10^{-12} s and hence over distances of the order of 10^{-8} cm . A neutron inelastic scattering experiment on water gives a composite picture of proton motions whereas in molecular dynamics one has the ability to study each aspect separately.

The mean square displacement of the center of mass of a molecule is defined in terms of its position $\mathbf{r}^{CM}(t)$ as

$$\langle \mathbf{r}^2 \rangle = \left\langle \frac{1}{N} \sum_{j=1}^N (\mathbf{r}_j^{CM}(t + \tau) - \mathbf{r}_j^{CM}(\tau))^2 \right\rangle_\tau. \quad (3.1)$$

In principle $\langle \mathbf{r}^2 \rangle$ contains all pertinent information about the process of self-diffusion. In practice however it is more profitable to consider its second derivative, the velocity autocorrelation function,

$$\langle \mathbf{V}(0) \cdot \mathbf{V}(t) \rangle = \left\langle \frac{1}{N} \sum_{j=1}^N \mathbf{V}_j^{CM}(t + \tau) \cdot \mathbf{V}_j^{CM}(\tau) \right\rangle_\tau. \quad (3.2)$$

The frequency spectrum of $\langle \mathbf{V}(0) \cdot \mathbf{V}(t) \rangle$ is denoted by $f_{CM}(\omega)$ and is given by

$$f_{CM}(\omega) = \int_0^\infty dt \cos \omega t \langle \mathbf{V}(0) \cdot \mathbf{V}(t) \rangle / \langle \mathbf{V}^2(0) \rangle. \quad (3.3)$$

Note that, as a matter of convenience, we have used $\langle \mathbf{V}^2(0) \rangle$ for normalizing the autocorrelation to unity at $t=0$.

The function $f_{CM}(\omega)$ is displayed in Figure 1. Note the clarity with which two regions of frequency stand out. There is a low frequency region at $\omega\tau=20$ (or 50 cm^{-1}) and a high frequency one at $\omega\tau=90$ (or 225 cm^{-1}). From Equation (3.3) we get $f_{CM}(0)=MD/k_B T$. From Figure 1, $f_{CM}(0)=0.0069\tau$ and hence $D=1.9\times 10^{-5}\text{ cm}^2\text{ s}^{-1}$. The region around $\omega\tau\sim 20$ corresponds to the motion of a molecule together with its immediate neighbors moving roughly as a 'cluster' while the region around $\omega\tau\sim 100$ corresponds to the oscillation of a molecule against its immediate neighbors.

The degree of damping however is so large (i.e., the width is comparable to the value of the frequency itself) that there is no tendency whatsoever for a molecule to

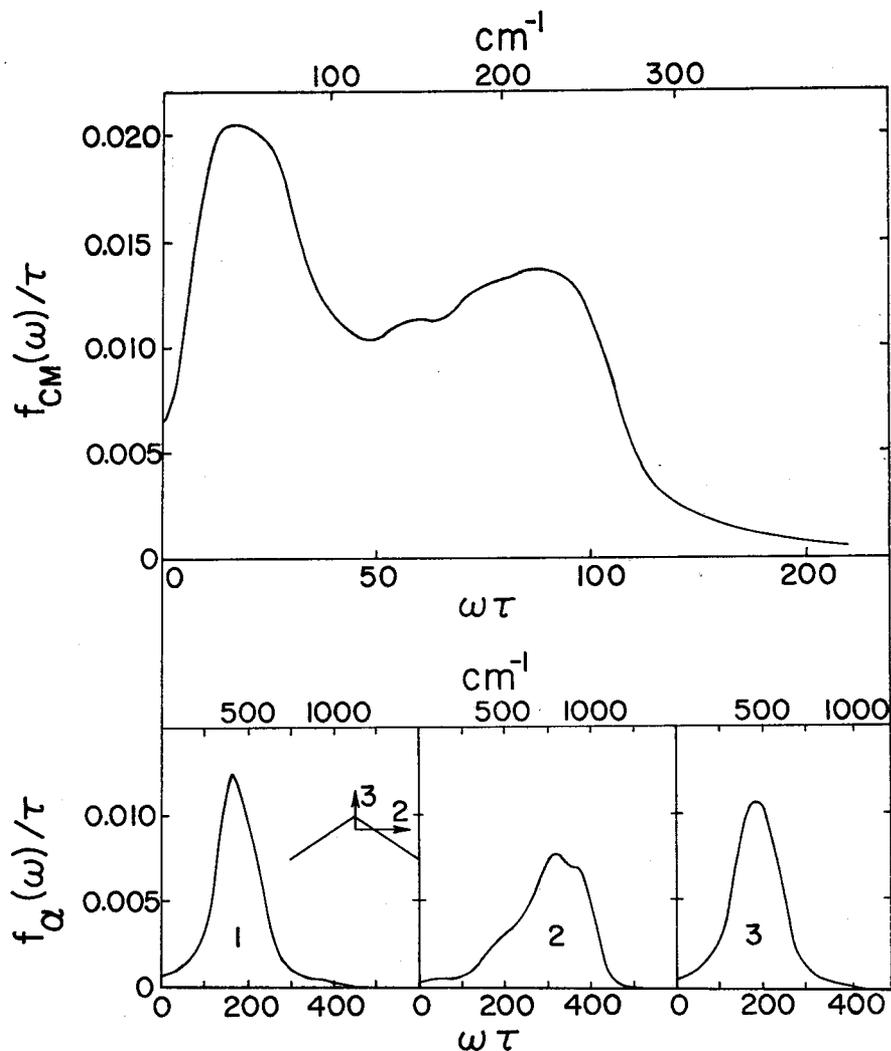


Fig. 1. Spectra $f_{CM}(\omega)$ [Equation (3.3)] and $f_{\alpha}(\omega)$ [Equation (3.4)]. Area under each curve is $\pi/2$. Unit of time $\tau = 2.126\text{ ps}$.

be localized around its momentary position for any recognizable length of time. In other words there is *no* evidence of the so-called 'solid-like' behavior.

If $\omega_\alpha(t)$ is the angular velocity of the molecule around a principal axis α , the auto-correlations $\langle \omega_\alpha(0) \omega_\alpha(t) \rangle$, $\alpha = 1, 2, 3$ are of interest in studying the librational characteristics of molecular motion. The frequency spectrum is denoted by $f_\alpha(\omega)$ and is given by

$$f_\alpha(\omega) = \int_0^\infty dt \cos \omega t \langle \omega_\alpha(0) \omega_\alpha(t) \rangle / \langle \omega_\alpha^2(0) \rangle. \quad (3.4)$$

A slow time dependence of $\langle \omega_\alpha(0) \omega_\alpha(t) \rangle$ indicates relatively free rotations whereas a rapidly oscillating behavior indicates the trapping of a molecule in a certain orientation by its neighbors. The lower part of Figure 1 shows the three functions $f_\alpha(\omega)$; the choice of axes is also shown there. The moments of inertia are such that $I_1 > I_3 > I_2$. The frequency at which the spectra $f_\alpha(\omega)$ show maxima are of course in the reverse order. The values of these frequencies are $\omega\tau = 165, 320-370$ and 180 (or $\sim 410 \text{ cm}^{-1}, 800-925 \text{ cm}^{-1}$, and 450 cm^{-1}). It was shown in our previous work [5] that the localization of the molecules around their momentary orientations is only marginal.

We refer the reader to Eisenberg and Kauzmann [7] where a summary of the experimentally observed characteristics of molecular motions in water is given. The five characteristic frequencies we have found in the molecular dynamics model of water ($50 \text{ cm}^{-1}, 225 \text{ cm}^{-1}, 410 \text{ cm}^{-1}, 450 \text{ cm}^{-1}, 800-925 \text{ cm}^{-1}$) are close enough to the experimental values for us to believe that the analysis and discussions in the following section do throw useful light on the neutron inelastic scattering technique for investigating the motion of molecules in water.

4. Theory of Neutron Inelastic Scattering from Water [8]

In the present context the relevant feature of the interaction between protons and neutrons is the fact that the neutron scattering cross section is dominated by the interference of waves scattered from the same proton at different times. Thus the neutron, when scattered from a hydrogenous material, samples the quantity $\mathbf{r}_j(t+\tau) - \mathbf{r}_j(\tau)$ where \mathbf{r}_j denotes the position of proton j . Thus we will be interested in the function

$$F_s(\boldsymbol{\kappa}, t) = \left\langle \frac{1}{N} \sum_{j=1}^N \exp \{ i\boldsymbol{\kappa} \cdot (\mathbf{r}_j(t+\tau) - \mathbf{r}_j(\tau)) \} \right\rangle_\tau, \quad (4.1)$$

for wave vector $\boldsymbol{\kappa}$, whose magnitude is denoted by κ . We shall further consider the Fourier transform of $F_s(\boldsymbol{\kappa}, t)$; namely $S_{\text{inc}}(\boldsymbol{\kappa}, \omega)$, given by

$$S_{\text{inc}}(\boldsymbol{\kappa}, \omega) = \int_0^\infty dt \cos \omega t F_s(\boldsymbol{\kappa}, t). \quad (4.2)$$

In the case of hydrogenous materials the cross section for scattering of a neutron, with momentum change $\hbar\kappa$ and energy change $\hbar\omega$, is directly related to $S_{\text{inc}}(\kappa, \omega)$.

We shall also consider the autocorrelation $C_s(\kappa, t)$ defined by

$$C_s(\kappa, t) = \frac{1}{\langle(\mathbf{\kappa} \cdot \mathbf{V})^2\rangle} \left\langle \frac{1}{N} \sum_{j=1}^N (\mathbf{\kappa} \cdot \mathbf{V}_j(t + \tau)) (\mathbf{\kappa} \cdot \mathbf{V}_j(\tau)) \times \exp\{i\mathbf{\kappa} \cdot (\mathbf{r}_j(t + \tau) - \mathbf{r}_j(\tau))\} \right\rangle_{\tau}, \quad (4.3)$$

where

$$\langle(\mathbf{\kappa} \cdot \mathbf{V})^2\rangle = \left\langle \frac{1}{N} \sum_{j=1}^N (\mathbf{\kappa} \cdot \mathbf{V}_j)^2 \right\rangle.$$

It is easy to show that

$$\frac{d^2 F_s(\kappa, t)}{dt^2} = -\langle(\mathbf{\kappa} \cdot \mathbf{V})^2\rangle C_s(\kappa, t). \quad (4.4)$$

The Fourier transform of $C_s(\kappa, t)$ is of course $\omega^2 S(\kappa, \omega) / \langle(\mathbf{\kappa} \cdot \mathbf{V})^2\rangle$. In the limit $\kappa \rightarrow 0$ we find that $\omega^2 S_{\text{inc}}(\kappa, \omega) / \langle(\mathbf{\kappa} \cdot \mathbf{V})^2\rangle$ becomes the Fourier transform, $f_p(\omega)$, of the proton velocity autocorrelation function; i.e.,

$$f_p(\omega) = \lim_{\kappa \rightarrow 0} (\omega^2 S_{\text{inc}}(\kappa, \omega) / \langle(\mathbf{\kappa} \cdot \mathbf{V})^2\rangle) = \int_0^{\infty} dt \cos \omega t \frac{\langle \mathbf{V}_p(0) \cdot \mathbf{V}_p(t) \rangle}{\langle \mathbf{V}_p^2(0) \rangle}. \quad (4.5)$$

The suffix p makes it explicit that we are concerned with the velocity of the proton.

As stated above \mathbf{V}_p is a composite of the translational and rotational motion of the molecules. There is no way, except through approximations in the interpretation of $S_{\text{inc}}(\kappa, \omega)$ or of $f_p(\omega)$ to separate the various components of molecular motion embedded therein.

In the limit $\kappa \rightarrow 0$ another property of $S_{\text{inc}}(\kappa, \omega)$ is of interest. For small κ only the large time behavior of $F_s(\kappa, t)$ remains relevant. In this limit $F_s(\kappa, t) \rightarrow \exp(-\kappa^2 \times (Dt + C))$ where D is the constant of self diffusion and C a constant with dimensionality (length)². Hence the half width of $S_{\text{inc}}(\kappa, \omega)$ at half height becomes $\kappa^2 D$.

In the limit $\kappa \rightarrow \infty$ the phase interference in the exponent of the right side of Equation (4.1) is so rapid that only the small time behavior of $F_s(\kappa, t)$ is relevant. In this limit we can write $\mathbf{r}_j(t + \tau) - \mathbf{r}_j(\tau) = t\mathbf{V}_j(\tau)$ and hence $F_s(\kappa, t) = \exp(-\langle(\mathbf{\kappa} \cdot \mathbf{V})^2\rangle \times t^2/2)$.

It is necessary to emphasize here that in general, except in the two limiting cases $\kappa \rightarrow 0$ and $\kappa \rightarrow \infty$, $F_s(\kappa, t)$ cannot be written as $\exp(-\kappa^2 W(t))$. An exception is provided by a harmonically vibrating solid; this exception is also peculiar in that $W(t)$ goes to a constant value for $t \rightarrow \infty$ thus allowing an expansion of $F_s(\kappa, t)$ in powers of $W(t) - W(\infty)$. This is the well known phonon expansion.

Before proceeding to the presentation of the results in the next section it is worthwhile to recall the manner in which experimental data for scattering of neutrons from water has been treated. Unfortunately the *only* unambiguous treatment of data is that of Sakamoto *et al.* [9]. These authors used the 'constant Q ' technique to get the $S_{\text{inc}}(\kappa, \omega)$ directly and then transformed their data first to get $F_s(\kappa, t)$ and then the Van Hove function $G_s(r, t)$ for the protons. These results are in overall accord with the molecular dynamics results already reported [5, 6]. No other experiment along these lines has been performed over the last ten years for improving the accuracy of the results in the ω wings of $S_{\text{inc}}(\kappa, \omega)$; i.e., for large energy transfers to the neutron. In our opinion the analysis of all other experiments is fraught with ambiguities and with assumptions that cannot be justified. Firstly, there has always been an attempt to separate out the so-called quasi-elastic scattering from the inelastic part; secondly, it has been almost invariably assumed that $F_s(\kappa, t)$ has the form $\exp(-\kappa^2 \langle r^2 \rangle / 6)$; thirdly, by combining the above two notions the scattering is expressed in terms of a phonon expansion involving a Debye-Waller factor which is not a definable quantity for motion of particles in a liquid. Another type of approach is one in which the proton is supposed to diffuse by a recognizable jump process between neighboring sites after a measurable stay at a site. Molecular dynamics data already published shows that none of the ideas mentioned above is valid for the purpose of describing the motion of protons in water. Also, the unambiguous analysis of their experimental data by Sakamoto *et al.* [9], in spite of the limited accuracy available at that time, does not give any hint that assumptions like the ones described above have any validity.

Once a molecular dynamics run of sufficient length has been made and the chronological sequence of positions and velocities of all the protons recorded, the calculation of $F_s(\kappa, t)$ or $C_s(\kappa, t)$, Equations (4.1) and (4.3), respectively, is quite a simple matter.

5. Molecular Dynamics Results

5.1. $F_s(\kappa, t)$

In Figure 2 we have plotted the function $\log F_s(\kappa, t)$ for a few values of κ , to bring out an important feature of its dependence on κ and t . It is quite clear that $F_s(\kappa, t)$ *cannot* be written in the form $\exp(-\kappa^2 \langle r^2 \rangle / 6)$. Hence any analysis of the data based on such a form would lead to erroneous conclusions regarding the behavior of $\langle r^2 \rangle$. To obtain the correct asymptotic behavior of $\langle r^2 \rangle$ for large t , and hence the constant of self diffusion, it is necessary to extract the small κ behavior of the function by a suitable extrapolation procedure. Figure 3 shows a plot of the same function as in Figure 2 but as a function of κ^2 for various values of t on the right end of Figure 2. Extrapolating to the value $\kappa=0$ one gets the values marked off on the ordinate of Figure 3. Using these values and plotting them back on Figure 2 one gets the dashed line shown there which therefore indicates the asymptotic behavior in time for $\kappa=0$. This gives a value of $D=2.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The difference between this value and the value $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ obtained from the motion of the center of mass and given in Section 3 is due to the fact that in Figure 2 the data needs to be taken further out

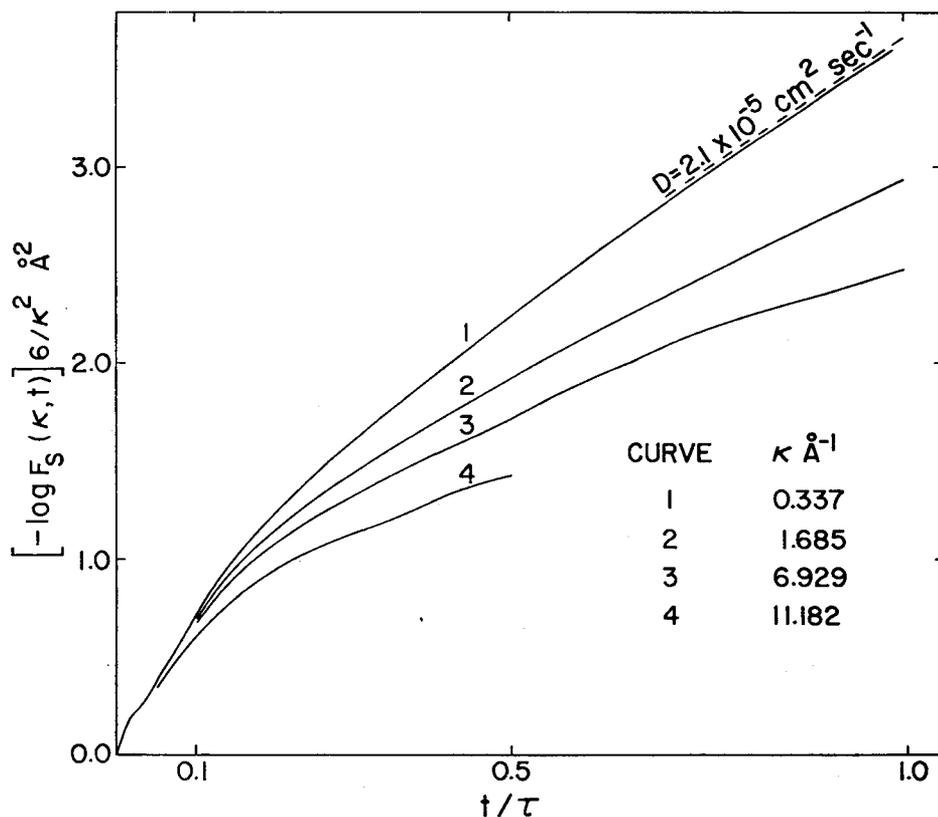


Fig. 2. Dependence of $F_s(\kappa, t)$ [Equation (4.1)] on t for various κ . A non-Gaussian distribution of proton displacements is clearly indicated; in other words $F_s(\kappa, t) \neq \exp(-\kappa^2 \langle r^2 \rangle / 6)$.

in time to allow for the long time that the molecule takes to complete one whole diffusive rotation.

Note that in Figure 2 the curve for $\kappa = 0.337 \text{ \AA}^{-1}$ indeed comes quite close to the curve for $\kappa = 0$. In other words an experiment made in the region of $\kappa \sim 0.3 \text{ \AA}^{-1}$ to obtain $F_s(\kappa, t)$ from $S_{\text{inc}}(\kappa, \omega)$ is in principle capable of giving at least the large time diffusive behavior of $F_s(\kappa, t)$ correctly. The small time behavior will be considered in subsection 5.4. below. Notice that at $t = 0.025 \tau$ there is an interesting structured region in $F_s(\kappa, t)$ and also that the overall curvature extends to about 0.3τ . This information will be contained in the high frequency region of $S_{\text{inc}}(\kappa, \omega)$.

5.2. $S_{\text{inc}}(\kappa, \omega)$

The function $S_{\text{inc}}(\kappa, \omega)$ is shown in Figure 4 for $\kappa = 0.337 \text{ \AA}^{-1}$. Notice that the intensity is almost entirely in the region $\omega\tau < 0.2$. The interesting region (Figure 1) beyond $\omega\tau \sim 10$ is very difficult to observe at present even with the best equipment of the neutron inelastic scattering method. In Figure 4 we have also shown $S_{\text{inc}}(\kappa, \omega)$ for

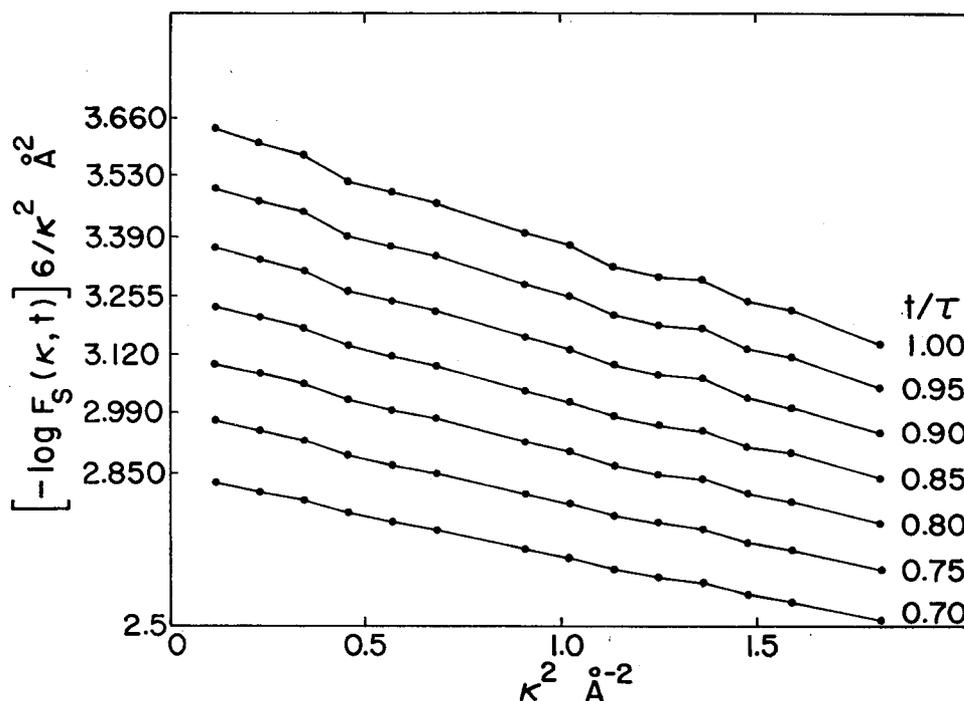


Fig. 3. Dependence of $F_s(\kappa, t)$ on κ^2 for various t between 0.7τ and τ . Extrapolation to the left gives the values indicated. These values are shown in Figure 2 as a dashed line.

$\kappa = 0.674 \text{ \AA}^{-1}$. This curve will be reconsidered further below in this subsection. The upper part of Figure 4 shows the half width at half height of $S_{\text{inc}}(\kappa, \omega)$ as a function of κ^2 . The discussion in Section 4 on the small κ behavior of $F_s(\kappa, t)$ shows that the half width at half height of $S_{\text{inc}}(\kappa, \omega)$ should go to zero as $\kappa^2 D$ when $\kappa \rightarrow 0$. From the upper graph in Figure 4 we see that to extract this information from $S_{\text{inc}}(\kappa, \omega)$ the region $\kappa \lesssim 0.5 \text{ \AA}^{-1}$ is a region of small enough κ . The diffusion constant derived from the graph in Figure 4 is indicated on the graph.

From the point of view of the main theme of this paper it is necessary to emphasize that the bending of the half-width-at-half-height curve away from the straight line has no simple explanation in terms of the behavior of the mean square displacement alone of the protons. It arises from the fact that the Van Hove function $G_s(r, t)$ for the protons departs appreciably from a Gaussian shape. This has already been shown explicitly in Figure 2. We therefore believe that the construction of models [10] for $\langle r_p^2 \rangle$, the mean square displacement of the protons, to account for an observed departure from the value $\kappa^2 D$ of the half-width-at-half-height of $S_{\text{inc}}(\kappa, \omega)$ is not useful; in fact it is an erroneous procedure. We have already drawn attention to this in previous publications [5, 11].

$S_{\text{inc}}(\kappa, \omega)$ for $\kappa = 0.674 \text{ \AA}^{-1}$ is shown in Figure 5 for large values of ω . The frequency scale in Figure 5 is 100 times that in Figure 4. The values of $S_{\text{inc}}(\kappa, \omega)$ fall by

3 orders of magnitude or more in going from $\omega\tau=0$ to $\omega\tau=50$ so that the numerical transformation procedure (to get $S_{\text{inc}}(\kappa, \omega)$ from $F_s(\kappa, t)$) starts to generate noise which is seen on the right hand part of Figure 5. However, even in such difficult circumstances the values shown contain some useful information (apart from the width information shown in Figure 4). Multiplying by ω^2 one gets the values shown on the top part of Figure 5. Note that a maximum at $\omega\tau=20$ is now discernible. This corresponds to the low frequency element of diffusive motion of a molecule shown in Figure 1. Apart from this no further information can be obtained from $S_{\text{inc}}(\kappa, \omega)$ for small κ due to the practical difficulty of calculating for large ω the low intensity wings of this function when κ is in the region $< 1 \text{ \AA}^{-1}$. A method of getting around this practical difficulty of numerical transformation is dealt with in subsection 5.4 below.

Regarding the overall shape of $S_{\text{inc}}(\kappa, \omega)$ we notice that there is no logical way of separating out the so-called quasi-elastic part from the inelastic part. The curve of

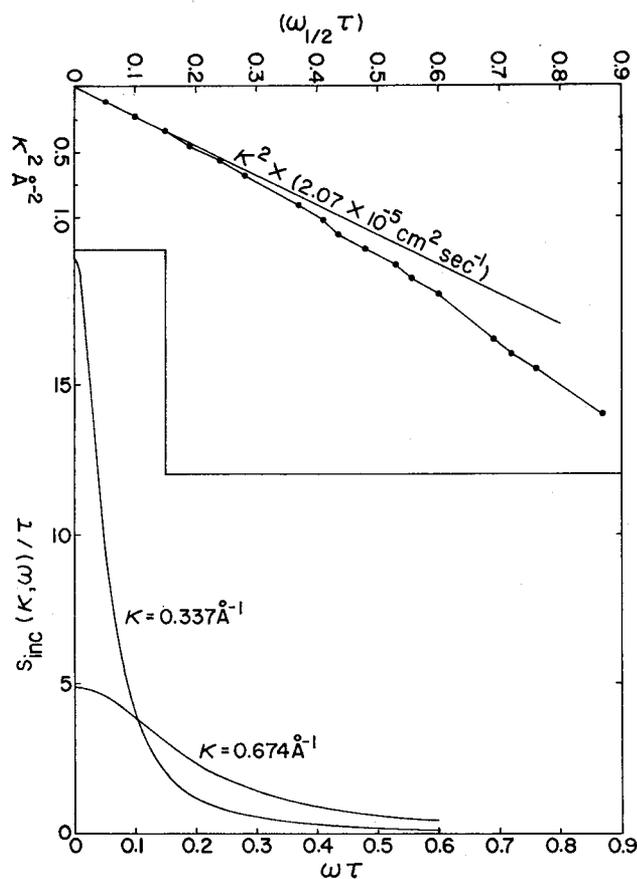


Fig. 4. Lower plot shows $S_{\text{inc}}(\kappa, \omega)$ for two small values of κ . The upper plot gives the half-width-at-half-height of $S_{\text{inc}}(\kappa, \omega)$ as a function of κ^2 ; the straight line behavior for small κ corresponds to $D = 2.07 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

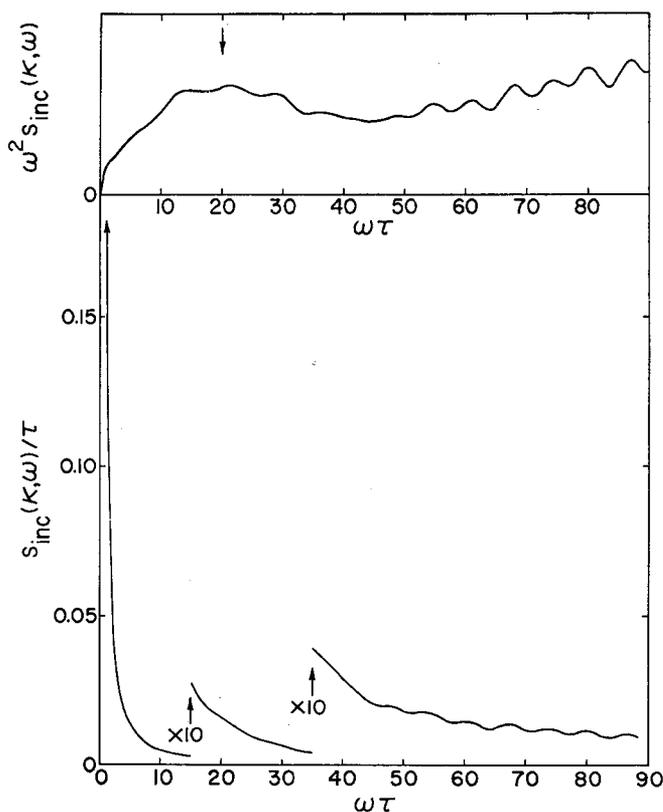


Fig. 5. $S_{\text{inc}}(\kappa, \omega)$ for $\kappa = 0.674 \text{ \AA}^{-1}$ (same as in Figure 4) is shown on an expanded scale. Note the large drop in intensity. The upper part shows $\omega^2 S_{\text{inc}}(\kappa, \omega)$ on an arbitrary scale. The arrow indicates the position of the first maximum in Figure 1.

$S_{\text{inc}}(\kappa, \omega)$ is one composite representation of the dynamics of the protons and has to be considered and analyzed in its entirety.

5.3. $\langle \mathbf{V}_p(0) \cdot \mathbf{V}_p(t) \rangle$

It is now clear that $S_{\text{inc}}(\kappa, \omega)$, in the small κ region, due to practical difficulties alluded to above, is just barely capable of bringing out a part of the interesting frequency characteristics of molecular motions shown in Figure 1. At this point therefore we revert to the primitive function itself; namely, $\langle \mathbf{V}_p(0) \cdot \mathbf{V}_p(t) \rangle$, the velocity autocorrelation function of the protons. The transform $f_p(\omega)$ defined in Equation (4.5) is shown in Figure 6. The frequency regions of importance taken from Figure 1 are indicated by arrows; as expected the proton gives a composite picture of the translational and rotational characteristics of the motion of water molecules. The shape of $f_p(\omega)$ is in overall accord with the available results from neutron inelastic scattering. However, in view of the experimental difficulties and methodological errors involved in extracting this spectrum from experimental data not much significance can be given to this accord.

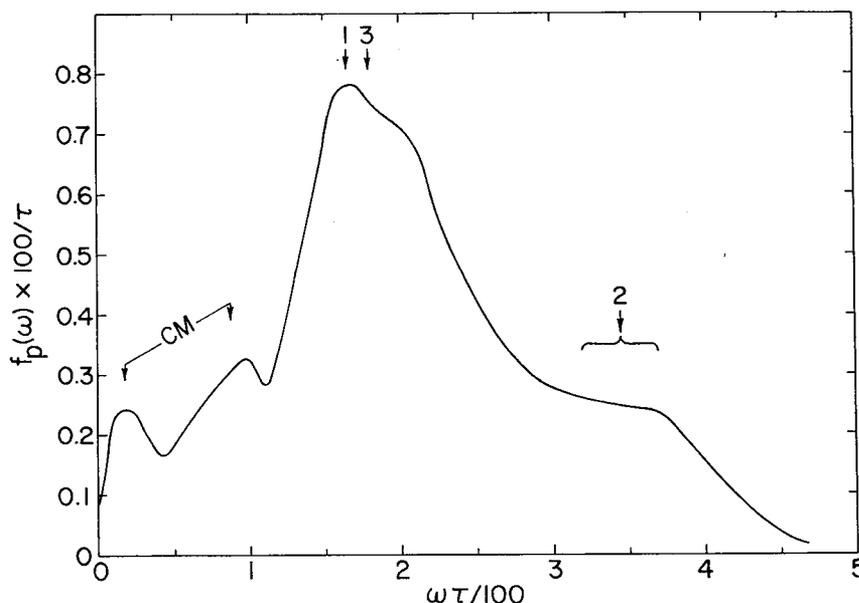


Fig. 6. Spectrum of the velocity autocorrelation of the proton. Arrows indicate expected positions of maxima from Figure 1. Librations around axes 1 and 3 are not separated. Their width makes the librations frequency around axis 2 and the high frequency component of center of mass motion appear only as shoulders in the spectrum.

In Figure 6 the only doubtful region is that of $\omega\tau \lesssim 2$. This is because the time a molecule takes to turn through a right angle is the Debye relaxation time ($\sim 2\tau$) and since $\langle \mathbf{V}_p(0) \cdot \mathbf{V}_p(t) \rangle$ has been calculated only up to $t = \tau/2$ there is a, residual, small negative tail of magnitude < 0.01 in the correlation function which, if included, would reduce the values calculated for $f_p(\omega)$ in the region $\omega\tau < 2$ by about 10%. This region of frequency is of no significance for the following discussion.

The peak at $\omega\tau = 20$ stands out quite clearly (compare Figures 1 and 6). However the maxima at $\omega\tau \sim 180$ are so broad that they overshadow the structure which one would have liked to see more clearly at $\omega\tau \sim 90$ (intermolecular vibrations) and $\omega\tau \sim 350$ (librations around principal axis #2).

5.4. $f_p(\omega)$ AND $\omega^2 S(\kappa, \omega) / \langle (\boldsymbol{\kappa} \cdot \mathbf{V})^2 \rangle$

As mentioned in Section 4, $\langle \mathbf{V}_p(0) \cdot \mathbf{V}_p(t) \rangle$ is the limiting form, for $\kappa \rightarrow 0$, of the autocorrelation function $C_s(\kappa, t)$ of Equation (4.3). It is interesting to know the degree to which the transforms of the two differ for $\kappa \sim 1 \text{ \AA}^{-1}$, since this is a convenient region of κ for experimental work with neutrons. The transform of $C_s(\kappa, t)$ is shown in Figure 7; the values obtained are very close to $f_p(\omega)$ shown in Figure 6.

The conclusion to be drawn from Figure 7 is that in the region of $\kappa \sim 1 \text{ \AA}^{-1}$, for $\omega\tau > 2$, $f_p(\omega)$ is extremely well represented by $\omega^2 S(\kappa, \omega) / \langle (\boldsymbol{\kappa} \cdot \mathbf{V})^2 \rangle$ which is the transform of $C_s(\kappa, t)$. The significance of this is that a neutron inelastic scattering experi-

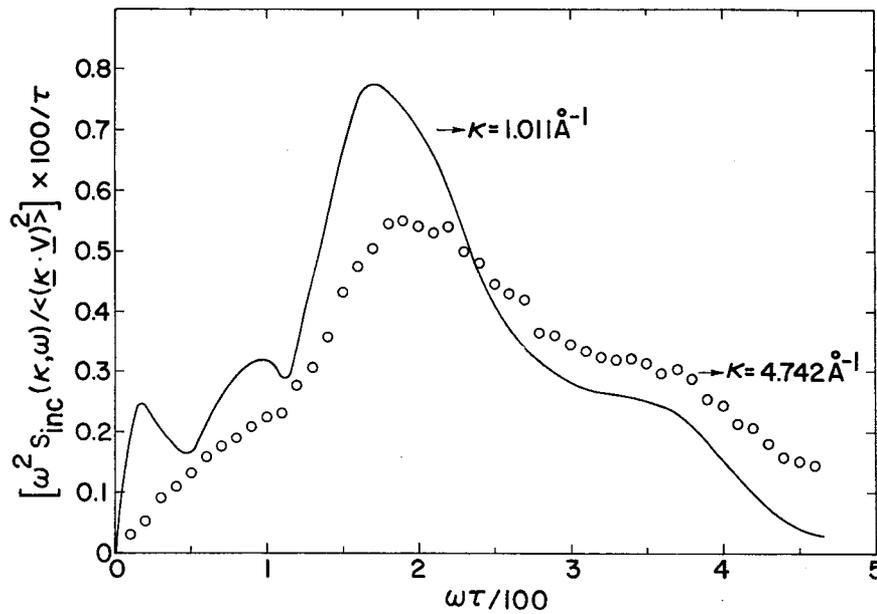


Fig. 7. Spectrum of $C_s(\kappa, t)$ [Equation (4.3)] for two values of κ . For $\kappa \sim 1 \text{ \AA}^{-1}$ this is a very good representation of $f_p(\omega)$ of Figure 6. For $\kappa \sim 5 \text{ \AA}^{-1}$ the departure from $f_p(\omega)$ is quite large.

ment made at $\kappa \sim 1 \text{ \AA}^{-1}$ to determine $S_{inc}(\kappa, \omega)$ will give $f_p(\omega)$ by simply taking $\omega^2 S_{inc}(\kappa, \omega)$ and normalizing the area to correspond to a convenient value. In this presentation the definitions of all the transforms (Equations (4.2), (4.5)) are such that the area under the transforms from $\omega=0$ to $\omega=\infty$ is $\pi/2$.

For large κ the difference between $f_p(\omega)$ and the transform of $C_s(\kappa, t)$ becomes more pronounced. For $\kappa = 4.742 \text{ \AA}^{-1}$ the results are shown in Figure 7. Here we have only a rough, qualitatively similar, behavior, with respect to $f_p(\omega)$.

5.5. CONCLUSIONS

It thus appears that up to $\kappa \sim 1 \text{ \AA}^{-1}$ an experimentally determined $S_{inc}(\kappa, \omega)$ simply multiplied by ω^2 (and the area $\int_0^\infty \omega^2 S(\kappa, \omega) d\omega$ suitably normalized) will give a reasonably faithful description of $f_p(\omega)$ and hence of the dynamics of the protons in the system. There is no question at all of a possible separation between the so-called quasi-elastic region and the inelastic region. Further, the notion of a phonon expansion is not only unnecessary but in fact it is incorrect for analyzing the data from liquid water.

6. Concluding Remarks

The outstanding difficulty in making neutron inelastic scattering experiments on water arises from multiple scattering in the sample. A good example of this is provided by the work of Blanckenhagen [12]; Figure 2 of Reference 12 shows the ratio of single

to multiple scattering. It is seen there that the contribution from multiple scattering is not a 'correction' to, but a major part of, what is observed. We hope to investigate this problem in the near future by using the $S_{\text{inc}}(\kappa, \omega)$ generated by molecular dynamics to simulate the multiple scattering phenomenon in an experiment with thin plate geometry with 90% transmission and an incident neutron beam of wave length 1 Å [13].

All our calculations have been based on a system obeying classical statistical mechanics. However, the nature of the conclusions drawn here about the difficulties inherent in the interpretation of neutron inelastic scattering data are still valid conclusions. Of course a direct comparison between actual data and our classically calculated results needs much greater care and justification. The first step in making such a direct comparison will be to symmetrize the experimental data by writing

$$S_{\text{inc}}^{\text{exp}}(\kappa, \omega) = \exp(-\hbar\omega/2k_B T) S_{\text{inc}}^{\text{sym}}(\kappa, \omega),$$

where $\hbar\omega$ denotes energy gain by the neutron. This ensures compatibility with the requirements of detailed balance [14]. The comparison will then have to be made between $S_{\text{inc}}^{\text{sym}}(\kappa, \omega)$ and our calculated results. To what quantitative extent this is sufficient to account for quantum mechanical corrections is a question which needs further study.

The presence of molecular vibrations gives a further contribution to the neutron inelastic scattering; this is excluded from our calculations since we have treated the molecules as rigid. This contribution occurs [15] at $\omega\tau \approx 600$ and at $\omega\tau \approx 1200$ (see ω scale on Figure 6). However, the main argument in this presentation will not be affected by this extension in the spectrum.

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DISCUSSION

Schofield: Referring to the historic past of ten years ago, may I point out that jump diffusion may have been a feature of the Rahman, Singwi and Sjölander model. It was not a feature of the Schofield-Egelstaff model! May I point out, however, that the jump diffusion model does not give a Gaussian $G_s(\mathbf{r}, t)$.

Rahman: I did mention during the talk that I was a participant in the development of some of the wrong approaches of ten years ago. May I recall that the Rahman-Singwi-Sjölander approach used a Gaussian quasi-crystalline model whereas the earlier Singwi-Sjölander model used a jump model. It is true that jump diffusion model leads to a non-Gaussian $G_s(\mathbf{r}, t)$ but the trouble with the jump model is that the consequent mean square displacement is not correct at all.

Sillescu: Can you calculate the propagator $P(\mathbf{r}_1(0)/\mathbf{r}_0(t))$ for protons of 2 water molecule 1 and 2 that have their closest distance of approach at time zero, and compare it with $P(\mathbf{r}_1(0)/\mathbf{r}_1(t))$ in order to check whether there is collective translational motion of water molecules?

Rahman: We are going to calculate the propagator of interest to NMR in the near future.

Brot: (1) Looking into your comparison of classical vs quantal correlation functions for a variety of simple systems, what is the better approximation for the classical CF: the real part of the quantal one or its modulus? The first choice corresponds to the symmetrized CF of Kubo of course, the second one to an assumption frequently made by experimentalists. There exists also a third possibility which is to take the geometric mean between the real and the imaginary part, as suggested by Schofield a few years ago.

(2) If your intermediate scattering function F_s is for the protons and not for the centers of gravity, much of its non-Gaussian character must arise from its rotational part. Supposing a Gaussian rotational F_s amounts to truncating its Sears expansion at the first spherical harmonic, a procedure which is frequently incorrect.

Rahman: Up to now we have only compared the real part of the *QM* result with the classical result. The other alternatives have not yet been considered. Regarding your second question, the F_s we calculated was of course for protons and the non-Gaussian behavior does arise mostly out of rotational motion.

Springer: You have described the H₂O intermolecular interaction simply in terms of Coulomb forces between a tetrahedral arrangement of electric charges. Does this imply that the 'hydrogen bonding' can be understood essentially in these terms?

Rahman: I have a very meagre knowledge of the varieties of ways in which chemists have found it useful to think of hydrogen bonds. One way is a simple coulombic approach. We have shown by MD calculations that a coulombic picture, using a distribution of a few point charges in the molecule, is quite a useful approach.

Yip: (1) Does your effective frequency distribution agree with those derived directly from neutron inelastic scattering measurements?

(2) Would you care to comment in the context of your results on the assumption that the validity of rotation-translation coupling effects can be ignored?

Rahman: The agreement is really quite good; reference to the recent work of Blankenhagen (see list of references in our paper) will show this quite clearly. Such a comparison was purposely left out of this presentation in favour of a focus on the difficulties that arise in the analysis of data obtained in a neutron experiment.

The separability, to a fairly good approximation, of the translational and rotational motions of the molecules was mentioned in our first paper on water. In view of the interest shown here in this regard we will try to give more attention to it in our future work and, if necessary, we will publish numerical details as well.

Chen: Regarding the quantum correction of the Van-Hove selfcorrelation function, if I calculate the correlation function classically, what is wrong by just hang on the detail balance factor?

Rahman: That is just what we are doing at present as you will see in the text of the paper. However, in the literature alternative, and essentially arbitrary, recipes are available. We would like to consider them as well.

Schofield: The relation

$$S_{cl} \approx \exp\left(-\frac{\hbar\omega}{2kT}\right) S_Q \left/ \cosh\left(\frac{\hbar\omega}{2kT}\right)\right.$$

comes from the quantum and classical versions of the Kubo-Wosi relaxation function theory. I think this particular choice is mainly an aesthetic one. In relation to the question of quantum vs. classical spectral functions, Berne has done calculations for rotational motion and has shown recurrences in the time correlation function which do not occur classically.

Litovitz: Do the hindered translational peaks depend strongly on temperature? Is your result consistent with that of Walrafen who uses the intensity of these peaks to estimate the extent of hydrogen bonding?

Rahman: The peaks do depend on temperature though I do not recall the details. I do not know how Walrafen connects this spectrum with the number of bonds. We shall surely look into it.

Magat: Il y a, à mon avis, deux questions qui sont probablement liées et pour lesquelles il n'y a pas eu jusqu'à présent des réponses entièrement satisfaisantes. (1) Pourquoi l'intensité des bandes Raman intermoléculaires 160, 170, 500 et 700 cm^{-1} décroît-elle très rapidement entre 20 et 60°C, comme je l'avais observé il y a 40 ans et comme l'a confirmé Walrafen, tandis que l'intensité de ces mêmes bandes en infrarouge est indépendante de la température? (2) La constante diélectrique complexe de l'eau peut être parfaitement représentée par un demi-cercle de Cole et Cole à condition de prendre $\epsilon_\infty = 5 \pm 0,5$. Or, d'une part n_{opt}^2 de l'eau liquide est $\sim 1,7$, la décroissance de ϵ_∞ de 5 à 1,7 se faisant au voisinage de 170 cm^{-1} (fréquence de vibration-elongation qui ne saurait être responsable de la variation de ϵ_∞); d'autre part ϵ_∞ de la glace est de 3,2. Je crains que, tant que nous n'aurons pas d'explication entièrement satisfaisante de ces observations, nous ne pourrions pas dire que nous 'comprendons' l'eau liquide et ceci malgré les progrès énormes (dus en grande partie à Rahman et Stillinger) qui ont été faits ces dernières années.

Rahman: Qualitatively speaking the intensity of an IR band should be less dependent upon the surroundings of a molecule than that of the corresponding Raman band; with increase in temperature the immediate surroundings of a molecule become less ordered, the hydrogen bonds become more ill defined and hence the derivative of the polarizability of the cluster consisting of a molecule and its immediate neighbors should vary rapidly with temperature. A quantitative study of this question will involve the very difficult task of calculating the appropriate quantum mechanical transition matrix elements as a function of local disorder.

As regards ϵ_∞ , (future) molecular dynamics calculations incorporating flexible water molecules will probably throw some useful light on the dielectric problem.

Friedman: Concerning the so-called translation-rotation coupling, one could imagine that your MD calculations were repeated for different proton masses, to see whether you get the large observed isotope effect (a factor of 1,2) for the change in diffusion coefficient or viscosity in going from H_2O to D_2O . If you do, then there must be translation-rotation coupling in your model fluid. If not, then in view of the excellence of your model, we could conclude that this particular isotope effect has a quantum mechanical origin. But the biggest quantal effect presumably comes from the librations ($\sim 500 \text{ cm}^{-1}$) so even the quantal effect would be a kind of translation-rotation coupling.

Rahman: These are very interesting points which we will pursue in further analysis of our data. It is possible that a small degree of coupling is enough to bring about the change you have mentioned.

Comment by M. R. Hoare

It would be a pity if no one were to mention the work of Zazar, Hasted and Chamberlain on sub-millimetre dielectric dispersion in water which will have appeared too recently for most participants to have seen it. (*Nature Phys. Sci.* **243**, 106 (1973)).

Interpreting their measurements of complex refractive index in the wave-number range 20–100 cm^{-1} they conclude that there is a second relaxation process with characteristic time 0.53×10^{-13} s, which they suggest arises from the rotation of whole molecules (or OH-groups) not breaking a hydrogen bond in the process.

It would be interesting to know whether such movements can be 'seen' in the latest molecular dynamics results.