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# Neutron Inelastic Scattering Study of Water

M. SAKAMOTO*, B. N. BROCKHOUSE, R. G. JOHNSON**
AND N. K. POPE

*Atomic Energy of Canada Limited*
*Chalk River, Ontario, Canada*

A large number of measurements of the energy distributions of neutrons scattered by $H_2O$ at 25°C and 75°C have been made under exceptionally high energy resolution ($2\times10^{-4}$ ev). From the results the scattering function $S(Q, \omega)$ has been obtained for $0.4\leq Q\leq 2\text{Å}^{-1}$ (75°C) and $0.4\leq Q\leq 2.6\text{Å}^{-1}$ (25°C). No trace is seen of discrete energy transfers reported by other workers. The measurements have been analyzed by means of the Van Hove transformation, and partial results of this analysis are reported. When the R.M.S. displacement of a proton exceeds the first neighbor distance the results seem to be describable by diffusion theory.

## Experimental results

Using the Chalk River rotating crystal spectrometer with 4.059 Å neutrons[1], a series of measurements have been made on thin specimens of $H_2O$ (transmission 78%) at 25°C and 75°C. The measurents were made in transmission in the symmetrical positions. About twenty distributions were taken at each temperature, at angles of from 15° to 114° at 25°C, and from 15° to 93° at 75°C. A specimen pattern was shown in one of References[1]. Fast neutron background comprised about 10% of the measured distributions and air scattering and beam contamination contributed amounts ranging from 15% at the smallest angle to 3% at the largest angles. After correction for these backgrounds, renormalization to the measured angular distribution, removal of frame overlap, correction for spectrometer (counter) efficiency, and conversion from time to energy distributions, the twenty measured distributions at each temperature were used to form a grid of values of the scattering functions $S(Q,\omega)$[1,2], at intervals in $Q=|k_0-k'|$ of $0.2\text{Å}^{-1}$, and in $\hbar\omega=E_o-E'$ of $0.5\times10^{-4}$ev. The energy resolution was $\sim2\times10^{-4}$ ev. Multiple scattering was removed from the measured scattering function by expanding it in powers of $Q^2$, viz: $A(\omega)+B(\omega)Q^2+C(\omega)Q^4\cdots$, over suitable ranges of $Q$. Since the initial term in the theoretical expansion of $S(Q,\omega)$ goes as $Q^2$, the term $A(\omega)$ is assigned to multiple scattering. It is probably a fair approximation to the real multiple scattering, which is believed on both experimental and theoretical grounds to be rather isotropic, and therefore, for a given $E_o$, to be approximately independent of $Q$. The ratio $\int A(\omega)d\omega/\int S(Q,\omega)d\omega$ was 0.4 in agreement with estimates for a flat specimen with a transmission of 78%, and the shape of $A(\omega)$ was reasonable. [For values of $|\hbar\omega|<5\times10^{-4}$ ev $A(\omega)$ was obtained by interpolation.]

After subtraction of the term $A(\omega)$, the functions $S(Q,\omega)$ for $H_2O$ at 25°C and 75°C (Fig. 1) were obtained. The functions are broadened by resolution in $\hbar\omega$ (resolution in $Q$ is not important). The resolution function in $\hbar\omega$ for each $Q$ (obtained from a series of measured distributions of the elastic incoherent scattering by vanadium metal) is also shown. These scattering functions were used to obtain the self correlation function $G_s(r,t)$ of the protons by a two dimensional Fourier transformation[2].

For larger values of $|\omega|$ $S$ was approximated by the function $B(\omega)Q^2+C(\omega)Q^4$. The measured functions $A$, $B$, $C$ are shown in Fig. 2. For clarity the points are omitted from $A$ and $C$. The comparatively poor statistics at large $|\omega|$ are largely introduced by the process of fitting the coefficients over a narrow range of $Q$ far from $Q=0$. For our purposes the statistical fluctuations were not important.

In all the patterns the now familiar dif-

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* Visiting scientist from Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan, now returned.

** Summer student (1960) from Queen's University, Kingston, Ontario.

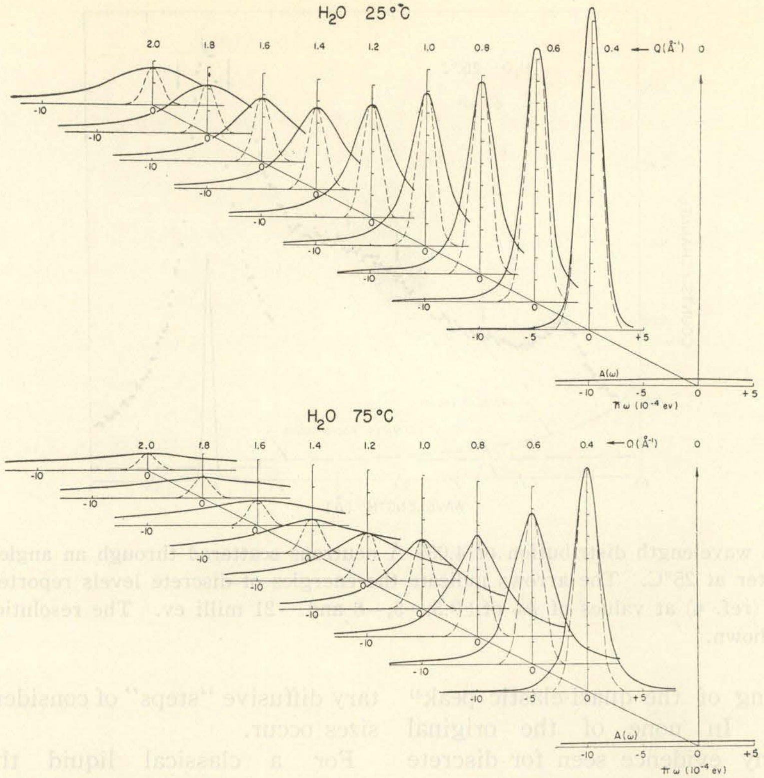


Fig. 1. The scattering function $S(Q,\omega)$ for water (a) at 25°C and (b) at 75°C for small values of $\hbar\omega$. The energy resolution functions are shown as dashed curves. The multiple scattering $A(\omega)$ which was subtraced is also shown.

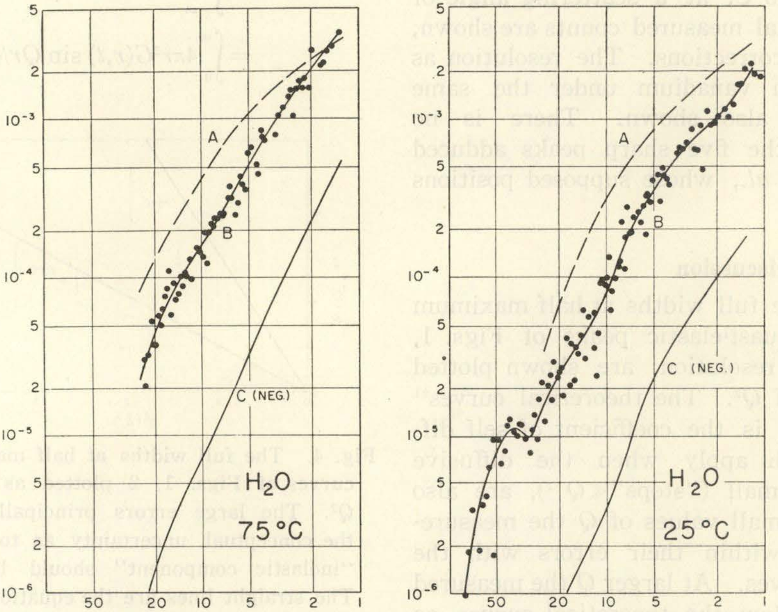


Fig. 2. The functions A, B, C measured for water at 25°C and 75°C. The ordinate scale is aranged to give correct normalization for $\hbar\omega$ in units of $10^{-4}$ ev.

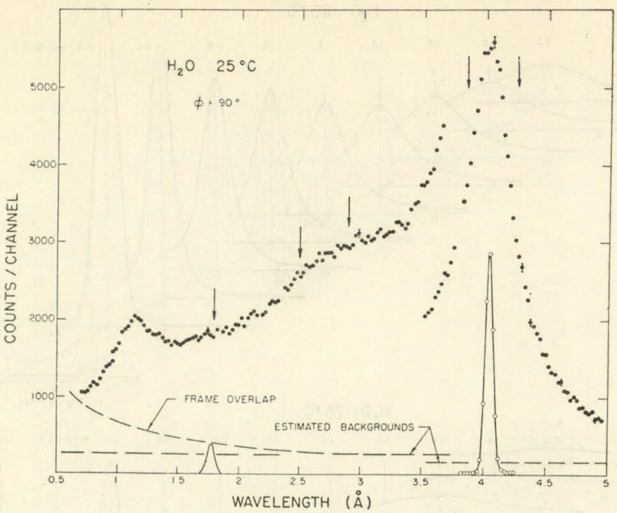


Fig. 3. The wavelength distribution of 4.059 Å neutrons scattered through an angle of 90° by light water at 25°C. The arrows indicate the energies of discrete levels reported by other workers (ref. 4) at values of $\hbar\omega$ of $\pm 0.5, -5, -8$ and $-21$ milli ev. The resolution function is also shown.

fusive broadening of the quasi-elastic peak[3] was observed. In none of the original patterns was any evidence seen for discrete peaks reported by Hughes *et al.*[4] in measurements using the filtered-beam, chopper method. In Fig. 3 we show a distribution measured with exceptionally high statistics on water at 25°C, at a scattering angle of 90°. The actual measured counts are shown, without any corrections. The resolution as measured with vanadium under the same conditions is also shown. There is no evidence for the five sharp peaks adduced by Hughes *et al.*, whose supposed positions are indicated.

## Analysis and discussion

In Fig. 4 the full widths at half maximum ($W$) of the quasi-elastic peaks of Figs. 1, corrected for resolution, are shown plotted as functions of $Q^2$. The theoretical curves[3] $W = 2\hbar DQ^2$ ($D$ is the coefficient of self diffusion[5]) which apply when the diffusive motions are small ("steps"$\ll Q^{-1}$), are also shown. At small values of $Q$ the measurements agree within their errors with the theoretical curves. At larger $Q$ the measured points fall below the theoretical curves, as noted earlier[3]. This fact was interpreted as showing that self diffusion in a liquid is a somewhat complex process in that elementary diffusive "steps" of considerably different sizes occur.

For a classical liquid the scattering function $S(Q,\omega)$ and the self correlation function $G_s(r,t)$ are related to an intermediate function $i(Q,t)$ by the equations:

$$i(Q,t) = \int_{-\infty}^{+\infty} S(Q,\omega)\cos\omega t d\omega$$
$$= \int_0^{\infty} 4\pi r^2 G(r,t) \sin Qr/Qr dr\ .$$

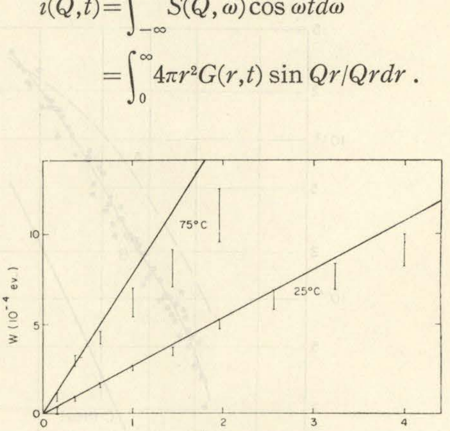


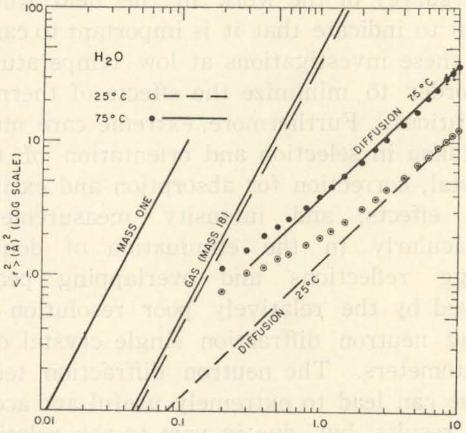
Fig. 4. The full widths at half maximum of the curves of Figs. 1, 2 plotted as a function of $Q^2$. The large errors principally arise from the conceptual uncertainty as to what, if any, "inelastic component" should be subtracted. The straight lines are the equations $W = 2\hbar DQ^2$ where the experimentol values of Simpson and Carr (5) were used for the self diffusion coefficient $D$. [$2.13 \times 10^{-5}$ cm²/sec at 25°C and 6.27 $\times 10^{-5}$ cm²/sec at 75°C.]

From a well known theorem on Fourier transforms the mean square displacement

$$\langle r^2\rangle=\int_0^\infty r^2 4\pi r^2 G_s(r,t)dr$$

$$=-3d^2/dQ^2\cdot i(Q,t)\,.$$

Experimentally $i(Q,t)$ is almost Gaussian in $Q$, except for a "tail" at large $Q$ amounting to a few percent of the initial value, $i(0,t)=1$. This fact enables us to obtain reasonably accurate values of $d^2/dQ^2\ i(Q,t)$, and thus of $\langle r^2\rangle$. The values of $\langle r^2\rangle$ deduced from the experiments are shown in Fig. 5. At large times good agreement with the calculated diffusion $\langle r^2\rangle=6Dt$ is obtained. This agreement breaks down for $\langle r^2\rangle<6\text{Å}^2$, that is, for an RMS displacement less than the distance of first neighbors in the liquid.



Fig· 5. The mean square displacement of a proton $<r^2>$ at comparatively large times, compared with theoretical calculations.

A complete report on this (and other) work on water will be submitted to Physical Review. We are grateful to Mr. E.A. Glaser for technical assistance, and to Mr. C. G. Gray and others for assistance in data handling.

## References

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4 D. J. Hughes, H. Palevsky, W. Kley and E. Tunkelo: Phys. Rev. **119** (1960) 872. Also K.E. Larsson, S. Holmryd and K. Otnes: Paper *I/S*15 IAEA Symposium, see reference 1.

5 J. H. Simpson and H. Y. Carr: Phys. Rev. **111** (1958) 1201.

## DISCUSSION

H. PALEVSKY: Do you remember the value of the diffusion constant used in making the calculated comparison diffusion broadening?

M. SAKAMOTO: We have used the experimental values of Simpson and Carr which are $2.13\times10^{-5}$ cm²/sec. at 25°C and $6.27\times10^{-5}$ cm²/sec. at 75°C.