Reply to "Comment on 'Spontaneous liquid-liquid phase separation of water'"

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Two different scenarios have been proposed on the phase separation occurring in the deeply supercooled liquid water. We discuss what we can derive from our simulation results for the two scenarios and propose a way for future investigation. We also demonstrate that the phase separation in the supercooled liquid water looks like the separation of liquid water and vapor just below the conventional critical point.

In our previous paper [1], it was reproduced by molecular dynamics simulations that deeply supercooled liquid water separates spontaneously into two liquids, one is high density and entropy, and the other is low density and entropy. Limmer and Chandler advocated that the transition observed in Ref. [1] is not a liquid-liquid separation but an ice coarsening from unstabilized supercooled liquid water, and our observation is in good agreement with their predictions [2,3]. However, our results are also consistent with the liquid-liquid hypothesis [4–8]. We would therefore like to clarify what is manifest and what is not from our simulation results.

Water at the initial stage of ice coarsening would be indistinguishable from so-called low-density liquid water. They share the same pressure-temperature region. They are therefore distinguishable only when there is a (metastable) phase transition between them, and if so, the transition must be first order and initiated by nucleation because of the difference in symmetries. We provided a movie as Supplemental Material of Ref. [1] to show how ice crystal grows. For those who advocate ice coarsening, it seems to be a continuous process of crystal growth from fine-grained ice [2]. However, we find a persistent nucleus of ice seems to appear at 500 ns in the low-density liquid region, which is long after the liquid-liquid separation. By that instant, the number of crystal fragments increases not monotonically but intermittently as shown in Fig. 3(b) of Ref. [1]. It is difficult to decide which interpretation is appropriate only from our simulation results. In order to clarify this point, one must prepare a pure low-density liquid (or finest-grained ice), perform large-scale long-time molecular dynamics simulations repeatedly, and watch whether ice suddenly nucleates (in case low-density liquid is a different phase from ice) or the grain size of ice grows continuously (in case they are identical). So far, we do not have enough numbers of trajectories for this purpose.

By the way, Limmer and Chandler commented that "Indeed, a finite surface tension would inhibit the *large* interfacial fluctuations observed in Ref. [1]." This statement is incorrect. The fact is that a finite surface tension inhibits *infinite* interfacial fluctuations. The surface tension is zero at the critical point and continuously increases with decreasing temperature. At a temperature slightly lower than the critical point, the surface tension is finite but very small. A large interfacial

fluctuation can be observed in such a condition. As an example, we show the interfacial fluctuation near the liquid-vapor critical point of TIP4P/2005 water at $T = 650$, 625, and 610 K in Fig. 1. We performed NVT simulations with 1000 water molecules at 0.31 g cm^{-1}. The critical point of this model is 641.4 K [9]. We see large interfacial fluctuations at $T = 625$ K. The surface fluctuations are suppressed at $T = 610$ K because of higher surface tension.

One may think that fluctuations seem small if the time window is too short compared with the structural reorganization time. In Fig. 1, the time axis is scaled by the relaxation time of hydrogen bonding τ_{HB}, defined by the time at which the hydrogen bond correlation function [10,11] becomes e^{-1}. This scaling ensures that the larger fluctuation at 625 K than at 610 K is indeed due to criticality. We perform the same analysis for ST2 water at $T = 250$, 240, and 235 K. The results are shown in Fig. 2. The density fluctuations shown in Fig. 2 are quite similar to those of water around the vapor-liquid supercritical point presented in Fig. 1. Both figures demonstrate that the density fluctuation of panel (c) is smaller than that of panel (b), and the difference in density between the high- and the low-density domains are larger for lower temperatures. Although the low-density domain found in supercooled water may be coarsening of ice as commented by Limmer and Chandler, this close similarity leads us to believe the existence of the liquid-liquid critical point between 240 and 250 K and the liquid-liquid coexistence below the critical point. Note that the scaled time t/τ_{HB} is much smaller in Fig. 2. This is not surprising because large translational displacements of molecules are required for the density fluctuation near the vapor-liquid critical point, whereas the conversion between low- and high-density domains can be caused by small changes in molecular orientation in supercooled water [1].

As noted by Binder [12], some special treatments are required to simulate the critical phenomena by molecular dynamics simulations because correlation length and time diverge at the critical point [13]. We do not intend to observe the criticality itself in the present Reply and Ref. [1]. Our simulations are designed so as to avoid the difficulty in reproducing the possible criticality at the hypothetical second critical point (if any) and to focus on the spontaneous separation of two liquids.

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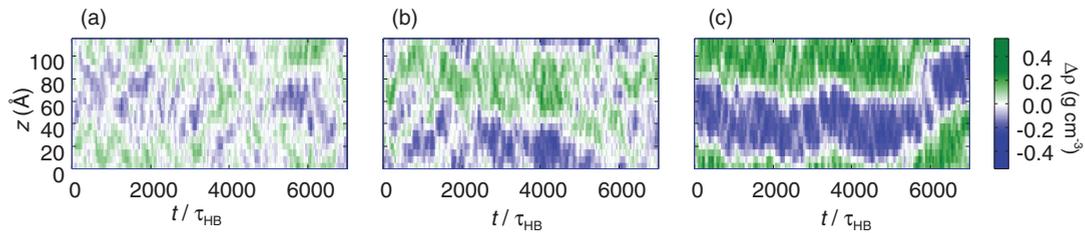[*]Corresponding author: vitroid@gmail.com

FIG. 1. (Color) Density profiles of water near the vapor-liquid critical point of TIP4P/2005 water. Panels (a)–(c) are the density profiles at $T = 650, 625$, and 610 K, respectively. NVT simulations were performed at 0.31 g cm^{-3}. The time axis is scaled by the relaxation time of the hydrogen bond correlation function. The relaxation times at 650, 625, and 610 K are 226, 258, and 280 fs, respectively. The reduced temperatures $T_r = T/T_c$ are 1.013, 0.974, and 0.951.
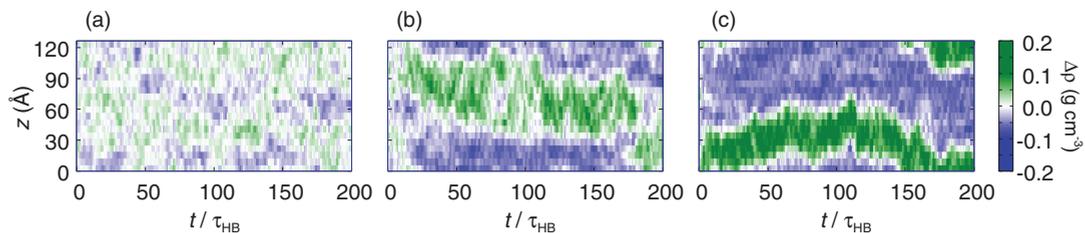

FIG. 2. (Color) Density profiles of supercooled ST2 water at (a) 250 K, (b) 240 K, and (c) 235 K. The trajectories are the same as those presented in Fig. 1 of Ref. [1]. The time axis is scaled by the relaxation time of the hydrogen bond correlation function. The relaxation times at 250, 240, and 235 K are 84, 311, and 1180 ps, respectively. The reduced temperatures T_r are 1.012, 0.972, and 0.951 ($T_c = 247$ K is taken from Ref. [14]).

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