Supplementary Material for 'Nuclear Quantum Effects on the Thermodynamic, Structural, and Dynamical Properties of Water'

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We provide additional results obtained from PIMD simulations of H_2O and D_2O using the q-TIP4P/F model. The main goal of this supplementary material is to show how sensitive the results in the main manuscript are to the (i) PIMD simulation time step dt, (ii) number of beads per polymer n_b, and (iii) collision frequency γ of the local PILE thermostat employed. The sensitivity of our results to dt is explored for both H_2O and D_2O for the cases $dt = 0.1, 0.25, 0.50$ fs (H_2O) and $dt = 0.25, 0.50$ fs (D_2O). The effects of varying n_b are also explored for both H_2O ($n_b = 32$, 72, 128) and D_2O ($n_b = 32$, 72). The effects of varying γ are studied only for the case of H_2O with $\gamma = 1.0 - 10^{-6}$ ps^{-1}; PIMD simulations for D_2O are all performed with $\gamma = 0.001$ ps^{-1}. The results for H_2O and D_2O included in the main manuscript correspond to $dt = 0.25$ fs, $n_b = 32$, 72, and $\gamma = 0.001$ ps^{-1}.

I. THERMODYNAMIC PROPERTIES

The densities of H_2O and D_2O as function of temperature are included in Fig. S1. Fig. S2 shows the enthalpy and isobaric heat capacity $C_P(T)$ of H_2O and D_2O; the corresponding isothermal compressibility $\kappa_T(T)$ and dielectric constant $\epsilon(T)$ are included in Figs. S3 and S4, respectively. The same symbol and color styles are employed in Figs. S1-S4 to denote the different system (H_2O and D_2O) and conditions (dt and n_b) considered.

The results can be summarized as follows. The reported $\rho(T)$ (Fig. S1), $\kappa_T(T)$ (Fig. S3), and $\epsilon(T)$ (Fig. S4) of H_2O and D_2O are not sensitive, within error bars, to the values of n_b and dt explored (i.e., $dt = 0.10 - 0.50$ fs and $n_b = 32 - 128$ for H_2O; $dt = 0.25 - 0.50$ fs and $n_b = 32 - 72$ for D_2O). However, the corresponding $C_P(T)$ vary considerably (by $5 - 20$ J/mol/K) depending on dt. Varying n_b in the range $32 - 128$ also alters the heat capacity of H_2O and D_2O. Briefly, from the thermodynamic properties studied, only C_P and the enthalpy are sensitive to the computational details and hence, its determination requires further studies.

A maximum in C_P is not observable for any of the values of dt and n_b explored. Instead, we confirm that the maximum in $\kappa_T(T)$ and $\epsilon(T)$ reported in the main manuscript is independent of dt and n_b. All of these extrema in thermodynamic properties are consistent with the possibility that water exhibits a liquid-liquid critical point at low temperatures and positive pressures [1]. Indeed, these maxima in the reported thermodynamic response functions are usually observed in classical computer simulations of water and water-like models that exhibit a LLCP [2, 3].

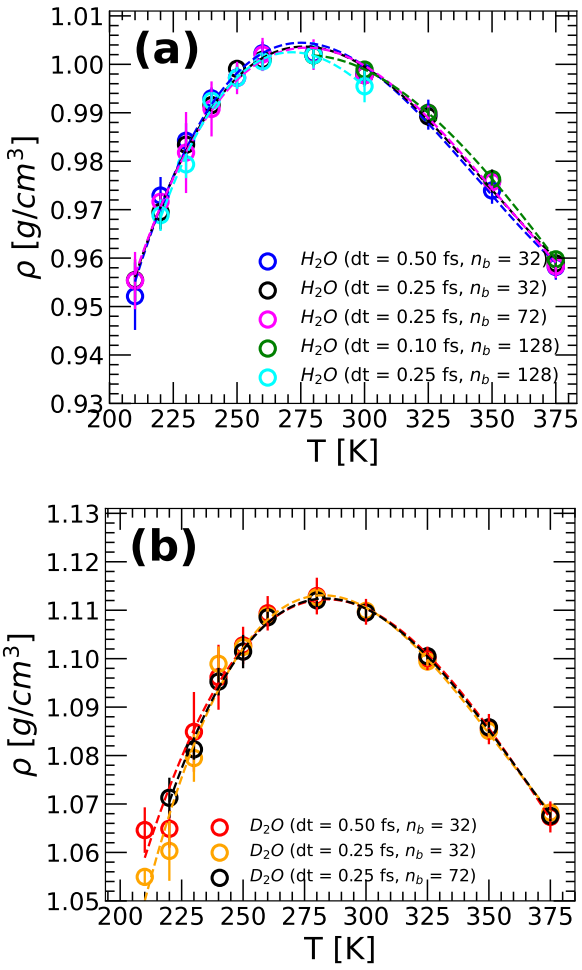

FIG. S1. Density of (a) H_2O and (b) D_2O as a function of temperature from PIMD simulations using the q-TIP4P/F model (P = 1 bar). In both cases, PIMD simulations using different number of beads per ring-polymer n_b and time step dt give similar density values.

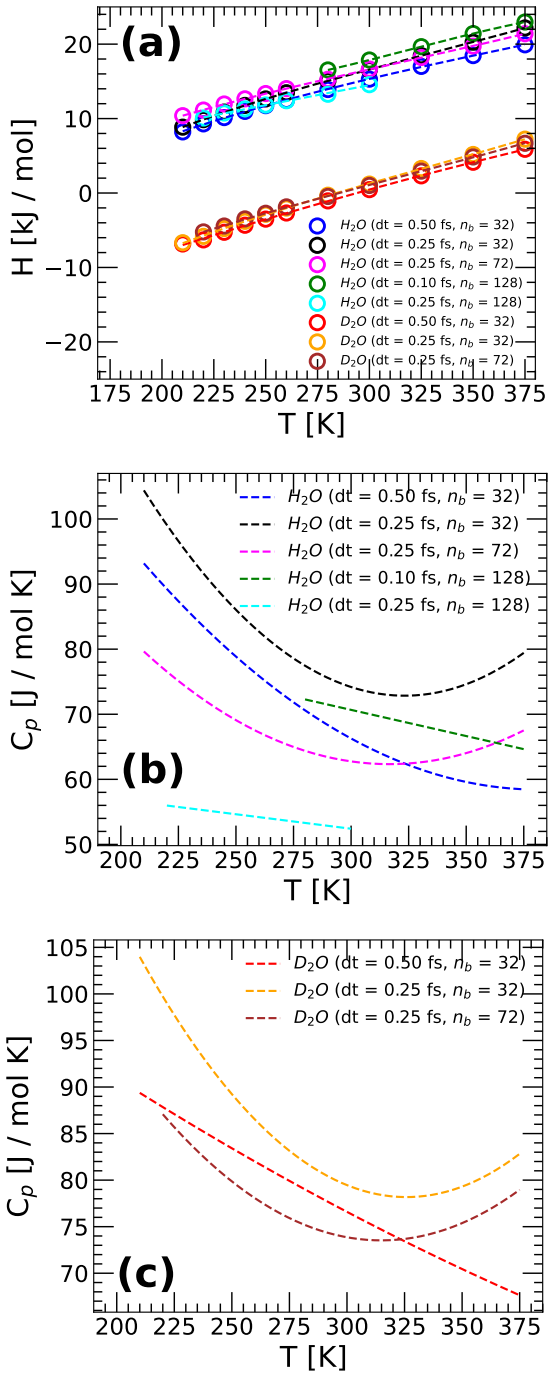

FIG. S2. (a) Enthalpy as a function of temperature for H_2O and D_2O (P = 1 bar) obtained from PIMD simulations using the q-TIP4P/F model. Results are for different time steps dt and number of beads n_b. Lines are obtained using third-order polynomial fits of the PIMD simulation results. (b) Heat capacity $C_P(T)$ of H_2O at different dt and n_b obtained from (a). (c) $C_P(T)$ for D_2O calculated from (a). $C_P(T)$ is very sensitive to both n_b and dt; varying these parameters can lead to a change in $C_P(T)$ of 5 - 50 J/mol/K and to the presence/absence of a minimum in $C_P(T)$.

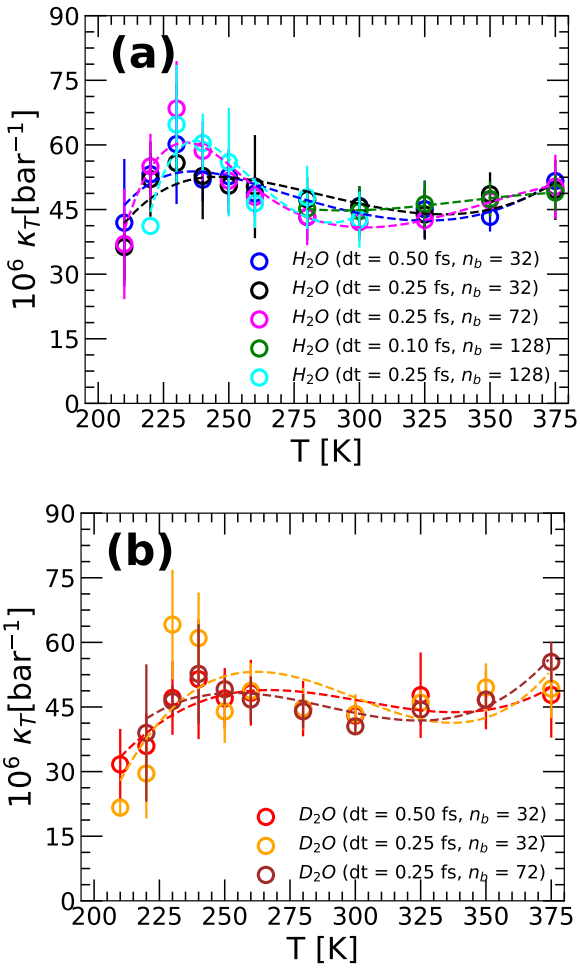

FIG. S3. Isothermal compressibility $\kappa_T(T)$ as a function of temperature for (a) H_2O and (b) D_2O (P = 1 bar). Results are from PIMD simulations using the q-TIP4P/F model and for different values of dt and n_b. The κ_T of both H_2O and D_2O are independent of the dt and n_b (within error bars).

II. DYNAMICAL PROPERTIES

The diffusion coefficient of H_2O and D_2O as a function of temperature are included in Fig. S5; the reported diffusion coefficients are practically independent of the time step employed (dt = 0.10, 0.25, 0.50 fs). The associated MSDs are included in Fig. S6a and S6b. As shown in Fig. S6c, the MSD, and hence the diffusion coefficients, are relatively independent of the number of beads n_b used. Fig. S7 shows the effects of the collision frequency γ on the MSD of H_2O for temperatures T = 220, 240, and 300 K. Hence, the diffusion coefficients obtained by using Eq. 8 in the main text are not affected by the thermostat used in the PIMD simulations.

We conclude by discussing briefly the methodology used in this work to calculate $D(T)$. In the RPMD technique, the diffusion coefficient is calculated from the Kubo-transformed velocity autocorrelation function

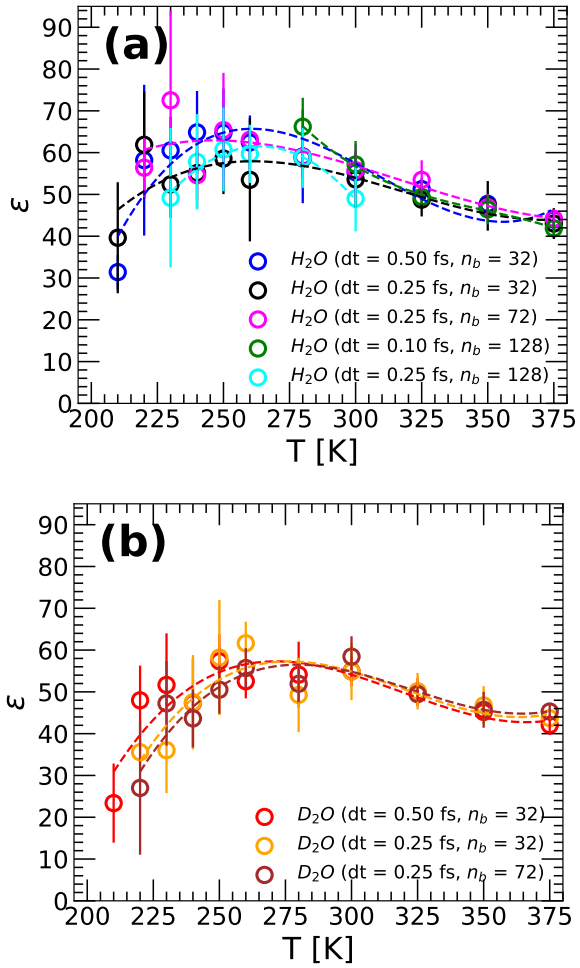

FIG. S4. Dielectric constant $\epsilon(T)$ as a function of temperature of (a) H_2O and (b) D_2O (P = 1 bar). Results are from PIMD simulations using the q-TIP4P/F model and for different values of dt and n_b. The $\epsilon(T)$ of both H_2O and D_2O are independent of dt and n_b (within error bars).

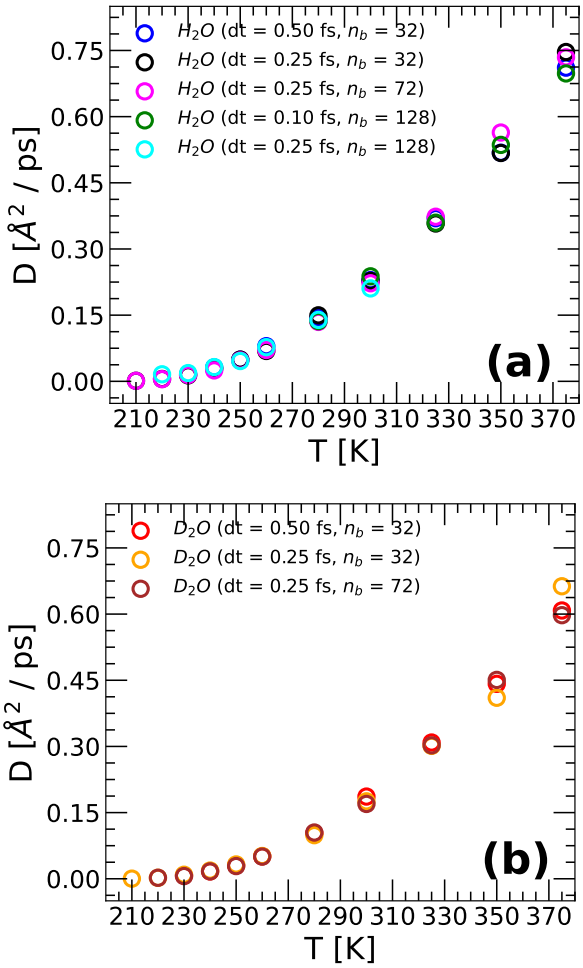

FIG. S5. Diffusion coefficient for (a) H_2O and (b) D_2O (P = 1 bar) obtained from PIMD simulations using the q-TIP4P/F model. Results are for different time steps dt and number of beads n_b. The diffusion coefficients of both H_2O and D_2O are independent of dt and n_b (within error bars) at $T < 350$ K.

(VACF); see manuscript, Eqs. 6 and 7. Moreover, the Kubo-transformed VACF is obtained from independent PIMD simulations at constant (N,V,E). In Fig. S8, we include the values of $D(T)$ calculated from RPMD. Specifically, we perform multiple PIMD simulations of H_2O in the NVE ensemble starting from configurations thermalized at T = 240, 280, 300, 325, 350, 375 K. From these NVE trajectories, we calculate the Kubo-transformed VACF, from which $D(T)$ is obtained (see Eq. 7 in the manuscript). At a given T, $\widetilde{c}_{v\cdot v}(t)$ is calculated from 10 independent trajectories (NVE ensemble) that vary in length depending on the temperature of the starting configuration. At T > 300 K, 75-ps trajectories were used; for T = 300 K and T < 300 K, trajectories of 100 and 150 ps were used, respectively. As shown in Fig. S8, the values of $D(T)$ reported in the main manuscript are identical (within error bars) to the values obtained using (true) RPMD.

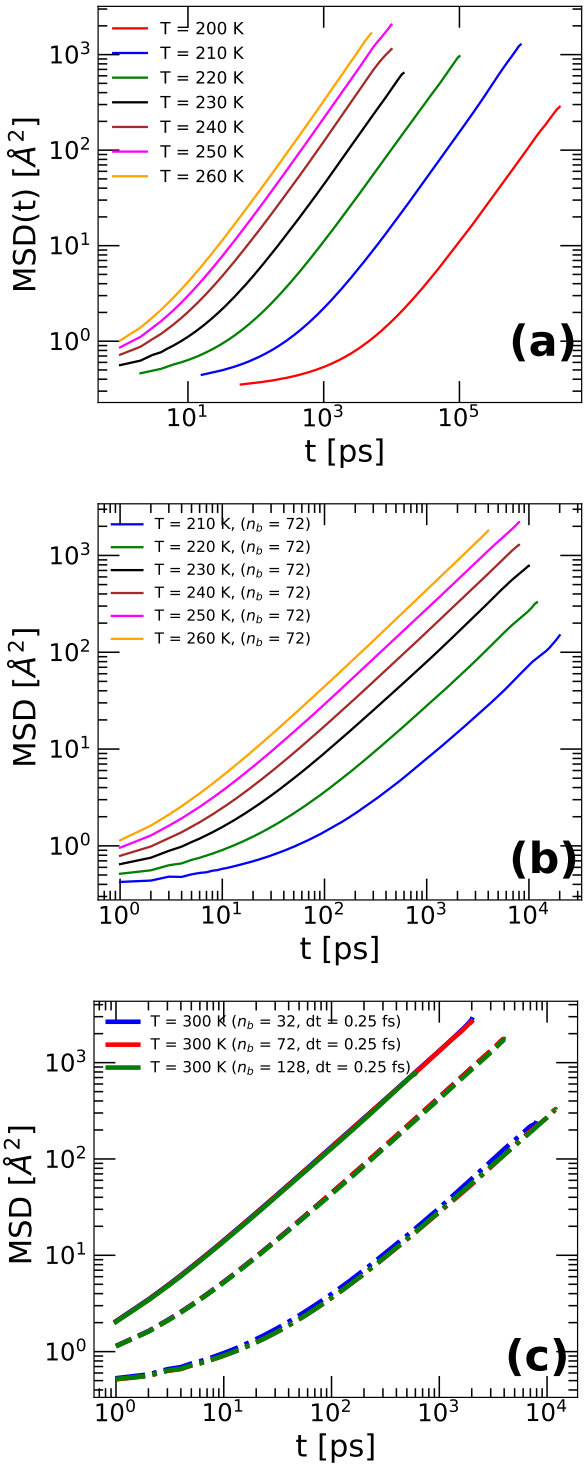

FIG. S6. MSD of water molecules from (a) classical MD and (b) PIMD simulations of q-TIP4P/F water (dt = 0.25 fs; n_b = 72). (c) Results from PIMD simulations are not sensitive to the number of beads n_b employed. Solid, dashed, and dot-dashed lines are, respectively, for T = 300, 260, and 220 K.

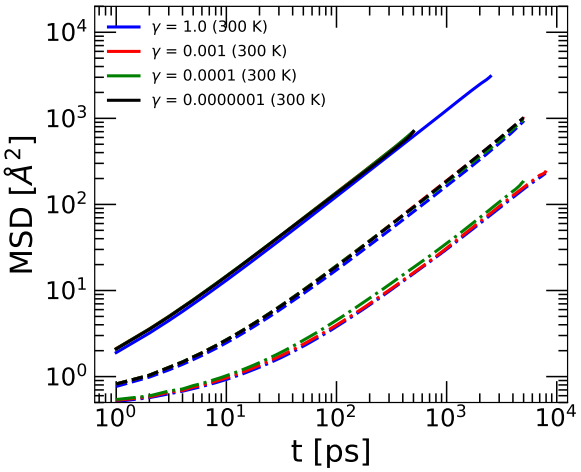

FIG. S7. Mean-square displacement of H_2O molecules obtained from PIMD simulations using the q-TIP4P/F model for different values of the thermostat collision frequency γ (dt = 0.50 fs and n_b = 32). Dashed and dotted lines correspond to T = 240 K and T = 220 K, respectively. The effects of γ on the dynamics of the system are negligible.

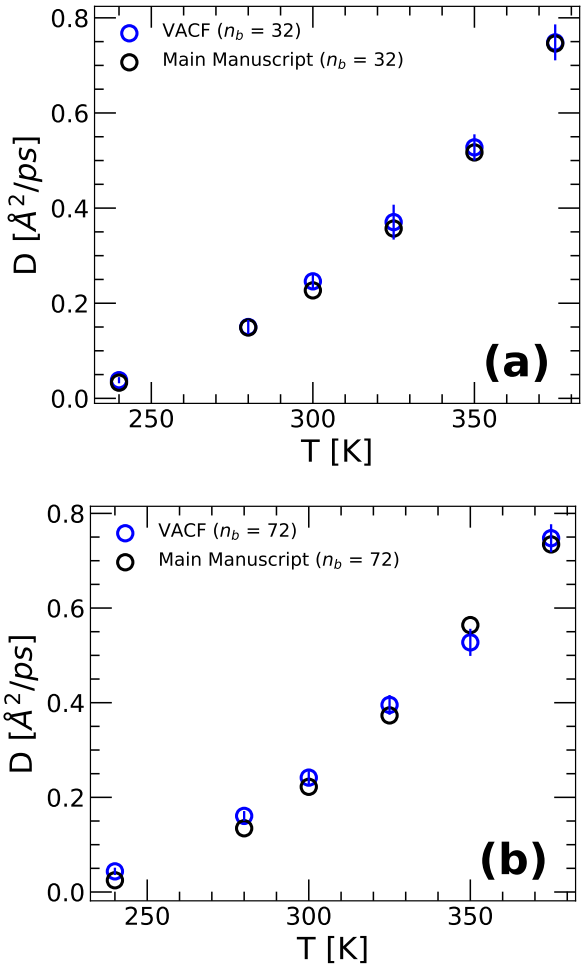

FIG. S8. (a) Diffusion coefficient of H_2O obtained from the Kubo-transformed velocity autocorrelation function $\widetilde{c}_{v \cdot v}(t)$ (blue circles) and from the slope of the MSD (black circles; Eq. 8 of the main manuscript) $n_b = 32$. (b) Same as (a) but for $n_b = 72$. Both methods provide practically the same results for D (within error bars) reported in the main manuscript.

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