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Diffusive Motions in Water and Cold Neutron Scattering*

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Using a model of liquid water in which a molecule, in its equilibrium position, performs an oscillatory motion for a mean time τ_0, and then diffuses by continuous motion for a mean time τ_1, and repeats this sort of motion, the differential scattering cross section for cold neutrons has been calculated. It is found that the shape of the "quasi-elastic" scattering is, in general, not Lorentzian. The formula for the broadening of the quasi-elastic peak assumes a simple form in two limiting cases: In case (i) $\tau_1 \gg \tau_0$, it reduces to the formula derived on the simple diffusion theory; and in case (ii) $\tau_1 \ll \tau_0$, the broadening is the same as in case (i) if $\kappa^2 D\tau_0 \ll 1$, and it approaches the asymptotic value $2\hbar/\tau_0$, if $\kappa^2 D\tau_0 \gg 1$, where $\hbar\kappa$ is the momentum transferred to the system and D is the diffusion coefficient of water. The observed value of the broadening can be explained for a value of $\tau_0 = 4\times 10^{-12}$ sec. Besides, the theoretical quasi-elastic scattering in case (ii) has certain interesting features which are in general agreement with experiment. In part II of this paper, inelastic scattering (hindered translations only) of cold neutrons has been calculated using two different models of water: (a) a gas model and (b) a Debye model; and the results have been compared with experiment.

The general shape of both the quasi-elastic and inelastic scattering of cold neutrons and the magnitude of the diffusive broadening seem to support a quasi-crystalline model of water.

I. INTRODUCTION

"COLD" neutron scattering has proved to be a powerful tool in the study of the dynamics of atomic motions in solids[1] and it is only very recently that this technique has been used to study the atomic motions in liquid water.[2–4] In contrast to solids, the atomic motions in liquids are very complex and there does not exist any satisfactory theory of the liquid state. Water, as compared with ordinary liquids, has many anomalous physical properties. It behaves in some respects more like a solid than like a liquid and this behavior, fortunately, makes water more easily amenable to a mathematical treatment. An important problem is to understand the nature of diffusive motions of the molecules in water. The present paper is an attempt in this direction and makes use of the available neutron scattering experimental results.

A general theory of neutron scattering by an arbitrary system of particles has been given by Van Hove.[5] In this theory, the differential scattering cross section is expressed as a four dimensional Fourier transform of the generalized distribution function, usually denoted as $G(\mathbf{r},t)$. In the classical limit, the interpretation of this function is that given an atom at the origin at time $t=0$, it defines the probability of finding an atom within a unit volume at the point $\mathbf{r}$, and at time t. The atom at the position $(\mathbf{r},t)$ may be the same that was at the origin at time $t=0$, or may be another atom. In the case of solids, it is possible to calculate the $G(\mathbf{r},t)$ function fairly exactly, which, unfortunately, is not the case for liquids.

The total scattering can be divided into a coherent part and an incoherent part, the former is given by the Fourier transform of $G(\mathbf{r},t)$ and the latter by the Fourier transform of the self-diffusion function $G_s(\mathbf{r},t)$. $G_s(\mathbf{r},t)$ defines the probability of finding a particle at the point $(\mathbf{r},t)$, if at time $t=0$, the same particle was at the origin. In water almost all the scattering is due to hydrogen for which the scattering is incoherent. The scattering, in the case of a solid, can be further divided into an inelastic part (phonon exchange) and an elastic part (no phonon exchange), the former arising as a result of rapid fluctuations in the distribution function for short times ($t \lesssim 10^{-13}$ sec); and the latter as a result of the distribution function being independent of time for long times ($t \gg 10^{-13}$ sec). Physically this means that after a time $t \gg 10^{-13}$ sec, the mean square displacement of an atom has attained its equilibrium value or in other words the atom has fully developed its thermal cloud. This physical fact is expressed by the familiar Debye-Waller factor in the expression for the scattering cross section. In liquids, on the other hand, the mean position of an atom is not stationary, but moves slowly, in other words the atom diffuses. Such a diffusive motion of an atom in a liquid gives rise to a broadening of the elastic peak. Thus in a liquid there is no true elastic scattering but only "quasi-elastic." The broadening of the elastic peak depends on the nature of the diffusive motions. In general, the diffusive motions may be quite complex but the two simple cases are: (i) diffusion by large independent jumps and (ii) diffusion by small motions according to the simple diffusion equation (continuous diffusion). Using the expression for the self-diffusion function obtained as a solution of the classical diffusion equation, Vineyard[6] has calculated the broadening in case (ii). Earlier,

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[1] For a general review of the subject see; L. S. Kothari and K. S. Singwi, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1959), Vol. 8, p. 109.

[2] B. N. Brockhouse, Suppl. Nuovo cimento **9**, 45 (1958).

[3] B. N. Brockhouse, Phys. Rev. Letters **2**, 287 (1959).

[4] D. J. Hughes, H. Palevsky, W. Kley, and E. Tunkelo, Phys. Rev. Letters **3**, 91 (1959).

[5] L. Van Hove, Phys. Rev. **95**, 249 (1954).

[6] G. H. Vineyard, Phys. Rev. **110**, 999 (1958).

Brockhouse[7] had also derived the same expression for the broadening.

Recent measurements of Brockhouse[3] for water show that the observed line broadening is somewhat less than that given by the simple diffusion theory and he concludes that case (ii) does not completely represent the mechanism of diffusion in water; and he further adds that a variety of diffusive motions must occur. More recent measurements of Hughes and collaborators[4] indicate that the experimental broadening is at least less than the theoretical value of Vineyard by a factor of three if not more. In fact, these authors conclude that their experiment shows no evidence of broadening related to diffusive motions and they further add that their result is in sharp contrast to that of Brockhouse.[3] In view of this contradiction and in view of the importance of the nature of the diffusive motions in the commonest of all liquids like water, the subject needs a more detailed theoretical study.

Using a model of liquid water in which a molecule executes an oscillatory motion for a mean time τ_0, and then diffuses by continuous motion for a mean time τ_1, and then repeats this sort of motion, we have calculated the differential scattering cross section for cold neutrons. The general formula for the broadening of the quasi-elastic component of the scattering that we have derived reduces in the case (i) $\tau_1 \gg \tau_0$, to the formula for the simple diffusion broadening deduced earlier by Vineyard[6]; and in the case (ii) $\tau_1 \ll \tau_0$, to a somewhat more complicated formula. The latter has some interesting features which should be checked experimentally and gives for $\tau_0 \simeq 4\times 10^{-12}$ sec a value of the broadening which is consistent with the experimental value of the Brookhaven group.[4] This value of the time τ_0 is supported by other independent experimental observations. An important feature of the theory is that it does not depend on the details of the model assumed. Cold neutron scattering in water should in principle enable us to determine not only the diffusion coefficient but also the mechanism of diffusion. The form of the quasi-elastic scattering and the magnitude of the line broadening seem to suggest a quasi-crystalline model of water, originally proposed many years ago by Bernal and Fowler.[8] In part II of this paper inelastic scattering of cold neutrons for a quasi-crystalline model and a gas model of water has been calculated and compared with the experiments of Hughes et al.[4] On the basis of this comparison, we conclude that a gas model for water for low neutron energies is a poor approximation and that a quasi-crystalline model is a better one to use.

2. MODEL FOR WATER

The model of water that has received considerable attention is the one originally proposed by Bernal and Fowler[8] and later modified by Lennard Jones and Pople.[9] In this model each water molecule is surrounded tetrahedrally by four other water molecules held together by hydrogen bonds, which can bend. The higher the temperature, the more is the bending. In water such a network of bonds extends throughout the liquid and they are continually breaking and reforming such that at any given instant all the molecules have their full quota of bonds. Based on such a model, Pople[10] was able to explain satisfactorily the temperature variation of the dielectric constant of water. It has also been proposed by Frank[11] that in contrast to the model of Lennard Jones and Pople, liquid water consists of flickering clusters of bonded molecules mixed with nonbonded fluid. In the former model one would expect that the diffusion mechanism will be primarily through big jumps corresponding to the mean distance between water molecules, whereas in the latter model the diffusion mechanism will be more complex. In Frank's model, a water molecule besides making an oscillatory motion, will also move as a free diffusing particle for a finite length of time. The parametric times τ_0 and τ_1 introduced in the present theory would take care of this fact.

3. MATHEMATICAL FORMULATION

Van Hove[5] has shown that the incoherent differential scattering cross section per atom per unit solid angle Ω and per unit energy $\hbar\omega$ is given by

$$\frac{d^2\sigma}{d\Omega d\omega}=a^2\frac{k}{k_0}\frac{1}{2\pi}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]G_s(\mathbf{r},t)d\mathbf{r}dt, \tag{1}$$

where a is the bound incoherent scattering length, $\mathbf{k}_0$ and $\mathbf{k}$ denote, respectively, the initial and final wave vectors of the neutron. The energy and momentum transfers are, respectively, given by

$$\hbar\omega=(\hbar^2/2m)(k_0^2-k^2),\quad \hbar\boldsymbol{\kappa}=\hbar(\mathbf{k}_0-\mathbf{k}), \tag{2}$$

m being the mass of the neutron. The self-diffusion function $G_s(\mathbf{r},t)$ is complex if quantum effects are taken care of and satisfies the relation[5]

$$G_s(\mathbf{r},t)=G_s^*(-\mathbf{r},-t). \tag{3}$$

The main problem is to calculate $G_s(\mathbf{r},t)$ or its Fourier transform. It is the latter which we shall calculate in the classical limit. We shall first define the following quantities: (a) $g(\mathbf{r},t)$ is the probability of finding a particle at the position $\mathbf{r}$ at time t, when it is performing an oscillatory motion about an equilibrium position, starting from the origin at time $t=0$; (b) starting from an oscillatory motion at time $t=0$, $p(t)$ gives the probability that the particle remains in the same oscillatory state at a later time t; (c) $h(\mathbf{r},t)$ is the probability of finding a particle at the position $\mathbf{r}$ at

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[7] B. N. Brockhouse, Acta Cryst. **10**, 827 (1957).

[8] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).

[9] J. Lennard Jones and J. A. Pople, Proc. Roy. Soc. (London) **A205**, 155 (1951).

[10] J. A. Pople, Proc. Roy. Soc. (London) **A205**, 163 (1951).

[11] H. S. Frank, Proc. Roy. Soc. (London) **A247**, 481 (1958).

time t, when it is performing a diffusive motion between two equilibrium positions, starting from the origin at time $t=0$; (d) starting from a state of diffusive motion at time $t=0$, $q(t)$ gives the probability that the particle remains in the same state of diffusive motion at a later time t; (e) $p(t)-p(t+dt)=-p'(t)dt$ gives the probability that the particle has left its oscillatory state during the time interval t and $t+dt$, and has gone into the diffusive state; and (f) $q(t)-q(t+dt)=-q'(t)dt$ gives the probability that the particle has left its diffusive state during the time interval t and $t+dt$, and has gone into the oscillatory state.

We now ask the question: what is the probability of finding a particle at the point $\mathbf{r}$ at time t, if at time $t=0$, the particle under consideration was at the origin; i.e., we ask for $G_s(\mathbf{r},t)$? Let us divide the motion into steps numbering $0, 1, 2, \cdots 2N, \cdots$. Starting from the origin where we assume that the particle is making an oscillatory motion, it could have arrived at the point $\mathbf{r}$ in time t after making $0, 1, 2, \cdots$ steps. The zeroth step corresponds to the oscillatory motion, step 1 to the succeeding diffusive motion, step 2 again to the oscillatory motion, step 3 to the diffusive motion and so on. Then $G_s(\mathbf{r},t)$ is given by

$$G_s(\mathbf{r},t)=\sum_i F_i(\mathbf{r},t), \quad t>0; \tag{4}$$

where the various F_i's are given by

$$\begin{aligned}
&\text{Step 0,} \quad F_0(\mathbf{r},t)=g(\mathbf{r},t)p(t),\\
&\text{Step 1,} \quad F_1(\mathbf{r},t)=-\int_0^t dt_1\int d\mathbf{r}_1\, q(t-t_1)h(\mathbf{r}-\mathbf{r}_1,\, t-t_1)p'(t_1)g(\mathbf{r}_1,t_1),\\
&\text{Step 2,} \quad F_2(\mathbf{r},t)=(-1)^2\int_0^t dt_2\int_0^{t_2} dt_1\int d\mathbf{r}_2 d\mathbf{r}_1\, p(t-t_2)g(\mathbf{r}-\mathbf{r}_2,\, t-t_2)q'(t_2-t_1)h(\mathbf{r}_2-\mathbf{r}_1,\, t_2-t_1)p'(t_1)g(\mathbf{r}_1,t_1), \qquad (5)\\
&\text{Step } 2N, \quad F_{2N}(\mathbf{r},t)=(-1)^{2N}\int_0^t dt_{2N}\int_0^{t_{2N}} dt_{2N-1}\cdots\int_0^{t_2} dt_1\int\cdots\int d\mathbf{r}_{2N}d\mathbf{r}_{2N-1}\cdots d\mathbf{r}_1\\
&\qquad\qquad \times p(t-t_{2N})g(\mathbf{r}-\mathbf{r}_{2N},\, t-t_{2N})q'(t_{2N}-t_{2N-1})h(\mathbf{r}_{2N}-\mathbf{r}_{2N-1},\, t_{2N}-t_{2N-1})\cdots p'(t_1)g(\mathbf{r}_1,t_1).
\end{aligned}$$

An important assumption which has been made in writing the expression (5) is that when the particle makes a transition from one step into the other, say from an oscillatory motion into a diffusive motion or vice versa, there is no correlation between the motions in the two steps. This seems to be a reasonable assumption in the particular case of water where the mean life time for the oscillatory motion is assumed to be large ($\sim 10^{-12}$ sec) compared to the period of vibration ($\sim 10^{-13}$ sec) and where the diffusion, as we shall see, is mainly through big jumps.

By substituting (5) in (4), it is possible in principle to calculate $G_s(\mathbf{r},t)$. However, what we are interested in is not $G_s(\mathbf{r},t)$ but its Fourier transform and therefore the Fourier transforms of the F_i's, which are easy to handle.

Let us consider the integral

$$\int_0^\infty dt\int d\mathbf{r}\, F_{2N}(\mathbf{r},t)\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)],$$

which can be written as

$$\begin{aligned}
&\int_0^\infty d\tau_{2N+1}\int_0^\infty d\tau_{2N}\cdots\int_0^\infty d\tau_1\int d\xi_{2N+1}\int d\xi_{2N}\cdots\int d\xi_1\\
&\qquad \times p(\tau_{2N+1})g(\xi_{2N+1},\tau_{2N+1})q'(\tau_{2N})h(\xi_{2N},\tau_{2N})\cdots p'(\tau_1)g(\xi_1,\tau_1)\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]. \qquad (6)
\end{aligned}$$

Expression (6) follows immediately by making the following change of variables for the time integrals;

$$t-t_{2N}=\tau_{2N+1}, \quad t_{2N}-t_{2N-1}=\tau_{2N}, \quad \cdots \quad t_2-t_1=\tau_2, \quad t_1=\tau_1;$$

and a similar change of variables for the space integrals. Hence,

$$\begin{aligned}
\int_0^\infty dt\int dr\,\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]F_{2N}(\mathbf{r},t)&=\int_0^\infty d\tau\int d\xi\,\exp[i(\boldsymbol{\kappa}\cdot\xi-\omega\tau)]p(\tau)g(\xi,\tau)\\
&\quad\times\left\{-\int_0^\infty d\tau'\int d\xi'\,\exp[i(\boldsymbol{\kappa}\cdot\xi'-\omega\tau')]p'(\tau')g(\xi',\tau')\right\}^N\\
&\quad\times\left\{-\int_0^\infty d\tau''\int d\xi''\,\exp[i(\boldsymbol{\kappa}\cdot\xi''-\omega\tau'')]q'(\tau'')h(\xi'',\tau'')\right\}^N=AC^ND^N; \qquad (7)
\end{aligned}$$

and similarly, it can be shown that

$$\int_0^\infty dt \int d\mathbf{r}\, \exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]F_{2N+1}(\mathbf{r},t)=BC^{N+1}D^N, \tag{8}$$

where

$$\begin{aligned}
A&=\int_0^\infty dt \int d\mathbf{r}\, \exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]p(t)g(\mathbf{r},t),\\
B&=\int_0^\infty dt \int d\mathbf{r}\, \exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]q(t)h(\mathbf{r},t),\\
C&=-\int_0^\infty dt \int d\mathbf{r}\, \exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]p'(t)g(\mathbf{r},t),
\end{aligned} \tag{9}$$

and

$$D=-\int_0^\infty dt \int d\mathbf{r}\, \exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]q'(t)h(\mathbf{r},t).$$

Now

$$\begin{aligned}
\int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} d\mathbf{r}\, \exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)] \sum_{N=0}^{\infty} F_N(\mathbf{r},t)
&=A\sum_{N=0}^{\infty}(CD)^N+BC\sum_{N=0}^{\infty}(CD)^N+\text{c.c.}\\
&=\frac{A+BC}{1-CD}+\text{c.c.},
\end{aligned} \tag{10}$$

where we have made use of the relation (3).

In deriving (10) we have tacitly assumed that at time $t=0$, all particles start with an oscillatory motion. This is in general not true and some of the particles will start their motion as free particles (i.e., with diffusing motion). In this case, following the same procedure as above, it can be shown that the corresponding expression to (10) is $B+AD/1-CD+\text{c.c.}$ Hence, the differential scattering cross section, using (10) and (1), is given by

$$\frac{d^2\sigma}{d\Omega d\omega}=\frac{a^2}{2\pi}\frac{k}{k_0}\left\{\frac{\tau_0}{\tau_1+\tau_0}\left(\frac{A+BC}{1-CD}\right)+\frac{\tau_1}{\tau_1+\tau_0}\left(\frac{B+AD}{1-CD}\right)+\text{c.c.}\right\}. \tag{11}$$

In (11), $\tau_0/(\tau_1+\tau_0)$ gives the fraction of particles performing an oscillatory motion, and $\tau_1/(\tau_1+\tau_0)$ gives the fraction of particles performing a diffusive motion at time $t=0$.

We shall now assume the following forms for the various functions occurring in (9):

$$\begin{aligned}
g(\mathbf{r},t)&=[2\pi\gamma(t)]^{-\frac{3}{2}}\exp[-r^2/2\gamma(t)],\\
p(t)&=e^{-t/\tau_0},\\
h(\mathbf{r},t)&=(4\pi D_1 t)^{-\frac{3}{2}}\exp[-r^2/4D_1 t],
\end{aligned} \tag{12}$$

and

$$q(t)=e^{-t/\tau_1},$$

where $\gamma(t)$ is the same as in a solid.

The form assumed for the function $g(\mathbf{r},t)$ is the same as for an atom in a solid. It is thus possible to calculate this function rigorously. It is reasonable to take such a form for water, since we assume that during the time τ_0 the motion of the molecule is very similar to what occurs in a solid. The time τ_0 is much greater than the period of vibration. Physically, this means that the thermal cloud of the atom has fully developed long before it had the chance to leave the oscillatory motion. For a normal liquid such a form of $g(\mathbf{r},t)$ will probably be incorrect. The function $h(\mathbf{r},t)$ is the solution of the usual classical equation of diffusion. In evaluating the expressions B and D in (9), we need to know the function $h(\mathbf{r},t)$ for all times from 0 to ∞. But the form of $h(\mathbf{r},t)$ assumed here is valid only for large times. For small times ($t\ll 10^{-13}$ sec), we know that the square of the width of the Gaussian distribution should vary as the square of the time; whereas for the function $h(\mathbf{r},t)$ it varies linearly with time. Thus, our $h(\mathbf{r},t)$ does not have the right form for very small times. To rectify this defect, one could use the distribution function obtained from the solution of the classical Langevin's equation, which forms the basis of the theory of the Brownian motion. The distribution function[12] so obtained has the correct limiting form for times both large and small compared to the characteristic time[12] β^{-1} of the liquid. It does not, however, mean that the distribution function for intermediate times is the correct one since the validity of the simple Langevin's equation for a liquid, where there are strong correlation effects, is rather doubtful. Besides, it is a classical equation of motion. An exact solution of the problem is probably very involved and has not been attempted so far. Fortunately, for water for which the foregoing theory is intended to be applied, the form of $h(\mathbf{r},t)$ as given by (12) is quite satisfactory. The use of the assumed $h(\mathbf{r},t)$ gives a correction to the broadening of the quasi-elastic peak [see Eq. (19)] which is of second order, the first order term depends only on τ_0.

We have treated the scattering classically, but it can be shown that quantum effects are negligible in the present case where we are interested in diffusion broadening which corresponds to an energy transfer much less than k_BT.

Using (12), the integrals in (9) are easily evaluated and we get

$$\begin{aligned}
A&=\exp[-\tfrac{1}{2}\kappa^2\gamma(\infty)]\frac{\tau_0}{1+i\omega\tau_0},\\
B&=\frac{\tau_1}{(1+\kappa^2 D_1\tau_1)+i\omega\tau_1},\\
C&=(1/\tau_0)A,\\
D&=(1/\tau_1)B.
\end{aligned} \tag{13}$$

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[12] S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943).

In evaluating the expression A we have written $\exp[-\frac{1}{2}\kappa^2\gamma(t)]$ as $\exp[-\frac{1}{2}\kappa^2\gamma(\infty)]\ \exp\{-\frac{1}{2}\kappa^2[\gamma(t)-\gamma(\infty)]\}$, and have expanded $\exp\{-\frac{1}{2}\kappa^2[\gamma(t)-\gamma(\infty)]\}$ as a power series and have retained only the first term. The first term gives the whole of the elastic peak in the broadening of which we are interested. The higher terms, which correspond to inelastic scattering, give only a smooth background.

The Debye-Waller factor in a solid, usually denoted by $2W$ is defined by the equation

$$2W=\tfrac{1}{2}\kappa^2\gamma(\infty). \tag{14}$$

Substituting the values of A, B, C, and D from (13) in (11) and using (14) we obtain, after some simplification,

$$\frac{d^2\sigma}{d\Omega d\omega}=\frac{a^2}{\pi}\frac{k}{k_0}\frac{e^{-2W}\tau_0}{1+\tau_1/\tau_0}\frac{(c+d\omega^2\tau_0^2)b}{b^2+\omega^2\tau_0^2(f+\omega^2\tau_0^2g)}, \tag{15a}$$

where

$$\begin{aligned} b&=1+\kappa^2D_1\tau_1-e^{-2W},\\ c&=1+\kappa^2D_1\tau_1+2\tau_1/\tau_0+(\tau_1^2/\tau_0^2)e^{2W},\\ d&=(\tau_1^2/\tau_0^2)e^{2W},\\ f&=(1+\kappa^2D_1\tau_1)^2+\tau_1^2/\tau_0^2+2(\tau_1/\tau_0)e^{-2W},\\ g&=\tau_1^2/\tau_0^2. \end{aligned} \tag{15b}$$

We observe from (15a) that the shape of the quasi-elastic scattering is, in general, not Lorentzian.

The diffusion coefficient D_1 as it occurs in (12) is defined by $l^2/6\tau_1$, where l^2 is the mean square displacement in time τ_1 during which continuous diffusion takes place. The actual diffusion coefficient D is given by

$$D=\frac{R^2+l^2}{6(\tau_0+\tau_1)}, \tag{16}$$

where R^2 is the mean square radius of the fully developed thermal cloud in the oscillatory motion. (16) follows directly from our $G_s(\mathbf{r},t)$ for large values of time. From (16) follows the relation

$$D_1\tau_1\simeq D\tau_0(1+\tau_1/\tau_0), \tag{17}$$

since $R^2\ll l^2$.

We shall now consider the two limiting cases of (15a): (i) $\tau_1\ll\tau_0$ and (ii) $\tau_1\gg\tau_0$.

Case (i). $\tau_1\ll\tau_0$

Using (17) and neglecting τ_1/τ_0 compared to unity, (15a) reduces to

$$\frac{d^2\sigma}{d\Omega d\omega}=\frac{a^2}{\pi}\frac{k}{k_0}\tau_0e^{-2W}\frac{[1-e^{-2W}/(1+\kappa^2D\tau_0)]}{\omega^2\tau_0^2+[1-e^{-2W}/(1+\kappa^2D\tau_0)]^2}. \tag{18}$$

The shape of the quasi-elastic peak is Lorentzian whose width at half maximum is given by

$$\Delta\epsilon=\frac{2\hbar}{\tau_0}\left(1-\frac{e^{-2W}}{1+\kappa^2D\tau_0}\right). \tag{19}$$

Now from (14), we have

$$\begin{aligned} 2W&=\tfrac{1}{6}\kappa^2R^2\\ &\simeq\kappa^2\left(\frac{\hbar^2}{2Mk_B\Theta}\frac{6T}{\Theta}\right), \end{aligned} \tag{20}$$

which follows from an analogy with solid. Θ is the Debye temperature of quasi-crystalline water, M is the mass of the water molecule, T is the temperature and k_B is the Boltzmann's constant. Expression (20) is valid for $T>\Theta$, which is true for water ($\Theta=135$°K, see Part II). Also

$$\kappa^2D\tau_0=\kappa^2l^2/6. \tag{21}$$

From (20) and (21), we have

$$2W=\kappa^2D\tau_0(R^2/l^2)\ll\kappa^2D\tau_0. \tag{22}$$

If $\kappa^2D\tau_0\ll1$, (19) reduces to

$$\Delta\epsilon=2\hbar\kappa^2D, \tag{23}$$

the broadening, which, as we shall see, is obtained when one uses the simple diffusion theory. If, however, $\kappa^2D\tau_0\gg1$, the broadening approaches the asymptotic value

$$\Delta\epsilon=2\hbar/\tau_0. \tag{24}$$

Case (ii). $\tau_1\gg\tau_0$

In this case, using (17), (15a) reduces to

$$\frac{d^2\sigma}{d\Omega d\omega}=\frac{a^2}{\pi}\frac{k}{k_0}\frac{\kappa^2D}{(\kappa^2D)^2+\omega^2}. \tag{25}$$

The broadening is thus given by

$$\Delta\epsilon=2\hbar\kappa^2D. \tag{26}$$

The expressions (25) and (26) were obtained earlier by Vineyard.[6]

Equation (25) follows immediately from (1) if we take for $G_s(\mathbf{r},t)$, the function $h(\mathbf{r},t)$ given by (12). We had mentioned earlier that $h(\mathbf{r},t)$ does not have the correct form for small times. Below, we shall derive an expression corresponding to (25) using for $G_s(\mathbf{r},t)$ the function as obtained from the solution of the Langevin's equation. The expression for $G_s(\mathbf{r},t)$ can be put in the form[12] [see Eq. (175), page 26 of reference 12].

$$G_s(\mathbf{r},t)=[2\pi\gamma(t)]^{-\frac{3}{2}}\exp[-r^2/2\gamma(t)],$$

where

$$\gamma(t)=(2D/\beta)(\beta t-1+e^{-\beta t}),\quad t>0, \tag{27}$$

and where the characteristic time β^{-1} is given by

$$\beta=k_BT/MD.$$

Substituting the foregoing expression for $G_s(\mathbf{r},t)$ in (1), it is easy to show that

$$\frac{d^2\sigma}{d\Omega d\omega}=a^2\frac{k}{k_0}e^x\sum_{\nu=0}^{\infty}{}'\frac{(-1)^\nu}{\nu!}x^\nu G_\nu(\omega), \tag{28}$$

where

$$G_\nu(\omega)=\frac{1}{\pi\beta}\frac{x+\nu}{(x+\nu)^2+\omega^2\beta^{-2}}, \tag{29}$$

and

$$x=\kappa^2D/\beta. \tag{30}$$

The term corresponding to $\nu=0$ in (28) is the same as (25). The higher terms give a correction to the simple diffusion formula (25). The broadening is less than that given by (26). The magnitude of the correction depends on the value of x and is on the whole very small.

4. DISCUSSION

Formula (15a) for the differential scattering cross section is somewhat involved to see the main features of the scattering. Let us now compare the expressions (18) and (25), the former is valid for case (i) $\tau_1 \ll \tau_0$, and the latter for case (ii) $\tau_1 \gg \tau_0$. There is an important difference between the two formulas, (18) has a form factor e^{-2W}, analogous to that in a solid, whereas in formula (25) there is no such factor. If we integrate (18) and (25) over an energy interval $\hbar\Delta\omega$ around the incident neutron energy such that $\hbar\Delta\omega$ is greater than the width of the quasi-elastic peak and if κ can be taken as constant within the range of integration, it will be seen that the intensity as given by (25) is independent of the scattering angle, whereas the intensity from formula (18) depends on the scattering angle through the factor e^{-2W}. Thus by measuring the intensity as a function of the scattering angle of the quasi-elastic peak, it should be possible to decide which of the two formulas (18) and (25) confirms to observations. Brockhouse,[2] using neutrons of wavelength 1.52 A has, indeed, observed that in the case of ordinary water the angular distribution of the quasi-elastic scattering is governed by a factor of the type e^{-2W} and has also estimated the numerical value of $2W$. Further, the measurements of Brockhouse indicate that the temperature dependence of the form factor is consistent with our equation (20). It would be worthwhile to repeat these experiments.

We shall now consider the broadening of the quasi-elastic peak which has been measured recently by Brockhouse[3] and Hughes and collaborators[4] and compare it with our theory. If we compare the two expressions (19) and (26) for the broadening, it is clear that they are very different. An important difference between the two is that the broadening given by (19) is, for $\kappa^2D\tau_0 \gg 1$, nearly independent of the scattering angle; whereas the broadening given by (26) is directly proportional to $\sin^2(\phi/2)$, ϕ being the scattering angle. The angle dependence of $\Delta\epsilon$ in (19) comes through the factor $e^{-2W}/(1+\kappa^2D\tau_0)$, which is in itself small. For $\kappa^2D\tau_0 \ll 1$, (19) and (26) give the same broadening and its angle dependence is given by $\sin^2(\phi/2)$. Thus an accurate experimental determination of the angular variation of the broadening would provide a test which of the two formulas (19) and (26) confirms to observations.

In Fig. 1, the broadening $\Delta\epsilon$ is plotted as a function of $\kappa^2D\tau_0$. Curve a corresponds to the values $\tau_0=3.6\times10^{-12}$ sec and $\tau_1/\tau_0=0$, and curve b to the same value of τ_0 but $\tau_1/\tau_0=1$. Curve c is plotted for $\tau_0=1.8\times10^{-12}$ sec and $\tau_1/\tau_0=0$. In the same figure, curve d represents the broadening given by formula (26) corresponding to case (ii), i.e., what one would expect on the simple diffusion theory. Curves a and c correspond to case (i) and, therefore, give the broadening expected on a purely jump mechanism of diffusion (formula 19). Curve b would correspond to a mechanism of diffusion between the above two extremes. It is clearly seen that for $\kappa^2D\tau_0 \ll 1$, all the four curves give the same broadening. For $\kappa^2D\tau_0 \gg 1$, curves a and c approach to an asymptotic value $2\hbar/\tau_0$ of the broadening. For values $0<\tau_1/\tau_0<1$, the broadening will lie between the two curves a and b. It is interesting to observe that even for a value of $\tau_1/\tau_0=1$, the increase in the broadening over that corresponding to $\tau_1/\tau_0=0$, is not more than twenty percent. In plotting these curves, we have taken the value[13] of the diffusion coefficient $D=1.85\times10^{-5}$ cm^2 sec^{-1} for 20°C temperature of water, and for $2W$ a value given by (20) for $\Theta=135$°K.

One immediately sees from the curves of Fig. 1 that for $\kappa^2D\tau_0>1$, the broadening as given by the curves a and c is much less than that given by curve d. Using

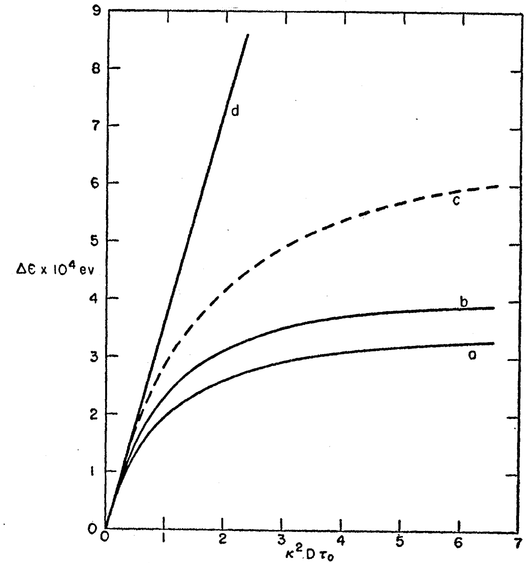

FIG. 1. Broadening $\Delta\epsilon$ of the "quasi-elastic" peak versus $\kappa^2D\tau_0$, for $D=1.85\times10^{-5}$ cm^2/sec and $\tau_0=3.6\times10^{-12}$ sec. The lower scale on the abscissa represents the corresponding scattering angle for neutrons of incident wavelength of 4 A. Curve a is plotted for $\tau_0=3.6\times10^{-12}$ sec, and $\tau_1=0$. Curve b is plotted for $\tau_1=\tau_0=3.6\times10^{-12}$ sec. Curve c is plotted for $\tau_0=1.8\times10^{-12}$ sec, and $\tau_1=0$; the value of the abscissa for curve c is half of what is shown in the figure. Curve d is based on simple diffusion model, formula (26).

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[13] J. H. Simpson and H. Y. Carr, Phys. Rev. **111**, 1201 (1958).

the sharp edge at 5.2×10^{-3} ev of the beryllium filtered neutrons, Hughes and collaborators[4] have measured the energy distribution of the neutrons scattered at 90°. These authors find that the broadening of the quasi-elastic peak is certainly less than 0.3×10^{-3} ev (limit of their resolution), whereas we should expect a value of 1.1×10^{-3} ev (for $D=1.85\times10^{-5}$ cm^2/sec) on the basis of the simple diffusion theory formula (26). If we now take $\tau_1/\tau_0=0$, and take the upper limit of the observed broadening as 0.3×10^{-3} ev, we can explain this broadening for a value of $\tau_0\simeq4\times10^{-12}$ sec. The experimental conditions of these authors correspond to a value of $\kappa^2D\tau_0\simeq3$. We shall see that the above value of τ_0 is supported by other independent experimental observations.

If one could improve the present experimental resolution, it should be possible to determine the diffusion coefficient D by measuring the broadening for small angles of scattering ($\kappa^2D\tau_0<1$). Measurements of the broadening for large angles of scattering such that $\kappa^2D\tau_0\gg1$, would give approximately the time τ_0. It seems, however, difficult to determine both τ_1 and τ_0 uniquely from an experimental curve of broadening versus $\kappa^2D\tau_0$.

If we take for τ_0 the value 4×10^{-12} sec and $D=1.85\times10^{-5}$ cm^2/sec, and use the relation $D=l^2/6\tau_0$, we get for l a value 2.2 A, which is reasonable since the mean distance between water molecules is nearly 3 A. The question is: is there any independent experimental evidence for such a value of τ_0? Hall[14] has attempted to explain the excess ultrasonic absorption in water as the result of a lag in the rearrangement of the molecules during an acoustic compression. The structural relaxation time for the rearrangement process which involves the breaking of intermolecular bonds in water has been estimated by him to be 2×10^{-12} sec at room temperature. Hall has also given an expression for the relaxation time as a function of the temperature of water. If we take the temperature variation of τ_0 as given by Hall and plot $\log\Delta\epsilon$ [see Eq. (24)] as a function of $1/T$ where T is the temperature, we get a straight line whose slope is the same as the slope of the experimental curve (Fig. 2, reference 3) of Brockhouse.[3] In view of the fact that the observed broadening is much greater than that predicted by our formula (24), it is difficult to say whether the above agreement has any significance. If we extrapolate the value of τ_0 for 100°C from the values given by Hall, we would estimate from formula (19) a diffusion broadening which is nearly six times the broadening for room temperature. The theoretical broadening at 100°C is estimated to be 2×10^{-3} ev, assuming that for 20°C the broadening is 3×10^{-4} ev. From the experimental[2] energy distribution of 30.8 $\times10^{-3}$ ev neutrons scattered through 28.3° by water at 100°C [Fig. 12(b) of reference 2], we estimate a broadening of 1.8×10^{-3} ev. Thus, the theory is in agreement with experiment. And this agreement is, indeed, significant in view of the fact that the broadening at 100°C is very large and as such the relative contribution of the experimental errors will be small.

In nuclear magnetic resonance experiments, the spin-lattice relaxation time T_1 in liquids is inversely proportional to the correlation time τ_c (for $\omega\tau_c\ll1$, ω being the Larmor frequency). Bloembergen, Purcell, and Pound[15] have estimated that for water at 20°C, τ_c is nearly 3.5×10^{-12} sec and that this time is consistent with the observed value of T_1.

M. Eigen and L. DeMaeyer[16] have considered various mechanisms of the protonic charge transport in water and have arrived at the conclusion that the rate determining step is the structural diffusion of the hydration complex ($H_9O_3^+$). The structural diffusion involves the formation (and disappearance) of several H bonds and a corresponding reorientation of the water molecules at the periphery of the complex. The average time of this process is of the order of 2×10^{-12} sec, which seems to account well for the mobility of the proton. This time is also related to the dielectric relaxation times, which also involve the liberation of a water molecule from its structure and its reorientation. The largest dielectric relaxation time for water observed by Lane and Saxton[17] is nearly 10^{-11} sec corresponding to an activation energy of 4.5 kcal/mole. These authors have also observed a relaxation time $<10^{-12}$ sec, corresponding to an orientation of more weakly bound H_2O molecules.

Thus, the structural relaxation time for excess ultrasonic absorption, the dielectric relaxation time, the time decisive for the drift mobility of the proton and the time τ_0 of the present theory are all of the same order of magnitude, as one would expect on physical grounds.

We had mentioned earlier in the introduction that there exists, according to Hughes and collaborators,[4] a real contradiction between their experimental value of the broadening of the quasi-elastic peak and that measured by Brockhouse.[3] Since the former authors used the sharp edge at 5.2×10^{-3} ev of the beryllium filtered neutrons, they were able to resolve the two small peaks near the incident energy and corresponding to an energy gain and loss of 0.7×10^{-3} ev, and which peaks Brockhouse has been unable to detect. Unfortunately, it so happens that the energy separation of these peaks from the incident energy is of the same order of magnitude as the theoretical diffusion broadening expected on the simple diffusion theory. It is very probable that Brockhouse has included these peaks in what he calls diffusion broadening and which indeed is not. Besides, we understand from Brockhouse[18] that his line patterns contain

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[14] L. Hall, Phys. Rev. **73**, 775 (1948).

[15] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).

[16] M. Eigen and L. DeMaeyer, Proc. Roy. Soc. (London) **A247**, 505 (1958).

[17] J. A. Lane and J. A. Saxton, Proc. Roy. Soc. (London) **A213**, 400 (1952).

[18] Private communication.

as much as 30% contribution from multiple scattering, which gives extra broadening. It is, therefore, understandable that Brockhouse has overestimated the diffusion broadening.

PART II: 1. INELASTIC SCATTERING

Here, we shall calculate the inelastic scattering of beryllium filtered neutrons (cutoff at $\lambda=3.96$ A) on the basis of two different models of water: (*a*) gas model and (*b*) Debye model, and compare the theoretical scattering with that observed by Hughes and collaborators.[4] It has almost become customary, chiefly among reactor physicists, to use for water a gas model of mass 18 for the calculations of thermal neutron spectra, which do give a very good fit with experiment. However, such calculations are a very insensitive test for deciding between a quasi-crystalline model and a gas model of water, since what one is looking for is an average effect and besides the mean neutron energy in a thermal spectrum is greater than $k_B\Theta$, where Θ is the Debye temperature of the quasi-crystalline model. We shall see that for cold neutron scattering, a gas model of water is not at all satisfactory and a quasi-crystalline model is a better one.

2. MATHEMATICAL FORMULAS

Assuming that for a quasi-crystalline model of water, the formula[19] for the differential inelastic scattering cross section is the same as that for a solid, we have

$$\frac{d^2\sigma}{d\Omega d\lambda}=a^2\frac{2(2m)^{\frac{1}{2}}}{h}\frac{E^2}{(E_0)^{\frac{1}{2}}E_D}e^{-2W-\beta(E-E_0)}\times\sum_{n=1}^{\infty}\frac{(2W)^n}{n!}\bar{G}_n(E-E_0),\quad(31)$$

where E_0 and E are, respectively, the energies of the incident and scattered neutrons and λ is the neutron wavelength corresponding to energy E. m is the neutron mass, h is Planck's constant and a is the incoherent scattering length. For a Debye model of a solid $\bar{G}_n$ functions are approximately (if $T/\Theta>1$) given by

$$\begin{aligned}\bar{G}_1(E-E_0)&=\tfrac{1}{2},\quad\text{for}\quad|E-E_0|/E_D<1,\\&=0\quad\text{for}\quad|E-E_0|/E_D>1,\end{aligned}\quad(32)$$

and

$$\bar{G}_n(E-E_0)=\frac{1.76}{(2\pi n)^{\frac{1}{2}}}\exp\left[-\frac{3.10}{2n}\left(\frac{E-E_0}{E_D}\right)^2\right],\quad(33)$$

for $n>1$. Also

$$\beta=1/2k_BT,\quad(34)$$

$$2W=\frac{\hbar^2\kappa^2}{2ME_D}\frac{6T}{\Theta}=\frac{m}{M}\frac{6T}{\Theta}\frac{E+E_0}{E_D},\quad(35)$$

if the scattering angle is 90°, and

$$E_D=k_B\Theta.\quad(36)$$

For a gas model the differential scattering cross section (including both elastic and inelastic scattering) is, as is well known, given by[19]

$$\frac{d^2\sigma}{d\Omega d\lambda}=\frac{a^2 2(2m)^{\frac{1}{2}}}{h}\frac{E^2}{\sqrt{E_0}}\frac{1}{(2\pi\Delta)^{\frac{1}{2}}}\times\exp\left\{-\frac{[E-E_0+(m/M)(E+E_0)]^2}{2\Delta}\right\},\quad(37)$$

where

$$\Delta=(m/M)(E+E_0)2k_BT,\quad(38)$$

and where in (37) and (38) the scattering angle has been taken to be 90°.

3. CALCULATIONS

The incident neutron spectrum as used in the experiments of Hughes and collaborators[4] can be approximately represented by

$$\begin{aligned}g(\lambda)&=4\lambda_0^4/\lambda^5\quad\text{for}\quad\lambda\geqslant\lambda_0,\\&=0\qquad\text{for}\quad\lambda<\lambda_0,\end{aligned}\quad(39)$$

where $\lambda_0=3.96$ A.

Formula (31) does not include the quasi-elastic scattering which is given by (18). For the Debye model we have made calculations for three different Debye temperatures $\Theta=125°$, 135°, and 150°K. For comparison with the observed spectrum both (31) and (37) are integrated over the incident neutron spectrum (39). Of the three calculations, we find that the differential scattering cross section corresponding to $\Theta=135°$K gives a most reasonable fit with the experimental values.

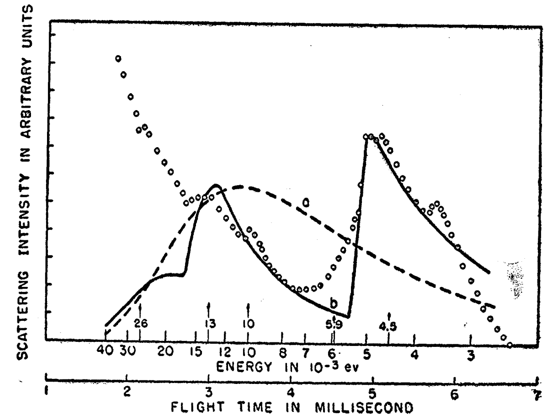

FIG. 2. Differential scattering cross section, in arbitrary units, of beryllium filtered neutrons (cutoff at 3.96 A) versus outgoing neutron energy for 90° scattering angle. The lower scale on the abscissa represents the time of flight. Curve *a* is calculated on a free gas model of mass 18. Curve *b* is calculated on a Debye model of a solid with $\Theta=135°$K. Experimental points of Hughes et al.[4] are marked with circles. The arrows in the figure indicate the energies at which various peaks have been observed by these authors.

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[19] Alf Sjölander, Arkiv Fysik 14, 315 (1958).

4. DISCUSSION

Results of these calculations are shown in Fig. 2 where $d^2\sigma/d\Omega d\lambda$ for 90° scattering angle is plotted, in arbitrary units, against the outgoing neutron energy (also flight time). Curve *a* shows the results for a gas model and curve *b* for a Debye model ($\Theta = 135°K$).

Experimental points of Hughes and collaborators[4] are marked with circles in the same figure. In plotting these points we have used the normalization that the experimental point at the top of the cutoff coincides with the corresponding theoretical value. In comparing the theoretical curves with the experimental curve, it must be borne in mind that the former do not include the contribution from any of the hindered rotations of the water molecule. What the theoretical curve *b* represents is the scattering arising from the continuous frequency distribution of the hindered translations (intermolecular), analogous to what occurs in a solid. On this continuum of frequencies, there may be superimposed a few more or less discrete frequencies.

Besides the well-known hindered rotation peak at 66×10^{-3} ev (not shown in Fig. 2; see Fig. 1 of reference 4), which has also been observed in the infrared spectrum, the experimental curve shows some other peaks whose positions have been indicated by arrows in Fig. 2. The peak at 26×10^{-3} ev [actual energy is $(26-5.2)\times10^{-3}$ ev] has also been observed in the infrared spectrum of ordinary ice ($\nu\sim160$ cm^{-1}) and may be assigned to another hindered rotation. The low frequency Raman spectrum of ordinary ice also shows a peak at 213 cm^{-1}. We should indeed compare our theoretical curve *b* with the experimental curve after subtracting from the latter the contribution of the above mentioned two hindered rotations. These peaks will, obviously, be fairly broad. If we assume that the contribution to the scattering from the hindered rotation at 26×10^{-3} ev does not extend below 15×10^{-3} ev, the agreement between the theoretical curve and the experimental curve is indeed good. The peak at 13×10^{-3} ev in the observed curve occurs almost nearly at the same energy as the maximum in the theoretical curve which corresponds mainly to one phonon peak. The occurrence of the other small peak at 10×10^{-3} ev in the experimental curve may be attributed, in analogy to a solid, to a subsidiary maximum in the actual frequency spectrum of quasi-crystalline water and corresponding to transverse vibrations. Such a bump will not obviously occur in the theoretical curve since we have assumed a Debye frequency spectrum for water. A slightly higher theoretical value at 13×10^{-3} ev is also understandable on the same grounds. Thus, it appears to us that these two peaks are perhaps not the result of hindered rotations of the water molecule but are the manifestations of the corresponding two maxima in the true frequency spectrum of water as a pseudocrystalline substance.

In the energy range between 7×10^{-3} ev and 5.5×10^{-3} ev, the experimental points lie above the theoretical curve. This discrepancy we attribute to the occurrence of a small peak at 5.9×10^{-3} ev in the observed curve. If we assume that the scattering intensity due to the motion corresponding to this peak is the same as that given by the theoretical curve *b* and if we further assume that the half-width of this peak is the same as the energy transfer (0.7×10^{-3} ev) to the neutron, we shall find that the resultant theoretical curve would agree very well with the experimental curve. The above remarks regarding the observed peak at 5.9×10^{-3} ev (in fact, there have been observed two peaks, the other is at 4.5×10^{-3} ev) are at present a mere guesswork since the reason of the occurrence[20] of the peak is not understood.

Even a casual inspection of Fig. 2 will show that the general shape of the scattering on the gas model (curve *a*) is very different from that given by the experimental curve.

In conclusion we would like to say that the inelastic scattering of cold neutrons can be understood better on a quasi-crystalline model of water than on a gas model. Further, as seen in Part I, the observed features of the quasi-elastic scattering are also consistent with such a model.

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[20] In a recent letter to the Physical Review [4, 131 (1960)] Borst has attempted to explain the occurrence of these two peaks (corresponding to an energy transfer of $\pm0.7\times10^{-3}$ ev) as the result of an ortho-para transition in liquid water similar to what occurs in H_2. This seems to us rather unlikely.