Wang et al. Reply:

Zhe Wang, Kao-Hsiang Liu, Peisi Le, Mingda Li, Wei-Shan Chiang, Juscelino B. Leão, John R. D. Copley, Madhusudan Tyagi, Andrey Podlesnyak, Alexander I. Kolesnikov, Chung-Yuan Mou, and Sow-Hsin Chen

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Wang *et al.* Reply: In the preceding comment [1], Formisano and De Panfilis expressed their concerns about the results reported in our Letter [2]. In this Reply, we will address their comments point by point.

The first point is the relation between the boson peak (BP) of the confined water studied in our Letter and the low-frequency excitations observed at ~ 6 meV (LFE6) in bulk water with inelastic X-ray scattering (IXS) [3] and in bulk heavy water with inelastic neutron scattering (INS) [4]. The LFE6s are the bumps observed in the coherent dynamic structure factor of the water sample $S_{coh}(Q,E)$. In early days, the origin of the LFE6 was tentatively assigned to the O-O-O bending vibrations [5]. The development of the high resolution IXS technique has brought an excellent tool for the investigation of LFE6. Thorough IXS studies strongly suggest that the LFE6s are collective transverse modes in water [3,6,7]. The BP in this Letter is referred to the bump at ~ 2 – 10 meV in the incoherent dynamic structure factor of the confined water $S_{inc}(Q,E)$. Due to the exceptionally large incoherent cross-section of H atom, the inelastic neutron scattering spectrum of H_2O is dominated by the incoherent signal and thus can be considered as $S_{inc}(Q,E)$. A similar definition can also be found in a recent computer simulation study [8]. In the literatures of amorphous materials, BP is usually referred to the excess part of the reduced vibrational density of state (vDoS) $g(E)$ over the Debye model [9-11]. Note that, for a classic system, $g(E)$ and $S_{inc}(Q,E)$ have the following relation [12]:

$$g(E) = \frac{G(E)}{E^2} \propto \lim_{Q\to 0} \frac{S_{inc}(Q,E)}{Q^2},$$

where $G(E)$ is vDoS. Recent studies show that the BP is related to the transverse modes [8-10]. However, directly comparing the BP and LFE6, as done in the preceding comment, is still improper, since they are related to $S_{inc}(Q,E)$ and $S_{coh}(Q,E)$ respectively and behave differently [9,11]. We emphasize that in our Letter we focus on the BP of the confined water, but not the LFE6 of the confined water.

We disagree with the comment, that INS "approximation is not satisfied at Q≈2.0 Å^{-1} and the purely incoherent approximation cannot be uncritically adopted as done in this Letter." In previous studies it was shown (see e.g. [13]) that the INS approximation for the materials containing mostly incoherent scattering atoms (like H_2O, where the ratio $\sigma_{inc}/\sigma_{coh}$=20.7) should work well.

The comment questions the linear interpolation method in determining T_B. Due to the smooth and monotonic change of the maximum of $\partial_E S_{th}(Q,E)$ as a function of temperature, the error of this estimation of T_B, evaluated with the method introduced in Ref. [14], is found to be quite small. The comment also mentions that the peak associated to low frequency has virtually no temperature dependence. This statement is fairly reasonable for the LFE6, the peak observed in $S_{coh}(Q,E)$ [15], but not for the BP. A recent study on the BP in the deeply-cooled confined water shows that the

temperature dependence of BP in confined water cannot be ignored [16].

In addition, the comment points out the difference of the inner pressure and outer pressure induced by the nano-confinement. We are aware of this difference and we did not directly assign the phase diagram of the confined water to bulk water. In fact, in our recent publications [17, 18], we compare the phase diagrams of the deeply-cooled confined heavy water and the deeply-cooled bulk heavy water. We find that the liquid-liquid transition lines of these two systems have a pressure difference of ~ 1 kbar. The order of this difference is consistent with a rough estimation with the Young-Laplace equation.

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[1] F. Formisano and S. De Panfilis, preceding comment.
[2] Z. Wang, K.-H. Liu, P. Le, et al., Phys. Rev. Lett. 112, 237802 (2014).
[3] F. Sette, G. Ruocco, M. Krisch, C. Masciovecchio, R. Verbeni, and U. Bergmann, Phys. Rev. Lett. 77, 83 (1996).
[4] C. Petrillo, F. Sacchetti, B. Dorner, and J. -B. Suck, Phys. Rev. E 62,3611 (2000).
[5] S. Sastry, F. Sciortino, and H. E. Stanley, J. Chem. Phys. 95, 7775 (1991).
[6] E. Pontecorvo, M. Krisch, A. Cunsolo, G. Monaco, A. Mermet, R. Verbeni, F. Sette, and G. Ruocco, Phys. Rev. E 71,011501 (2005).
[7] A. Cunsolo, G. Ruocco, F. Sette, C. Masciovecchio, A. Mermet, G. Monaco, M. Sampoli, and R. Verbeni, Phys. Rev. Lett. 82, 775 (1999).
[8] P. Kumar, K. T. Wikfeldt, D. Schlesinger, L. G.M. Pettersson, and H. E. Stanley, Sci. Rep. 3, 1980 (2013).
[9] H. Shintani and H. Tanaka, Nat. Mater. 7, 870 (2008).
[10] A. I. Chumakov, G. Monaco, A. Monaco et al., Phys. Rev. Lett. 106, 225501 (2011).
[11] A. I. Chumakov, I. Sergueev, U. van Bürck, W. Schirmacher, T. Asthalter, R. Rüffer, O. Leupold, and W. Petry, Phys. Rev. Lett. 92, 245508 (2004).
[12] S.-H. Chen, K. Toukan, C.-K. Loong, D. L. Price, and J. Teixeira, Phys. Rev. Lett. 53, 1360 (1984).
[13] J. M. Carpenter and C. A. Pelizzari, Phys. Rev. B 12, 2397 (1975).
[14] https://en.wikipedia.org/wiki/Linear_interpolation
[15] E. Mamontov, A. De Francesco, F. Formisano, A. Laloni, L. Sani, B. M. Leu, A. H. Said, and A. I. Kolesnikov, J. Phys.: Condens. Matter, 24, 064102 (2012).
[16] A. Cupane, M. Fomina, and G. Schirò, J. Chem. Phys. 141, 18C510 (2014).
[17] Z. Wang, K.-H. Liu, L. Harriger, J. B. Leão, and S.-H. Chen, J. Chem. Phys. 141, 014501 (2014).
[18] Z. Wang, K. Ito, J. B. Leão, L. Harriger, Y. Liu, and S.-H. Chen, J. Phys. Chem. Lett. 6, 2009 (2015).