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Massively parallel molecular dynamics simulation of formation of ice-crystallite precursors in supercooled water: Incipient-nucleation behavior and role of system size

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Ice-crystallite precursor formation in supercooled water was studied via molecular dynamics for systems ranging from $\sim 10^6$ to 8.6×10^6 molecules, using a tetrahedrally biased single-site "mW" model. This has established system-size effects in the early onset of nucleation, so as to study often-transient precursors' beguiling propensity to "flicker" into instantaneous locally ordered molecular arrangements redolent of ice. In addition, the adoption of solidlike and liquidlike bimodal local configurational-energy distributions was observed, characteristic of early nucleation. Larger systems favored a higher probability of precursor formation, although such ones were not usually longer lived relative to those in smaller systems (which themselves are rather transient). It was concluded tentatively that subtle effects of differences in systemwide density fluctuations and accessible lower-frequency modes tend to favor precursor formation in larger systems, although not necessarily the precursor's kinetic stability.

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I. INTRODUCTION

Water has various anomalous, intriguing characteristics which cannot be explained easily from a simple liquid's perspective; the mechanisms underpinning (homogeneous) nucleation constitute a particular challenge. Certainly, supercooled-water thermodynamics presents intriguing anomalies [1], tempting speculation that water displays a liquid-liquid transition between high- and low-density liquid (HDL and LDL) [2–10] to explain these anomalies [1]. The "two-liquid hypothesis" has been recast not in terms of coexisting, but rather different local hydrogen-bonding environments [11,12], implying the existence of distinct local structures. An apparent fractional Stokes-Einstein relationship in liquid water has been interpreted as a two-liquid picture of water [13]. Recently, it would appear that a metastable liquid-liquid transition has been identified for the ST2 model from thermodynamic analysis [14], with the suggestion of spontaneous separation of ST2 water into two thermodynamically distinct liquid phases under appropriate conditions [15]. However, these suggestions and analyses for two-liquid behavior in Refs. [2–16] are highly contested [17–27]. In particular, Limmer and Chandler have interpreted appearance of two-liquid behavior for the ST2 model as evidence of coarsening behavior [21–24,26], while Kühne and Khaliullin have recast experimental x-ray spectra of water in terms of electronic effects representing asymmetric features [27].

In any event, of interest to incipient nucleation in supercooled water, the direct homogeneous nucleation of water has been reported via molecular dynamics (MD), using a small simulation box containing a few hundred molecules, neglecting long-range electrostatic interactions [28]. In an insightful study, Moore and Molinero [29] have recently reported via coarse-grained MD with their tetrahedrally biased single-site "mW" model (bereft of electrostatics) [30] that an increase in the fraction of four-coordinated molecules rationalizes supercooled water's anomalous thermodynamics, and controls the rate and mechanism of ice nucleation (simulated for 4096-molecule systems), suggesting fastest crystallization at 202 K; below this, ice nuclei formed faster than liquid water equilibrates, implying a lower metastability limit below the homogeneous-nucleation temperature (∼231 K), but much higher than glass transition (∼136 K) [29]. mW has been used to study heterogeneous ice formation and growth in 32 768-molecule systems [31], given its computational tractability [30]. Interestingly, crystallization has been found to occur faster for mW than any equilibration of LDL [29,31], while mW free-energy maps suggest no metastable liquid state below 205 K [24].

Finite-size effects constitute a particular, historic challenge for simulation of crystallization. Although small-system thermodynamic-scaling techniques can be applied more easily for equilibrium, static properties [32], nonequilibrium systems *ipso facto* are more elusive: For instance, in ice-water systems, diffuse interfaces [33] would be expected to affect crystallites' periodic- "replicae" influence on each other, under periodic boundary conditions (PBCs). PBCs' "tyranny" introduces severe length restrictions, possibly limiting MD's validity for elucidating crystallization mechanisms [34]; natural fluctuations in density, phonons, and dipolar interactions occur over tens of nanometers. For instance, English and Tse have studied density fluctuations in liquid water by million-molecule MD for both ambient and supercooled conditions, establishing spatial correlation length for local density and time scales of local high- and low-density regions [35]; compared to smaller, historic sizes, they found finite-size effects are problematic in describing density fluctuations in small systems, due to phonon wavelengths permitted by artificially small box sizes and PBC restrictions [36,37]. English *et al.* have studied system-size effects on methane hydrates [38] and planar liquid methane-water interfaces [39] and ice crystallization and melting [40] on systems with up to around 8×10^6 molecules, finding omission of (lower-frequency) vibrations in smaller systems led to artificial suppression of methane hydrate precursor [39] and ice-crystal [40] formation.

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Here, we perform massively parallel MD to model mW-potential icelike precursor formation in supercooled water, given its ice *Ih* melting point is 274 K, also predicting ice *Ih* as the most stable, ambient-pressure phase [31]. We apply this to systems ranging in size from $\sim 10^6$ to 8.6×10^6 molecules, establishing system-size effects upon the precursors' "flickering" into instantaneous locally ordered icelike molecular arrangements, and to study the development of local configurational-energy distributions to assess any possible incipient nucleation. To be clear, we study explicitly the development of icelike precursors rather than density fluctuations *per se*, given that these are separate physical processes, although we do speculate on the contribution of these fluctuations in incipient nucleation. We are not motivated by any study of putative two-liquid behavior, given the mW model does not display it below 205 K with the disappearance of a metastable liquid state, in terms of free-energy-surface considerations [24].

The faster diffusivity of mW is problematic for bulk water [30] and ice-formation kinetics [29–31,40]; together with absence of electrostatics and explicit rotational motion, this limits quantitative realism. Given water's highly polar nature, long-range electrostatic effects affect structural ordering, as would reorientation and changes in hydrogen bonding, although mW's tetrahedral biasing mitigates this to some extent [30]. Admittedly, mW has serious drawbacks, but we seek *grosso modo* qualitative insights into icelike precursor formation in multimillion-molecule systems; computational expediency is *sine qua non*.

II. METHODOLOGY

Large-scale Atomic/Molecular Massively-Parallel Simulator (LAMMPS) was used on IBM Blue-Gene platforms [41] for MD [42,43] with a time step of 10 fs. Cubic simulation boxes, each containing $\sim 10^6$, 2.5×10^6, 5×10^6, and 8.6×10^6 liquid-phase molecules, were generated, relaxed from replication of smaller systems (containing up to 10^6 molecules) on which approximately 100 ns of *NPT*-ensemble MD had been performed at 274 K and ambient pressure, with mild barostat-thermostat coupling (respective periods of 5 and 1 ps [44,45]). The box lengths were ~323, 430, 538, and 646 Å, and were relaxed for a further 50 ns in the *NVT* ensemble at 274 K with a Nosé-Hoover thermostat of period 1 ps [44]. Following this, four Maxell-Boltzmann–generated sets of velocities at 225 K were used to launch *NPT*~1–1.4 μs "production" runs; the volume had stabilized within ~10 ns in each case, although no crystallites were observed in this time. This temperature was chosen due to the desire to study the early stages of nucleation, given the previous observation of Moore and Molinero of mW crystallization at a rate accessible within less than a microsecond at ~225 K [29].

Báez-Clancy ice-liquid distinction criteria were employed [46,47], where an angular order parameter quantifies tetrahedrality of bonding for nearest-neighbor molecules, followed by potential recognition of five-membered rings (present in clathrates but absent in liquid water and ice)—in any event, no five-membered rings were identified here, as expected. This preliminary classification is refined by grouping icelike molecules into precursors, taking into account the identities of neighboring molecules. To verify the robustness of Báez-Clancy ice-liquid distinction criteria, the CHILL algorithm was used for selected trajectories to identify icelike precursors, given its success at distinguishing ice phases, be they hexagonal, cubic, or interfacial, from liquid water [48]—similar conclusions were found (*vide infra*). It should be noted that since the density of bulk ice and liquid water is markedly different, it was found from an analysis of the local density of icelike precursors identified by these criteria (both Báez-Clancy and CHILL) at $\sim 0.94\ \mathrm{g/cm^3}$ that these were closer to bulk ice density than the surrounding liquid. In terms of density fluctuations, as opposed to density *per se*, these are taken into account implicitly in parametrization and development of these various geometric icelike and liquidlike recognition criteria, in that these have been developed empirically from molecular-simulation studies of ice- and hydrate-liquid systems in Refs. [46–48], in which density fluctuations are inherently present.

III. RESULTS AND DISCUSSION

Figure 1 displays typical behavior of the evolution of icelike precursors for individual systems, with a system of 10^6 molecules ("1 M"), displaying the number of precursors, number of molecules therein, and number in the largest. The beguiling flickering of occasional precursors into a transient appearance belies the rich tapestry of underlying molecular rearrangements. In particular, there is a "waiting" time of circa 0.8 μs, after which there is a gradual transition towards a substantially greater number of precursors redolent of an adoption of a more glassy state. Given that the simulations are run below the homogeneous-nucleation temperature (~231 K) [49], coupled with mW's relatively reliable temperature-density relationship [30], this renders early-onset, incipient preordering prior to homogeneous nucleation likely within accessible submicrosecond time scales even in larger systems: This is evident by the increasing presence of precursors in Fig. 1. After this "transition", precursors appear more persistent—this point is confirmed by persistence-time distributions and configurational-energy distributions (*vide infra*). There is consolidation of the largest precursor towards 30 or more molecules, in contrast to 14 to ~24 in the earlier stages, albeit with the development in parallel of further secondary, smaller precursors in the 14– ~ 24-molecule range—this is also confirmed below. The more prominent O-O-O bending mode in supercooled water [50,51] appears to stabilize (subcritical) precursors; this is consistent with ordering mediated by four-coordinated "patches" [28,29]. This O-O-O and four-coordinated ordering was more prominent in the simulations' latter stages where some precursor formation has occurred, detected in spectra of velocity autocorrelation functions.

Importantly, the CHILL criteria identified almost identical clusters in terms of molecular identities as the icelike precursors of the Báez-Clancy criteria. However, these were usually of interfacial-ice type in the case of CHILL, underscoring the nonbulk nature of the precursors, which makes good sense; indeed, this insight would not have been achieved with Báez-Clancy criteria alone, underscoring the very-useful nature of CHILL. Quantitatively, incipient-nucleation probabilities were found to be almost the same for CHILL as with the Báez-Clancy approach.

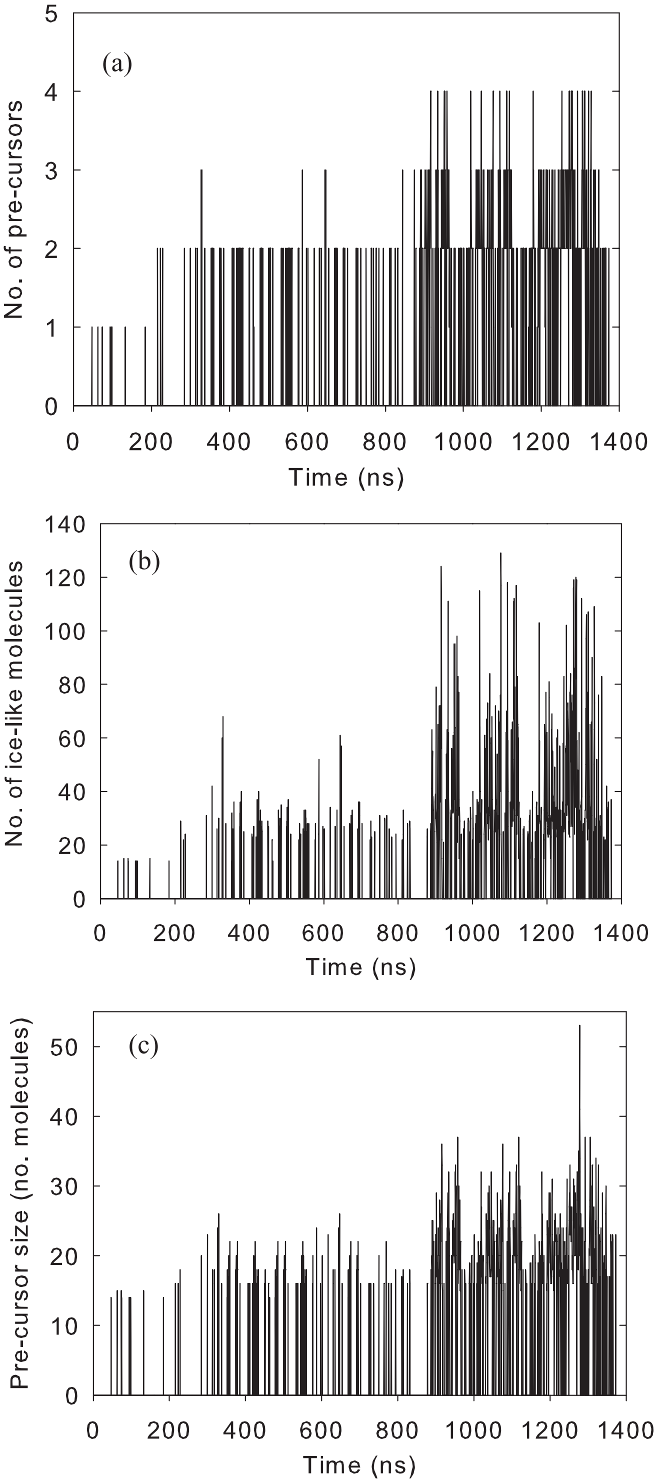

FIG. 1. Typical example of the evolution of “icelike” precursor behavior in an individual trajectory in the 10^6 molecule system. (a) Number of precursors; (b) total number of molecules present in all precursors; (c) number of molecules in the largest precursor.

Figure 2 shows evolution of percentage probability of molecules being in icelike precursors for varying system sizes, averaged over 50-ns windows. There is a marked increase in propensity to form precursors in larger systems, particularly the 8.6×10^6 molecule one (8.6 M). There is a greater likelihood of precursors forming per unit volume, and of so doing more rapidly *vis-à-vis* 1 M; this probability increases with system size. Strikingly, the waiting time for transition to a more coarse state with enhanced O-O-O and four-coordinated ordering occurs earlier upon increasing size, with a dramatically lower value of 0.5 μs for the 8.6 M case (0.8 μs for 1 M).

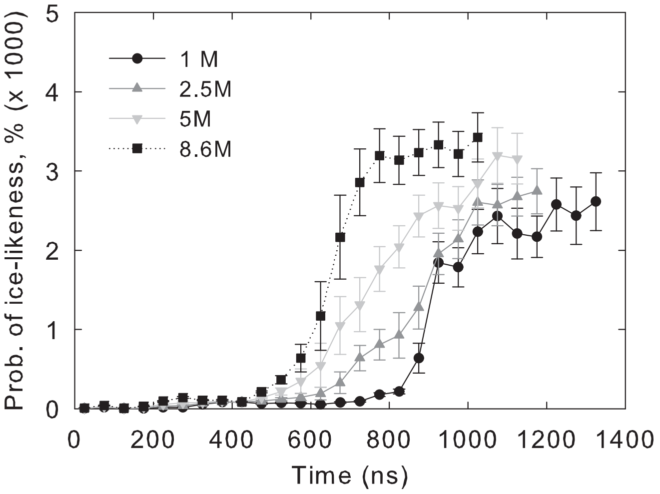

FIG. 2. Evolution of percentage probability of molecules being in icelike precursors for varying system sizes, averaged over trajectories in 50-ns windows, with standard deviations indicated.

Figure 3 shows distributions of precursors’ size, in terms of number of molecules, averaged over all such precursors and trajectories, before and after the transitions evident in Figs. 1 and 2. In terms of run-to-run variability, broadly consistent distributions in precursor size were seen over each independent trajectory, given that they were run for relatively long periods of time (i.e., around a microsecond). The averaged profiles belie the temporary reassignment to the liquid phase of certain tranches of the “interface,” observed in individual runs; the precursors evolve dynamically, buffeted by density fluctuations. They are classified back and forth between liquid and precursor on subnanosecond time scales, with the same “core” of molecules sometimes reappearing as a precursor tens or even hundreds of nanoseconds later. Other molecules in regions not previously associated with precursors are assigned on occasion thereto, in what appears to be a semirandom pattern. In Fig. 3, the probability distributions of precursors’ sizes at various stages, before and after the transition observed in Figs. 1 and 2, reveal the development of a set of larger precursors containing ∼40 water molecules (greater than one hydration shell) as a key event after this point, which would tend to be subcritical in size, although approaching this. This is slightly more pronounced in larger systems, but what is more striking is that larger systems appear to facilitate the development of many smaller precursors, i.e., favoring homogeneous nucleation to a greater extent rather than the consolidation of (subcritical) precursors. This general phenomenon, and development of this typical behavior in precursors’ sizes over time was observed in nearly all of the independent runs.

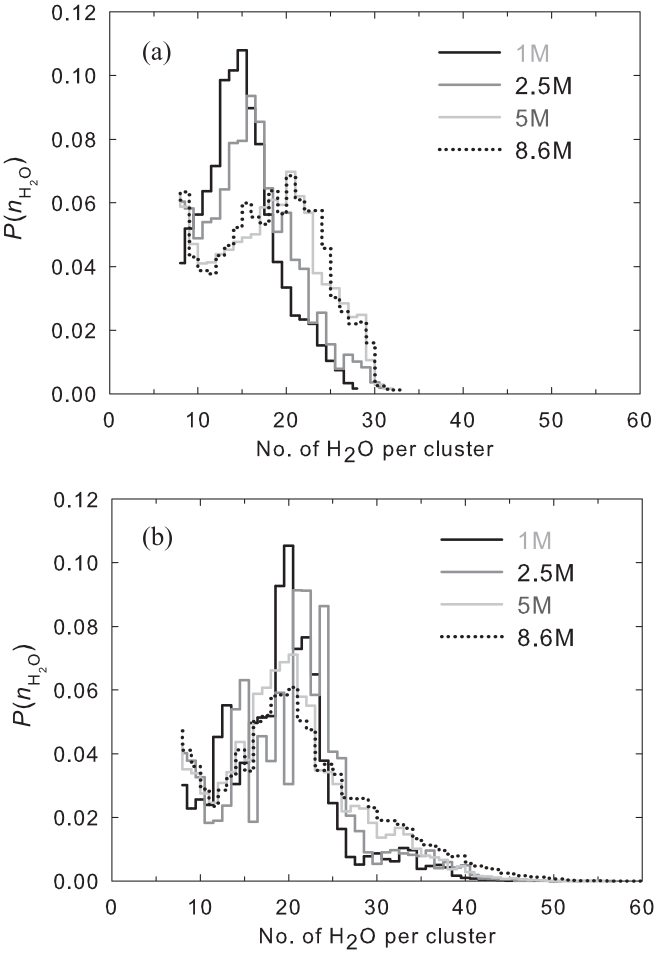

FIG. 3. Normalized probability distributions of sizes of icelike precursors, averaged over all such precursors and trajectories, during (a) 400–450 ns, and (b) 1000–1050 ns, i.e., essentially "before" and "after" the transitions to a larger number of precursors. There was reasonably consistent behavior between individual runs, so standard-deviation bars are omitted for clarity.

We have also considered evolution of the probability distribution of each molecule's interaction energy with the rest of the system for the 1 and 8.6 M cases, but also at the higher temperatures of 250 and 275 K for the 1 M system over ∼1 μs (i.e., for supercooling, yet above the homogeneous-nucleation temperature, and also for just 1 K above the melting point, respectively). We see in Fig. 4 that there is a gradual development of a bimodal distribution at 225 K, and more especially in the larger system [cf. Fig. 4(a) vs 4(b)], as there is a development of ice precursors; this is consistent with Figs. 1 and 2. Again, in terms of run-to-run variability, broadly consistent distributions were evident given the relatively long periods of MD in each run. At 250 K, it is only in the latter half of the ∼1 μs trajectory that the first, "faint," presence of icelike precursors is evident, given the weaker degree of subcooling [cf. Fig. 4(c)], while any hint of evolution towards a bimodal distribution is absent at just (∼1 K) above the melting point [cf. Fig. 4(b)], as expected. Indeed, the long relaxation time for this process (far greater than the circa-microsecond time scales of the present

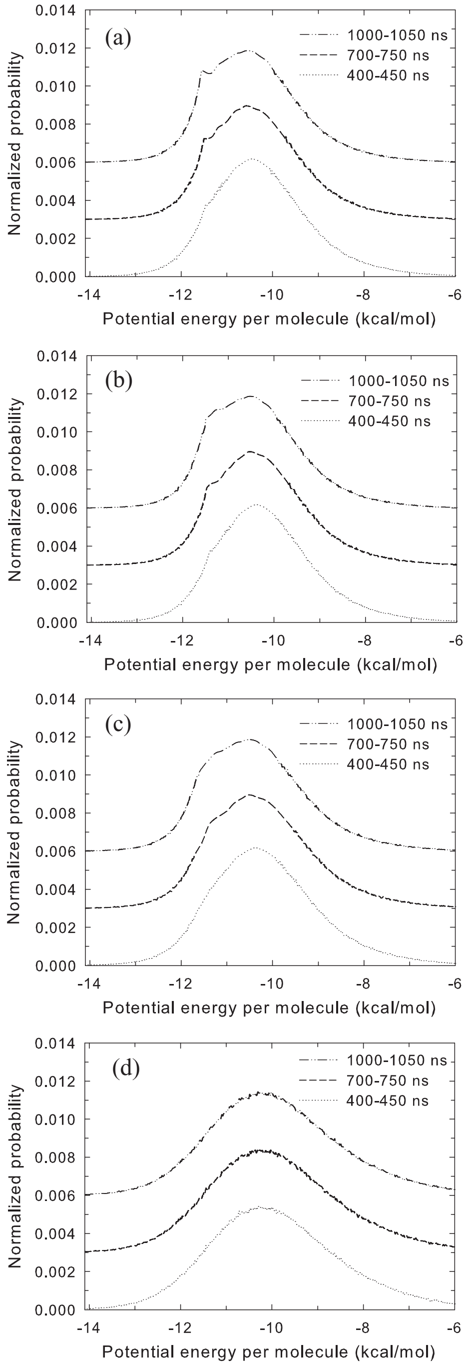

FIG. 4. Evolution of normalized probability distribution of each molecule's interaction energy with the rest of the system, each averaged over trajectories in 50-ns windows (displaced vertically upwards for ease of viewing). (a) 8.6 M and (b) 1 M systems, at 225 K; note the development of the icelike kink at ∼−11.5 kcal/mol, which is slightly lower in energy (by ∼0.02–0.04 kcal/mol) and more "jagged" for the larger system. (c) 1 M system, at 250 K: Note the relatively weak, indistinct icelike kink at ∼ − 11.5 kcal/mol [compared to the more aggressively supercooled 225 K case in (b)], in the second half of the ∼1 μs trajectory. (d) 1 M system, at 275 K (just around 1 K above the melting point for the mW model, i.e., no longer supercooled): Note absence of any icelike peak and the same distribution. In all cases, there was reasonably consistent behavior between individual runs, so standard-deviation bars are omitted for clarity.

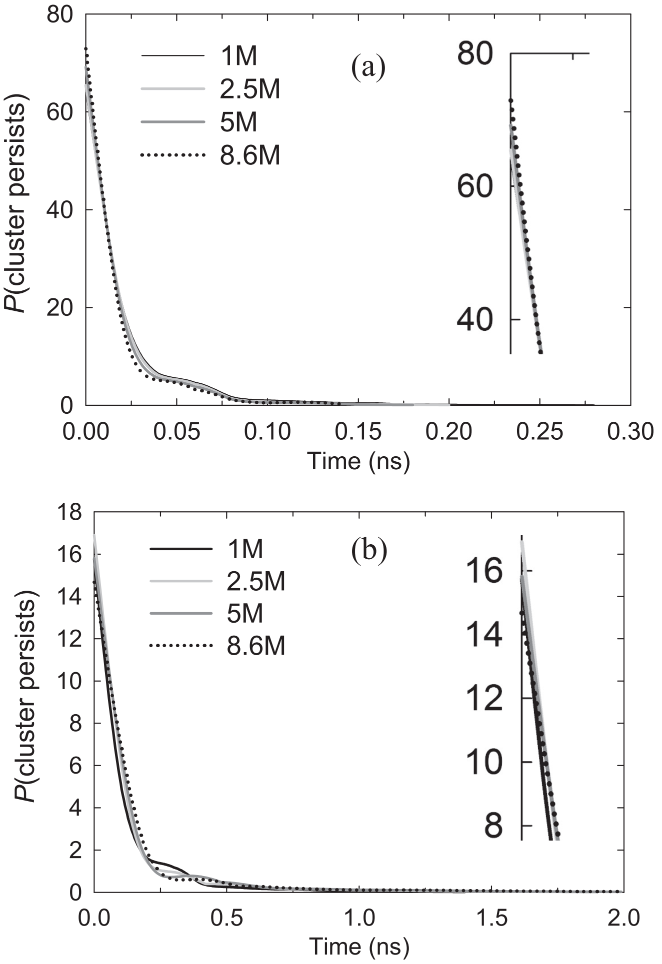

FIG. 5. Normalized probability distributions of persistence times of individual precursors, averaged over all such precursors and trajectories for varying system sizes, during (a) 0–50 ns, and (b) 200–250 ns. The earlier-time behavior is enlarged in the inset to the right.

work) may serve to rationalize controversial debates regarding appearance of two-liquid behavior [52].

Although there is a clear trend evident in Figs. 1–4 suggesting a greater likelihood of a water molecule being in an icelike precursor in larger systems, together with a preponderance of some larger precursors, Fig. 5 shows that the probability distribution of persistence times of the precursors remains somewhat shorter in larger systems. This leads to the conclusion that smaller systems induce artificial time stability to precursors less experienced in larger systems. Run-to-run variability was relatively low, with consistent distributions for the precursors' lifetimes. This is similar in terms of lack of substantial variability for distributions in time scales of density fluctuations in water [35], sampled from atomistic MD.

Considering the above evidence, a consistent picture emerges. The inherent problem of smaller systems is the limiting of lowest-frequency vibration (akin to a phonon [53]) so its wavelength is half the box size. Therefore, smaller simulation boxes with a length L_α in a given Cartesian direction, α, render k-vectors k_α lower than $2\pi/L_\alpha$ inaccessible. We conjecture that this truncation of density fluctuations in smaller systems to exclude longer-wavelength fluctuations appears to inhibit the development of locally ordered O-O-O and four-coordinated arrangements necessary for transient flickering of icelike (subcritical) precursors. This would favor the development, and consolidation of precursors in larger systems, where they experience a fuller panoply of (lower-frequency) density fluctuations; this precursor consolidation is evident in Fig. 3. Indeed, similar findings have been uncovered for the development of methane hydrate precursors at large planar water-methane interfaces [39]. However, an intriguing aspect to the present precursors is the finding that temporal stability is not enhanced in larger systems; if anything, the reverse is found (albeit not dramatically so) with greater, artificial persistence in smaller systems. This would appear to indicate that the full gamut of lower-frequency density fluctuations enhances local ordering in larger systems to render it more likely that many more "homogeneous" nucleation events occur (from liquidlike to smaller precursors in the ∼14–20 molecule size), with some consolidation of larger precursors (yet still tantalizingly subcritical), rendering it more likely that an aggregate distribution of persistence times will be more biased to shorter durations *vis-à-vis* smaller systems.

In terms of how this picture fits in with the more established corpus of nucleation theory from analytic, numerical, or simulation approaches, the long-range size effects evident here are inconsistent with the formulation of classical nucleation theory [54]. According to our conjecture, the origin of these finite-size effects appear to lie in low-frequency, long-wavelength local-density fluctuations arising from vibrational modes more accessible to larger systems [35], and these have been shown recently to have a noticeable effect on ice-crystallization kinetics (both growth and dissociation) using the mW model in identical system sizes to that pursued here (i.e., 1 M- to 8.6 M-sized systems) [40], and indeed for similar-sized interfacial systems of liquid methane and water with the mW model containing millions of molecules [39].

IV. CONCLUSIONS

MD was used to study precursor formation and dynamic evolution of ordering prior to incipient homogeneous-nucleation events in supercooled water in systems of $(\sim 1\text{–}8.6) \times 10^6$ molecules. Larger systems were found to favor precursor formation, although such ones were not usually longer lived relative to those in smaller systems (which themselves are rather transient). The evolution of a bimodal molecular energy distribution emphasizes early stages of nucleation. It would appear that subtle effects of more accessible lower-frequency modes tend to favor precursor formation in larger systems, although not necessarily their kinetic stability.

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