Note: Microsecond long atomistic simulation of supercooled water

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Supercooled water is a metastable phase of liquid water below the melting temperature.[1] In this regime, the transition to the solid phase is irreversible once the process is activated. An interesting discussion recently developed on the relationship between crystallization rate and the time scales of equilibration within the liquid phase.[2,3] Calculations using a coarse grained monatomic model of water, the mW model, suggested that equilibration of the liquid below the temperature of homogeneous nucleation $T_H \approx 225$ K is slower than ice nucleation.[3] This observation has important consequences to a proposed theory of water anomalies, predicting a second critical point below T_H where a liquid-liquid phase transition occurs.[4] Although it has attracted attention,[5–8] this theory is not without problems. If the speed of ice nucleation is faster than liquid relaxation, the liquid-liquid transition would lose sense from a thermodynamical point of view, being the liquid phase not equilibrated.[2]

Here, a 3 μs long molecular dynamics simulation of the TIP4P-Ew water model is presented to investigate the relaxation properties of an atomistic model in the supercooled region below T_H. The length of this calculation is one order of magnitude larger than the 350 ns used to study freezing with the mW model.[3] A box of 1024 molecules was simulated with GROMACS.[9] The Berendsen barostat,[10] velocity rescale thermostat[11] and PME (Ref. 12) were used for pressure coupling, temperature coupling, and long-range electrostatics, respectively. The simulation was run at 190 K and 1250 atm. These values are close to the estimated liquid-liquid critical point for the TIP4P-Ew,[13] congruous with recent calculations on the similar TIP4P/2005 model.[6]

In these conditions, freezing was not observed as shown by the time series of the potential energy E_p (Fig. 1(a)). Fluctuations are of the order of 0.5 kJ/mol with no systematic drift. It has been observed that once freezing is activated the energy drifts very quickly to low values of the potential energy, with large energy changes (e.g., roughly 5 and 2 kJ/mol for TIP4P at 230 K (Ref. 14) and TIP4P/2005 at 242 K,[15] respectively).

The time series of the density ρ and the tetrahedral order parameter Q_T (Ref. 17) are shown in Figs. 1(b) and 1(c). They, respectively, correlate and anticorrelate with the potential energy (Pearson correlation coefficient $r = 0.69$ and -0.86). The distributions of both ρ and Q_T show an appreciable bump at one of the tails (see right panel of Figs. 1(b) and 1(c)), suggesting the presence of a subpopulation. For the case of the tetrahedral order parameter, the subpopulation emerges at values around 0.873 (red dashed line and right side of Fig. 1(c)). This fluctuation is localized in a time window between 2.3 and

2.6 μs in correspondence to a decreasing of both the density and the potential energy. It is interesting to note that density subpopulations have been interpreted by some[18] as a signature of the aforementioned liquid-liquid transition.

To check whether this fluctuation corresponded to an ice nucleation attempt, the Q_6 order parameter[2,16,19] was calculated (Fig. 1(d)). In the time window between 2.3–2.6 μs the value of the parameter is around 0.025, with no signs of ice nucleation. Moreover, no correlation with the energy was found ($r = 10^{-6}$). With a value of Q_6 for hexagonal ice expected to be one order of magnitude larger,[16] no evidence for ice nucleation is found in the present trajectory.

Finally, the oxygen mean-square-displacement (MSD) was calculated (Fig. 2). At timescales shorter than one ns, water shows a subdiffusive behavior (dotted line in Fig. 2). For larger times the system enters a diffusive regime, following the linear relationship MSD $\approx t$ (dashed line), with a maximum average displacement of 3.47 nm after 3 μs. Taking into account that the molecular diameter is around 0.3 nm, water
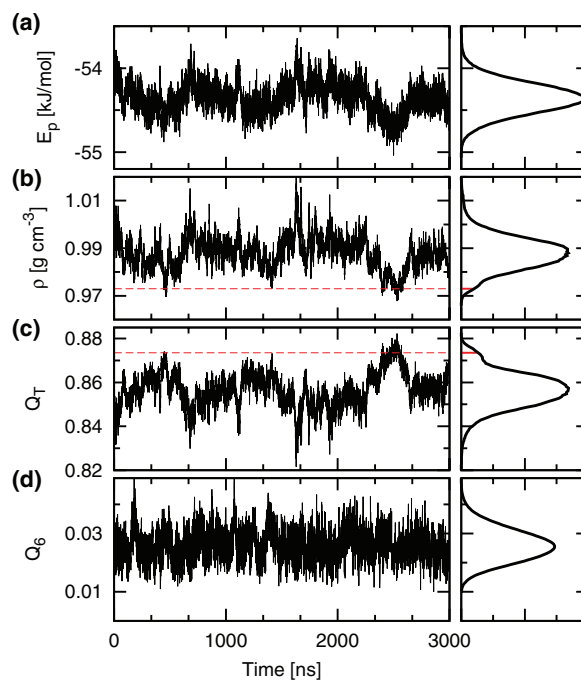

FIG. 1. Time series for the 3 μs trajectory. (a) Potential energy; (b) density; (c) tetrahedral order parameter Q_T; (d) Q_6 parameter (calculated as in Refs. 2 and 16). Right panels show the probability distribution of the respective quantities. Dashed lines represent deviations from the mean fluctuations, with values of 0.972 and 0.873 for ρ and Q_T, respectively.
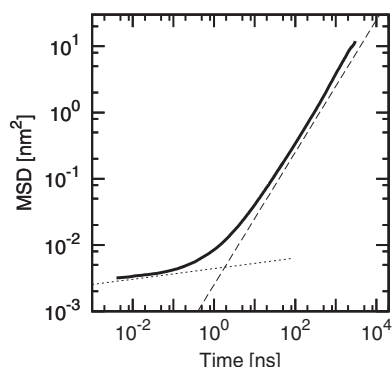
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FIG. 2. Oxygen mean square displacement (MSD). The dashed and dotted lines represent a linear and a power-law (exponent equal to 0.1) regression, respectively. The diffusion coefficient extracted from the linear regime is of 6.6×10^{-9} cm^2/s. The g_msd function of GROMACS was used with 150 windows to improve statistics.

molecules have diffused for about 11.5 molecular diameters (the average box side length is of 3.14 nm).

Apart from a rare fluctuation unrelated to nucleation, the converged distribution of the potential energy, density, and structural order parameters (Fig. 1), together with the fact that water dynamics is not glassy (Fig. 2) provide evidence that the liquid phase has equilibrated before the transition to ice. Our finding is in agreement with another μs long simulation of supercooled water with a 5-site model,[18] suggesting that equilibration of the liquid phase below T_H is a common feature of atomistic models. The mW model has shown to reproduce several properties of water, including density and phase diagram.[20] But the lack of hydrogens, and consequently of molecular reorientations,[21] might considerably speed up the time scales. We speculate that the differences in the relaxation kinetics between atomistic models and the mW model are due to the lack of molecular reorientations in the latter. Clearly, further experimental validation is needed to clarify which proposed mechanism (if any) is closer to real water.

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