H1. HYDROGEN-BOND DYNAMICS IN BULK WATER

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Water is a simple molecule made up of three atoms in a V configuration displaying an electronic distribution almost perfectly spherical. However, the properties of the liquid are very complex and not totally understood despite a huge number of experimental and simulation studies. In a very general way, one may say that the so-called "anomalous" behaviour of water derives from hydrogen bonds (HB) which generate an anisotropic potential and strong although fragile inter-molecular forces.

Historically, many experiments tried to catch and understand the topological and dynamic properties of HB and the way they may be related to the thermodynamic and transport properties of the liquid. Alternatively, the remarkable development of simulations of molecular dynamics made very popular "efficient potentials" to describing complex liquids such as water. For most of such potentials, the anisotropy of the potential is indirectly taken into account by the assumption of a molecular anisotropy fixed ad hoc in order to reconstitute, at the best and within classical concepts, the room temperature properties of liquid water. As a consequence, HB are poorly described because they are nothing more than a consequence of Coulombic forces between point charge molecules.

We have been among the experimentalists who, in the past, tried to identify the important role of hydrogen bonds, particularly studying the dynamics of supercooled water, i.e. at temperatures where they represent the determining factor. It is relatively difficult to isolate the dynamics of HB in a way that is, as much as possible, model independent. The performances of the spin-echo spectrometer MUSES, that measures the intermediate function $I(Q,t)$, gave us the opportunity of using an original way to studying HB dynamics in a way that is almost independent of other contributions to the scattered intensity.

We took profit of the good knowledge of the partial structure factors of heavy water (D_2O). Looking into detail to the Q dependence of the three factors, one realizes that, by accident, at $Q = 3.7$ Å^{-1}, $S_{DD}(Q)$ is the only partial that contributes significantly to the scattered intensity. Consequently, the measurement of $I(Q,t)$ at this value of the momentum transfer, yields a specific information about the dynamics of deuterium atoms directly implied in HB, and without any important contribution of the diffusion movements of the molecular centres of mass. In order to establish a convincing comparison, we measured as well $I(Q,t)$ at $Q = 1.9$ Å^{-1}, i.e. at the vicinity of the structural peak in $S(Q)$, where the scattered intensity is maximum and all the motions contribute to the signal.

The two main results are depicted on the figure. The two time dependences take place in very different time domains. As expected, the dynamics of the DD pairs is naturally faster than the molecular motions. But, the more important evidence concerns the temperature dependences, which are dramatically different. While at $Q = 1.9$ Å^{-1} we retrieve the well known non-Arrhenius temperature dependence of all the transport properties of water, at $Q = 3.7$ Å^{-1} the temperature dependence is much weaker and follows a classical Arrhenius law, demonstrating that, at the level of HB, there is no anomalous temperature dependence. This rather direct experimental determination of HB dynamics in liquid water reminds how important are all studies of bonds in water that can relate the two observed dynamics without calling for analytical, sometimes exotic models.

At this point, one may admit that the glass transition temperature of water (130 K) corresponds to the "freezing" of the motion of hydrogen atoms which remain extremely mobile even under 228 K, a virtual temperature that corresponds to numerical extrapolations of transport properties and that, actually, can be associated to the temperature of homogeneous nucleation of ice. In our view, this experimental result is a strong argument to say that temperatures obtained by extrapolations or from simulations reflect simply the increase of the number of HB with decreasing temperature and the formation of embryos