Collective Dynamical Properties of Liquid Water

M. A. Ricci
Dipartimento di Fisica, Università della Calabria, Rende, Italy

D.Rocca
Dipartimento di Fisica, Università "La Sapienza", Roma, Italy

G. Ruocco
Dipartimento di Fisica, Università di L'Aquila, L'Aquila, Italy

R. Vallauri
Istituto di Elettronica Quantistica del Consiglio Nazionale delle Ricerche, Firenze, Italy

(Received 16 March 1988)

A theoretical and computer simulation analysis suggests that two collective modes can propagate in liquid water for wave vectors $k > 0.64$ Å^{-1}. The low-frequency mode (ordinary sound) turns out to be associated with the oxygen density fluctuations, whereas the hydrogen density fluctuations are found to be governed by both modes, thus indicating that the high-frequency collective motion is related to fast librational oscillations. This allows a simply physical interpretation of the existing experimental and computer simulation data.

PACS numbers: 61.20.Ja, 62.12.Bt

The study of collective dynamical properties of liquid water has received great attention in recent years. The dynamical structure factor of D_2O has been measured by Bosi *et al.*[1] and Teixeira *et al.*[2] Moreover, a computer simulation (CS) has been used to evaluate the density-density correlation function by adopting different potential modes,[3-5] and its Fourier transform has been compared with the experimental data. The present seemingly confused situation is summarized in Fig. 1, where the peak frequency of $S(k,\omega)$ is reported as a function of the wave vector k (dispersion relation).

Rahman and Stillinger,[3] using a four-point-charge potential model superimposed to a Lennard-Jones interaction between oxygens, found that the calculated $S(k,\omega)$ (Fourier transform of the center-of-mass density correlation function), presents two distinct peaks, which yield two branches in the dispersion relation, the lower one corresponding to ordinary sound propagation. These data are in quantitatively good agreement with the behavior of $\omega(k)$ measured by Bosi *et al*[1] in a neutron-scattering experiment performed with low incident flux, which prevented any measurement at high frequencies. The second branch found by Rahman and Stillinger[3] at higher frequency, on the other hand, lies on the curve reported by Teixeira *et al.*,[2] who measured $S(k,\omega)$ with an experimental setup which allows only the measurement of the high-frequency region of the spectrum. The fourth set of data was obtained by Wojcik and Clementi,[5] who performed a CS using the so-called Matsuoka-Clementi-Yoshimine (MCY) potential[6] which consists of three atom-atom potentials supplemented by the electrostatic interaction between charges $-\frac{1}{2}Q$ at the H sites and Q placed on the main symmetry axis at a distance δ from the O atom. In extracting $S(k,\omega)$ from the same correlation function evaluated by Rahman and Stillinger,[3] by a suitable version of the maximum entropy method, MCY found that only one peak is present,

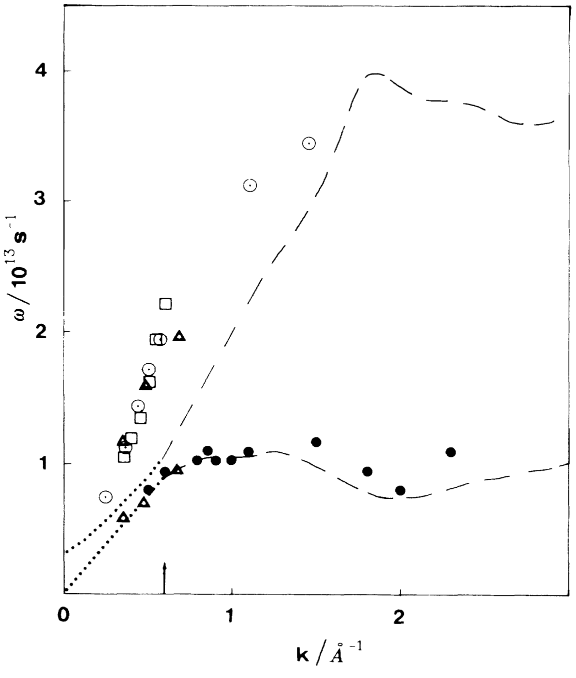

FIG. 1. Peak frequency of $S(k,\omega)$ as a function of the wave vector k; filled circles: experimental data from Ref. 1, open squares: experimental data from Ref. 2, open triangles: CS results from Ref. 3, open circles: CS results from Ref. 5. Lower and upper dashed lines represent the results of the present theoretical investigation, $\omega_1(k)$ and $\omega_2(k)$. The arrow indicates the smaller k value ($k_{\min} = 0.64$ Å^{-1}) accessible to our CS.

whose k evolution lies on the upper branch (higher frequency). This result is in agreement with a CS reported by Impey, Madden, and McDonald (obtained by using the same MCY potential), as well as with the experimental findings of Teixeira *et al.*[2] The physical interpretation of these results, given by various authors, leads to two distinct pictures of the collective properties of liquid water. From one side, Rahman and Stillinger[3] and Teixeira *et al.*[2] assert that their results indicate the presence of a fast sound mode ($c \approx 3300$ m/s) associated with the density fluctuations of the light species (H). Similar behavior has been found in a different context by Bosse *et al.*[7] in a $\mathrm{Li_{0.8}Pb_{0.2}}$ alloy. Their CS and theoretical analysis has shown that an additional propagating collective mode (which is supported by the light particles alone), confined to high frequencies and large wave vectors, can exist. On the other side, Wojcik and Clementi[5] interpreted their results in the framework of generalized hydrodynamics, concluding that the ω vs k dependence can be understood as a consequence of positive dispersion. However, this interpretation overlooks the experimental data of Ref. 1.

In order to shed some light on the physical interpretation of the existing data and eventually arrive at an unambiguous view of the dynamical processes involved in neutron scattering from liquid water, we have performed a theoretical and a CS study to ascertain: (i) whether a high-frequency mode can propagate in liquid water and (ii) what is the physical nature of such a mode.

The theoretical approach is based upon the Mori-Zwanzig[8] formalism applied to a two component dynamical variable

$$\rho_k(t) = \begin{bmatrix} \rho_k^{(\mathrm{O})}(t) \\ \rho_k^{(\mathrm{H})}(t) \end{bmatrix},$$

where $\rho_k^{(\mathrm{O})}(t)$ and $\rho_k^{(\mathrm{H})}(t)$ are the spatial Fourier transforms of the density fluctuations of the O and H atoms, respectively, i.e.,

$$\rho_k^{(\mathrm{O})}(t) = \textstyle\sum_i \exp\{-i\mathbf{k}\cdot\mathbf{r}_i^{(\mathrm{O})}(t)\} - (2\pi)^3 N/V\delta(k),$$

$$\rho_k^{(\mathrm{H})}(t) = \textstyle\sum_i (\exp\{-i\mathbf{k}\cdot\mathbf{r}_i^{(\mathrm{H_1})}(t)\} + \exp\{-i\mathbf{k}\cdot\mathbf{r}_i^{(\mathrm{H_2})}(t)\}) - (2\pi)^3 2N/V\delta(k),$$

where $\mathbf{r}^{(\mathrm{O})}(t)$, $\mathbf{r}^{(\mathrm{H_1})}(t)$, and $\mathbf{r}^{(\mathrm{H_2})}(t)$ represent the vector positions of the individual O and H atoms of molecule i. The sum runs over the N molecules of the system confined in a volume V. In the following calculation, as well as in the CS, the molecule is supposed to be rigid and its geometry is schematically shown in Fig. 2. Within this theoretical framework, the correlation function matrix $\mathbf{C}(k,t) = \langle \rho_k(t)\cdot\rho_k^\dagger(0)\rangle$ obeys the generalized Langevin equation

$$\frac{d}{dt}\mathbf{C}(k,t) = -\int_0^t d\tau\, \mathbf{C}(k,t-\tau)\cdot\mathbf{K}(k,\tau), \tag{1}$$

where $\mathbf{K}(k,\tau)$ represents the memory function matrix.

In terms of a Laplace transform Eq. (1) reads

$$\hat{\mathbf{C}}(k,z) = [z\mathbf{I} + (z\mathbf{I} + \hat{\mathbf{K}}'(k,z))^{-1}\cdot\mathbf{K}(k,0)]^{-1}\cdot\mathbf{C}(k,0), \tag{2}$$

with $\hat{\mathbf{K}}'(k,z)$ the Laplace transform of the memory function matrix of $\mathbf{K}(k,t)$ and $\mathbf{I}$ the unit matrix. In Eq. (2),

$$\mathbf{K}(k,0) = \langle \dot{\rho}_k(0)\cdot\dot{\rho}_k^\dagger(0)\rangle\cdot\langle \rho_k(0)\cdot\rho_k^\dagger(0)\rangle^{-1}.$$

The evaluation of these matrix elements, although lengthy, is straightforward, and details of this calculation will be reported elsewhere. $\mathbf{C}(k,0)$ expresses the $t=0$ value of the correlation matrix, which is given in terms of the partial structure factors, namely,

$$C_{11}(k,0) = \langle \rho_k^{(\mathrm{O})}(0)\rho_{-k}^{(\mathrm{O})}(0)\rangle = NS_{\mathrm{OO}}(k) = N\left[1 + (N/V)\int d^3r \exp\{i\mathbf{k}\cdot\mathbf{r}\}[g_{\mathrm{OO}}(r) - 1]\right], \tag{3a}$$

$$C_{12}(k,0) = C_{21}(k,0) = \langle \rho_k^{(\mathrm{O})}(0)\rho_{-k}^{(\mathrm{H})}(0)\rangle = 2NS_{\mathrm{OH}}(k) = 2N\left[\frac{\sin(kr_{\mathrm{OH}})}{kr_{\mathrm{OH}}} + (N/V)\int d^3r \exp\{i\mathbf{k}\cdot\mathbf{r}\}[g_{\mathrm{OH}}(r) - t]\right], \tag{3b}$$

$$C_{22}(k,0) = \langle \rho_k^{(\mathrm{H})}(0)\rho_{-k}^{(\mathrm{H})}(0)\rangle = 4NS_{\mathrm{HH}}(k) = 4N\left[\frac{1}{2} + \frac{\sin(ka)}{2ka} + (N/V)\int d^3r \exp\{i\mathbf{k}\cdot\mathbf{r}\}[g_{\mathrm{HH}}(r) - 1]\right]. \tag{3c}$$

In $(3a)$–$(3c)$, the $g_{\alpha\beta}(r)$ represent the various pair distribution functions and the other symbols are defined in Fig. 2. By neglecting the damping [i.e., $\hat{\mathbf{K}}'(k,z) \equiv 0$], one can obtain the eigenfrequencies of the system by finding the solutions $\omega_1(k)$ and $\omega_2(k)$ (with $z = i\omega$) of the secular equation $\det[\mathbf{K}(\mathbf{k},0) - \mathbf{I}\omega^2] = 0$.

In order to understand the physical nature of the two solutions, we perform the limit as $k \to 0$ (hydrodynamic regime); one obtains:

$$\omega_1^2(k) = \frac{k_{\mathrm{B}}T}{M}\frac{1}{S(0)}k^2, \tag{4a}$$

$$\omega_2^2(k) = \frac{2}{3}\frac{k_{\mathrm{B}}t}{I}h^2\frac{1}{S''(0)} + \mathrm{const}\,k^2. \tag{4b}$$

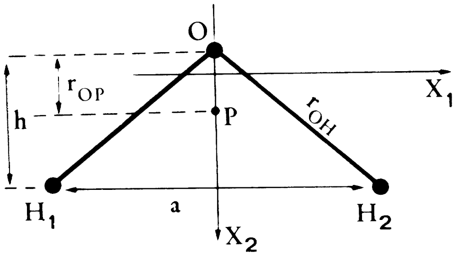

FIG. 2. Schematic representation of the water molecule. X_1 and X_2 represent the two coplanar principal axes. P indicates the position where the negative charge of the TIP4P potential model is located. The values of the parameters are: $a = 1.51$ Å, $h = 0.586$, Å, $r_{OH} = 0.957$ Å, and $r_{OP} = 0.15$ Å.

In Eq. (4a) M is the mass of the molecule and $S(0) = S_{OO}(0) = S_{HH}(0) = S_{OH}(0)$ is the $k=0$ value of the partial structure factors, which are all coincident, and related to the isothermal compressibility χ_T [$S(0) = \rho k_B T \chi_T$]. The first solution $\omega_1(k)$ gives the ordinary-sound dispersion law with a velocity of sound $c_0 = [M\rho\chi_T]^{-1/2}$ dependent on the isothermal instead of adiabatic compressibility because energy fluctuations have not been taken into account. In Eq. (4b) one has $I^{-1} = I_1^{-1} + I_3^{-1}$, where I_1, I_2, and $I_3 = I_1 + I_2$ are the moments of inertia referred to the principal axes of the molecule (see Fig. 2), and $S''(0)$ is defined as $S''_{OO}(0) + S''_{HH}(0) - 2S''_{OH}(0)$, where $S''_{\alpha\beta}(0)$ indicates the second derivative of $S_{\alpha\beta}(k)$ with respect to k, evaluated at $k=0$. Therefore, in this limit, the second solution has a finite value which depends upon the moments of inertia of the molecule, thus indicating that the second mode is related to the collective rotational motion of the molecules in the system. This second propagating mode will be shown to be connected with the motion of H atoms, having negligible influence on the collective dynamics of the O density fluctuations.

In order to find the k dependence of the two solutions, we have performed a CS of liquid water to evaluate the partial structure factors. The interaction potential (TIP4P[9]) used in the simulation is modeled by two positive charges over the H atoms ($q = 0.52e$), a negative charge ($q = -1.04e$) on the site P shown in Fig. 2, plus a Lennard-Jones interaction between the O sites ($\sigma = 0.3154 \times 10^{-9}$ m, $\epsilon = 0.1077 \times 10^{-20}$ J). The simulation is carried out on a system of 256 molecules at a temperature $T = 309$ K and a density $\rho = 10^3$ Kg/m^3, so that the cubic box length is $L = 18.71$ Å. The time step is 10^{-15} s and the averages are obtained over a run of 10000 steps.

The results for $\omega_1(k)$ and $\omega_2(k)$ are reported in Fig. 1; the lower k value accessible to our CS is $k_{\min} = 0.64$ Å^{-1} so that the extrapolations to lower wave vectors are somehow arbitrary and have been indicated by dotted lines. As is apparent the lower frequency branch $\omega_1(k)$ follows closely the experimental values of Bosi *et al.*[1] as well as the Rahman and Stillinger[3] CS data. It extrapolates to zero k with a slope which is in good agreement with the ordinary sound velocity $c_0 \approx 1500$ m/s. The high-frequency branch $\omega_2(k)$ appears to be markedly distinct from the lower one, reaching a plateau value at $k = 2$ Å^{-1} which is 4 times higher than the plateau of $\omega_1(k)$. Although the comparison with the existing high-frequency data shows only qualitative agreement, the present calculation, in any case, demonstrates that a high-frequency mode can propagate in the system. This conclusion is reinforced by the analysis of the contributions of the two modes to the O and H density correlation functions. If one writes

$$C_{11}(k,t) = \langle \rho_k^{(O)}(t)\rho_{-k}^{(O)}(0)\rangle = NS_{OO}(k)\{I_{OO}^{(1)}(k)\cos[\omega_1(k)t] + I_{OO}^{(2)}(k)\cos[\omega_2(k)t]\},$$

$$C_{22}(k,t) = \langle \rho_k^{(H)}(t)\rho_{-k}^{(H)}(0)\rangle = 4NS_{HH}(k)\{I_{HH}^{(1)}(k)\cos[\omega_1(k)t] + I_{HH}^{(2)}(k)\cos[\omega_2(k)t]\},$$

the quantities $I_{\alpha\beta}^{(j)}(k)$ give the relative weight of the jth mode to the particular density correlation function and can be easily evaluated from Eq. (2). Again it is worthwhile to examine their behavior as $k \to 0$: One finds that $I_{OO}^{(2)}(k \to 0) = I_{HH}^{(2)}(k \to 0) = 0$. This exact result is encouraging since it is physically plausible. Indeed, at long wavelengths the position of the reference point over the molecule becomes inessential and one regains the hydrodynamic results: only one mode with $\omega(k \to 0) = c_0 k$ can propagate, since the higher-frequency one is completely depleted. The k dependence of the intensities, which is reported in Fig. 3, is also illuminating. First of all we notice that $I_{OO}^{(2)}(k)$ is virtually zero at all k's, thus indicating that the O density fluctuations are propagating according to the lower-frequency mode $\omega_1(k)$. On the contrary, $I_{HH}^{(2)}(k)$ increases as k increases, so that a fast modulation of the H density fluctuations becomes of major importance at

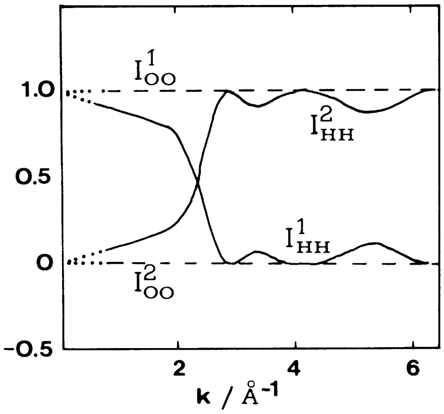

FIG. 3. k dependence of the amplitudes of the two modes in the oxygen (dashed lines) and hydrogen (solid lines) density correlation functions for the low-frequency mode $I^{(1)}(k)$ and the fast-frequency mode $I^{(2)}(k)$.

larger wave vectors [and, of course, is detected in the experimentally measured $S(k,\omega)$]. This result naturally leads to the physical interpretation that the high-frequency mode is related to the rapid collective librational motion of H atoms, which can exist only on a finite length scale and cannot be present at long wavelengths.

In conclusion, the analysis of collective dynamical properties of liquid water in terms of a two-variable theory, which accounts for the density fluctuations of the two species (oxygen and hydrogen) forming a water molecule, suggests that two collective modes can be supported by the system, one of which is strictly related to the number density fluctuations and gives the proper behavior of the system in the hydrodynamic regime ($k \rightarrow 0$). The second one involves a higher-frequency oscillation and is related to the faster collective librational motion of hydrogen atoms, which occurs on a shorter length scale. The possibility of detecting this fast sound mode by a coherent neutron-scattering experiment is, of course, much hampered by the fact that the damping of this wave can be very high, as already stressed by the experimental results[2] which show that the width at half-height of the second mode becomes comparable with the frequency shift at $k \approx 0.6$ Å^{-1}. Nevertheless, we believe that the present investigation allows one to interpret the experimental and the CS data on physical grounds, having pointed out the dynamical properties underlying the propagating density fluctuations.

The authors wish to thank Dr. U. Balucani and Professor S. W. Lovesey for many stimulating discussions. Part of the computing time was made available under convention between CNR (Consiglio Nazionale delle Ricerche) and CINECA (Centro Interuniversitario di Calcolo Automatico).

[1] P. Bosi, F. Duprè, F. Menzinger, F. Sacchetti, and M. C. Spinellli, Lett. Nuovo Cimento **21**, 436 (1978).

[2] J. Teixeira, M. C. Bellissent-Funel, S. H. Chen, and B. Dorner, Phys. Rev. Lett. **54**, 2681 (1985).

[3] A. Rahman and F. H. Stillinger, Phys. Rev. A **10**, 368 (1974).

[4] R. W. Impey, P. A. Madden, and I. R. McDonald, Mol. Phys. **46**, 513 (1982).

[5] M. Wojcik and E. Clementi, J. Chem. Phys. **85**, 6085 (1986).

[6] O. Matsuoka, E. Clementi, and M. Yoshimine, J. Chem. Phys. **64**, 2314 (1976).

[7] J. Bosse, G. Jacucci, M. Ronchetti, and W. Schirmacher, Phys. Rev. Lett. **57**, 3277 (1986).

[8] B. J. Berne, in *Statistical Mechanics,* edited by B. J. Berne (Plenum, New York, 1977), P. B, p. 233.

[9] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, J. Chem. Phys. **79**, 926 (1983); M. A. Ricci, G. Ruocco, and M. Sampoli, to be published.