Interplay between Time-Temperature Transformation and the Liquid-Liquid Phase Transition in Water

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We study the new water model proposed by Mahoney and Jorgensen [J. Chem. Phys. **112**, 8910 (2000)], which is closer to real water than previously proposed classical pairwise additive potentials. We simulate the model in a wide range of deeply supercooled states and find (i) the existence of a nonmonotonic "nose-shaped" temperature of maximum density line and a nonreentrant spinodal, (ii) the presence of a low-temperature phase transition, (iii) the free evolution of bulk water to ice, and (iv) the time-temperature-transformation curves at different densities.

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Much effort has been invested in exploring the overall phase diagram of water and the connection among its liquid, supercooled, and glassy states [1–3], with particular interest in understanding the origin of the striking anomalies at low temperatures, such as the T dependence of the isothermal compressibility K_T, the constant pressure specific heat C_P, and the thermal expansivity α_P.

The "stability limit conjecture" attributes the increase of the response functions upon supercooling to a continuous retracing spinodal line bounding the superheated, supercooled, and stretched (negative pressure) metastable states [4]. This line at its minimum intersects the temperature of maximum density (TMD) curve tangentially. More recently, a different hypothesis has been developed, for which the spinodal does not reenter into the positive pressure region, but rather the anomalies are attributed to a critical point below the homogeneous nucleation line [5]. The TMD line, which is negatively sloped at positive pressures, becomes positively sloped at sufficiently negative pressures and does not intersect the spinodal. A line of first order phase transitions—interpreted as the liquid state analog of the line separating low and high density amorphous glassy phases [3,5]—develops from this critical point.

Simulations of supercooled metastable states are possible because the structural relaxation time at the temperatures of interest is several orders of magnitude shorter than the crystallization time. It is difficult, but not impossible [6], to observe crystallization in simulations of molecular models [7] because homogeneous nucleation rarely occurs on the time scales reachable by present-day computers. Bulk water simulations have been crystallized by applying a homogeneous electric field [8] or placing liquid water in contact with preexisting ice [9,10], but spontaneous crystallization of deeply supercooled model water has not been observed in simulations.

In contrast, experimental measurements of metastable liquid states are strongly affected by homogeneous nucleation. The nucleation and growth of ice particles from aqueous solution has been extensively studied, and the "nose-shaped" time-temperature-transformation (TTT) curves have been measured [1,11,12]. The nonmonotonic relation between crystallization rate and supercooling depth results from the competition between the thermodynamic driving force for nucleation and the viscous slowing down [1]. Crystallization hinders direct experimental investigation of pure metastable liquid water below the homogeneous nucleation line; only indirect measurements can be made by studying the metastable melting lines of ices [3].

This work attempts to unify the phenomena connected with the existence of a liquid-liquid phase transition and homogeneous nucleation in a single molecular dynamics simulation study. We simulate a system of $N = 343$ molecules interacting with the transferable intermolecular potential with five points (TIP5P) [13]. TIP5P is a five-point, rigid, nonpolarizable water model, not unlike the five-point ST2 model [14]. The TIP5P potential accurately reproduces the density anomaly at 1 atm and exhibits excellent structural properties when compared with experimental data [13,15]. The TMD shows the correct pressure dependence, shifting to lower temperatures as pressure is increased. Under ambient conditions, the diffusion constant is close to the experimental value, with reasonable temperature and pressure dependence away from ambient conditions [13].

We perform equilibration runs at constant T (Berendsen's thermostat), while we perform production runs in the microcanonical (NVE where N is the number of particles, V is volume, and E is energy) ensemble. After thermalization at $T = 320$ K we set the thermostat temperature to the temperature of interest. We let the system evolve for a time longer than the oxygen structural relaxation time τ_α, defined as the time at which $F_s(Q_0, \tau_\alpha) = 1/e$, where $F_s(Q_0, t)$ is the self-intermediate scattering function evaluated at $Q_0 = 18\ \mathrm{nm}^{-1}$, the location of the first peak of the static structure factor. In the time τ_α, each molecule diffuses on average a distance of the order of the nearest

neighbor distance. We use the final configuration of the equilibration run to start a production run of length greater than several τ_α and then analyze the calculated trajectory. We check that no drift in any of the studied quantities and no crystallization occurs during the production run.

In Fig. 1 we show results for pressure along isotherms. At lower temperatures an inflection develops, which becomes a "flat" isotherm at the lowest temperature, $T = 215$ K. The presence of a flat region indicates that a phase separation takes place, and we estimate the critical temperature $T_{C'} = 217 \pm 3$ K, the critical pressure $P_{C'} = 340 \pm 20$ MPa, and the critical density $\rho_{C'} = 1.13 \pm 0.04$ g/cm^3.

In Fig. 2(a) we plot the pressure along isochores. The curves show minima as a function of temperature; the locus of the minima is the TMD line, since $(\partial P/\partial T)_V = \alpha_P/K_T$. It can be seen that the pressure exhibits a minimum if the density passes through a maximum ($\alpha_P = 0$). It is clear that, as in the case of ST2 water, TIP5P water has a TMD that changes slope from negative to positive as P decreases. Notably, the point of crossover between the two behaviors is located at ambient pressure, $T \approx 4$ °C, and $\rho \approx 1$ g/cm^3.

We also plot the spinodal line. We calculate the points on the spinodal line fitting the isotherms (for $T \geq 300$ K) of Fig. 1 to the form $P(T, \rho) = P_s(T) + A[\rho - \rho_s(T)]^2$, where $P_s(T)$ and $\rho_s(T)$ denote the pressure and density of the spinodal line. This functional form is the mean field prediction for $P(\rho)$ close to a spinodal line. For $T \leq 250$ K, we calculate $P_s(T)$ by estimating the location of the minimum of $P(\rho)$. The results in Fig. 2 show that the liquid spinodal line is not reentrant and does not intersect the TMD line [16].

A supercooled liquid is metastable with respect to the crystal, so it is driven to crystallize [1]. However, crystallization of model water has not been found in simulations because the homogeneous nucleation time far exceeds the CPU time. Fortunately, for TIP5P, crystallization times lie within a time window accessible to present-day simulations, and we observe crystallization at densities $\rho = 1.15$ and 1.20 g/cm^3 for a wide range of temperatures (Fig. 3).

To quantify the crystallization process, we analyze four independent configurations thermalized at temperature $T = 320$ K and instantaneously quenched to the temperature of interest. We monitor the potential energy as well as the time evolution of the structure factor $S_{\vec{Q}}(t) \equiv \langle \rho_{\vec{Q}}(t) \rho^*_{\vec{Q}}(t) \rangle / N$ at all wave vector $\vec{Q}$ values, ranging

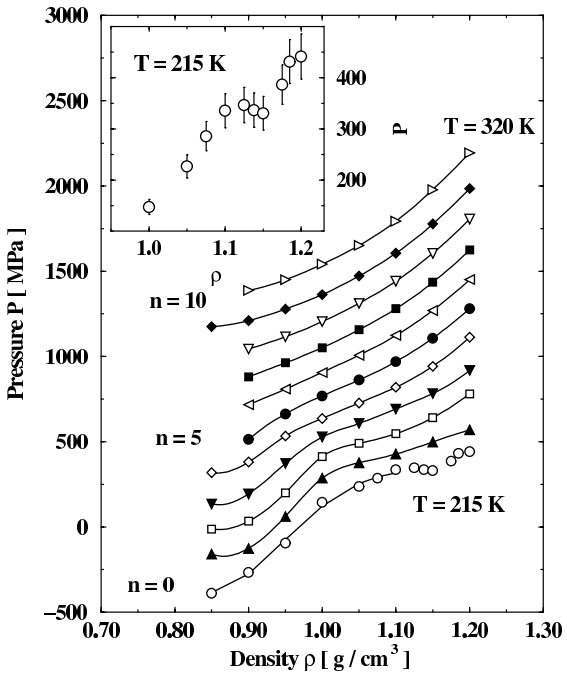

FIG. 1. Dependence on density of the pressure at all temperatures investigated ($T = 215$, 220, 230, 240, 250, 260, 270, 280, 290, 300, and 320 K, from bottom to top). Each curve has been shifted by $n \times 150$ MPa to avoid overlaps. An inflection appears as T is decreased, transforming into a "flat" coexistence region at $T = 215$ K, indicating the presence of a liquid-liquid transition. Inset: A detailed view of the $T = 215$ K isotherm.

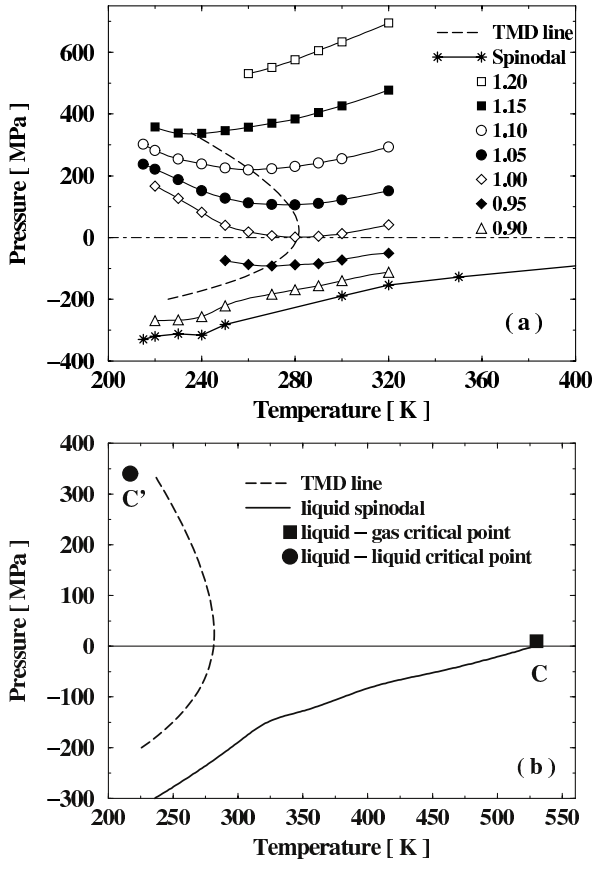

FIG. 2. (a) Pressure along seven isochores; the minima correspond to the temperature of maximum density line (dashed line). Note the "nose" of the TMD line at $T = 4$ °C. Stars denote the liquid spinodal line, which is not reentrant and terminates at the liquid-gas critical point. (b) The full phase diagram of TIP5P water. The liquid-gas critical point C is indicated by the filled square [16] and the liquid-liquid critical point C' by the filled circle.

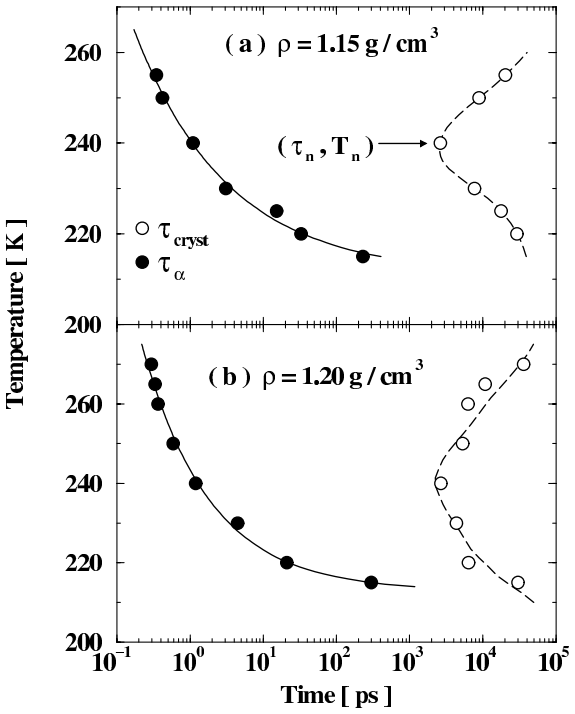

FIG. 3. Average crystallization time (open circles) as a function of temperature at the two densities (a) 1.15 g/cm^3 and (b) 1.20 g/cm^3. A well-defined nose shape is visible, as measured for water solutions [11]. We also show the structural relaxation times τ_α as calculated from the self-intermediate scattering function $F_s(Q,t)$ (closed circles). Shown as solid lines are the mode-coupling theory power law fits with $T_c = 211$ K, $\gamma = 2.9$ for $\rho = 1.15$ g/cm^3, and $T_c = 213$ K, $\gamma = 2.13$ for $\rho = 1.20$ g/cm^3. The interplay between these two curves is discussed in the text.

from the smallest value $2\pi/L$ allowed by the side L of the simulation box up to 50 nm^{-1}. The oxygen density fluctuation $\rho_{\vec{Q}}(t)$ is defined as $\sum_{i=1}^{N} \exp(i\vec{Q}\vec{r}_i)$, where $\vec{r}_i$ is the oxygen coordinate of molecule i. The onset of crystallization coincides with the occurrence of (i) a sudden drop in potential energy and (ii) a sharp increase in the density fluctuations at one or more wave vector values. When crystallization occurs, the value of $S_{\vec{Q}}(t)$ jumps from $\mathcal{O}(1)$ in the liquid to $\mathcal{O}(\mathrm{N})$.

Defining the crystallization time is somewhat arbitrary because of the stochasticity which accompanies the onset of crystallization and the definition of the critical nucleus. We define τ_{cryst} as the time at which *any* density fluctuation $S_{\vec{Q}}(t)$ grows above a threshold value $S^* = 15$ and remains continuously above the threshold for a time exceeding $t^* = 40$ ps. This threshold prevents transient density fluctuations from being attributed to crystallization. We also perform calculations for other definitions of S^* and t^*, but the above values are sufficient to unambiguously identify the onset of crystallization without requiring excessive simulation time. Figure 3 shows the crystallization times τ_{cryst}, averaged over the four independent runs, for two different densities and for a broad range of T. The resulting TTT curve shows a characteristic nose shape, arising from the competition between two effects, the thermodynamic driving force for nucleation and the viscous slowing down [1,6]. As temperature is lowered, both the thermodynamic driving force and the relaxation time increase, and it becomes more difficult for particles to diffuse to the energetically preferred crystalline configuration. For both densities, $\rho = 1.15$, and 1.20 g/cm^3, the T at which nucleation is fastest is around 240 K. At this T, the onset of crystallization requires about 3 ns. At the lowest studied T, the crystallization time has grown to 30 ns.

Figure 3 also shows the relaxation times τ_α. The T dependence of τ_α can be described by a power law $\tau_\alpha \propto (T - T_c)^\gamma$, in agreement with the prediction of mode coupling theory [17]. Since the relation $\tau_\alpha \ll \tau_{\mathrm{cryst}}$ holds at each temperature, including in the deeply supercooled region, "equilibrium" studies of metastable water can be achieved before nucleation takes place. The liquid can be connected to the deeply supercooled state via equilibrium metastable states if we choose a quench rate larger than the critical cooling rate $\mathcal{R}_c \equiv (T_m - T_n)/\tau_n$, where T_m is the melting T and T_n and τ_n locate the nose in the TTT curve [1]. For TIP5P, $\mathcal{R}_c \approx 10^{10}$ K/s at the two studied densities. For $\rho = 1.10$ g/cm^3 and $T = 240$ K, we observe only one (out of four) crystallization event within a time of 70 ns. For densities smaller than $\rho = 1.10$ g/cm^3, we observe no crystallization events within a time of 60 ns and hence we can only estimate that $\mathcal{R}_c$ is smaller than 10^9 K/s (the experimental value for water at ambient pressure is $\mathcal{R}_c \approx 10^7$ K/s [18]).

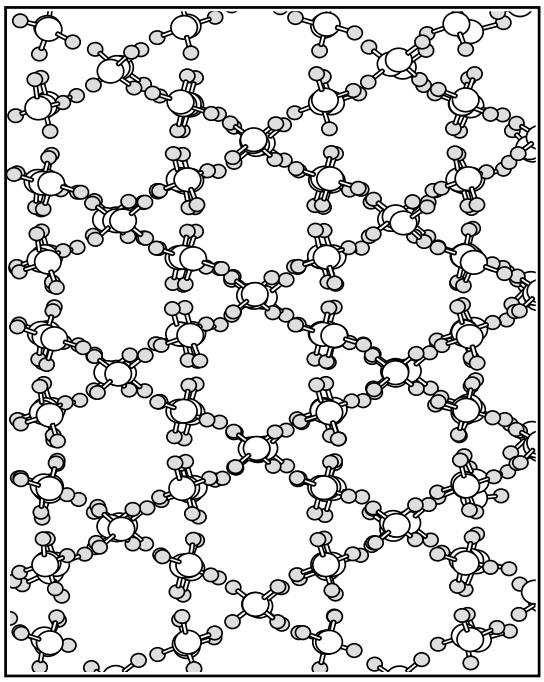

FIG. 4. For $\rho = 1.20$ g/cm^3, the energy minimum configuration, viewed along the c axis, of a crystal formed at $T = 270$ K.

In Fig. 4 we show a typical crystal configuration. The crystal structure, after energy minimization at constant volume, is a proton-ordered structure similar to ice B, first observed by Baez and Clancy [10]. Ice B is a variant of the ice IX structure, which is the proton-ordered form of ice III. The density of ice IX and ice III is in fact 1.16 g/cm^3, close to our value.

We have shown that the liquid-liquid phase separation can be observed in metastable equilibrium (i) if the cooling rate is faster than $\mathcal{R}_c$ and (ii) if the observation time is shorter than the crystallization time at the critical point. While both such conditions can be realized in numerical simulations—as shown here—they cannot be met in experiments. Our simulations also show that a continuity of states between liquid and glassy phases of water exists [19]. Liquid states below the homogeneous crystallization temperature can be accessed provided the cooling rate exceeds $\mathcal{R}_c$.

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Note added.—Recently, Matsumoto *et al.* have reported molecular dynamics simulations of ice nucleation and growth processes for a system of 512 water molecules interacting with the TIP4P potential [20,21].

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