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DYNAMICS OF SUPERCOOLED WATER STUDIED BY NEUTRON SCATTERING

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Résumé - Nous présentons des résultats d'expériences de diffusion incohérente de neutrons, quasi-élastique et inélastique, par de l'eau en phase surfondu. L'analyse du spectre quasi-élastique permet de déterminer deux temps caractéristiques et leur dépendance en température. La diffusion est expliquée par le modèle de saut et un mécanisme de rupture de la liaison hydrogène est proposé. Le spectre inélastique est étendu jusqu'à 600 meV montrant, pour la première fois, la raie due aux vibrations intramoléculaires de stretching.

Abstract - Incoherent quasi-elastic and inelastic neutron scattering by water was performed in a temperature range extending to the supercooled state. The analysis of the quasi-elastic spectrum separates two main components and gives two characteristic times. Their temperature analysis justifies the use of the Jump Diffusion model and suggests a mechanism for the hydrogen bond breaking. The inelastic spectra extend until 600 meV, i.e., covering the intramolecular vibration region showing, for the first time, the stretching band.

As many other liquids, water molecules form between them hydrogen bonds. However, some peculiarities make its behaviour very specific. Firstly, the hydrogen bond framework is very dense. Actually, even at room temperature, as much as 80% of the possible bonds are formed /1/. Secondly, the hydrogen bonds are fragile, i.e., extremely temperature and pressure dependent, because of their energy and directional character. Finally, the bonds form locally a tetrahedral lattice, i.e., a very open structure where each molecule is surrounded by about four next neighbours.

When the temperature is decreased, the number of bonds increases /1/, the angular correlations also increase /2/ and consequently the observed anomalies in the behaviour of water are more pronounced. At low temperatures, say below room temperature and in the supercooled state, the structural aspects dominate and the properties of water can be explained from geometrical considerations /3/. It follows, as a consequence, that in this low temperature range, the nature of the potential used, for instance in numerical simulations is not very crucial and different choices can give good results, as far as the tetrahedral structure is reproduced.

Because of the importance of hydrogen bonding, one can ask the following question: what is the dynamical behaviour of an hydrogen bond and how is it related with the transport properties of liquid water?

Clearly, there is no simple way to isolate the hydrogen bond from the molecular dynamics. Actually, most of the techniques are mainly sensitive to the molecule as a whole and the separation of the hydrogen bond behaviour is hazardous.

However, incoherent quasi-elastic and inelastic neutron scattering appears to be
rather appropriate because one is there sensitive to the proton dynamics, then to the hydrogen bond.

In a typical neutron scattering experiment, a beam of monoenergetic neutrons is scattered by the sample. Angular and energy analysis of the scattered neutrons provide information on both structure and dynamics at a molecular and atomic level. Incoherent neutron scattering, in particular, is related with the dynamic structure factor, $S_s(Q,E)$, and can be expressed in terms of the atomic individual movements. Because of the very high incoherent cross section of hydrogen atoms, the scattering by $H_2O$ molecules can be assumed to be originated by hydrogen atoms and the observed energy spectrum measures the proton dynamics.

The experimental determination of the incoherent inelastic spectrum is a compromise between the amplitude of the energy transfer range and the energy resolution. We present here two sets of experiments quite different from this point of view.

One set of experiments used the Intense Pulsed Neutron Source at Argonne (U.S.A.). The incident neutron energy was 800 meV which allows one to reach energy transfers equal to 600 meV at reasonable $Q$ values (smaller than 8 Å⁻¹).

In Fig.1 we show the function

$$G(Q,E) = \frac{E^2}{Q^2} S_s(Q,E)$$

(1)

(where $E$ is the energy transfer and $Q$ the wave vector) obtained at -15°C, i.e. with a supercooled sample. For this purpose we used a set of 150 Pirex capillaries 0.8 mm i.d.

From the figure we identify clearly three main bands: the librational band at 96 meV, the intramolecular vibrational bending band at 207 meV and the intramolecular
stretching band at 418 meV. From the temperature analysis (between 80°C and -15°C), of these bands, we conclude that:
1) the librational band shifts towards high frequencies when temperature decreases.
2) the bending line is almost temperature independent.
3) the stretching line shifts towards low frequencies with decreasing temperature.
In contrast with the equivalent peak in the Raman spectrum, it cannot be separated in different components. All these results indicate that the proton motion in water molecules is strongly affected by the formation of hydrogen bonds. In particular it is the origin of the librational band which is not present in gas phase. The temperature variation of the librational band can also be explained noting that the hydrogen bond network is more distorted when temperature increases and will be better understood with the quasi-elastic spectrum analysis we present below.

A more detailed analysis of this set of results will be presented elsewhere /4/.

Another set of experiments was performed at the Institut Laue-Langevin (Grenoble). The incident neutron energy was 3.14 meV, in order to obtain a resolution high enough to study the quasi-elastic component of the incoherent spectrum, even at low temperatures. The sample was composed of about 80 Pyrex capillaries (i.d. = 0.3 mm) in order to decrease the temperature down to -20°C. Spectra were recorded at nine different temperatures below room temperature, and for 19 different angles corresponding to elastic wave-vectors Q extending from 0.25 to 2 Å⁻¹. An example of the obtained spectra is given in Fig.2.

Fig 2 - Typical quasi-elastic spectra, obtained at -5°C. The energy of the incident neutrons was 3.14 meV. Points represent the experimental data. The solid lines are the best fit. The dashed lines represent the resolution function.

The fit was done assuming two dynamic processes each of them described by lorentzians:

\[ S_S(\omega) = e^{-\langle u^2 \rangle Q^2 / 3} T(Q,\omega) \ast R(Q,\omega) \]  

The first term is the Debye-Waller factor, \( \langle u^2 \rangle \) is the vibrational amplitude and
* means convolution. The mathematical form of the other terms are:

\[ T(Q, \omega) = \frac{1}{\pi} \frac{\Gamma(Q)}{\Gamma(Q)^2 + \omega^2} \]  

(3)

\[ R(Q, \omega) = j_0(Qa) \delta(\omega) + \frac{1}{\pi} \sum_{l=1}^{\infty} (2l+1) \ j_{2l}^2(Qa) \ \frac{\ell(\ell+1)D_F}{[\ell(\ell+1)D_F]^2 + \omega^2} \]  

(4)

In this expressions the energy transfer is now represented by \( \omega \), \( j_0(Qa) \) are spherical Bessel functions and \( a = 0.98 \ \text{Å} \) (the O-H distance) is a radius of gyration for the rotation.

\( T(Q, \omega) \) is a lorentzian with \( \text{HWHM} = \Gamma(Q) \) and, in a classical picture, is associated with diffusion processes. We analysed the width \( \Gamma(Q) \) within the Jump Diffusion model /5/:

\[ \Gamma(Q) = \frac{DQ^2}{1 + DQ^2 \tau_0} \]  

(5)

where \( D \) is the self-diffusion coefficient and \( \tau_0 \) represents a residence time. Fig.3 shows the result of this fit at different temperatures between 20°C and -20°C.

![Fig.3 - HWHM of the translational lorentzian at different temperatures. The solid lines represent the best fit. For \( T = 20°C \) the self-diffusion line is shown.](image)

The broad components \( R(Q, \omega) \) are normally associated with rotational relaxation. They are \( Q \) independent. If we define a characteristic time \( \tau_1 \) given by:

\[ \tau_1 = \frac{1}{6} \frac{D}{D_F} \]  

(6)

we obtain an Arrhenius behaviour for its temperature dependence (Fig.4).

Finally, we determined the Debye-Waller parameter. It is, within the experimental
Dielectric relaxation time, \( \tau_d \), and orientational relaxation time, \( \tau_o \), are determined in our experiment. Different transport properties and relaxation times are shown together.

The vibrational amplitude is \( \langle u^2 \rangle = 0.484 \, \text{Å} \). We must emphasize that all the data are fitted with a typical error of 1% with three free parameters: \( \langle u^2 \rangle \), \( \Gamma \), and \( D_0 \). In Fig. 2 the solid lines represent the final fit.

From this features, it is possible to justify a mechanism for the proton motion. As we pointed out above, water molecules are instantaneously connected with most of their neighbours through hydrogen bonds. However, each hydrogen bond is very directional and the libration amplitude is very large. Molecular dynamics computer simulations of Impey et al. /6/ indicate that, when the amplitude of libration is above 25°, the bond is broken. This estimation is in very good agreement with the value \( \langle u^2 \rangle^{1/2} = 0.484 \, \text{Å} \) we deduced from the Debye-Waller factor.

When a bond is broken, the molecule can form a bond with another neighbour. Then, the time \( \tau_1 \) is a measure of this characteristic time, and we justify the use of Eq. (4) in the fitting procedure, noting that this process corresponds to a rotational movement. Independent determinations of the hydrogen bond life-time /7/ lead to values with the same order of magnitude (Fig. 4), but what must be emphasized is that in both cases one finds an Arrhenius temperature dependence. This normal behaviour is different from those of all other properties of water and it is certainly a manifestation of the hydrogen bond dynamics.

On the other hand, the diffusion of the molecule is possible only when a sufficient number of bonds is broken simultaneously. With decreasing temperature, the fraction of mobile molecules becomes extremely small and consequently the temperature dependence of all the transport properties is strongly non-Arrhenius. A simple picture based on the geometrical properties of the hydrogen bond framework has been proposed /3/ to relate the hydrogen bond lifetime and the transport properties and used with success in the interpretation of the dielectric relaxation time /8/. In our
experiments, the anomalous temperature behaviour is followed by the residence time \( \tau_0 \) (Fig.4).

It is worth noting moreover that a characteristic jump length \( L \) can be defined in the classical way from Eq.(5) by

\[
L = (6D\tau_0)^{1/2} \tag{7}
\]

The temperature dependence we obtain for \( L \) is given in Fig.5. Its value is in average

![Graph showing temperature dependence of jump length](image)

Fig.5 - Temperature dependence of the jump length \( L \) defined by Eq.(7). Note that it is in average close to 1.6 Å, the distance between the two protons in water molecule.

equal to 1.6 Å, which suggests that the diffusion is made by rotational jumps. Actually this distance corresponds to the distance between two protons, then to two possible bonds of the water molecule. The small temperature dependence can be understood if we remember that at high temperatures the hydrogen bond framework is more deformed and the distance \( L \) is reduced.

Fig.4 shows plotted together different relaxation times and dynamic properties of liquid water. While transport properties and molecular relaxation times are not Arrhenius temperature dependent, a shorter time is observed in depolarized light Rayleigh scattering /7/ and in our experiment. The temperature dependence of the hydrogen bond lifetime deduced by Bertolini et al /8/ has also a small temperature dependence with an associated activation energy close to that of \( \tau_1 \). The activation energy deduced from Rayleigh scattering is slightly higher perhaps because it is there associated with the molecular polarizability.

We described above a mechanism to relate the two different behaviours in temperature of the characteristic times \( \tau_0 \) and \( \tau_1 \). However, our approach is certainly too crude, in particular, writing Eq.(2). Actually, the model we propose is not compatible with the convolution of the diffusion and rotation components which supposes that the
two processes are not coupled. A more precise model must take into account the coupling between vibrations, rotations and diffusion, which is certainly strongly temperature dependent. With such a specific model, it will be possible to precise more quantitatively the molecular dynamics of water. Our analysis represents in this sense a first order approximation.

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