

## Neutron scattering from polycrystalline ice (Ih): Some keys to understanding the collective behavior of liquid water

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(Received 4 March 1993)

The phonon dispersion in the second Brillouin zone of polycrystalline ice (Ih) has been measured. The results confirm the predictions of a previous lattice-dynamics calculation [A. Criado, F. J. Bermejo, M. García-Hernández, and J. L. Martínez, *Phys. Rev. E* **47**, 3516 (1993)] where anomalously steep dispersion curves of an apparent acoustic origin were found. The relevance of the present findings for explaining some apparently anomalous features concerning the collective dynamics of liquid water is finally discussed.

PACS number(s): 61.20.-p, 64.70.-p

The possible existence of “fast-sound” modes in liquids composed by particles with disparate masses has recently been the focus of a considerable research effort from theoretical [1], computer simulation [2], and experimental [3] approaches. Because of the rather different atomic masses of its constituent atoms, liquid water was early expounded as a suitable candidate for the detection of these modes of “kinetic” origin [2]. As a matter of fact, computer molecular-dynamics (MD) simulations [4–7], evidenced from the very outset [4] the presence of steep dispersion curves of an apparent sonic origin, a fact which led some authors [8] to interpret their experimental findings as evidences of such phenomenon.

On the other hand, calculations based upon the Mori formalism [7, 9] have shown that a dispersion curve reminiscent of those calculated for simple liquids (i.e., leading to the true hydrodynamic value for the sound velocity) results from plots of the eigenmode frequencies versus wave vector, while the steep dispersion still appears in plots of the maxima of the scattering functions calculated from the analysis of the MD trajectories.

Led by previous experience with the analysis of inelastic-neutron-scattering spectra (INS) of relatively complex liquids [10] and glasses [11], where it became clear that the origins of such anomalously steep curves were caused by the mixing of excitations of optical origin with truly acoustic modes due to the orientational averaging, a lattice-dynamics (LD) calculation for a polycrystalline form of solid water [12] was recently carried out. As a result, it was shown that plots of the frequencies cor-

responding to the maxima of either the  $S(Q, \omega)$  dynamic structure factors, or those appearing in the current-current autocorrelation function  $J_I(Q, \omega) = \frac{\omega^2}{Q^2} S(Q, \omega)$  (frequently used to display the results calculated by MD) versus wave vector, revealed a pattern of frequencies far exceeding those corresponding to a prolongation of hydrodynamic sound. In fact, as probed in a previous study [12], the shape of the “dispersion curves” calculated by such a procedure was reminiscent of those reported for liquid water, once the appropriate softening of the elastic constants are taken into account.

Because of the steepness of the calculated dispersions [12], direct measurement of the polycrystalline  $S(Q, \omega)$  seemed to be precluded by the kinematic restrictions inherent to conventional present-day INS spectrometers. However, as it will be commented below, the ratio between the lattice parameters of hexagonal ice enables the measurement of such a dispersion curve within the second Brillouin zone.

The purpose of the present paper is therefore to report the comparison between the calculated results described in Ref. [12] with those obtained from experimental means, and therefore, to validate the previous calculations, something which will enable us to draw some conclusions about what can be expected to be seen in experiments (either scattering or MD) regarding the normal or supercooled liquid phases.

The rationale behind the present effort lies in the fact that if such a steep dispersion is present in the polycrystal, where the mostly translational and rotational man-

ifolds cover well-defined frequency ranges (i.e., below 10 THz the vibrational density of states is composed by excitations of mostly translational character which do not show a large isotopic effect [12], whereas for frequencies above 15 THz the excitations are clearly related to hydrogen motions), then the origin of such an anomalous dispersion as arising from rotational motions involving the hydrogens while leaving the center of mass at rest, as postulated in Ref. [2] cannot be sustained.

The INS measurements were performed at the high flux reactor at Petten (The Netherlands), using the triple-axis thermal spectrometer located at the beam tube HB1. The measurements were performed in the constant  $k_i = 5.37 \text{ \AA}^{-1}$  mode with the spectrometer set in the W configuration and collimations of 30 min (in pile), 30 min (monochromator to sample), and 30 min (sample to analyzer), at  $T = 88 \text{ K}$ . The achieved resolution in energy transfer using such a setup measured with a vanadium standard was about 1.2 THz (half width at half maximum).

The sample consisted in 99.95% deuterated water placed inside an aluminum cell of 2 cm external diameter. A liquid-nitrogen cryostat was employed, and the sample was frozen from the room-temperature liquid at a rate fast enough to prevent as much as possible the preferential orientation of the crystallites. Because of the relatively weak excitation peaks which are superimposed on the broad translational band [13], relatively large counting times were required (10 000 monitor counts, i.e., about 9 min of counting per data point). Several runs were performed in order to assess the quality and positioning of the sample by means of measurements of the strictly elastic  $S(Q, \omega = 0)$  static structure factor, a sample of which is shown in Fig. 1. From a qualitative comparison of the Bragg intensities with those of pulverized samples [14], it seems clear that some amount of texture is present in the sample although the low  $Q$ -resolution of the present measurement hinders any further comparison.

The spectra were finally corrected for absorption and

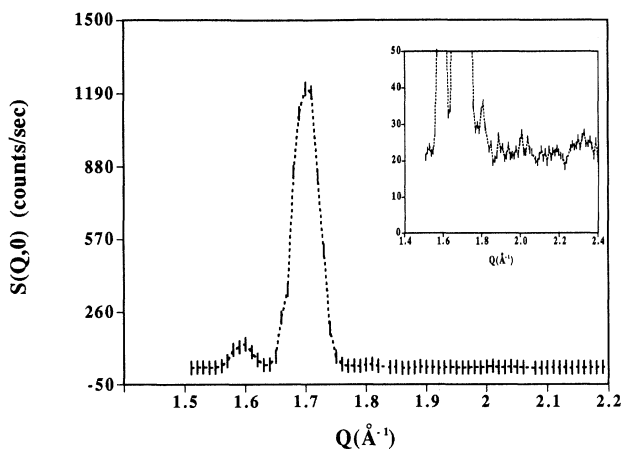


FIG. 1. The measured strictly elastic  $S(Q, \omega = 0)$  structure factor. The inset shows an enlargement showing some additional reflections.

container scattering effects by means of conventional procedures.

A set of the most relevant neutron groups measured in the present experiment is shown in Fig. 2 covering the useful range of momentum transfers. The spectra for wave vectors below  $1.9 \text{ \AA}^{-1}$  were basically composed by a monotonic decaying envelope arising from the ridge of the translational manifold and measurements of finite-frequency features away from this contribution were precluded by the contamination of the direct beam.

The origin of the finite-frequency feature appearing in the INS spectra can be easily understood by consideration of the fact that two of the dimensions of the primitive cell of hexagonal ice (Ih) are not far from being one-half of the third ( $a = b = 4.513 \text{ \AA}$ ,  $c = 7.355 \text{ \AA}$ ). As a consequence, the zone boundary for the in-plane directions ( $Q_p \approx 1.4 \text{ \AA}^{-1}$ ) will be close to the lower harmonics of the other direction ( $Q_p \approx 1.71 \text{ \AA}^{-1}$ ), something which result after the orientational (polycrystalline) averaging in an effective zone boundary about  $Q_p = 1.41 \text{ \AA}^{-1}$ . The wave vectors corresponding to the observed excitations can therefore be displaced by subtraction of  $Q_p$ , down to the first Brillouin zone, something which will enable a comparison of the present results with those calculated by means of LD given in Ref. [12]. A comparison of the wave-vector dependence of the position in frequency of the peak maxima  $\omega_{\max}$  for both experimental and LD results is given in Fig. 3, along with the dispersion of subsidiary maxima which also appear in the orientationally averaged  $S(Q, \omega)$ . Even if the comparison can only be made in semiquantitative terms because of the purely harmonic nature of the LD calculation (a decrease in frequencies is then expected), it seems clear that the shape of the steep “dispersion curve” found from the LD results is borne out by the experimental measurement.

The dominance of modes belonging to optical manifolds can be gauged from comparison of the steep curve shown in Fig. 3 with those identified as arising from mainly longitudinal- or transverse-acoustic excitations, also shown in the figure.

The collective dynamical properties of liquid water have been a matter of strong controversies for a number of years. Although some relevant progress have been registered during the past decade [15] regarding the understanding of transport and relaxation processes at hydrodynamic and mesoscopic scales, the microscopic origin of the excitations occurring at scales accessible by INS or computer simulations still remains a widely disputed area. As a matter of fact, it seems difficult to reconcile, in some respects, the dynamical information obtained using different experimental techniques, a fact due in part to the oversimplified terms on which the analysis of experimental data is customarily performed.

A comparison between the results obtained in the present work for polycrystalline ice and those derived from computer simulation results for the liquid, from where the existence of a “fast-sound” mode was inferred is finally shown in Fig. 4. A remarkable similitude between the shape of the MD curves for liquid water and those calculated by LD or measured by INS is clearly seen, and, as a matter of fact, the maximum frequen-

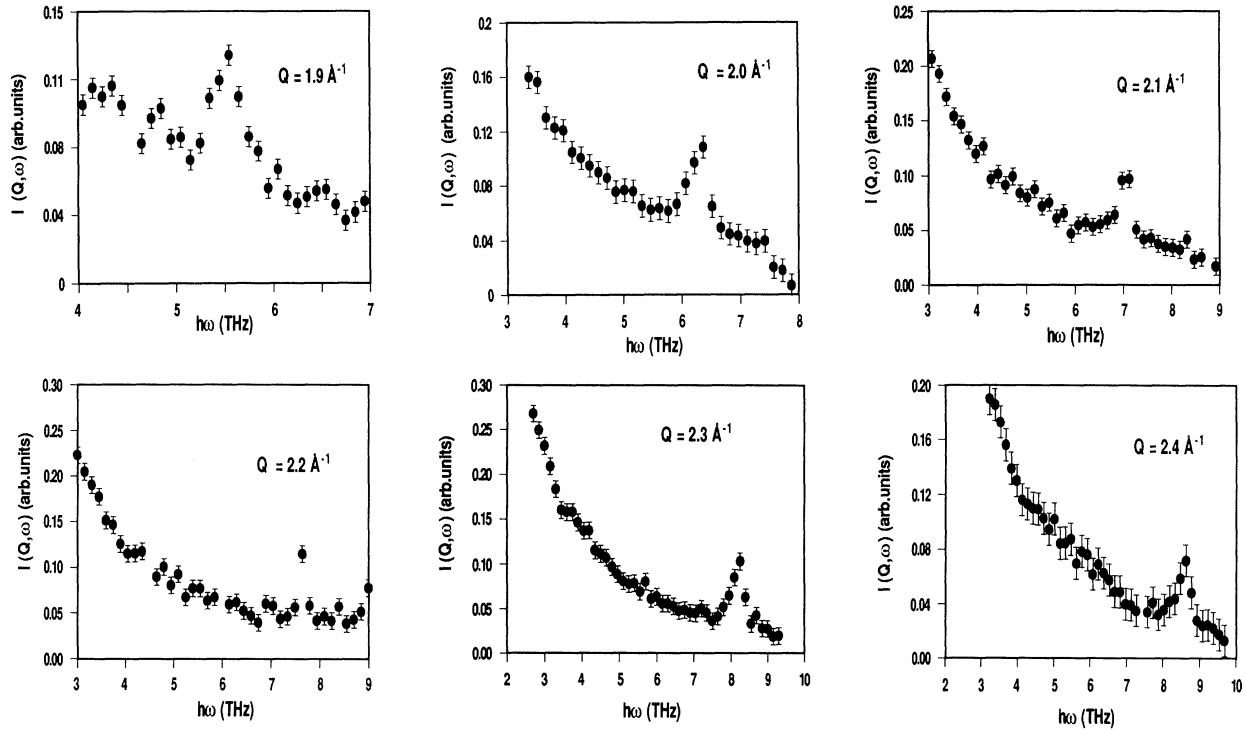


FIG. 2. A representative set of neutron groups for several different values of momentum transfers (given in the insets).

cies of the curve corresponding to supercooled water are rather close to those derived from experiments.

If the slopes of the steep dispersions were interpreted in terms of propagation of sound, values far in excess of those corresponding to hydrodynamics would obviously result (i.e.,  $3235 \text{ ms}^{-1}$  for liquid water versus the ultrasonic value of  $1510 \text{ ms}^{-1}$ , and  $6857 \text{ ms}^{-1}$  from experiment or  $7170 \text{ ms}^{-1}$  from LD versus the light-scattering value of  $3940 \text{ ms}^{-1}$  for polycrystalline ice). Such an anomalously large value for the sound velocity of normal liquid water was first reported by Impey, Madden, and McDonald [5] from MD simulation data, and later found by Teixeira *et al.* [8] from the analysis of their INS results, the origin of which was tentatively interpreted as arising from excitations of dense patches of bonded molecules. Taken with respect to the dispersion of longitudinal hydrodynamic sound [16] it can be seen that the ratios of the slopes of the steep curves to the ordinary sound is about 1.8 in ice (1.76 experimental and 1.84 LD), which is rather close to the value of 2.14 for liquid water.

The results reported herein show that the case of liquid or polycrystalline water represents an extreme case with respect to other molecular materials [17], where the pullout towards high frequencies in plots of  $\omega_{\text{max}}$  vs wave vector seems to depend strongly on both the molecular shape and the nature of the interparticle potential. In fact, such an apparent anomaly in the dispersion curves of the polycrystalline material is absent in the examined crystals composed by molecules interacting through basically Lennard-Jones potentials (i.e., oxygen or carbon tetrachloride), but is evidenced in cases where the intermolecular interactions proceed via strongly directional

forces, as it was evidenced in MD, LD, and INS studies on another hydrogen-bonded material such as methanol [10, 11] in both liquid and glassy states.

As a main conclusion, it seems clear that the steep

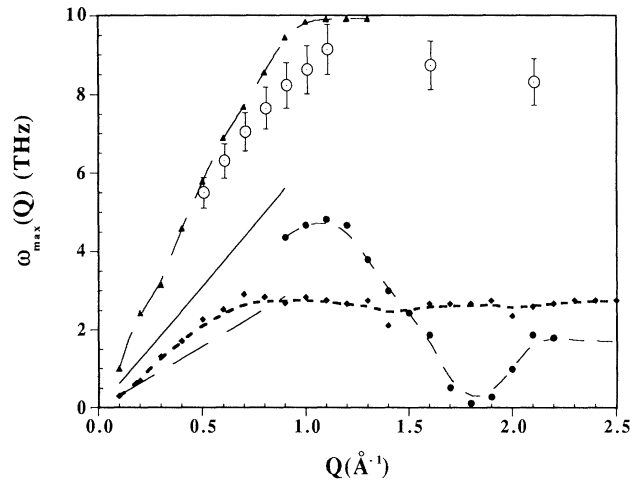


FIG. 3. The experimental data points [after displacing them  $Q = 1.4(1) \text{ \AA}^{-1}$ ] are shown by open circles. The curves shown by filled symbols represent the peak maxima found from the polycrystalline  $S(Q, \omega)$  calculated from the LD results. Filled triangles represent the manifold of modes that becomes dominant above  $0.35 \text{ \AA}^{-1}$ , filled ovals show the dispersion of a peak covering modes of mostly transverse-acoustic (TA) character, whereas filled circles are identified with mostly longitudinal-acoustic (LA) modes. The solid and dashed lines represent extrapolations of longitudinal and transverse hydrodynamic sound.

dispersion curves reported for liquid water are a consequence of the mixing of different dispersion branches within the translational manifold, due to orientational averaging. From inspection of graphs given in a previous paper [12], it can be seen that two small peaks which can be assigned to sound propagation on the basis of their dispersion behavior, which is shown in Fig. 3, are visible in  $S(Q, \omega)$  but nearly disappear when the  $J_I(Q, \omega)$  current autocorrelation is computed since multiplication by  $\omega^2$  results in a transfer of the spectral power towards higher frequencies. A similar behavior can be expected to be followed by the same quantities regarding supercooled or liquid water, where, at length scales larger than about  $60 \text{ \AA}$  (below  $Q = 0.1 \text{ \AA}^{-1}$ ) such an apparently anomalous dispersion curve should merge with that corresponding to hydrodynamic sound, from where true estimates of the elastic constants of the medium could be deduced. Unfortunately, such kinematic conditions are extremely difficult to meet with present day instrumentation, although it may be explored by MD simulations using nonconventional geometries for the simulation box (i.e., a parallelepiped with one of the directions far larger than the other two).

It seems finally clear that the next step in the direction taken would be to consider the collective dynamics of amorphous ice in relation with the MD results for liquid water. From comparison of the generalized vibrational density of states [18] of amorphous and hexagonal ices, it becomes clear that the main differences are the substantial broadening of the higher frequency peaks within the translational manifold. The lack of information regard-

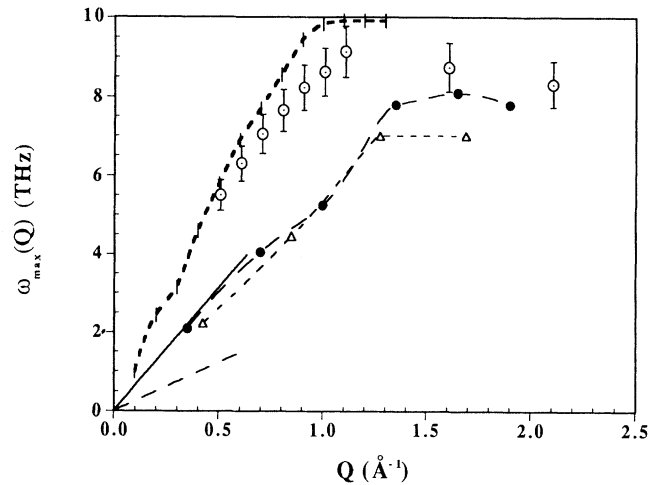


FIG. 4. A comparison between the present results (thick dotted line and open circles) with reported data from MD simulations on supercooled [6] (filled circles) and normal liquid [7] (open triangles) water. The hydrodynamic longitudinal sound linear dispersions are shown by the solid (ice) and dashed (liquid) lines.

ing the wave-vector dependence of the neutron inelastic spectra precludes any further comparison.

This work has been supported in part by DGICYT Grant No. PB89-0037-C03, and EEC Grant No. SC1-CT91-0714 (TSTS). A. Bontenbal gave us invaluable help during the course of the measurements.

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