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COLLECTIVE DYNAMICS IN LIQUID WATER

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Abstract: A theoretical analysis of the hydrogen and oxygen density correlation functions in liquid water predicts that, besides the ordinary sound mode, a high frequency "optical-like" collective mode propagates through the hydrogen atoms. Computer simulations of the same quantities confirm the theoretical predictions and allow a clear interpretation of the experimental neutron scattering data.

1. Introduction

The collective dynamical properties of liquid water have recently been investigated by neutron scattering experiments [1] and by computer simulation (CS) [2,3]. The analysis of the experimental spectrum $S(k,\omega)$ indicates the presence of a highly broadened peak in the wavevector range $0.3 < k < 1.5$ A^{-1}, whose frequency changes almost linearly with the wavevector [1]. The resulting high sound velocity ($\approx$ 3200 m/s), suggests an interpretation of the nature of the underlying collective excitation; namely the possibility that a "fast sound" mode can propagate in the small patches of highly bonded water molecules [1].

A similar dispersion relation has been observed by Wojcik and Clementi [3] in a CS study which makes use of the MCY interaction potential between two water molecules at liquid density. They evaluate the intermediate scattering function

$$F(k,t) = \frac{1}{N} \langle \sum_i [e^{i\underline{k}\cdot\underline{r}_i^{(c)}(t)}] \sum_j [e^{i\underline{k}\cdot\underline{r}_j^{(c)}(0)}] \rangle \qquad (1)$$

where $\underline{r}_i^{(c)}$ represents the vector position of the centre of mass of molecule i and N is the number of particle in the system. The Fourier transform of $F(k,t)$, i.e. $S(k,\omega)$, shows a rather well

defined peak the frequency of which agrees quite satisfactorily with the experimental findings in the explored wavevector range. The interpretation of the dispersion relation is nevertheless different in that they claim a positive dispersion of the ordinary hydrodynamic mode to be the origin of such a behaviour, thus extending to molecular systems the concepts invoked to account for similar (but less evident) results in monatomic liquids [4].

In a previous CS of liquid water, using the ST2 potential model, Rahman and Stillinger [5] had found that the centre of mass $S(k,\omega)$ presents two peaks ; one at low frequency corresponding to the ordinary sound and a second one at higher frequency. The latter was suggested to be the print of a "fast" mode propagating through the hydrogen atoms.

Recently we have presented a theoretical analysis of the collective properties of liquid water [6] in which the density fluctuations of both the oxygen and hydrogen atoms are separately considered in order to clarify the nature of the propagating modes and eventually arrive at a definitive interpretation of the neutron scattering measurements.

We present here the results of the above mentioned theoretical approach which, under simplifying assumptions, leads naturally to the prediction of two propagating modes. The dispersion relation of these two modes, in the limit of vanishing wavevector, will be discussed in order to understand the nature of the two collective excitations. Finally the results for the oxygen and hydrogen intermediate scattering functions evaluated by CS will be presented and compared with the theoretical and experimental findings.

2. Theoretical analysis and CS results

We consider the density fluctuations of the oxygen and hydrogen atoms to be the components of the relevant dynamical variable. By applying the projection operator formalism developed by Mori and Zwanzig and neglecting the damping, one can write down a secular equation, whose solutions give the eigenfrequen-

cies of the resulting two modes. For a complete evaluation of these two solutions only the knowledge of static quantities is required; namely the partial structure factors (PSF) as a function of the wavevector k and the second time derivatives of the intermediate scattering functions that can be built up from the dynamical variable under investigation. The expression of these latter quantities are the same as that reported in eq. (1) where now $\underline{r}_i^{(c)}$ is replaced by the vector position either of the oxygen or the hydrogen atoms. Extensive details of the calculations will be reported elsewhere [7].

The dispersion relation for the two eigenfrequencies $\omega_1(k)$ and $\omega_2(k)$ is reported in Fig. 1. The PSF have been obtained by performing a CS with N = 108 molecules at T = 310 K and ϱ = 1.0 g/cm³. We have adopted the potential model TIP4P [8] which gives a realistic description of liquid water in a wide range of temperature and pressure [9].

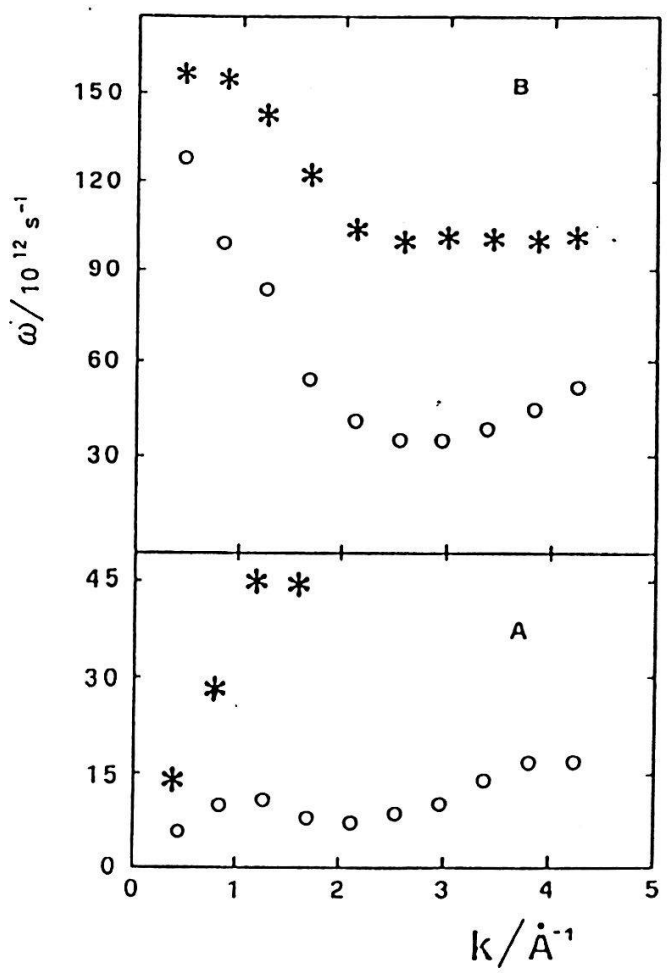

Figure 1.
Dispersion relation for the eigenfrequencies of the two modes.
A) the low frequency "acoustic" mode $\omega_1(k)$:
B) the high frequency "optical-like" mode $\omega_2(k)$.
Open circles refer to the solution of the secular equation under the assumption of zero damping; the stars refer to the peak positions of $\omega^2 S(k,\omega)$.
The spectra are obtained by Fourier transforming the oxygen and hydrogen intermediate scattering functions evaluated by computer simulation.

The nature of the two solutions predicted by the theoretical analysis is more easily understood by exploring their behaviour in the limit of $k \to 0$. One finds [6]

$$\omega_1^2(k\to 0) = K_B T/[MS(0)]\ k^2 \tag{2}$$

$$\omega_2^2(k\to 0) = K_B T\ h_{12}^2/[3IS''(0)] \tag{3}$$

In eq. (2) M is the total mass of the molecule and S(0) is any of the three PSF, being at k = 0 all coincident. The mode propagating at frequency $\omega_1(k)$ (see fig. 1A) is recognizable as the ordinary sound mode and indeed its dispersion relation is found to be very close to $\omega_1(k) = k\sqrt{[K_B T/MS_{OO}(k)]}$ in the whole range of explored wavevectors ($S_{OO}(k)$ being the oxygen-oxygen PSF). From eq. (3) it appears that the second solution has a finite value at k = 0 and therefore the second mode can be recognized as an "optical-like" mode. The observed dispersion behaviour (see fig. 1B) stresses its collective nature. In eq. (3) $S''(0) = S''_{OO}(0) + S''_{HH}(0) - 2S''_{OH}(0)$, where $S''_{\alpha\beta}(k)$ represents the second derivative of $S_{\alpha\beta}(k)$ at k = 0, h_{12} is the distance between the oxygen atom and the line joining the hydrogen ones, I is a combination of the principal momenta of inertia. This result points out that the rotational degrees of freedom of the molecule are involved in the dynamics of this high frequency mode. In fact the frequency values of this mode appear to be in the range proper to the librational motion of the molecule, i.e. $10^{14}\ s^{-1}$. The evaluation of the relative contributions of the two modes to the oxygen and hydrogen density autocorrelation functions (DACF) reveals that only the latter ones are influenced by the high frequency mode [6]. This theoretical prediction is confirmed by the direct evaluation of these DACF performed by CS and of the corresponding spectra. In Fig. 2 we compare $\omega^2 S(k,\omega)$ for oxygen and hydrogen. The variation of the low frequency peak is reported in fig. 1A. It appears to be higher than $\omega_1(k)$ and in agreement both with the experimental [1] and CS results [3]. In view of the nature of this low frequency mode we can conclude that this is nothing but the ordinary sound mode which suffers from anomalous dispersion as pointed out in Ref. 3. The hydrogen spectrum shows a high

frequency maximum which varies with k as reported in fig. 1B, i.e. in good agreement with the theoretical estimate.

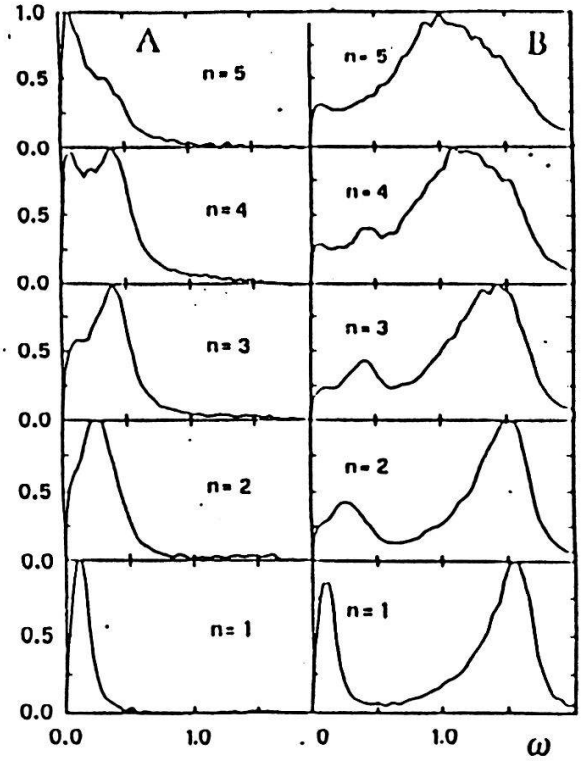

Figure 2.
$\omega^2 S(k, \omega)$ normalized to their maximum values as a function of the frequency (in units 10^{14} s^{-1}) at several wavevectors. A and B refer to the oxygen and hydrogen spectra respectively. The wavevector k is of the form $k = 2\Pi n/L$ where L is the cubic box length of the computer simulation. The value of L = 14.78 Å of the present simulation leads to a minimum wavevector k_{min} = 0.4251 $Å^{-1}$ for n = 1.

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