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Dynamical properties of liquid water

U Balucani[†], J P Brodholt[‡] and R Vallauri[§]

[†] Istituto di Elettronica Quantistica del CNR, Via Panciatichi 56/30, I-50127 Firenze, Italy

[‡] Department of Geological Sciences, University College of London, Gower Street, London WC1E 6BT, UK

[§] Istituto Nazionale per la Fisica della Materia e Dipartimento di Fisica dell'Università di Trento, I-38050 Povo (Trento), Italy

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Abstract. The collective dynamical properties of water are discussed with reference to recent inelastic scattering data as well as to simulation results reported here for the first time. Some striking features (notably the so-called 'fast sound') which aroused in the past a considerable debate now appear to be rather well understood. In contrast, there are other additional aspects (in particular, the character of a nearly flat mode at $10\text{--}12\text{ ps}^{-1}$ present both in water and in ice) which undoubtedly require a better understanding.

1. Introduction

In the last two years the amount of data concerning the dynamical properties of liquid water at a microscopic level has increased considerably, mostly after the performance of new inelastic scattering experiments with both 'traditional' probes such as thermal neutrons [1, 2] as well as 'new' ones such as x-rays generated by powerful synchrotron sources [3–5]. The appearance of all these data provides the possibility of replacing, at least in principle, purely phenomenological descriptions of the dynamics of hydrogen-bonded systems with suitable extensions of the frameworks so successful in simple fluids [6]. Remarkable progress along these lines has in fact recently been reported, even by recourse to suitably designed molecular dynamics (MD) simulations [2, 7–11]. Despite all this, several important aspects of the microscopic motions in water remain still unclear, or even controversial. The present work encompasses the recent advances in the field, and tries to extract a reasonably unified interpretation from all the data reported up to now. Even so, some features cannot be given a sound explanation, and here we must limit ourselves to a straight account of the findings, from both real and MD experiments. We conclude with a short account of the aspects successfully clarified, as well as of the points for which a satisfactory interpretation is still lacking.

In the present work, most of the above programme will be achieved by referring to MD data, reported here for the first time. These simulations should clearly be such as to mimic as closely as possible the real liquid of water molecules, at least for the properties sampled in the experiments. This is indeed possible by adopting suitable 'models' for the intermolecular potential: in the following, we shall mostly refer to a rather sophisticated potential model which deals with polarizable water molecules [12], but in most cases comparable results and conclusions can be obtained by using well known simpler potentials such as the TIP4P [13] and SPC/E [14] models.

In the following we shall mainly focus our attention on the more ‘spectacular’ (and controversial) dynamical features of liquid H₂O and D₂O at room temperature. The most part of these features is found to probe the *collective* motions of the molecules at the level of the molecular centres of mass. Of course, in a strongly interacting system any peculiar behaviour of the microscopic dynamics can be expected to have some importance even for other quantities, such as for example the ‘single-molecule’ dynamics probed by incoherent inelastic neutron scattering [2], or the velocity autocorrelation function (VACF) which controls the value of the diffusion coefficient [11]. Although we shall briefly comment even on the indirect effects as felt by this second class of properties, the main emphasis of the present work will be placed on the genuine collective properties. For the latter, it is convenient to follow the traditional classification into: (i) quantities associated with the dynamics of density fluctuations, such as the dynamic structure factor $S(k, \omega)$ or the related longitudinal current spectrum $C_L(k, \omega) \equiv \omega^2 S(k, \omega)$; and (ii) quantities associated with viscous effects and/or shear motions, such as the transverse current spectrum $C_T(k, \omega)$. All these quantities have the conventional definitions (see for example [6]), and provide a full account of the collective dynamics of the centres of mass as probed over space and time ranges given by $2\pi/k$ and $2\pi/\omega$, respectively.

2. Longitudinal correlations

After a number of experimental corrections, from the measured coherent inelastic scattering cross section it is possible to extract the dynamic structure factor $S(k, \omega)$ (in the neutron case, owing to the large incoherent cross section of the proton, this is in practice possible only by using deuterated samples). Both for neutrons and x-rays, the minimum accessible wavevectors k are about two or three orders of magnitude larger than those typical of the ordinary hydrodynamic range (the ones usually probed by light scattering). Given these premises, the fact that the measured $S(k, \omega)$ is substantially different with respect to the Navier–Stokes predictions is not surprising. At wavevectors $k > 0.3 \text{ \AA}^{-1}$, both the experimental (neutron and x-ray) and the MD spectra appear superficially to be rather structureless. However, particularly at the lowest k there are in the spectral wings clear pieces of evidence of ‘shoulders’ located at frequencies which increase with the wavevector. This suggests that some dispersive, acoustic-like, feature is buried into the spectrum. Two procedures have been employed to extract this information. The first one (usually adopted in the experimental work) focuses on the wings, which are fitted to a functional shape strictly valid for a single-damped-harmonic-oscillator model. Alternatively, in the MD work one frequently considers the longitudinal current spectrum $C_L(k, \omega) \equiv \omega^2 S(k, \omega)$ which always exhibits a peaked structure. Since both procedures emphasize the contribution of relatively high frequencies, the outcomes are expected to be not very different (and indeed one can show that there are circumstances, approximately valid for in liquid water, in which the two procedures give basically identical results [15]). Whichever method is adopted, the important quantity which is deduced is the position ω_L of a ‘Brillouin-like’ peak at different wavevectors. A closer analysis of the dispersion relation $\omega_L(k)$ for $k > 0.3 \text{ \AA}^{-1}$ reveals a surprising feature: the phase velocity of this ‘longitudinal sound’ is $\approx 3200 \text{ m s}^{-1}$, more than twice larger than the ordinary sound velocity in the liquid ($\approx 1500 \text{ m s}^{-1}$) as measured in the hydrodynamic region.

Since the first observation of this peculiar feature by inelastic neutron scattering [16], followed by further evidence obtained by MD simulations [7, 8, 17, 18] and inelastic x-ray scattering [3–5], several possible speculative suggestions for the origin of this *fast sound*

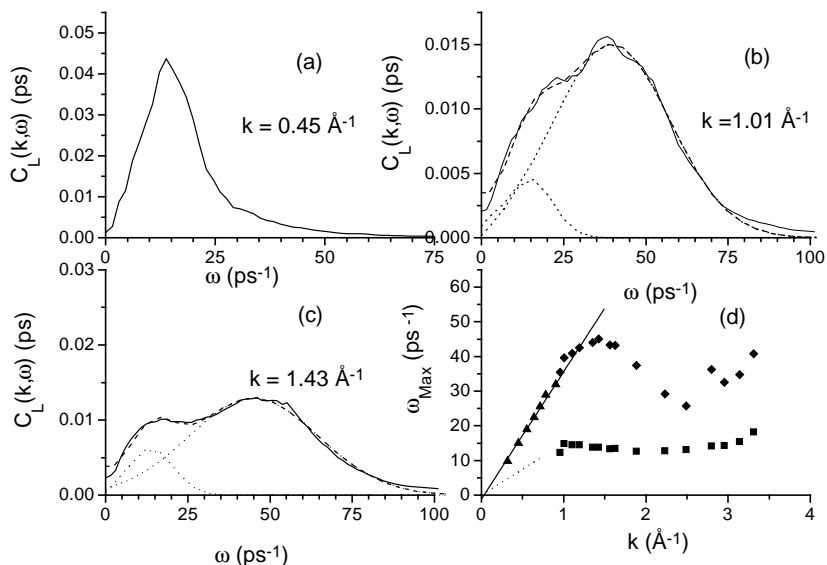


Figure 1. (a), (b), (c): the full lines denote the longitudinal current spectra $C_L(k, \omega)$ at selected values of k as obtained by our simulations. All the curves have been normalized to unit area. Whereas at the lowest wavevector (a) a best-fit analysis yields only a single component, in (b) and (c) at least two components (dotted lines) are required in order to have a reasonable fit (dashed line). The dispersion relation of the peaks deduced from such a procedure is plotted in (d), at both low (triangles) and high wavevectors (squares and diamonds). The full and dotted straight lines correspond to phase velocities of 3500 m s^{-1} and of 1500 m s^{-1} , respectively (the latter being the ‘hydrodynamic’ value).

have been made. Nowadays there is an almost general consensus that (i) the effect is *not* associated with the presence of a separate acoustic branch with high velocity coexisting with the ‘ordinary’ one; (ii) there is instead a single longitudinal acoustic branch in which the phase velocity gradually increases from the hydrodynamic result up to the values observed both in the experiments and in the simulations (‘positive dispersion’); (iii) the fast-sound effect is visible over a rather limited wavevector range: even with the previous artifices, for k larger than, say, 1.8 \AA^{-1} the definiteness of the excitation deteriorates so much that any reference to it as a sound mode becomes increasingly meaningless. Some of these findings are illustrated in figure 1, which refers to our new MD simulation data obtained with the polarizable potential model implemented in [12].

A consistent theoretical interpretation of the fast-sound phenomenon is currently available [7, 8]. Basically, the positive dispersion is argued to stem from *viscoelastic effects* similar to those present in simple liquids. That is, as the wavevector (and correspondingly the frequency of the mode) increases, the dynamical properties of the system gradually evolve from liquid-like or viscous (the realm of ordinary hydrodynamics) to solid-like or elastic (a situation characterized by an instantaneous response of the system). This transition is ideally complete when the frequency exceeds a suitable relaxation rate ruling the dynamic relevance of viscous effects. In principle, this mechanism is present in any liquid; in water, the huge magnitude of the positive dispersion is traced back to a particularly high value of

the limiting infinite-frequency velocity and of the so-called ‘Einstein frequency’, which in turn follow directly from the peculiar structural properties of a hydrogen-bonded fluid [7]. On the basis of all these arguments, one expects that the value of the ‘fast-sound’ velocity in liquid water is of the same order as the ‘ordinary’ longitudinal sound velocity of ice.

Summing up, the above picture appears rather satisfactory; however, a glance to figure 1 indicates that in the longitudinal current spectra the dispersive fast-sound peak is not the full story. At increasing wavevectors, a second spectral feature begins in fact to appear at a position of 10–12 ps⁻¹ (see figure 1). Our analysis of the collective dynamics in terms of $C_L(k, \omega)$ makes the observability of this additional peak rather poor at low k ; even so, on the whole the wavevector dependence of the new feature appears to be modest, or even negligible. In liquid water, this feature was originally observed as a broad shoulder in Raman spectra [19] detected in a number of MD simulations using different potential models [7, 18]; in particular, in reference [18] it was attributed to a bending mode involving three oxygen atoms. Subsequently, the presence of a mode at $\omega \approx 10$ ps⁻¹ has been reported for $k > 0.5 \text{ \AA}^{-1}$ in a neutron scattering experiment [1], and misinterpreted as an extended sound mode propagating with a velocity close to the hydrodynamic value. Finally, very recent, high-resolution x-ray inelastic scattering data [5] have confirmed the presence in the liquid of *both* the fast-sound mode and the new (almost non-disperse) feature. In reference [5], some clue to the understanding of the nature of the new mode is provided by a measurement of $S(k, \omega)$ in Ih ice. Here the translational symmetry makes it possible to access even transverse excitations, provided that k exceeds a suitable boundary of the first Brillouin zone, reported at $\approx 0.75 \text{ \AA}^{-1}$. The authors of reference [5] in fact detected in ice a feature at about the same position as in water, and assigned it to a *transverse optical mode*. Since in liquids the absence of Brillouin zones prevents the observability in $S(k, \omega)$ of purely transverse excitations, the experimental findings seem to indicate either that the above mode acquires in water a partly longitudinal character, or that ‘loose’ Brillouin zones can be defined even in a dense liquid (as happens, for example, in the well known ‘de Gennes’ narrowing effect). However, in both cases we must admit that we deal with qualitative arguments rather than with a satisfactory (fundamental) interpretation.

3. Transverse correlations

In an effort to understand the rather complicated situation mentioned at the end of the last section, by our MD simulations in liquid H₂O we have evaluated even the transverse current correlation spectra $C_T(k, \omega)$. Such a quantity, not directly accessible by real experiments, should shed some light over the nature of shear excitations in a wavevector range considerably larger than the one reported previously [8, 9], and hopefully clarify the interplay (if any) between the nominal ‘longitudinal’ and the ‘transverse’ spectra.

The MD transverse current spectra as obtained at a few typical wavevectors are reported in figure 2. The relatively small size of our system (and hence the magnitude of the minimum probed wavevector) prevents us from accessing the genuine hydrodynamic region where $C_T(k, \omega)$ is known to be a Lorentzian with a peak at $\omega = 0$ and a width determined by the kinematic viscosity coefficient of the system. However, for our purposes this low- k regime (which in the case of water has been investigated in [8]) is not particularly interesting. As in any other liquid, the consideration of wavevectors beyond the hydrodynamic ones is known to give rise to the presence of well defined inelastic peaks in $C_T(k, \omega)$, showing that at finite k the liquid is able to support transverse modes of the same type as those present in the crystalline phase. This phenomenon has a ‘viscoelastic’ origin similar to that

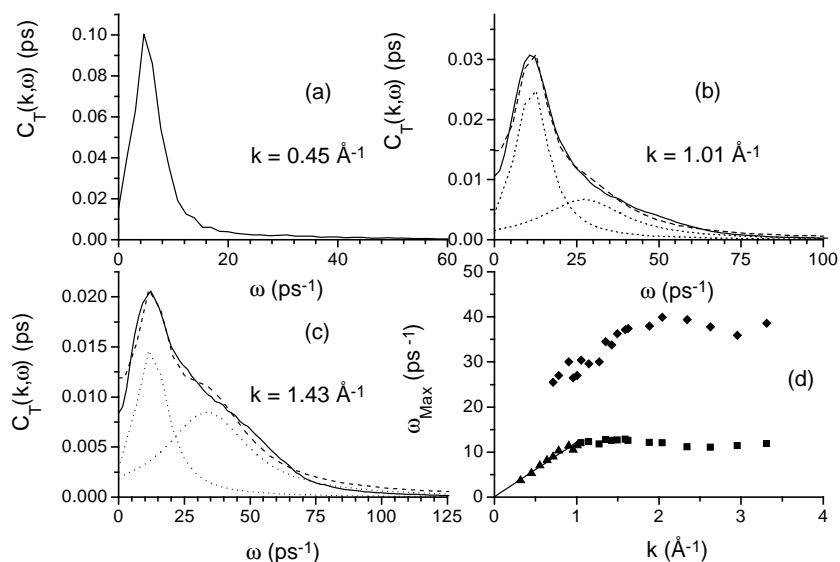


Figure 2. As figure 1, but for the transverse current spectra $C_T(k, \omega)$. In (d), the straight line corresponds to a phase velocity of 1200 m s^{-1} .

responsible for the positive dispersion of the longitudinal spectra. Our data in figure 2 in fact show the clear emergence of inelastic peaks in $C_T(k, \omega)$; plotting the corresponding dispersion relation (figure 2(d)) we find a transverse sound velocity of about 1200 m s^{-1} , to be compared with the value 1900 m s^{-1} reported for polycrystalline hexagonal ice [20].

However, even in this case the analysis of the spectra at increasing wavevectors shows the presence of an additional feature which coexists with the previous dispersive ‘acoustic’ mode. Looking at figure 2(d), one indeed notes that as k approaches $\approx 0.8 \text{ \AA}^{-1}$, $C_T(k, \omega)$ can be best fitted only by including a *second*, nearly flat feature at $\approx 12 \text{ ps}^{-1}$. At first sight, this is clear evidence for a transverse, optic-like excitation present even in the liquid phase. This supports the speculation in section 2 that the ‘bending mode’ (purely transverse in ice [5]) does indeed have a mixed character in the liquid. However, this picture does not explain the presence at high k of an additional high-frequency dispersive excitation, evident in figure 2, and needed to account for the intensity in the wings of $C_T(k, \omega)$. Although the dispersion of this new feature is about the same as that of the ‘ordinary’ transverse acoustic branch, its position appears to be shifted to much higher frequencies (see figure 2(d)). Possible ‘interference’ effects between the two branches cannot be excluded at this stage, but again we must recognize the absence of a satisfactory interpretation.

4. Concluding remarks

In this paper we have discussed some of the recent developments in the study of the collective dynamics of water at room temperature, as brought about by both new experimental and simulation data. Some of the latter are actually reported here for the first time. On the whole, a satisfactory interpretation emerges for several features which

have aroused much interest (and controversial debates) in the past few years. One of these is undoubtedly the phenomenon of ‘fast sound’, whose existence and ultimate origin now appear to be reasonably clear.

In contrast, even at the ‘global’ level of centres of mass several features are found which demand either a consistent framework of interpretation, or simply a less cursory understanding. The aforementioned feature occurring in water at 10–12 ps⁻¹ is a typical example of this situation: its dominant transverse character seems rather clear, and is confirmed from a recent analysis of the VACF spectrum (a single-particle property akin to the density of states) which can be split into longitudinal and transverse contributions [11]. However, the ultimate mechanism responsible for the observation of this feature in $S(k, \omega)$ or in $C_L(k, \omega)$ for water remains unclear. The presence of a high-frequency transverse ‘acoustic’ branch, as reported in figure 2, is even more puzzling. Nevertheless, on the basis of the rapid and substantial progress recently seen by this field, one can be reasonably confident that even a solution of these intriguing aspects is not too far off.

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