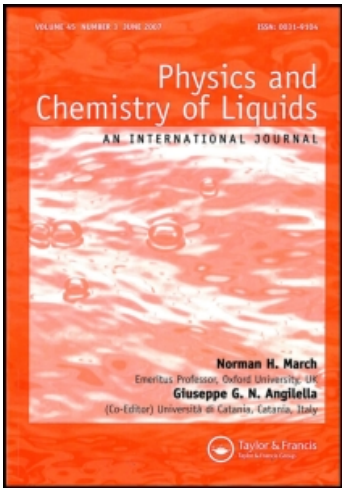

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Viscoelastic Model for the Transition from Normal to Fast Sound in Water

V. Tozzini[a]; M. P. Tosi[b]
[a] Istituto Nazionale di Fisica della Materia and Classe di Scienze, Pisa, Italy [b] International Centre for Theoretical Physics, Trieste, Italy

To cite this Article Tozzini, V. and Tosi, M. P.(1996) 'Viscoelastic Model for the Transition from Normal to Fast Sound in Water', Physics and Chemistry of Liquids, 33: 3, 191 — 198
To link to this Article: DOI: 10.1080/00319109608039820
URL: http://dx.doi.org/10.1080/00319109608039820

Phys. Chem. Liq., 1996, Vol. 33, pp. 191–198
Reprints available directly from the publisher
Photocopying permitted by license only

Letter

VISCOELASTIC MODEL FOR THE TRANSITION FROM NORMAL TO FAST SOUND IN WATER

V. TOZZINI[a] and M. P. TOSI[b]

[a]*Istituto Nazionale di Fisica della Materia and Classe di Scienze, Scuola Normale Superiore, I-56126 Pisa, Italy;* [b]*International Centre for Theoretical Physics, P. O. Box 586, I-34014 Trieste, Italy*

(Received 9 July 1996)

The cross-over from hydrodynamic to fast sound in water at 5 C has recently been mapped experimentally by means of inelastic X-ray scattering. We show that a viscoelastic model gives a good account of both the longitudinal-current autocorrelation function and the dynamic structure factor in the region of the cross-over. Evidence is also given for a weakly dispersing excitation observed in these experiments being a liquid state remnant of an oxygen-related optic mode in ice.

Keywords: Dynamical structure of liquids; vibrational modes in disordered systems

The propagation of sound in water has received much attention since a molecular dynamics study by Rahman and Stillinger [1] showed that the spectrum of density fluctuations in a mesoscopic region of wave number k exhibits a secondary maximum at a much higher frequency than that appropriate to hydrodynamic sound. The so-called high-frequency sound has been the object of several other studies by molecular dynamics [2–4] and has been observed in liquid D_2O by neutron inelastic scattering [5] and in liquid H_2O by high-resolution X-ray scattering [6]. By the latter technique it has also been demonstrated that sound waves with wavelength in the range between 0.5 and 3 nm propagate at the same velocity in water and ice [7]. Very recently Sette *et al.* [8] have used X-rays with even higher energy resolution to follow the evolution of excitations in the longitudinal acoustic-like dynamics of water as their velocity of propagation goes from 2000 m/s at $k = 1\ \mathrm{nm}^{-1}$ to the fast

sound value $v_\infty = 3200$ m/s at $k \geqslant 4$ nm^{-1}. This experiment provides almost a full mapping of the cross-over from hydrodynamic to high-frequency sound, the former having speed $v_0 = 1500$ m/s approximately.

The main purpose of the present letter is to examine the inelastic scattering spectrum of water in the region of the cross-over with the help of a simple viscoelastic model for density fluctuations [9]. As in much previous work on the dynamical structure of classical liquids including water [4], the model is first applied to describe the autocorrelation spectrum of longitudinal current density fluctuations. Closer contact with the data is then made by applying the model directly to describe the dynamic structure factor of water in the mesoscopic region of wave number and frequency where the cross-over from hydrodynamic to fast sound occurs. We also discuss the origin of a weakly dispersing spectral component which was observed in the X-ray scattering experiments outside the region of the cross-over.

The viscoelastic model yields for the density response function $\chi(k,\omega)$ of the fluid the expression

$$\chi(k,\omega) = \frac{nk^2}{m}\left[\omega^2 - \omega_0^2(k) + i\omega\frac{\omega_\infty^2(k) - \omega_0^2(k)}{-i\omega + 1/\tau(k)}\right]^{-1} \tag{1}$$

where n is the number density, m is the molecular mass and $\omega_0(k)$, $\omega_\infty(k)$ and $\tau(k)$ are three k-dependent parameters of the dynamics of the fluid. In the present case we set $\omega_\infty(k) = v_\infty k$ and $\omega_0(k) = v_0 k$, while we treat $\tau(k)$ as a phenomenological relaxation time to be obtained from a fit of the inelastic X-ray scattering data.

Equation (1) leads via the fluctuation-dissipation theorem to the following expression for the longitudinal-current autocorrelation function $C_L(k,\omega)$ in the classical limit,

$$C_L(k,\omega) = \frac{2k_B T k^2}{m}\frac{\omega^2\tau(k)[\omega_\infty^2(k) - \omega_0^2(k)]}{[\omega^2 - \omega_0^2(k)]^2 + [\omega\tau(k)]^2[\omega_\infty^2(k) - \omega^2]^2} \tag{2}$$

The peak frequency $\bar{\omega}(k)$ of this function and the relaxation time are related to each other by

$$\tau^2(k) = \frac{\bar{\omega}^4(k) - \omega_0^4(k)}{2\bar{\omega}^4(k)[\omega_\infty^2(k) - \bar{\omega}^2(k)]} \tag{3}$$

and for frequencies $\omega \approx \bar{\omega}(k)$ the longitudinal-current spectrum takes the Lorentzian form

$$C_L(k,\omega) = \frac{2k_B T k^2}{m} \frac{\bar{\omega}^2(k)\,\tau(k)\,[\omega_\infty^2(k) - \omega_0^2(k)]}{[\omega^2 - \bar{\omega}^2(k)]^2 + \omega^2 \Gamma^2(k)}. \tag{4}$$

A dispersion relation having the simple form

$$\bar{\omega}(k) = k\left[v_\infty + \frac{v_0 - v_\infty}{1 + (k/k_0)^2}\right] \tag{5}$$

ensures that the width parameter $\Gamma(k)$ is proportional to k^2 in the long wavelength limit, as is appropriate in the Brillouin scattering regime [10], and tends to a constant for $k \to \infty$.

Figure 1 reports the observed peak frequencies for the acoustic-like dynamics of water in the X-ray scattering experiments of Sette *et al.*, [6, 8] together with the two limiting linear dispersion curves for hydrodynamic and fast sound and with the fit of the observed peak frequencies given by eqn (5) with the fitting parameter k_0 chosen to have the value $k_0 = 2.0\ \mathrm{nm}^{-1}$ over the whole range of wave number up to $10\ \mathrm{nm}^{-1}$. A clearer view of the goodness of the fit can be obtained from Figure 2a, which compares the curve resulting from the fit for the k-dependent sound velocity $v(k) \equiv \bar{\omega}(k)/k$ with the scattering data. The curve in Figure 2b shows the corresponding values of $\tau(k)$ from eqn (3). Finally, the inset in Figure 1 reports the calculated values of $\bar{\omega}(k)\tau(k)$, showing that this quantity increases towards and above unity as the wave number increases from 1 to $4\ \mathrm{nm}^{-1}$ across the transition from hydrodynamic to high-frequency sound.

From the continuity equation the longitudinal-current spectrum $C_L(k,\omega)$ is related to the dynamic structure factor $S(k,\omega)$ by $C_L(k,\omega) = \omega^2 S(k,\omega)$. Of course, the dominant feature in the measured $S(k,\omega)$ is its central quasi-elastic peak, which Sette *et al.* [6, 8] represent by a Lorentzian curve in order to isolate the contribution coming from the collective sound-wave excitation. In the viscoelastic model we write

$$S(k,\omega) = \frac{2\hbar k^2}{m}[n(\omega) + 1] \frac{\omega\tau(k)\,[\omega_\infty^2(k) - \omega_0^2(k)]}{[\omega^2 - \omega_0^2(k)]^2 + [\omega\tau(k)]^2\,[\omega_\infty^2(k) - \omega^2]^2} \tag{6}$$

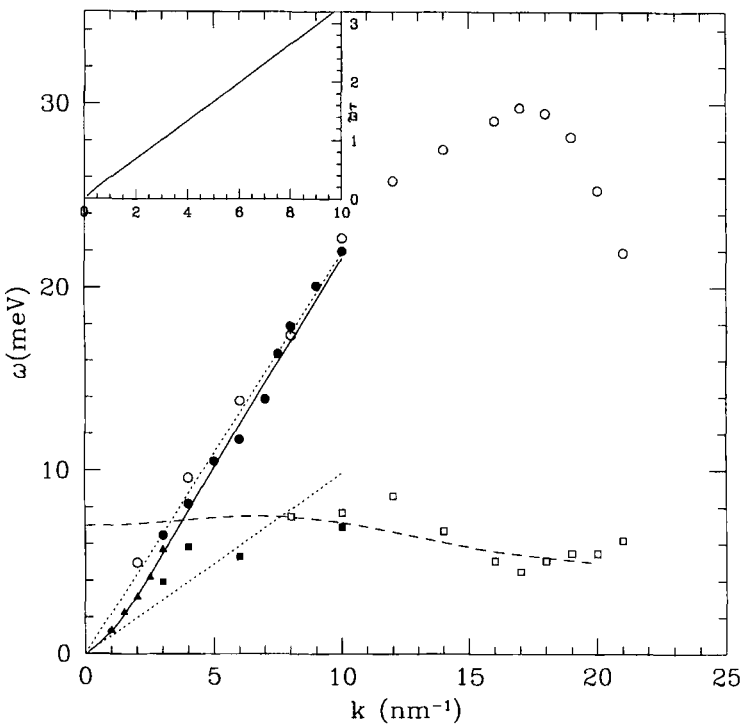

FIGURE 1 Excitations in water and ice of relevance to the present discussion. Acoustic-like peak frequencies measured in X-ray inelastic scattering experiments are shown as triangles (from ref. 8) and as filled circles (from ref. 6) for water and as empty circles (from ref. 7) for ice. The short-dashed straight lines show the dispersion relations for hydrodynamic and fast sound. The filled squares report the peak frequencies of a weakly dispersive mode observed in water, while the empty squares refer to a transverse optic phonon in ice (from ref. 8). The long-dashed curve shows our results for an oxygen-related transverse optic mode in polycrystalline ice, after reduction to the first Brillouin zone. The inset reports the values of $\bar{\omega}\tau$ from the viscoelastic model for the longitudinal-current autocorrelation function.

with $n(\omega)$ the Planck distribution factor. The low-frequency expansion of eqn (6) reads

$$S_{qe}(k,\omega) \approx 2k_B T k^2 \tau(k) \frac{\omega_\infty^2(k) - \omega_0^2(k)}{\omega_0^4(k)}$$

$$\left[1 + \omega^2 \frac{\omega_\infty^4(k)\tau^2(k) - 2\omega_0^2(k)}{\omega_0^4(k)}\right]^{-1} \tag{7}$$

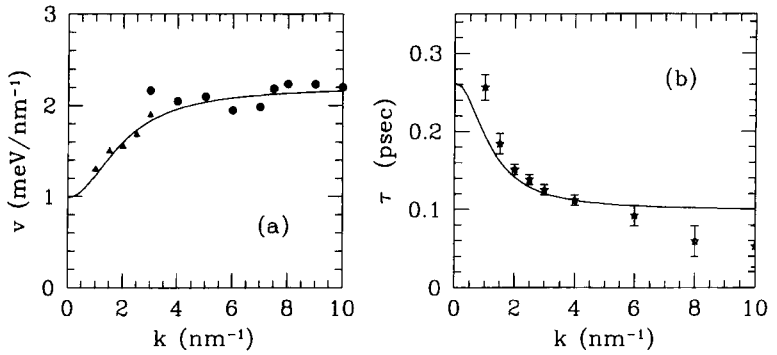

FIGURE 2 Velocity $v(k) \equiv \bar{\omega}(k)/k$ of acoustic-like excitations in water (a) and viscoelastic relaxation time $\tau(k)$ (b) *versus* wave number k. The curves are from our analysis of the longitudinal-current spectrum. Triangles and dots in (a) are from the X-ray scattering experiments reported in ref. 8 and in ref. 6, respectively. Stars with estimated error bars in (b) are from the sound-wave component of the dynamic structure factor $S(k,\omega)$.

The difference $S_{sw}(k,\omega) = S(k,\omega) - S_{qe}(k,\omega)$ gives the model expression for the contribution of the sound wave excitation to the scattering cross section, allowing $\tau(k)$ to be redetermined by fitting either the position of the peak in $S_{sw}(k,\omega)$ or its width to the data on the side peak in the measured scattering cross section. These two alternative procedures yield very similar results, which are reported in Figure 2b as stars with estimated error bars and compared with our earlier determination of $\tau(k)$ from $C_L(k,\omega)$. Figure 3 reports the viscoelastic $S(k,\omega)$ as well as its quasielastic and sound-wave components at $k = 2.5\ \text{nm}^{-1}$ and $k = 4\ \text{nm}^{-1}$. The latter component is seen to be in excellent agreement with the X-ray scattering data, whereas the width of the quasi-elastic component tends to be overestimated in the viscoelastic model.

We turn next to the transverse optic phonon measured by Sette *et al* [8] in ice. Its relatively low frequency (see empty squares in Fig. 1) indicates that it is associated with relative motions of the molecules within the lattice cell. To evaluate its dispersion curve we use the density functional approach developed in earlier work [11] on alkali halides, expressing the mode frequency in terms of the centre-of-mass-centre-of-mass (essentially oxygen-oxygen) structure factor $S_{CC}(k)$ in water near freezing and of the Debye-Waller factor in ice. For simplicity we replace the I_h structure of ice by the diamond structure, containing two molecules

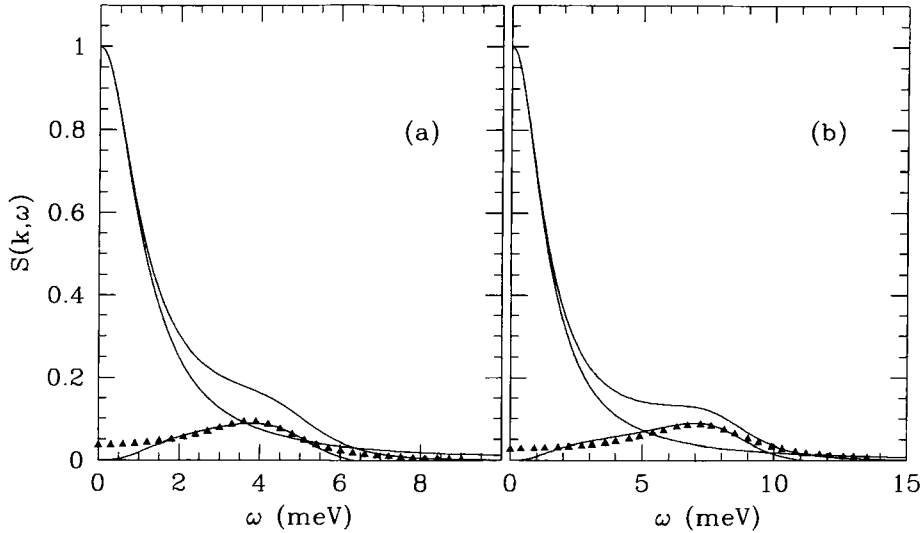

FIGURE 3 Dynamic structure factor $S(k,\omega)$ of water versus frequency ω at values of the wave number $k = 2.5\ \text{nm}^{-1}$ (a) and $k = 4\ \text{nm}^{-1}$ (b). The full curves report the viscoelastic structure factor and its quasi-elastic and sound-wave components. The triangles show the sound-wave component reported in ref. 8 from a damped-harmonic-oscillator fit of the X-ray scattering data. The theoretical curves are normalized by the condition $S(k,0) = 1$, while the data have been normalized to agree with the theoretical result at the peak frequency.

per unit cell. The expression for the dispersion relation of the mode within the first Brillouin zone is

$$\omega_T^2(q) = \sum_G \frac{1}{2}[1 - \cos(\mathbf{G}\cdot\mathbf{d})] \int d\Omega(\mathbf{q}) F(|\mathbf{q}+\mathbf{G}|)[(\mathbf{q}+\mathbf{G})\cdot\hat{\varepsilon}_q]^2$$

$$- \sum_{G\neq 0} \frac{G^2}{6}[1 + \cos(\mathbf{G}\cdot\mathbf{d})] F(G) \tag{8}$$

where

$$F(k) = \frac{n_s k_B T}{n_l M}\left[\frac{1}{S_{CC}(k)} - 1\right]\exp(-d^2 L^2 k^2/3) \tag{9}$$

In these equations n_s and n_l are the number densities of ice and water, **M** is the molecular mass, **G** are the reciprocal lattice vectors of the f.c.c lattice, **d** is the vector joining first neighbours within the unit cell, $\hat{\varepsilon}_q$ is the eigenvector of the mode and L is the Lindemann parameter of ice, for which we have adopted the classical value $L \approx 0.17$. Equation (8) contains an angular average over the direction of the wave number **q**, accounting for the fact that the measurements were taken on polycrystalline ice.

The calculated dispersion curve is given by the long-dashed curve in Figure 1. It is seen there that the results agree with the measured frequencies in ice and are only somewhat higher than the frequencies of the weakly dispersive mode observed in the X-ray scattering experiments on water (filled squares). This provides evidence that the weakly dispersive mode in water is a liquid-state remnant of the intermolecular transverse optic mode in ice, as suggested by Sette *et al.*[8].

In summary, we have shown that a simple viscoelastic model gives a satisfactory description of the observations on the cross-over from hydrodynamic to fast sound in water. Consistent values for the viscoelastic relaxation time τ governing the transition from the hydrodynamic regime $\omega\tau \ll 1$ to the high-frequency regime $\omega\tau \gg 1$ have been obtained from alternative determinations based on the longitudinal-current correlation spectrum and on the full dynamic structure factor. Remnants of the collective excitations of ice are seen to persist across melting both in the longitudinal acoustic-like dynamics and in the transverse oxygen-related dynamics of water.

Acknowledgements

One of us (VT) wishes to thank Giancarlo Ruocco for providing the X-ray scattering data prior to publication and for useful discussions.

References

[1] Rahman, A. and Stillinger, F. H. (1974). *Phys. Rev. A*, **10**, 368.
[2] Impey, R. W., Madden, P. A. and McDonald, I. R. (1982). *Molec. Phys.*, **46**, 513.
[3] Balucani, U., Ruocco, G., Torcini, A. and Vallauri, R. (1993). *Phys. Rev. E*, **47**, 1677.
[4] Sciortino, F. and Sastry, S. (1994). *Molec. Phys.*, **100**, 3881.
[5] Teixeira, J., Bellissent-Funel, M. C., Chen, S. and Dorner, B. (1985). *Phys. Rev. Lett.*, **54**, 2681.
[6] Sette, F., Ruocco, G., Krisch, M., Bergmann, U., Masciovecchio, C., Mazzacurati, V., Signorelli, G. and Verbeni, R. (1995). *Phys. Rev. Lett.*, **75**, 850.
[7] Ruocco, G., Sette, F., Bergmann, U., Krisch, M., Masciovecchio, C., Mazzacurati, V., Signorelli, G. and Verbeni, R. (1996). *Nature*, **379**, 521.
[8] Sette, F., Ruocco, G., Krisch, M., Masciovecchio, C., Verbeni, R. and Bergmann, U. *Phys. Rev. Lett.*, **77**, 83.
[9] See, for instance Copley, J. R. D. and Lovesey, S. L. (1975). *Repts. Progr. Phys.*, **38**, 461.
[10] Teixeira, J. and Leblond, J. (1978). *J. Phys. (Paris,)* **39**, L-83.
[11] Tozzini, V. and Tosi, M. P. (1995). *Phil. Mag.* B **72**, 577.