

COMMENTARY

Reply to “Comment to ‘Dynamics of supercooled confined water measured by deep inelastic neutron scattering’ by Y. Finkelstein and R. Moreh”

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We reply to the comment [*Front. Phys.* 14(5), 53605 (2019)] by Y. Finkelstein and R. Moreh on our article [*Front. Phys.* 13(1), 138205 (2018)]. We agree with some of their criticisms about our calculation of the temperature effect on the kinetic energy of hydrogen atoms of supercooled confined water; we also agree with their statement that, in view of the current sensitivity of the technique, possible effects of the liquid–liquid water transition are hardly detected with deep inelastic neutron scattering (DINS). However, we disagree with their use of the translational mass ratio of a single water molecule and, in general, with their underestimation of collective effects.

Keywords supercooled water, liquid–liquid transition, deep inelastic neutron scattering, libration, vibrational density of states, proton kinetic energy

In the comment [1], Y. Finkelstein and R. Moreh criticized our attempt [2] to obtain evidence for the existence of a liquid–liquid transition in supercooled water by using DINS. They accepted our experimental data but they criticized our calculation of the expected effect of temperature on the kinetic energy of hydrogen atoms of supercooled confined water.

Two main points are raised:

- First, the contribution of librations to $\text{Ke}(\text{H})$, expected to occur at ~ 200 to 1250 cm^{-1} for condensed H_2O , was ignored.
- Second, the kinetic energy fraction S_{T_r} (shared by the water protons in the translation) used for calculating $\text{Ke}(\text{H})$ is not correct.

We agree with the first point: indeed, contributions coming from librations are missing in our calculation. We thank the authors for pointing out this to us and to the scientific community.

As far as the second point is concerned, we disagree with the value $S_{\text{T}_r} = 0.0556 = 1/18$ used by the authors. This number originates from considering the translation of a single water molecule and reflects the mass ratio of the proton to the entire water molecule. In our case, we are considering the effect of collective low-frequency *vibrational* modes that give origin to the so-called boson peak experimentally observed in supercooled confined water. Although there is an ongoing debate in the literature

about the physical origin of the boson peak (harmonic excitations of a disordered lattice [3], anharmonic local modes of a “soft potential” with distributed parameters [4], quantum excitations in glasses intrinsic of their non-equilibrium character [5], etc.) no one has ever traced its origin to *translations*. It has to be stressed also that in our INS experiment on the boson peak of confined water [6], contributions coming from translations fall into the so-called quasi-elastic peak and have been carefully subtracted before obtaining the VDOS. So, our value of $S_{\text{T}_r} = 1$ is most probably overestimated (also in view of the violation of the sum rule pointed out by the authors), but surely the value $S_{\text{T}_r} = 0.0556$ used by the authors is not justified.

More in general, a similar criticism can also be made about the other S values used in the Comment; indeed, as reported in previous publications by the same authors (see e.g., Ref. [7]), these values are calculated from the translation, rotation and vibration of a single water molecule, and effects of collective behavior of water molecules (especially relevant in the supercooled confined state) are not taken into account.

We would like to stress also the following point. At the beginning of their comment the authors criticize our suggestion concerning the liquid–liquid transition in our supercooled confined water and state: “The reasoning behind this suggestion relied on the assumption that the seemingly higher $\text{Ke}(\text{H})$ value at 210 K, compared to that at 250 K, indicates that at 210 K the water pro-

tons experience a stiffer intermolecular potential than at 250 K, in contradiction to the expectation that water at 210 K and 250 K should be mainly in high and low density liquid states respectively". It is clear that the authors mis-interpreted our suggestion. Indeed, in our paper we suggested that water hydrogens experience a stiffer intermolecular potential at 210 K than at 250 K, *in agreement* with the expectation that water at 210 K should be mainly in the low density liquid state, while at 250 K it should be mainly in the high density liquid state; this is opposite to what the authors seem to believe.

In conclusion,

- we agree with the fact that the calculation reported in Ref. [2] is not correct, and we also agree with the statement made in the Abstract that "the current sensitivity of the deep inelastic neutron scattering (DINS) method cannot detect with confidence small differences in the proton kinetic energy, $K_e(H)$, involved in a liquid–liquid transition in supercooled water confined in nanoporous silica". Indeed, although such effects could have been expected in view of the recent results by F. Perakis *et al.* (Ref. [8]), our new experiments that extend the temperature range investigated to the 170–325 K range [9] clearly show that the liquid–liquid transition *is not* observed in DINS experiments and that the contribution of the low frequency collective vibrational motions responsible for the boson peak is indeed very weak.
- We disagree with the unjustified use of the translational mass ratio of a single water molecule to take into account the kinetic energy fraction arising from the low frequency collective vibrational modes responsible for the Boson peak and, more in general, with the underestimation of the collective behavior of water molecules.

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