Collective excitations in liquid water at low frequency and large wave vector

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There is considerable interest in the possibility of a "second sound" excitation in liquid water.[1–6] Evidence supporting this possibility stems from molecular dynamics (MD) studies[1,3] using the ST2 potential, in which the observation of both the "normal sound" and a "second sound'" mode at roughly twice the frequency are reported. However, MD simulations based on other intermolecular potentials and neutron scattering experiments find evidence only for the "second sound" mode at large values of wave vector q.

In this note we show that the peak in the dynamic structure factor $S(q,\omega)$ that had previously been identified with the extension of normal sound in the large q region[1,3] in ST2 water is due to the O–O–O bending mode. We show that the peak position of this low frequency mode is q independent in a wide q range, and we discuss the implication of this result on the interpretation of the "second sound" mode.

The difficulties in both experiments and MD are related to the broadening of the central quasielastic peak and to the superposition of the intense bending and stretching bands. The latter makes the "self" contribution to the structure factor $S(q,\omega)$ relevant, especially in the case when small systems are simulated. In order to overcome these difficulties, we have analyzed a simulation of 216 ST2 water molecules[7] at $T = 235$ K and average density $\rho = 0.95$ g/cm^3. With this choice, the intensity of the quasielastic central peak is very small in the frequency range of interest.[8] We have calculated $S(q,\omega)$ for other values of T and ρ, and with other model potentials (TIP4P, SPC) and have obtained consistent results. Thus the conclusions drawn here are not restricted to temperatures and densities close to the one for which we present data.

To calculate $S(q,\omega)$ we first calculate the space Fourier transform $\rho(k,t)$ of the oxygen density for several 40 ps time intervals. $S(q,\omega)$ is then obtained using the maximum entropy method for power spectrum estimation.[9] We average $S(q,\omega)$ with respect to three q vectors with the same magnitude along the x, y, and z directions. To ensure that the features observed are not spurious we have studied these spectra in conjunction with straightforward calculations using the Wiener–Khinchin theorem.

Figure 1 shows $S(q,\omega)$ for six q values. We observe two peaks at finite values of ω except for the smallest value of q ($q_0 = 0.3316$ Å^{-1}). At this q value, the two peaks are coincident. These results are in contrast with the results in Refs. 1 and 3, where the low ω peak could not be observed for q larger than 0.6 Å^{-1} due to the broadening of the central peak. We make the important observation that the low frequency peak is q independent. We note, in passing, that the higher frequency peak moves to larger ω linearly with q (with a velocity of 3500 m/s), in full agreement with previous work.[1,3–5]

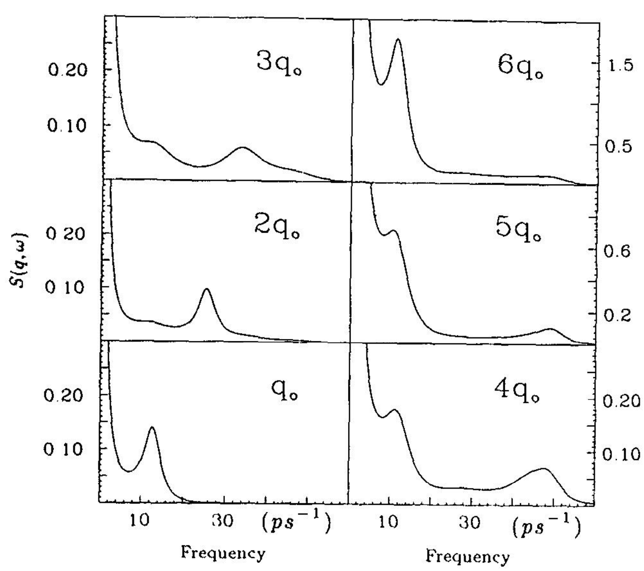

FIG. 1. $S(q,\omega)$, measured in arbitrary units for different q values (shown in units of $q_0 = 0.3316$ Å^{-1}), and shown as a function of ω (in ps^{-1}). The maximum entropy method (Ref. 9) was used to obtain these curves.

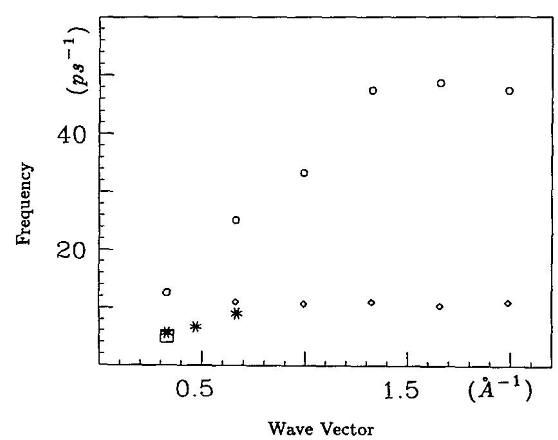

FIG. 2. Position of the maxima of $S(q,\omega)$ as a function of q. The lower frequency peaks are denoted by ◇, and the higher frequency peaks by ○. Also shown are the corresponding results from Ref. 1 (*) and Ref. 3 (□).

Figure 2 shows the positions of the maxima of $S(q,\omega)$ as a function of q. Also shown in the figure are the lower frequency peaks in $S(q,\omega)$ from Refs. 1 and 3.

Comparing with known ω values for q-independent modes in water, we find that the value of the low frequency q-independent peak in $S(q,\omega)$ corresponds to the O–O–O bending mode at 60 cm^{-1} or 11 ps^{-1}. We have confirmed this by calculating the "self" part of $S(q,\omega)$. We are thus led to conclude that the association of this peak for q close to q_0 with normal sound in Refs. 1 and 3 was due to its fortuitous observation in a very small q range, yielding a velocity close enough to the normal sound velocity. Since these were the only studies where normal sound and the higher frequency sound propagation had been observed simultaneously, our result leaves the interpretation of the higher frequency mode more open. In particular, the possibility that this mode is a continuation of the normal sound mode, with positive dispersion accounting for the higher velocity, would seem to be more plausible.[4]

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[8] The molecular self-diffusion in water [controlling the width of the quasi-elastic peak in $S(q,\omega)$] has a strong temperature and density dependence. At ambient pressure the diffusion coefficient appears to vanish at 227 K. See C. A. Angell, in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1981), Vol. 7. The density dependence is also discussed in A. Geiger, P. Mausbach, and J. Schnitker, in *Water and Aqueous Solutions*, edited by G. W. Neilson and J. E. Enderby (Adam Hilger, Bristol, 1986).

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