Comment on "Boson Peak in Deeply Cooled Confined Water: A Possible Way to Explore the Existence of the Liquid-to-Liquid Transition in Water"

In their Letter, Wang *et al.* [1] report on an inelastic neutron scattering (INS) experiment where they describe the pressure evolution of a low energy ($E \sim 6$ meV) excitation, emerging in confined protonated water only below 230 K at an exchanged momentum $Q = 2.0$ Å^{-1}. Water confinement was used to overcome the unavoidable crystallization occurring below ~250 K in bulk water. The authors report that a similar finding was also obtained in both bulk (numerical simulations [2]) and confined water at ambient pressure. They refer to this low temperature excitation as a boson peak (BP) [3], and relate its occurrence to the Widom line, concluding that the observed pressure behavior of the BP reveals the signature of the high-density liquid (HDL) to the low-density liquid (LDL) transition proposed [4], though severely questioned [5], for bulk water. We believe these claims to be unconvincing for the following reasons.

Comparison with corresponding findings in liquid water.—The authors not only overlook commenting on the actual density of confined liquid water [6–9], but they also neglect to establish any physical relationship with the well known excitations of coherent or incoherent origin occurring at similar energies in bulk liquid water. Since the seminal Raman scattering room temperature studies by Bolla [10], a mode in the ~5–7 meV range has indeed been regularly observed with optical [11–14], numerical [15], and inelastic x-ray scattering [16–18] and INS techniques [19,20] over a wide thermodynamic range (0–2 kbar, 250–450 K) in both H_2O and D_2O (see Fig. 4 in Ref. [21]). The microscopic nature of such a mode, underdamped and still well defined at $Q = 2.0$ Å^{-1}, is the subject of controversial single-particle [12,22,23] or collective [21,24] interpretations. Irrespective of its incoherent or coherent nature, this evidence is unquestionable and cannot be ignored. This mode is not easily detectable in high temperature neutron spectra from H_2O because of the overwhelming quasielastic contribution. However, its presence always emerges in calculating the hydrogen vibrational density of states, as was done in Ref. [22] at $T = 256$ K, and in bulk or confined H_2O from 300 K down to 242 K [25], but not mentioned in Ref. [1]. This mode, but not the BP, was also observed when investigating the vibrational dynamics in amorphous ices [26,27]. Moreover, a bulklike excitation not dependent on temperature was observed down to 205 K in an INS measurement on slightly salty liquid water [28].

Data analysis and treatment.—(i) INS probes at the same time the coherent and incoherent properties of matter with a weight given by their respective neutron cross section and dynamic structure factor. H_2O is considered as an incoherent scatterer by reason of the high $\sigma_{\mathrm{inc}}/\sigma_{\mathrm{coh}}$ ratio. Yet, this approximation cannot be uncritically adopted as was done in Ref. [1] and a proper estimation of the related ratio $S_{\mathrm{inc}}(Q,\omega)/S_{\mathrm{coh}}(Q,\omega)$ at the thermodynamic (P, T) and kinetic (Q,ω) investigated point should be addressed. (ii) An arbitrary interpolating metric is adopted to determine the locus of the BP appearance: the T_B parameter is a clumsy, large-error quantity inherent in the slowing down of the thermal diffusion. The peak associated with the low energy—and virtually temperature independent (see Fig. 4 of Ref. [1])—excitation is enhanced by the narrowing of the quasielastic signal upon lowering the temperature. (iii) The exact internal pressure existing in such tiny pores is not directly related to the He applied pressure and is therefore unknown [29]. As a consequence, the confined water phase diagram and properties cannot be unconditionally assigned to those of bulk water. (iv) In order to support the authors' claims at a less speculative level, the correct BP shape should be determined by calculating the vibrational density of states in excess of that of the corresponding crystalline phase.

In conclusion, the whole large body of numeric and experimental investigations on the single particle and collective properties of liquid water report the presence of a weakly dispersing excitation in the 5–7 meV range. We believe that, in order to use the BP as a marker of the HDL or LDL bulk water phases, the authors should perform a more complete data treatment and establish a relation, if any, between the supposed BP peak they observe in a confined environment and the well established bulk mode present in a wide portion of the phase diagram at the same energy.

F. Formisano[1] and S. De Panfilis[2]
[1]Consiglio Nazionale delle Ricerche
Istituto Officina dei Materiali
Operative Group in Grenoble (OGG)
c/o Institut Laue Langevin F-38042 Grenoble Cedex
France
[2]Centre for Life Nano Science IIT@Sapienza
Istituto Italiano di Tecnologia
I-00161 Roma, Italy

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[1] Z. Wang, K.-H. Liu, P. Le, M. Li, W.-S. Chiang, J. B. Leão, J. R. D. Copley, M. Tyagi, A. Podlesnyak, A. I. Kolesnikov, C.-Y. Mou, and S.-H. Chen, Boson Peak in Deeply Cooled Confined Water: A Possible Way to Explore the Existence of the Liquid-to-Liquid Transition in Water, Phys. Rev. Lett. **112**, 237802 (2014).
[2] P. Kumar, K. T. Wikfeldt, D. Schlesinger, L. G. M. Pettersson, and H. E. Stanley, The boson peak in supercooled water, Sci. Rep. **3**, 1980 (2013).
[3] A. I. Chumakov, G. Monaco, A. Monaco, W. A. Crichton, A. Bosak, R. Rüffer, A. Meyer, F. Kargl, L. Comez, D. Fioretto, H. Giefers, S. Roitsch, G. Wortmann,

M. H. Manghnani, A. Hushur, Q. Williams, J. Balogh, K. Parliński, P. Jochym, and P. Piekarz, Equivalence of the Boson Peak in Glasses to the Transverse Acoustic Van Hove Singularity in Crystals, Phys. Rev. Lett. **106**, 225501 (2011).

[4] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Phase behaviour of metastable water, Nature (London) **360**, 324 (1992).

[5] S. Fanetti, M. Pagliai, M. Citroni, A. Lapini, S. Scandolo, R. Righini, and R. Bini, Connecting the water phase diagram to the metastable domain: High-pressure studies in the supercooled regime, J. Phys. Chem. Lett. **5**, 3804 (2014).

[6] A. K. Soper, Density profile of water confined in cylindrical pores in MCM-41 silica, J. Phys. Condens. Matter **24**, 064107 (2012).

[7] A. K. Soper, Density minimum in supercooled confined water, Proc. Natl. Acad. Sci. U.S.A. **108**, E1192 (2011).

[8] Y. Zhang, A. Faraone, W. A. Kamitakahara, K.-H. Liu, C.-Y. Mou, J. B. Leo, S. Chang, and S.-H. Chen, Reply to Soper: Density measurement of confined water with neutron scattering, Proc. Natl. Acad. Sci. U.S.A. **108**, E1193 (2011).

[9] A. Taschin, P. Bartolini, A. Marcelli, R. Righini, and R. Torre, A comparative study on bulk and nanoconfined water by time-resolved optical Kerr effect spectroscopy, Faraday Discuss. **167**, 293 (2013).

[10] G. Bolla, Sulla forma della banda Raman dell'acqua, Nuovo Cimento **9**, 290 (1932).

[11] R. W. Impey, P. A. Madden, and I. R. McDonald, Spectroscopic and transport properties of water, Mol. Phys. **46**, 513 (1982).

[12] S. Krishnamurthy, R. Bansil, and J. Wiafe-Akenten, Low-frequency Raman spectrum of supercooled water, J. Chem. Phys. **79**, 5863 (1983).

[13] G. E. Walrafen, Raman spectrum of water: transverse and longitudinal acoustic modes below $\approx$300 cm^{-1} and optic modes above $\approx$300 cm^{-1}, J. Phys. Chem. **94**, 2237 (1990).

[14] G. E. Walrafen, Y. C. Chu, and G. J. Piermarini, Low-frequency Raman scattering from water at high pressures and high temperatures, J. Phys. Chem. **100**, 10363 (1996).

[15] A. Rahman and F. H. Stillinger, Propagation of sound in water. A molecular-dynamics study, Phys. Rev. A **10**, 368 (1974).

[16] F. Sette, G. Ruocco, M. Krisch, C. Masciovecchio, R. Verbeni, and U. Bergmann, Transition from *Normal* to *Fast* Sound in Liquid Water, Phys. Rev. Lett. **77**, 83 (1996).

[17] E. Pontecorvo, M. Krisch, A. Cunsolo, G. Monaco, A. Mermet, R. Verbeni, F. Sette, and G. Ruocco, High-frequency longitudinal and transverse dynamics in water, Phys. Rev. E **71**, 011501 (2005).

[18] Inelastic x-ray scattering as well contains an incoherent contribution, e.g., see G. Monaco, A. Cunsolo, G. Ruocco, and F. Sette, Viscoelastic behavior of water in the terahertz-frequency range: An inelastic x-ray scattering study, Phys. Rev. E **60**, 5505 (1999).

[19] P. Bosi, F. Dupré, F. Menzinger, F. Sacchetti, and M. C. Spinelli, Observation of collective excitations in heavy water in the 10^8 cm^{-1} momentum range, Lett. Nuovo Cimento **21**, 436 (1978).

[20] C. Petrillo, F. Sacchetti, B. Dorner, and J.-B. Suck, High-resolution neutron scattering measurement of the dynamic structure factor of heavy water, Phys. Rev. E **62**, 3611 (2000).

[21] A. Cunsolo, C. N. Kodituwakku, F. Bencivenga, M. Frontzek, B. M. Leu, and A. H. Said, Transverse dynamics of water across the melting point: A parallel neutron and x-ray inelastic scattering study, Phys. Rev. B **85**, 174305 (2012).

[22] S.-H. Chen and J. Teixeira, Structure and dynamics of low-temperature water as studied by scattering techniques, Adv. Chem. Phys. **64**, 1 (1986).

[23] S. Sastry, F. Sciortino, and H. E. Stanley, Collective excitations in liquid water at low frequency and large wave vector, J. Chem. Phys. **95**, 7775 (1991).

[24] M. Sampoli, G. Ruocco, and F. Sette, Mixing of Longitudinal and Transverse Dynamics in Liquid Water, Phys. Rev. Lett. **79**, 1678 (1997).

[25] M.-C. Bellissent-Funel, S. H. Chen, and J.-M. Zanotti, Single-particle dynamics of water molecules in confined space, Phys. Rev. E **51**, 4558 (1995).

[26] M. M. Koza, H. Schober, S. F. Parker, and J. Peters, Vibrational dynamics and phonon dispersion of polycrystalline ice XII and of high-density amorphous ice, Phys. Rev. B **77**, 104306 (2008).

[27] M. M. Koza, Vibrational dynamics of amorphous ice structures studied by high-resolution neutron spectroscopy, Phys. Rev. B **78**, 064303 (2008).

[28] E. Mamontov, A. De Francesco, F. Formisano, A. Laloni, L. Sani, B. M. Leu, A. H. Said, and A. I. Kolesnikov, Water dynamics in a lithium chloride aqueous solution probed by Brillouin neutron and x-ray scattering, J. Phys. Condens. Matter **24**, 064102 (2012).

[29] F. Caupin, Escaping the no man's land: Recent experiments on metastable liquid water, J. Non-Cryst. Solids **407**, 441 (2015).