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## Dynamics of water studied by neutron scattering

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**Abstract.** Quasi-elastic incoherent neutron scattering data on liquid water are analysed in terms of two dynamical processes. They give the residence time and the characteristic lifetime of a hydrogen bond. Percolation theory for low temperature water relates the Arrhenius behaviour of the hydrogen bond temperature dependence to the anomalous transport properties of liquid water.

The molecular dynamics of water has been studied by different spectroscopic techniques, *ab initio* calculations and computer simulations [1] (CMD). The main theoretical problem put by such studies is the large and unusual temperature and pressure dependences of the transport properties of liquid water, in particular at low temperatures. Only *ad hoc* effective potentials reproduce, more or less, such properties. As an example, the Arrhenius slope for self diffusion,  $-d(\ln D)/d(1/T)$ , changes from 4 kcal mol<sup>-1</sup> at 30 °C to 9 kcal mol<sup>-1</sup> at -30 °C. Roughly speaking, *ab initio* calculations [2] are unable to describe the low temperature properties of water, because its characteristic tetrahedral structure is not conveniently taken into account. On the contrary, most of the CMD over emphasise such structure in order to reproduce the thermodynamic properties but disagree with the microscopic structure as measured by scattering techniques.

As first shown by Geiger *et al* [3], the hydrogen bond network in liquid water is so dense that it can be seen as forming a transient gel, at times comparable to the lifetime,  $\tau_{\text{HB}}$ , of a hydrogen bond, that is, around 1 ps. It is plausible that this network plays a central role in the physics of water at very low temperatures and one simple approach consists of visualizing and making statistics of the connectivity properties of the hydrogen bond network as a function of temperature, using concepts issued from percolation theories [4].

As far as thermodynamics properties are concerned, a semi-empirical equation gives the temperature dependence of the number of 'intact bonds':

$$p = 1.8 - 0.004 T \quad (1)$$

for H<sub>2</sub>O. This expression can also be seen as the linearization of the Arrhenius temperature dependence of  $(1 - p)/p$ , with an activation energy for the hydrogen bond formation equal to 3.3 kcal mol<sup>-1</sup>. In the temperature region extending from room temperature down to -30 °C,  $p$  changes typically from 0.60 to 0.85. One can consider

that each water molecule can form with its next 4 neighbours a number of bonds between 0 and 4. The populations of the five possible classes of molecules follow the binomial distribution, a result confirmed by CMD using the ST2 potential [5].

In order to describe the temperature dependence of the transport properties of low temperature liquid water, one makes two assumptions: (i) the dynamics of an individual hydrogen bond has a classical temperature dependence, i.e. is described by an Arrhenius equation; (ii) molecular rotations and diffusion motions can be accomplished only by zero or single bonded molecules. The temperature dependence of this population,  $F_M$ , is given by  $F_M = (1 - p)^4 + 4(1 - p)^3 p$  and the proportion of 'immobile' molecules at a given time of the order  $\tau_{HB}$ , is:

$$F_I = 1 - F_M = 6p^2 - 8p^3 + 3p^4.$$

Considering a labelled molecule of the set  $F_I$ , at time  $t = 0$  and following its time evolution, it is possible to deduce that the probability of it remaining immobile for a time  $\tau_0$  is given by  $(F_I(p))^{\tau_0/\tau_{HB}}$ . This result gives the temperature dependence of  $\tau_0$ :

$$\tau_0(T) = \tau_{HB}(T) \frac{A}{\ln(F_I(p))} \quad (2)$$

where  $A$  is a number that can be taken either as a constant [4] or, more exactly, as a function of  $p$  [6]. Assuming for  $\tau_{HB}(T)$  an Arrhenius law, the main temperature dependence of the residence time  $\tau_0$ , comes from the denominator in equation (2). In particular,  $\tau_0(T)$  diverges when  $p \rightarrow 1$ .

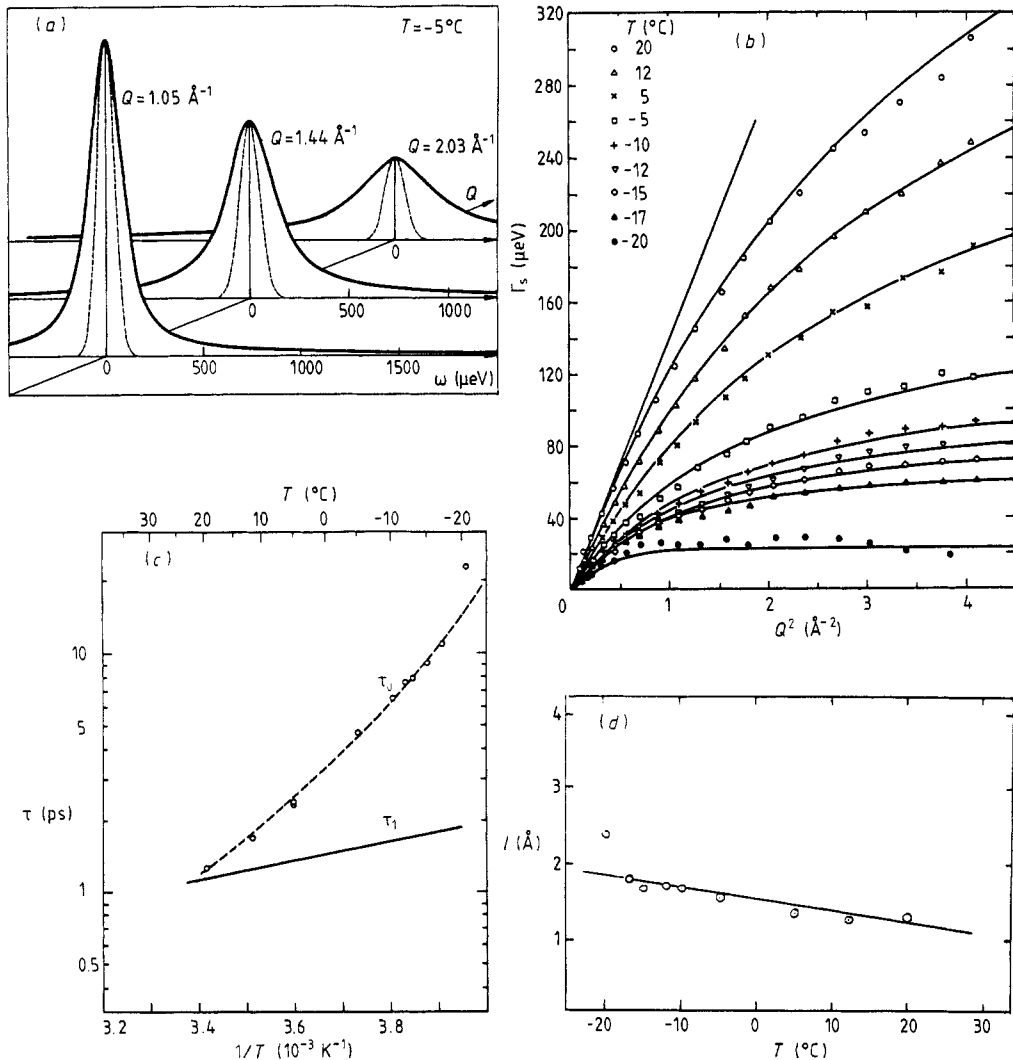
Equation (2) is in very good agreement with the temperature dependence of all the transport properties such as self-diffusion, dielectric relaxation time or shear viscosity. One goal of the experiment is then to isolate and identify the microscopic time  $\tau_{HB}$ .

Quasi-elastic incoherent neutron scattering (QENS) and inelastic neutron scattering (INS) are spectroscopic techniques appropriate to the study of microscopic movements. The important incoherent cross section of hydrogen nuclei strongly relates the scattered intensity to individual protonic motions.

The classical way to analyse the quasi-elastic scattered intensity assumes the decoupling between vibrations, rotations and diffusion motions. In liquid water, such decoupling is certainly not correct at room and high temperatures when rotational and diffusion motions are coupled. However, at low temperatures this approximation is justified. Within this approximation, the scattered intensity  $I(Q, \omega)$  depends on the momentum transfer  $Q$  and energy transfer  $\omega$  in the following way:

$$\begin{aligned} I(Q, \omega) &= \exp(-Q^2 \langle u^2 \rangle / 3) T(Q, \omega) * R(Q, \omega) \\ T(Q, \omega) &= (1/\pi) \Gamma(Q) / [\omega^2 + (\Gamma(Q))^2] \\ R(Q, \omega) &= (1/\pi) \sum_{i=1}^{\infty} (2i+1) j_i^2(Qa) i(i+1) D_r / \{\omega^2 + [i(i+1)D_r]^2\} \\ \Gamma &= DQ^2 / (1 + DQ^2 \tau_0) \\ \tau_1 &= (6D_r)^{-1} \\ l &= \sqrt{6D\tau_0} \end{aligned} \quad (3)$$

where the first term of  $I(Q, \omega)$  is the Debye–Waller factor,  $R(Q, \omega)$  accounts for the



**Figure 1.** (a) The scattered intensity for three values of the elastic momentum transfer. The full curves represent the fit by equation (3) and the experimental data fall inside the width of the line. The broken curves represent the instrumental resolution. (b) The width of the translational line plotted against the momentum transfer. The straight line corresponds to the hydrodynamic limit of self-diffusion. (c) Arrhenius plot of the residence time,  $\tau_0$ , and of the hindered rotations characteristic time,  $\tau_1$ . This last time can be associated with the hydrogen bond lifetime. (d) Temperature dependence of the jump length, which is close to the distance between the two hydrogen atoms in a water molecule (from [7]).

hindered rotations and  $T(Q, \omega)$  for the translation movements,  $*$  denotes frequency convolution, and  $j_i(x)$  are the spherical Bessel functions.  $\langle u^2 \rangle$  is the mean square amplitude of the vibrations (mainly, the librational movements),  $\Gamma$  is the width of the translational line,  $D$  is the self-diffusion (low- $Q$  limit of  $\Gamma$ ),  $\tau_0$  is the residence time (inverse of the high- $Q$  limit of  $\Gamma$ ),  $\tau_1$  is the hindered rotations characteristic time,  $a$  the oxygen-hydrogen intramolecular distance and  $l$  is the mean square jump length, assuming a

jump diffusion mechanism. The fit of the experimental data, obtained at spectrometer IN6 of the Institut Laue–Langevin (Grenoble, France) [7] is given in figure 1.  $\langle u^2 \rangle^{1/2} = 0.48 \text{ \AA}$  is temperature independent. The characteristic time  $\tau_1$  has an Arrhenius temperature dependence. Since it is associated with hindered rotational movements, we interpret this time as the typical hydrogen bond lifetime. Moreover, the large amplitude of the librational movements suggests that the breaking of hydrogen bonds is due to large amplitude librational movements. Considering the value of  $\langle u^2 \rangle^{1/2}$  and the hydrogen–oxygen distance, the critical angle beyond which the hydrogen bond can be considered as a broken bond is around  $30^\circ$ . When at least 3 bonds are simultaneously broken, diffusion is possible, but the temperature dependence of the residence time  $\tau_0$  is anomalous and given by equation (2).

Another argument in favour of this description of the molecular motions in liquid water is obtained from INS in the stretching region [8] around 500 meV. A simulation performed by Toukan and Rahman [9] predicts two lines at 427 meV and 510 meV corresponding to stretching vibrations with and without simultaneous breaking of the hydrogen bond. These two lines are observed and their intensity is proportional to  $p$  and  $1 - p$  as expected from the proposed model.

In conclusion, the approximation based on the connectivity of the hydrogen bond network can take into account the anomalous behaviour of water at low temperatures and is well confirmed by neutron spectroscopic techniques.

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