Supporting Information for: Direct observation of liquid-liquid phase coexistence in deeply supercooled water using an accurate polarizable multipole model

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Table S1: Selected validation properties of the iAMOEBA model. Self-diffusion, shear viscosity, and surface tension are at 298.15 K, 1.0 atm. A more extensive table of validation properties can be found in Ref. 1.

Property	iAMOEBA	Experiment	% Diff.
Ice Ih melting point (1 atm)	261 K	273 K	-4.4%
Surface tension (mN m^{-1})	68.4	71.7	-4.6%
Self-diffusion (10^{-5} cm s^{-2})	2.54	2.30	10.4%
Shear viscosity (mPa s)	0.85	0.896	5%
Diffusion activation energy (kJ mol^{-1})	18.8	18.4	-2.2%

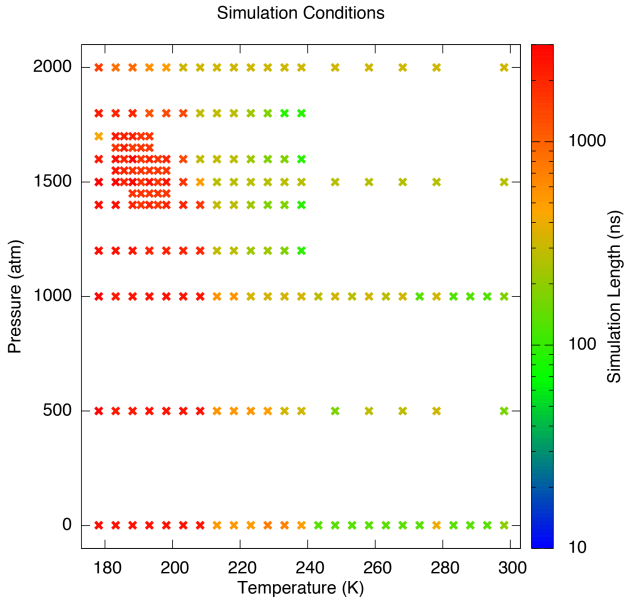

Figure S1: The bulk MD simulations that were carried out to generate the thermodynamic data shown in Figure 1 and Figure S1. Colors of $\times$ symbols indicate simulation length.

Construction of initial structure for direct coexistence simulations

The initial structure for the LDL portion of the coexistence simulation was derived from a simulation of a cubic box of 500 molecules at NPT conditions (178.15 K, 1800 atm). A proposed LDL structure was extracted from the trajectory corresponding to $t = 2.4$ μs where the box side-length was 24.976 Å and the instantaneous density was 960 kg m^{-3}. The LDL structure was used to initiate another NPT simulation at elevated temperature (188.15K, 1800 atm) corresponding to the HDL regime; this simulation was run for 40 ns and used an anisotropic barostat in which only the z-axis was allowed to vary. At the end of this run, a proposed HDL structure was extracted from the trajectory, in which the side-lengths of the tetragonal box were $(24.976, 24.976, 22.279)$ Å corresponding to $\rho = 1076$ kg m^{-3}. Each simulation box was replicated twice in the x, y, z dimensions to create a pair of 4000-molecule supercells. The two supercells were then stacked along the z-direction with a 2.5 Å spacing to create the starting structure of the direct coexistence simulation with a total of 8000 molecules.

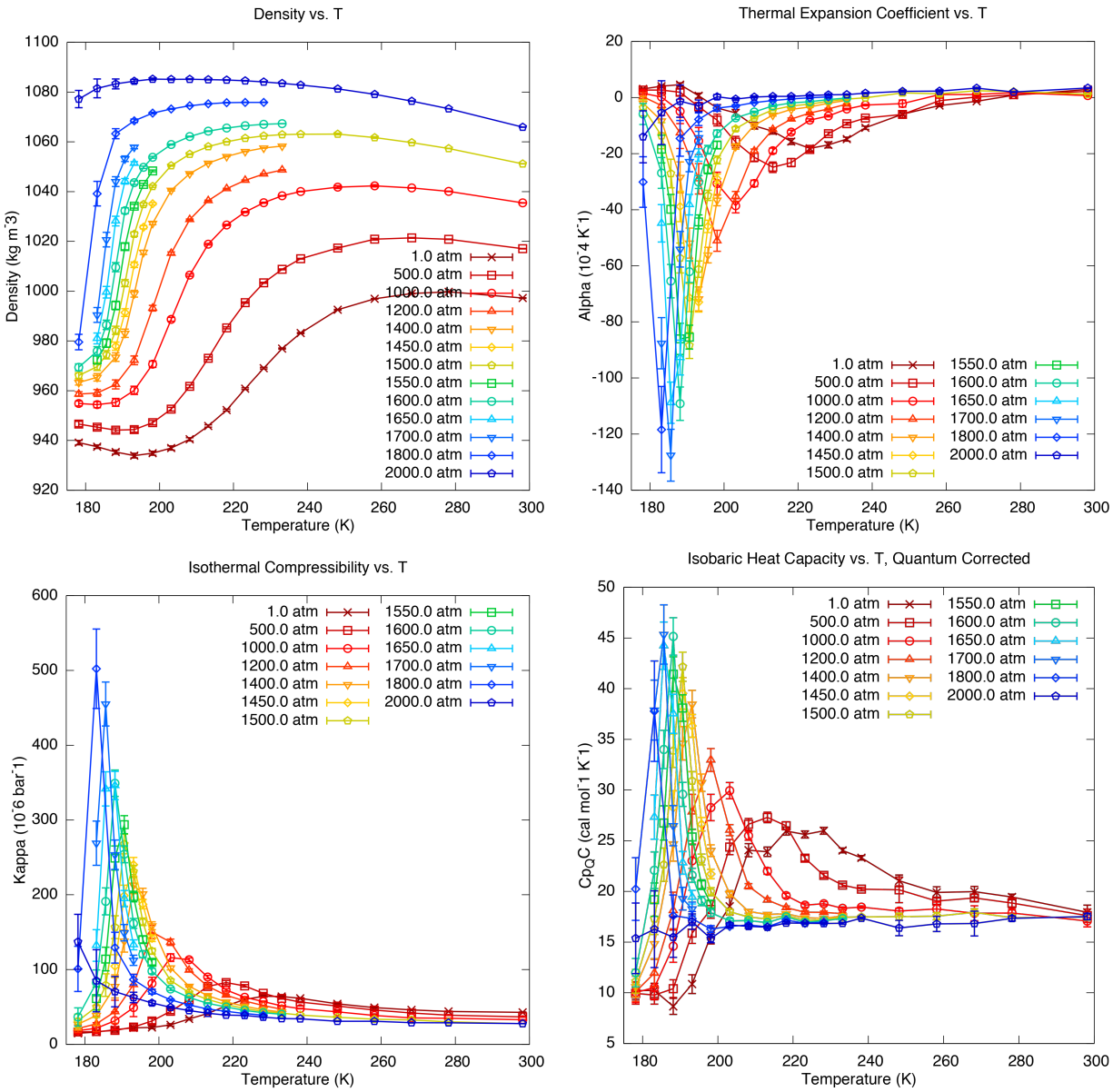

Figure S2: Thermodynamic properties iAMOEBA water as a function of temperature and pressure. The data shown is the same as in Fig. 1.

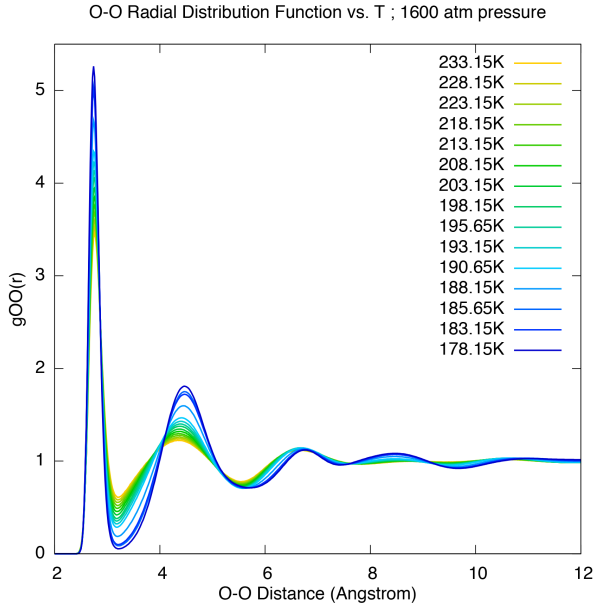

Figure S3: The temperature dependence of the iAMOEBA O-O radial distribution function at 1600 atm pressure. The rapid change in the first trough and second peak of the RDF near 188.15 K is indicative of potential LLCP behavior.

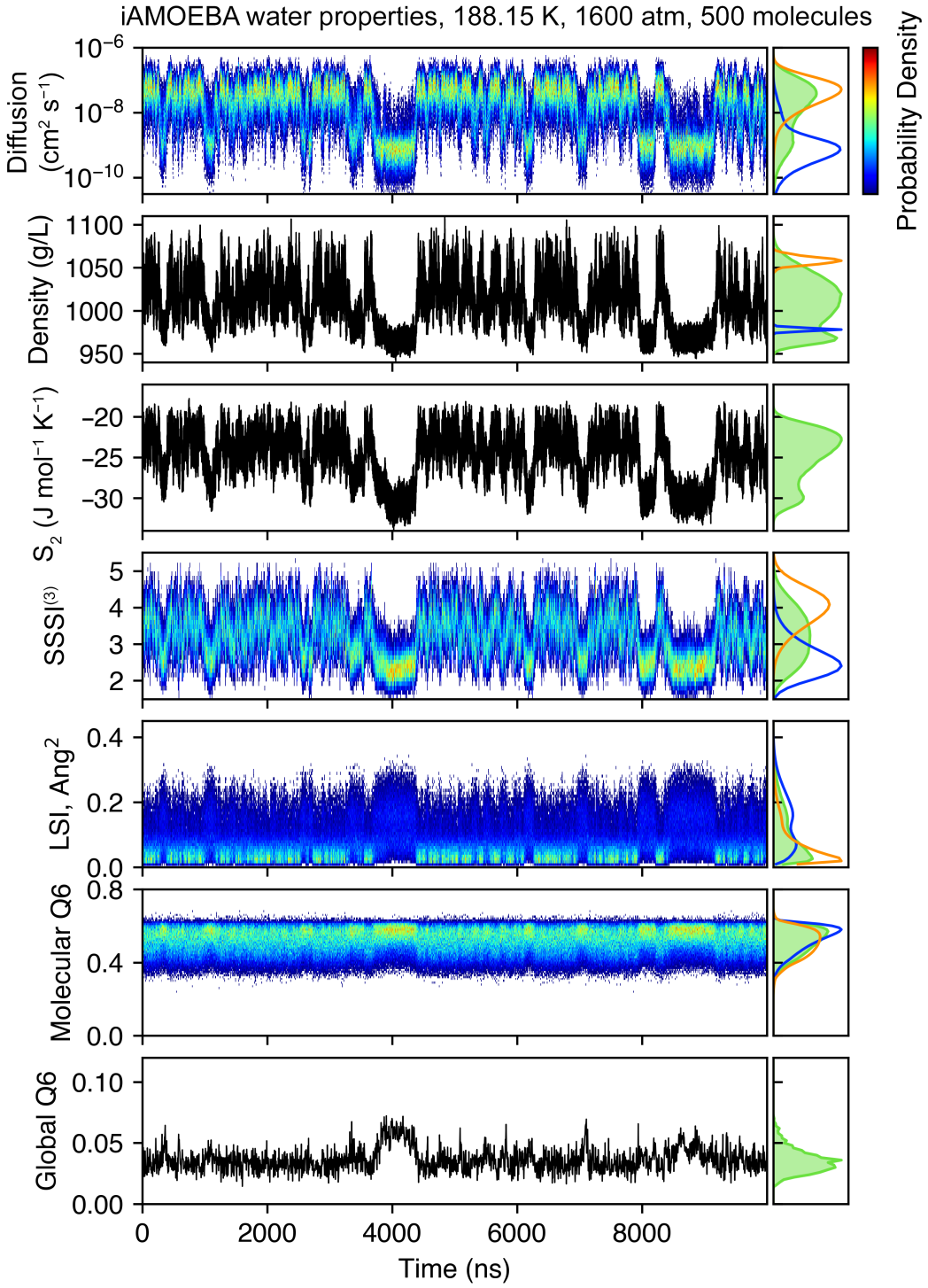

Figure S4: Trajectory analysis of 500 iAMOEBA water molecules at 188.15 K and 1600 atm.

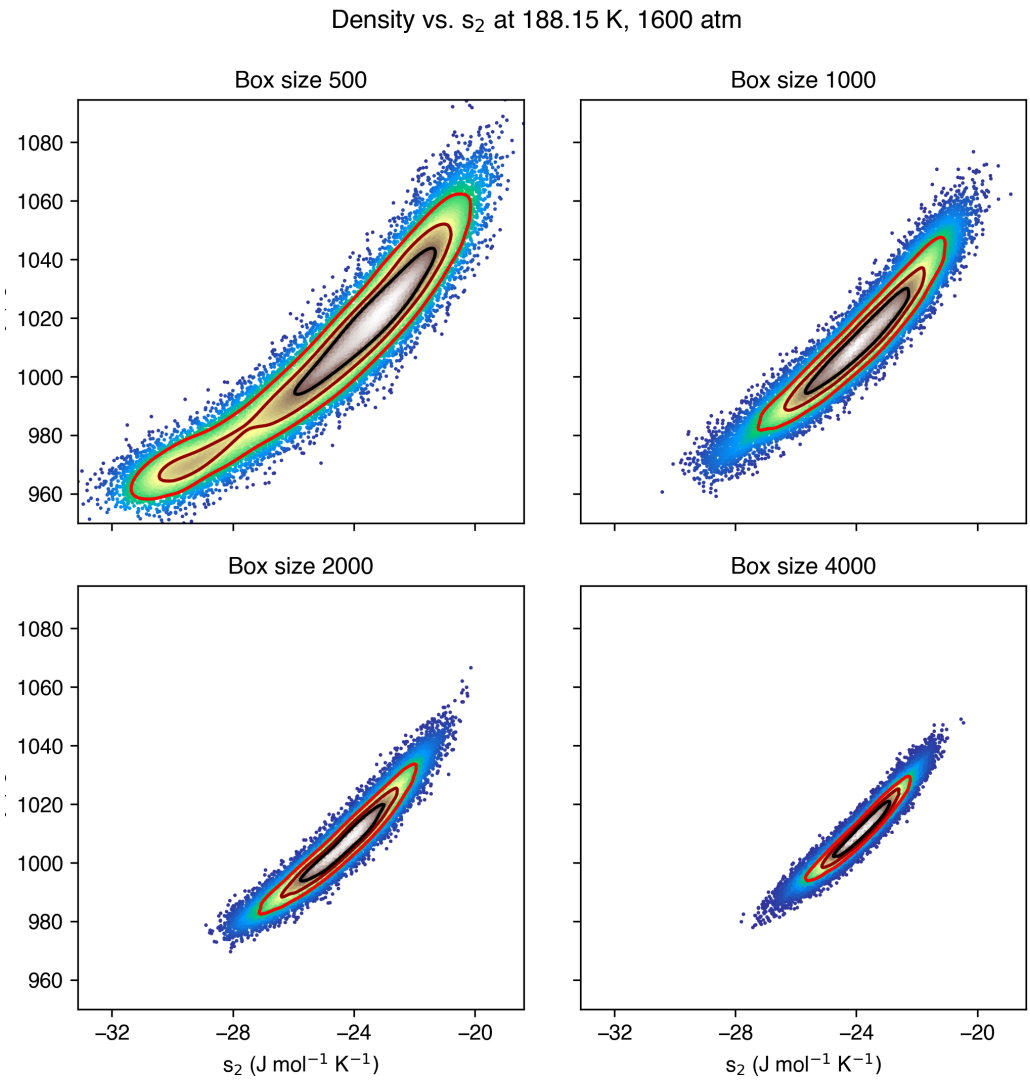

Figure S5: Scatter plot of density vs. S2 for simulations containing 500, 1000, 2000 and 4000 molecules. The contours are drawn at $\Delta G = 0.5$, 1.0 and 2.0 kJ/mol relative to the minimum. The free energy is calculated as $\Delta G = -k_B T \ln P/P_{\max}$ where P is calculated using the `scipy.stats` kernel density estimator.

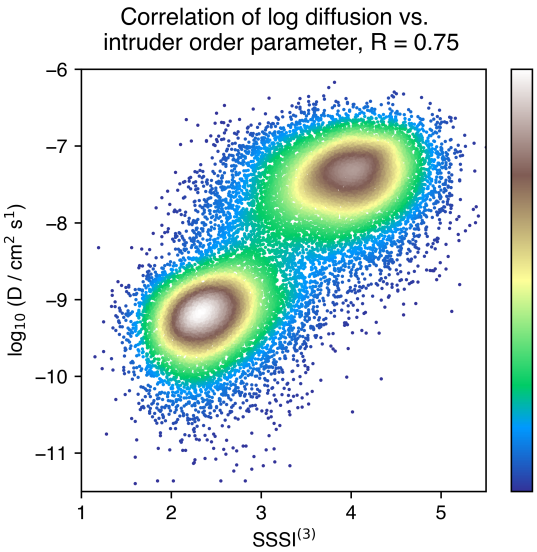

Figure S6: Scatter plot of SSSI(3) vs. log diffusion coefficient using molecules taken from simulations at two different conditions: lower left = 180.15K, 1800 atm (LDL); upper right = 184.15 K, 1800 atm (HDL).

References

(1) Wang, L.-P.; Head-Gordon, T.; Ponder, J. W.; Ren, P.; Chodera, J. D.; Eastman, P. K.; Martinez, T. J.; Pande, V. S. Systematic Improvement of a Classical Molecular Model of Water. *J. Phys. Chem. B* **2013**, *117*, 9956–9972.