LETTER

REPLY TO HEAD-GORDON AND PAESANI:
Liquid water, a branched polymer with ∼100-fs short-lived heterogeneous hydrogen bonds

Saber Naserifar[a] and William A. Goddard III[a,1]

The letter by Head-Gordon and Paesani (hereafter HG-P) (1) contains several confusions about our results that we clarify here.

The title claiming that liquid water is not a dynamic polydisperse branched polymer is not supported by any information in their letter.

Their first paragraph alleges that the oxygen–oxygen radial distribution function (g_{OO}) from neutron scattering is not as accurate as the best X-ray analysis from Skinner et al. (2) (X-ray2). Since H and D have different neutron scattering lengths isotope-substitution techniques (3) can be used to extract the g_{OO} directly from neutron scattering (4). In contrast, X-ray is affected by the electron distribution and other methods (such as classical simulations) are used to obtain g_{OO}. However, X-ray2 uses a combination of neutron and X-ray to obtain a reliable g_{OO} which is close to the neutron g_{OO}. In fact, our RexPoN is in even better agreement with X-ray2 than neutron (Fig. 1).

In their second paragraph HG-P claim that correcting MB-Pol (N_{OO} = 6.2) for nuclear quantum effects (NQE) using path-integral molecular dynamics (PIMD), MB-pol-PIMD (N_{OO} = 4.8), leads to better agreement with experiment, which is true, but as shown in Fig. 1*B* the peak is still too high. In contrast, correcting the RexPoN for NQE using PIMD leads to a g_{OO} with N_{OO} = 4.6, nearly identical to the g_{OO} of X-ray2 with N_{OO} = 4.5 (Fig. 1*A*). Therefore, as opposed to their claim, correcting RexPoN for NQE provides an even better description of water structure. The details of RexPoN-PIMD were given in section A.2 of the supplementary information in ref. 5.

The height of the second peak of g_{OO} (g2) indicates the structural ordering of molecules in the second coordination shell. Figures S1 and S6 of ref. 5 show that RexPoN obtains the g2 close to experiment. The radial position of g2 (4.2 Å) is a little shorter than X-ray2 (4.5 Å) but very similar to other experimental data (6).

Their fourth paragraph seems confused. HG-P claim that water is homogeneous without structural motifs. It is homogeneous over large time scales (nanoseconds and longer). However, the dynamic heterogeneity we report is at the 90-fs time scale. Indeed, 2D Raman-THz experiments (7) find hydrogen-bond lifetimes of 75 to 95 fs for 298 to 276 K, confirming the time scale and heterogeneity observed with RexPoN.

HG-P are correct about the work of Kim et al. (8). They only observed a compressibility maximum at 227 K and 1 bar that confirms the existence of a Widom line. They suggested it could support the liquid–liquid critical point hypothesis.

HG-P mention that MB-pol can describe the supercooled state of water very well but their citations do not support such a claim. In addition, we show in Table 1 that it is less accurate than RexPoN.

Summarizing, our RexPoN force field for water leads to incredibly accurate properties in excellent agreement with experiment (9). RexPoN shows that at 298 K water is a dynamic polydisperse branched polymer at time scales of 90 fs. Nothing in the HG-P letter disproves this conclusion.

Acknowledgments

S.N. was supported by the Joint Center for Artificial Photosynthesis, a Department of Energy (DOE) Energy Innovation Hub, supported through the Office of Science of the US DOE under Award DE-SC0004993. W.A.G. was supported by the Computational Materials Sciences Program funded by the US DOE, Office of Science, Basic Energy Sciences, under Award DE-SC00014607. The calculations were carried out on the Extreme Science and Engineering Discovery Environment, which is supported by National Science Foundation Grant ACI-1548562.

[a]Materials and Process Simulation Center, California Institute of Technology, Pasadena, CA 91125

Author contributions: S.N. and W.A.G. designed research; S.N. performed research; S.N. and W.A.G. analyzed data; and S.N. and W.A.G. wrote the paper.

The authors declare no conflict of interest.

[1]To whom correspondence may be addressed. Email: wag@caltech.edu.

First Published September 10, 2019.

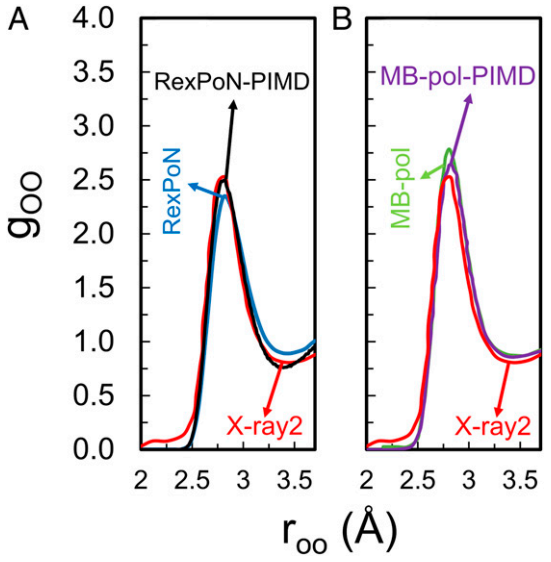

Fig. 1. Comparison of the first peak in the oxygen–oxygen radial distribution function (g_{OO}) extracted from Skinner et al. (2) experiments (X-ray2) at $T = 298$ K and 1 atm pressure with the predictions from (*A*) RexPoN and RexPoN-PIMD and (*B*) MB-pol and MB-pol-PIMD. This shows that RexPoN-PIMD is nearly identical to X-ray2 experiment, much closer than MB-pol-PIMD, and that RexPoN is far closer than MB-pol. For more comparisons see figure 1 of ref. 5.

Table 1. Summary of predicted properties from RexPoN compared to experimental data, PBE-DFT, MB-pol (10), and MB-pol-PIMD

Property	Experiment	RexPoN	DFT-PBE	MB-pol	MB-pol-PIMD
T_{melt}	273.15	273.3	420	263.5	—
S^0	69.9	68.43	51.32	—	—
ρ	0.9965	0.9965	0.944	1.007	1.001
ε	78.4	76.1	112	68.4	—
ΔH_v	10.52	10.36	6.2	10.93	10.1

The melting temperature T_{melt} (kelvin) at 1 atm pressure. Standard molar entropy S^0 (joules per mole kelvin), density ρ (grams per cubic centimeter), static dielectric constant ε, heat of vaporization ΔH_v (kilocalories per mole), all at $T = 298$ K, pressure = 1 atm.

1 T. Head-Gordon, F. Paesani, Water is not a dynamic polydisperse branched polymer. *Proc. Natl. Acad. Sci. U.S.A.* **116**, 13169–13170 (2019).
2 L. B. Skinner *et al.*, Benchmark oxygen-oxygen pair-distribution function of ambient water from x-ray diffraction measurements with a wide Q-range. *J. Chem. Phys.* **138**, 074506 (2013).
3 J. E. Enderby, G. W. Neilson, Structural properties of ionic liquids. *Adv. Phys.* **29**, 323–365 (1980).
4 A. H. Narten, W. E. Thiessen, L. Blum, Atom pair distribution functions of liquid water at 25 °C from neutron diffraction. *Science* **217**, 1033–1034 (1982).
5 S. Naserifar, W. A. Goddard, 3rd, Liquid water is a dynamic polydisperse branched polymer. *Proc. Natl. Acad. Sci. U.S.A.* **116**, 1998–2003 (2019).
6 A. K. Soper, Joint structure refinement of x-ray and neutron diffraction data on disordered materials: Application to liquid water. *J. Phys. Condens. Matter* **19**, 335206 (2007).
7 A. Berger, G. Ciardi, D. Sidler, P. Hamm, A. Shalit, Impact of nuclear quantum effects on the structural inhomogeneity of liquid water. *Proc. Natl. Acad. Sci. U.S.A.* **116**, 2458–2463 (2019).
8 K. H. Kim *et al.*, Maxima in the thermodynamic response and correlation functions of deeply supercooled water. *Science* **358**, 1589–1593 (2017).
9 S. Naserifar, W. A. Goddard, 3rd, The quantum mechanics-based polarizable force field for water simulations. *J. Chem. Phys.* **149**, 174502 (2018).
10 S. K. Reddy *et al.*, On the accuracy of the MB-pol many-body potential for water: Interaction energies, vibrational frequencies, and classical thermodynamic and dynamical properties from clusters to liquid water and ice. *J. Chem. Phys.* **145**, 194504 (2016).