Comment on "Transition from *Normal* to *Fast* Sound in Liquid Water"

In a recent Letter, Sette *et al.* [1] claim to have detected the origin of some transition from *normal* to *fast* sound in liquid water by means of inelastic scattering of x rays. Such a result is adduced from measurements of the $I(Q, \omega)$ (uncorrected by the atomic form factors and the large multiphonon contribution) spectral response of liquid water and hexagonal ice.

The data exemplify the progress achieved in instrument development, registered within an astoundingly short lapse of time (i.e., for comparison see [2]). However, the conclusions hinge on several assertions on the dynamics of Ih ice which run counter to the experience accumulated over years, as well as on a rather simplified procedure for data reduction and analysis. Consequently the main results of such a Letter should be qualified in its essence for reasons that are explained below.

The microscopic dynamic response of a polycrystalline molecular solid is substantially complicated by the orientational averaging of the different and numerous crystal modes (up to 21 in ice Ih) which leads to an average dynamic structure factor $\langle S(Q, \omega)\rangle_{\text{avg}}$ showing features which represent *envelopes over modes*, and consequently the frequency corresponding to their maxima cannot be directly assigned as the one corresponding to a well defined crystal excitation. To see this, one can compare the $\langle S(Q, \omega)\rangle_{\text{avg}}$ of a polycrystalline model of ice shown in Fig. 2 of [3] with those reported for ice in Fig. 4 of [1], and realize their proximity once the different ratios of peak intensities due the disparate character of the two techniques to sample the dynamics is accounted for. Since the character of individual modes is known, it can be verified that the quantities $\omega_{\max}(Q)$ of peak maxima in $\langle S(Q, \omega)\rangle_{\text{avg}}$ encompass a wide mixture of polarizations and therefore cannot be interpreted in terms of a well defined physical frequency, but have to be considered as a valid means to describe the data only. Therefore, the assignment of transverse-optic (TO) or longitudinal-acoustic (LA) character to the polarizations of both peaks in $I(Q, \omega)$ does not seem to be justified. It also runs counter to neutron scattering work [4] where the lowest frequency feature, which corresponds to the strongest peak in the density of states and shows basically no isotopic effect (i.e., represents the feature where the collective effects are strongest), was characterized as *dominantly* transverse acoustic (TA). Also it opposes the measurement of Renker [5] on ice-Ih single crystals, where it is shown that the frequency of the LA mode at the zone boundary never exceeds some 19.5 meV, whereas the peak frequencies shown in Fig. 4 of [1] are significantly above such a figure ($\approx$30 meV).

The steep behavior of the $\omega_{\max}(Q)$ corresponding to the higher-frequency peak comes as a consequence of the orientational averaging of intensities corresponding to modes with rather different polarizations [5,6]. Its rise up to frequencies well above hydrodynamic sound while retaining a phase velocity substantially below that of hydrodynamic sound comes as a mere consequence of fitting the spectrum of excitations within the 10–40 meV range with only one spectral function (the experimental densities of states show at least three peaks [4]) and in no way can be interpreted in terms of "coupling" between modes [1] or the existence of some "mesoscopic" domain in ice and water [7] where sound propagation becomes decoupled from the elastic properties of the media (i.e., a common value of 3200 ± 100 m s^{-2} is found for the phase velocity in water at 21 °C, 4 °C, and ice at -20 °C, whereas the hydrodynamic sound velocity goes from $\approx$1500 to $\approx$1420 m s^{-1} and $\approx$4000 m s^{-1} for the same three temperatures).

It then seems clear that what is being sampled contains a large contribution of higher-lying modes which because of its highly localized nature become effectively decoupled from the dramatic changes in the elastic properties of the sample occurring upon crossing the freezing transition. If what is sampled and assigned as a LA mode were of mostly acoustic origin, the stationary condition of the sound waves would have caused a strong bend of the "dispersion" curve leading to a vanishing (or at least rather small) group velocity at the Brillouin zone boundary, that is, $Q \approx 0.75$ Å^{-1} [8].

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