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Experimental determination of the nature of diffusive motions of water molecules at low temperatures

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Extensive and high-quality quasi-elastic incoherent neutron scattering data were obtained for water in the temperature range extending from room temperature down to $-20\,^{\circ}\mathrm{C}$ in the supercooled state. The analysis generally confirms findings of our previous experiment [S. H. Chen, J. Teixeira, and R. Nicklow, Phys. Rev. A **26**, 3477 (1982)], but in particular three new results have been obtained: (a) two relaxation times are clearly identified, which are related to the short-time and intermediate-time diffusion of water molecules, respectively, and their temperature dependence has been determined; (b) one of these relaxation times is associated with jump diffusion of the protons, and the temperature dependence of the jump length has been qualitatively determined; (c) the Q dependence of the scattering intensity integrated over the quasi-elastic region gives a Debye-Waller factor which is temperature independent.

I. INTRODUCTION

The microscopic motions involved in diffusion of hydrogen containing molecules can be most effectively studied by quasi-elastic incoherent neutron scattering. This potential has been exploited already in the early days of development of neutron scattering techniques by Sakamoto *et al.* in the particular case of water.[1] Ever since then, there have been many attempts to improve the measurement, each with variable degrees of success. But the result of the analysis of these data has never led to an unequivocal characterization of the nature of the microscopic diffusive motion of water molecules (see summary by Blanckenhagen[2]).

The case of water presents a particular complication because of the extensive hydrogen bonding existing already at room temperature.[3] The diffusive motion of hydrogen-bonded water molecules is expected to be much more complicated than that, for example, of liquid argon, especially at short times. The interpretation of the neutron quasi-elastic spectra is accordingly complicated especially when only a narrow range around room temperature is explored.

In our previous study,[4] we pointed out the fact that the rapid completion of hydrogen bonding in water as the temperature goes below $0\,^{\circ}\mathrm{C}$ can be effectively used to separate two time scales associated with microscopic diffusive motion of water molecules. In this extended temperature range, it is easier experimentally to separate the two time scales and identify their respective temperature dependences. However, because of the limited neutron flux available for our experiment, the statistical accuracy was not high enough to allow us to study the temperature dependence of the broad line. Our main finding was, however, that the sharp line can be well interpreted as due to the jump diffusion of the proton across the tetrahedral angle with a characteristic jump length of about $L = 1.23$ Å, which is rather temperature independent. We therefore decided to repeat the experiment at the high-flux reactor at the Institut Laue Langevin where the effective cold neutron flux at the sample is as much as 100 times larger.

We now report findings of the first analysis of this result which clearly identify the two time scales and their temperature dependence from room temperature down to $-20\,^{\circ}\mathrm{C}$. We were also able to study the attenuation of the quasi-elastic intensity as a function of the elastic momentum transfer $Q = 4\pi(\sin\theta)/\lambda$, where λ is the incident neutron wavelength and θ is half the scattering angle. From this, we are able to identify the mean-square vibrational amplitude of the protons transverse to the hydrogen bond. Based on this analysis we can now propose a qualitative model of the proton motions associated with the microscopic diffusion of water molecules.

II. EXPERIMENT

The experiment was carried out at the Institut Laue Langevin (ILL) in Grenoble using the focusing time-of-flight spectrometer IN6. The characteristics of this spectrometer are its high flux at the sample position ($\phi = 3.3 \times 10^7 n\ \mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ at $\lambda = 5.1$ Å without choppers), large momentum transfer range ($0.25 < Q < 2$ Å^{-1}), and a relatively good energy resolution ($\Delta E = 100\ \mu\mathrm{eV}$ at $\lambda = 5.1$ Å). The typical data collection time was about 8 h which gives a peak count of about 2×10^5 at $Q = 1 \pm 0.05$ Å^{-1}.

The sample was made from 80 glass capillary tubes assembled in a planar geometry. The capillaries were made of Pyrex with sizes i.d. 0.3 mm and o.d. 0.4 mm. The dimension of the sample was 5×5 cm^2. The sample was mounted in a cryostat which maintained the temperature at $T\pm0.1$°C. The use of capillary tubes was necessary for achieving the supercooling but it has the additional advantage of reducing the multiple scattering by the fact that Pyrex contains a significant amount of boron which absorbs low-energy neutrons. The transmission from the water was 95% while that of the empty capillaries was 93%. We estimate the multiple scattering to be less than 5% of the scattered intensity.

The experiment was done in nine temperatures: 20, 12, 5, -5, -10, -12, -15, -17, and -20°C. A separate empty-cell run was made at room temperature, the result of which was used to correct the signal. Another separate run was made with the same sample frozen to ice at -10°C so that comparison with supercooled water data could be made to ascertain that we do not accidentally freeze the sample during the run.

Both quasi-elastic and inelastic spectra were taken simultaneously. The extrapolation of the inelastic signal due to the hindered vibrations of water molecules to the quasi-elastic region indicates that the contribution due to the inelastic scattering was negligible. Typical examples of the spectra are given in Fig. 1.

III. METHOD OF DATA ANALYSIS

Since we are concerned with analysis of spectra in the quasi-elastic region ($0<\hbar\omega<3000$ μeV), the inelastic contribution can be very well approximated by a Debye-Waller factor. Therefore we write the intermediate scattering function for the proton motion as

$$F_s(Q,t)=\exp(-Q^2\langle u^2\rangle/3)R(Q,t)T(Q,t) \tag{1}$$

where the first factor (Debye-Waller factor) gives the probability that the neutron is elastically (or quasi-elastically) scattered, the second factor $R(Q,t)$ represents the contribution from the low-frequency rotational motions of the molecule, and the third factor $T(Q,t)$ represents the contribution from the translational motion.

We are forced to assume a decoupling of rotational and translational motions of the molecules as a necessity for having a tractable analytical model of the diffusion of the water molecules. We write

$$R(Q,t)=j_0^2(Qa)+3j_1^2(Qa)\exp[-t/(3\tau_1)] + 5j_2^2(Qa)\exp(-t/\tau_1)\ , \tag{2}$$

$$T(Q,t)=\exp[-\Gamma(Q)t]\ . \tag{3}$$

$R(Q,t)$ represents the first three terms of the well-known expansion due to Sears[5] for the classical rotational diffusion of a molecule. a here stands for radius of the rotation and in this case we take it as 0.98 Å, which is the O-H distance in a water molecule, τ_1 is a relaxation time associated with the rotation diffusion, $j_1(x)$ are the spherical Bessel functions, and the higher-order terms in the Sears expansion are, in practice, negligible for the given value of a in our experimental Q range. We take $\Gamma(Q)$ in Eq. (3) to be:[6]

$$\Gamma_{(Q)}=\frac{DQ^2}{1+DQ^2\tau_0}\ , \tag{4}$$

which is an expression for a random-jump-diffusion model, where τ_0 represents the residence time. The translational diffusion constant D is given in terms of the mean-square jump length $\langle l^2\rangle_{\text{av}}^{1/2}$ by

$$D=\frac{\langle l^2\rangle_{\text{av}}}{6\tau_0}\ . \tag{5}$$

This model may be an oversimplification for representing the short- and intermediate-time diffusion of the water molecule but we were able to show that it can be made to fit all the data remarkably well by an appropriate choice of three parameters: quasi-elastic intensity, Γ, and τ_1, all of which are *a priori* Q and temperature dependent. What is even more remarkable is that these three parameters can be interpreted in a rather consistent manner based on our intuitive picture of the short- and intermediate-time diffusion of water molecules.

In fitting the data, we Fourier transform the $F_s(Q,t)$ to obtain $S_s(Q,\omega)$ and then fold it with the Q- and ω-dependent resolution function determined independently by a vanadium calibration run. The resolution-broadened $S_s(Q,\omega)$ is then transformed into the double differential cross section appropriate for the time-of-flight spectra and it is then compared with the data scaled by an amplitude factor A. In principle, A should depend only on the number of hydrogen atoms in the sample and the cross section of a hydrogen atom. The result of our fit confirms that the factor A is Q independent and that it is proportional to the amount of water in the sample for different runs, the temperature dependence being negligible. The detail of this data treatment uses existing computer programs available from the Institut Laue Langevin computer library.[7] In practice, these data treatments are nontrivial because there are 337 detectors in the spectrometer IN6, which covers an angular range from 10° to 115°.

IV. RESULTS

The fitting of data to the theory was done in two stages. In the first fit we determined quasi-elastic intensity $\Gamma(Q)$ and τ_1 for each measured temperature. From this fit we concluded that τ_1 follows an Arrhenius behavior and is well described by

$$\tau_1=\tau_1^0\exp(E_A/k_BT) \tag{6}$$

with the prefactor $\tau_1^0=0.0485$ ps and the activation energy $E_A=1.85$ kcal mol^{-1}.

We then performed the second fit in which Eq. (6) for τ_1 was imposed. The new values obtained for the quasi-elastic intensity and $\Gamma(Q)$ do not differ significantly from those obtained in the first fit, but they are slightly more precise. Points in Fig. 2 show the final results obtained for $\Gamma(Q)$.

The linewidth $\Gamma(Q)$ was then analyzed according to Eq. (4) and the best values for D and τ_0 at each temperature evaluated. Figure 3 shows an Arrhenius plot of τ_0 and τ_1 vs $1/T$.

We want to point out that the determination of D by

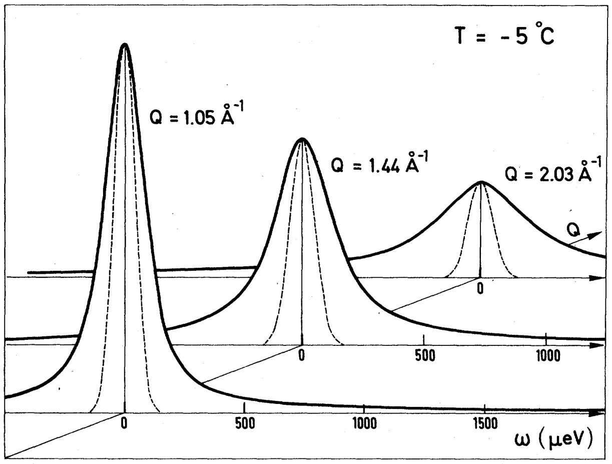

FIG. 1. Quasi-elastic incoherent neutron spectra from water at $-5\,^{\circ}\mathrm{C}$ for three different values of Q. ——: best fit. — — —: resolution function. Experimental points are within the thickness of the solid line.

this procedure does not give accurate numerical values of D at low temperature. This is because D is mainly determined by $\Gamma(Q)$ at small Q where the linewidth is significantly lower than the half width at half maximum (HWHM) of the resolution function of the instrument which for $Q < 0.5$ Å^{-1} is 35 μeV in the scale given in Fig. 2. However, it is also worth noting that at high temperatures the D values are rather well determined and they agree with the NMR determinations.

The Q dependence of the quasi-elastic intensity at each temperature follows accurately a functional dependence $\exp(-Q^2\langle u^2\rangle/3)$ with a fitted value of $\langle u^2\rangle^{1/2}=0.484$ Å which is temperature independent throughout the measured temperature range. This result is in good agreement with the previous measurements of Irish *et al.*[8] We summarize in Table I the ensemble of parameters for each temperature. The mean jump length, $L=\langle l^2\rangle_{\mathrm{av}}^{1/2}$, is obtained from Eq. (5) using the NMR values of D by Gillen *et al.*[9]

We note the following points.

(1) Figure 1 clearly shows the quality of the fit to the theory presented in Sec. II. The statistical accuracy of the experimental data $I(Q,\omega)$ is about 1% and the fitted curve was uniformly within the statistical error. In fact, the four parameters given in Table I are sufficient to reproduce all the experimental data at each temperature.

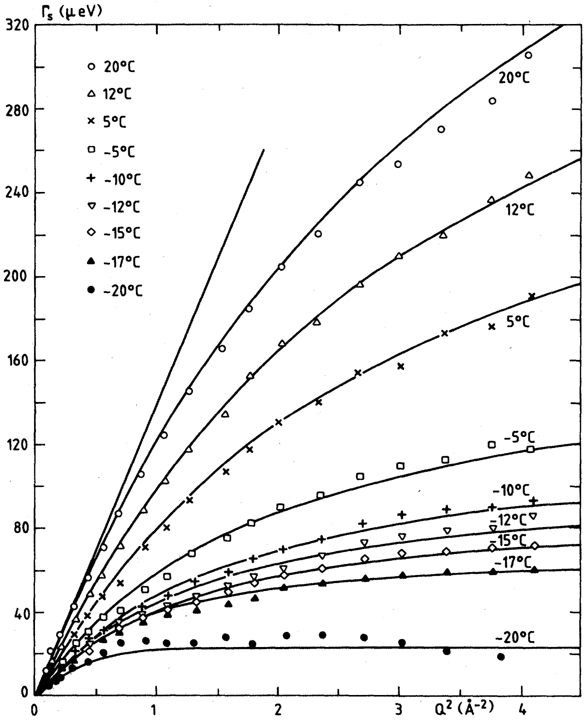

FIG. 2. Linewidth Γ of the translational component of the spectrum vs Q^2. Note that a one-Lorentzian fit, as commonly done, gives much larger linewidths with a different Q dependence. ——: best fit using Eq. (4). The straight line gives the self-diffusion constant at 20 °C.

(2) The low-temperature linewidths $[\Gamma(Q)]$ as a function of Q^2 (Fig. 2) show an initial linear region and then rapidly flatten out to a constant value given by $1/\tau_0$. This is a striking confirmation of the jump-diffusion model for the intermediate-time diffusion in water. In the literature there have been controversies on this point due to the incorrect analysis of the linewidth as mentioned in the Introduction. Our high-quality data combined with the analysis finally settled this question in the affirmative.

(3) From Fig. 3 it is clear that, near room temperature, the two relaxation times τ_0 and τ_1 are close. Thus, it is understandable that analysis of data near room temperature is not unique, as was the case in the past. The greatest advantage in our experiment is that we were able to supercool water down to $-20\,^{\circ}\mathrm{C}$, thus clearly establishing the separation of the two relaxation times. It should

TABLE I. Parameters for each measured temperature.

T (°C)	τ_0 (ps)	τ_1 (ps)	L(Å)	$\langle u^2\rangle^{1/2}$ (Å)
20	1.25		1.29	
12	1.66		1.25	
5	2.33	$0.0485\exp(E_A/k_BT)$	1.32	
-5	4.66		1.54	
-10	6.47	$E_A=1.85$ kcal mol^{-1}	1.65	0.48
-12	7.63		1.70	
-15	8.90		1.73	
-17	10.8		1.80	
-20	22.7		2.39	

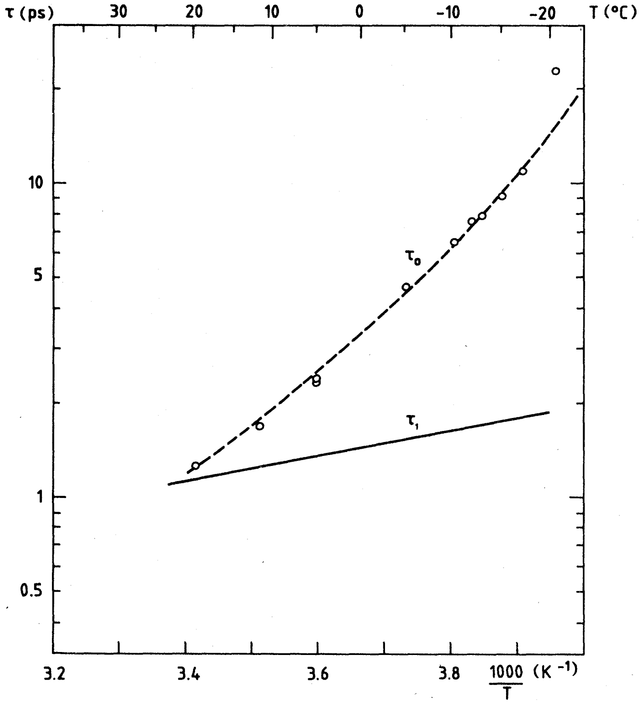

FIG. 3. Residence time τ_0 of the jump diffusion and an Arrhenius plot of the relaxation time τ_1 defined by Eq. (6).

also be remarked that because of the closeness of the values of τ_0 and τ_1 near room temperature, the determination of each of them as presented in Fig. 3 is subjected to a significant amount of error.

V. CONCLUSION

Based on the above observations, we can now present a qualitative picture of diffusion of water molecules at the microscopic level. We first make some comments about the theory presented in Sec. II for the analysis of data. Certainly, the treatment of the rotational part of the intermediate scattering function is oversimplified and the only justification of it is based on the observation that it provides an excellent fit to the data. We have tried a number of alternative analysis procedures but none of them gave a consistent result. Referring back to Eq. (2), we can remark that in a more rigorous theory, taking into account the local condition of protons in a hydrogen-bonded water molecule, the form of $R(Q,t)$ would be similar to that of Eq. (2), except the weighting functions for each of the three terms would not be as simple as the spherical Bessel functions. The Q dependence of these weighting functions will have to reproduce more accurately the local ordering of the protons. Perhaps our choice of $a = 0.98$ Å was an effective value which happens to represent this Q dependence approximately. With this reservation in mind we can now describe the short-time motions of the proton as follows.

It is generally accepted that, at room temperature and below, each water molecule is, on the average, hydrogen bonded to four or less neighbors. Thus, at short times when not all of the hydrogen bonds are broken, the motion of the proton can be described by an overdamped harmonic oscillator confined to a spherical surface around the oxygen atom. This is a kind of low-frequency motion we try to describe by Eq. (2) with a characteristic relaxation time τ_1 around 1 ps. At the intermediate-time scale, where a sufficient number of hydrogen bonds are broken, the proton can then jump to the nearest site which is at an average distance of about 1.6 Å (see Table I for L). This intermediate-time scale is characterized by the second relaxation time we called τ_0, and the motion of the protons is well described by the random-jump diffusion model.[6]

The vibrational contribution to the dynamic structure factor in the quasi-elastic region is given in terms of the Debye-Waller factor with an average vibrational amplitude of 0.484 Å. To see that these parameters we determined are reasonable, we offer the following supporting observations.

(1) The relaxation time τ_1 has an Arrhenius behavior with an activation energy $E_A = 1.85\ \text{kcal}\,\text{mol}^{-1}$, which is perhaps associated with the fluctuation of the hydrogen bond. This kind of Arrhenius behavior has been observed for water only in one other case which comes from the short-time linewidth of the depolarized Rayleigh scattering.[10] Absolute magnitudes of the times in these two experiments cannot be directly compared because of some arbitrariness of the definition of τ_1 in the case of Rayleigh scattering. For rotational diffusion we have $\tau_1 = 1/6D_r$, where D_r is the rotational diffusion constant.

(2) The relaxation time τ_0 is strongly temperature dependent and is non-Arrhenius. This certainly is associated to the motion of the water molecule as a whole and its behavior is similar to many other relaxation times derived from transport properties such as self-diffusion, viscosity, dielectric relaxation, spin-spin relaxation in NMR, etc.[11]

(3) The average jump distance L, as can be seen from Table I, is temperature dependent being smaller at higher temperature. This can be interpreted in terms of the random network model of water.[12] At higher temperature, the distribution of hydrogen bonds is on the average more deformed and the jump distance of the proton would be smaller than the distance across the tetrahedral angle, which is equal to 1.6 Å.

(4) The mean-square displacement $\langle u^2 \rangle^{1/2}$, deduced from the Debye-Waller factor, can be interpreted as the maximum vibrational amplitude perpendicular to the hydrogen bond. According to a computer simulation by Impey *et al.*,[13] the critical angle for breaking of the hydrogen bond is about 30° which corresponds to a vibrational amplitude of $2(0.98 \sin 15°) \simeq 0.5$ Å, in agreement with our value.

Note added. We admit that our interpretation of the spectra remains controversial. Nevertheless, we believe some of these questions can be answered with further work at even higher resolution, in progress at this time.

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