

COMMENTARY

Comment to “Dynamics of supercooled confined water measured by deep inelastic neutron scattering”

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We comment on the findings of “Dynamics of supercooled confined water measured by deep inelastic neutron scattering”, by V. De Michele, G. Romanelli, and A. Cupane [*Front. Phys.* 13, 138205 (2018)]. We show that the current sensitivity of the deep inelastic neutron scattering (DINS) method, cannot detect with confidence small differences in the proton kinetic energy, $\text{Ke}(\text{H})$, involved in a liquid-liquid transition in supercooled water confined in nanoporous silica. We also criticize the calculation of $\text{Ke}(\text{H})$ carried out in *Front. Phys.* 13, 138205 (2018).

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

An attempt to capture the liquid liquid transition (LLT) in H_2O was recently reported by a deep inelastic neutron scattering (DINS) study [1]. In that paper, the proton kinetic energy was measured, using a sample of deeply supercooled water (SCW) nanoconfined in silica Xerogel of ~ 20 Å effective pore dimension (hereby denoted as SCW@SX). The results were [1]: $\text{Ke}(\text{H}) = (157 \pm 3)$ meV at 210K and (156 ± 2) meV at 250K. This small and statistically insignificant 1 ± 1.8 meV difference in $\text{Ke}(\text{H})$, complemented with a quantum harmonic semi empirical (SE) calculation of the temperature effect on $\text{Ke}(\text{H})$ in SCW@SX, was suggested in Ref. [1] to indicate the occurrence of a liquid–liquid transition (LLT). 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 protons 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. This conclusion seems however to be doubtful because the current level of sensitivity of the DINS technique [2] cannot detect with confidence the $\text{Ke}(\text{H})$ differences at 210 K and 250 K related to variations in the density of the liquid.

In addition, the general known trend of variation of $\text{Ke}(\text{H})$ in water between 200 K and 260 K, covering the above T range is a slowly increasing one [3, 4], as also supported in a very recent report on the same system [5].

In this commentary, we examined the calculated T -effect made in Ref. [1], revealing some difficulties which seem to invalidate its conclusions.

The $\text{Ke}(\text{H})$ value in *condensed* H_2O phases may be cal-

culated using the well-established SE method [3]; it may be expressed as

$$\text{Ke}(\text{H}) = \sum_i S_i \text{Ke}(\text{H})_i, \quad (1)$$

where the indices $i = \text{T}_r, \text{L}, \text{B}, \text{SS}, \text{AS}$ respectively refer to translation (T_r) and libration (L) of the whole H_2O molecule, and to its internal modes: HOH bending (B), and symmetric (SS) and asymmetric (AS) OH stretching. The S_i coefficients in Eq. (1) correspond to the kinetic energy fractions respectively shared by the proton in the above modes of motion; the details of calculation may be found elsewhere [6].

In Ref. [1] the T -effect of $\text{Ke}(\text{H})$ in SCW@SX was calculated by adopting the measured *internal* modes of liquid H_2O of Ref. [7], together with their corresponding SE calculated kinetic energy fractions. To account for the contribution of the *external* (lattice) modes of the confined H_2O , the normalized integral of the vibrational density of states (VDOS), measured by inelastic neutron scattering (INS) for the same system [1] (of 20 Å pore diameter and a 0.4 hydration level - gr $\text{H}_2\text{O}/\text{gr SiO}_2$) [8], was utilized. The results of Ref. [1] are reproduced in Fig. 1 (blue curve). The measured [1] DINS values are shown as green data points in Fig. 1.

Note that the calculated blue curve of $\text{Ke}(\text{H})$ vs. T of Ref. [1] (Fig. 1) suffered from two drawbacks [9]: First, only the translational contribution to $\text{Ke}(\text{H})$ was accounted for while ignoring that of libration occurring at ~ 200 to 1250 cm^{-1} . As a result, the kinetic energy fraction S_{T_r} (shared by the H_2O protons in translation) used to calculate $\text{Ke}(\text{H})$ came out wrong.

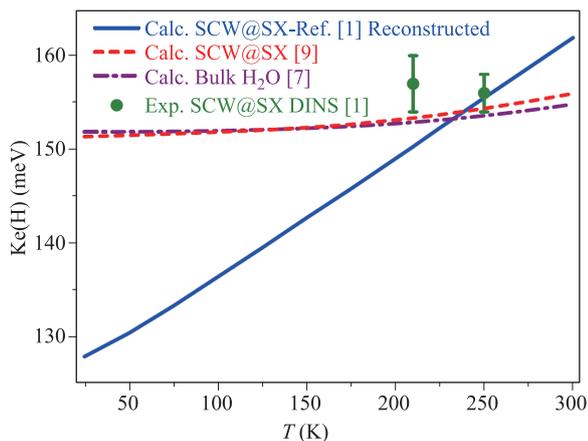


Fig. 1 The effect of temperature on $\text{Ke}(\text{H})$: presently reconstructed SE calculation of Ref. [1] for SCW@SX (solid blue curve). The corrected [9] calculation of $\text{Ke}(\text{H})$ vs. T (dash red). Also depicted is the SE calculation of Ref. [7] for ordinary H_2O (dot-dash purple). Green data points with error bars are the DINS measured $\text{Ke}(\text{H})$ values reported in Ref. [1].

Table 1 Experimental vibrational frequencies of ice Ih (in cm^{-1} units). T_r , L, B, SS, AS denote translation, libration, bending, symmetric, and asymmetric stretch respectively. Note that the sum rule of the energy fractions in Ref. [1] is different from 1.0.

		External modes		Internal modes [7]			Sum rule
		T_r [8]	L [10]	B	SS	AS	
	ν_i (cm^{-1})	44	636	1645	3280	3490	
Ref. [1]	S_i	1	0	0.463	0.459	0.485	1.469
Present	S_i	0.0556	0.475	0.463	0.459	0.485	1.00

Table 1 lists the frequencies of the five modes of motion of the H_2O molecules together with the calculated energy fractions of the protons used in Ref. [1] and in the present work. A check for the correctness of the energy fractions is usually made by calculating the sum rule which should add up to unity. This sum rule may be written as [3]

$$S_{T_r} + S_L + \frac{1}{3} \sum_{i=1}^3 S_i = 1. \quad (2)$$

It is fulfilled for the present calculation but not for that of Ref. [1] where the sum of the energy fractions is 1.47 (see Table 1).

Altogether, the calculated T -effect of the $\text{Ke}(\text{H})$ values of Ref. [1] was severely underestimated in particular at low T , and gradually increases with T (see blue curve in Fig. 1).

To correct for the missing librational mode, we accounted for the INS measured librational frequency of a closely related system of nanoconfined water, namely H_2O nanoconfined in 14 Å single wall carbon nanotubes (SWC-

NTs) [10]. In addition, the corrected values of S_{T_r} and S_L were used to account for the kinetic energy fraction of the proton in the translational and librational motions. The result of these two corrections on the calculated value of $\text{Ke}(\text{H})$ vs. T is shown as the dash red curve in Fig. 1 (see also Ref. [9]).

Note the huge deviation between the T -effect originally calculated in Ref. [1] (solid blue curve in Fig. 1) and that of its corrected version (dash red curve in Fig. 1). Note also the excellent agreement between the calculation of Ref. [9] and that of ordinary H_2O (dot-dash purple curve) [7], as well as the good agreement with the measured DINS values of Ref. [1] (shown as green data points in Fig. 1).

The fact that the T -effect of ordinary H_2O practically coincides with that of SCW@SX, strongly questions the conclusion made in Ref. [1] regarding the LLT.

Finally it is very interesting to note that in a very recent paper by the authors of Ref. [1], the values of $\text{Ke}(\text{H})$ were measured in a wider T range 170–325 K and an excellent agreement with the calculations of Ref. [9] was obtained [5]. This again confirms our present conclusion regarding the LLT. It should be noted however that differently from $\text{Ke}(\text{H})$, the kinetic energy of the *electrons* in water is indeed sensitive to temperature variations between 256 K and 293 K, showing a strong increase upon supercooling from 277 K to 256 K [11].

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