Second inflection point of water surface tension in deeply supercooled regime revealed by entropy anomaly and surface structure using molecular dynamics simulations

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Electronic supplementary information (ESI†)

Relationship between the thickness of surface and the number of molecules in the simulated systems

Vins et al. [1] compared their results for 4 choices of N (the number of water molecules in the simulation, and the one in our study is 4142 as pointed out in our main text). They find that the surface tension is independent of N, but the interface thickness t increases systematically with N. Here, we plot t^2 against $ln(N)$ at ~350 K, and these data are from Vins et al.'s [1], Vega and Miguel [2], Sega and Dellago's [3] and our studies (Fig. S5). The relationship between them is as Eq. S1

$$t^2 = 0.0408 \times ln(N) - 0.1066 \quad \text{(S1)}$$

This N-dependence of t^2 is a simple consequence of Eq. 10a. Of course, writing N as the product of the bulk water density times the volume of the water slab, and noting that volume scales with the third power of the linear dimension L, one has that $ln(N) = 3\ln(L) + constant$. The prefactor 0.0408 indeed is rather close to the prefactor that Eq. 10a then would predict. Thus, the N-dependence of t^2 provides a further independent test of the estimated surface tension.

List of figures.

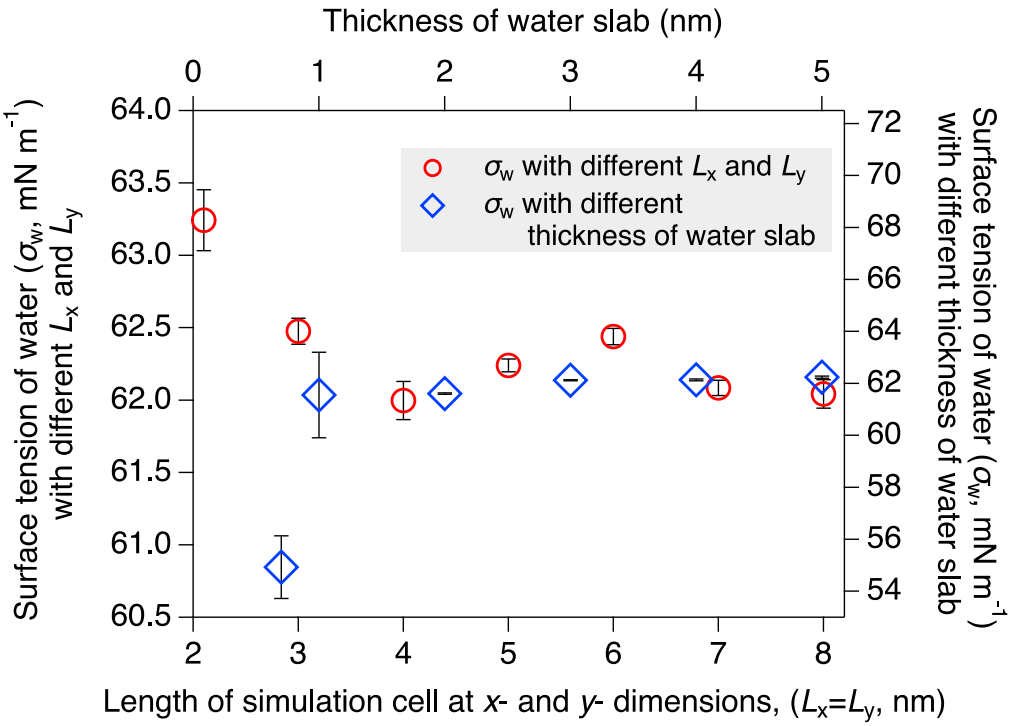

Fig. S1. Surface tension of water (σ_w) at 298.15 K for systems with different sizes. The red circles represent the simulated σ_w with different length of simulation cell at x- and y- directions ($L_x = L_y$), but the length at z-direction (L_z) and the thickness of water are fixed with 20 nm and 5 nm, respectively. The blue diamonds represent the simulated σ_w with different thickness of water slab, but simulation cell is with a fix size ($L_x = L_y$ = 5 nm and L_z = 20 nm). The black error bars are the standard error of three individual simulations.

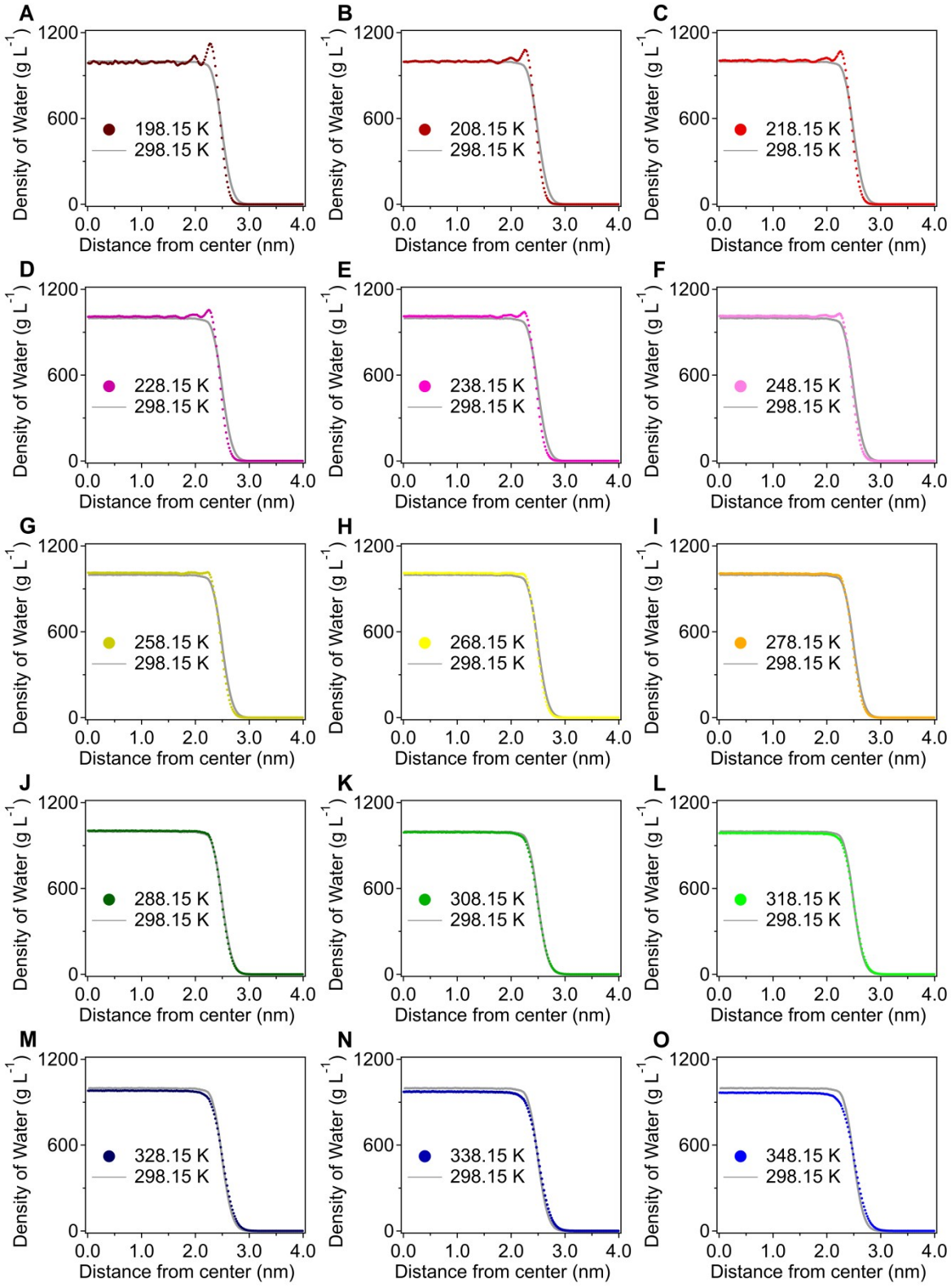

Fig. S2. The MD simulated density profiles of water at different temperature. The density profile at 298.15 K is always plotted with grey line as a reference.

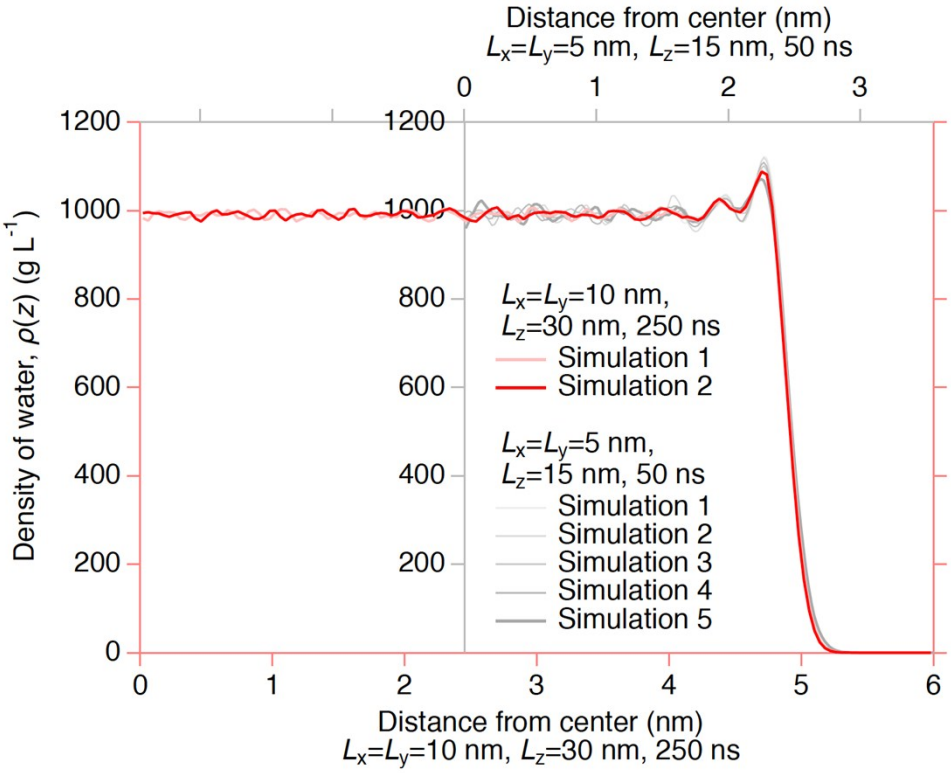

Fig. S3. Stability and repeatability of the 'apophysis' and the compact water layer near the surface. The density profiles of the supercooled water at 198.15 K obtained from two individual simulations in a larger cell ($L_x = L_y$ = 10 nm, L_z = 30 nm, 250 ns, reddish colored lines), as well as from five individual simulations in a smaller cell ($L_x = L_y$ = 5 nm, L_z = 15 nm, 50 ns, greyish colored lines), which is the one that we used in our study.

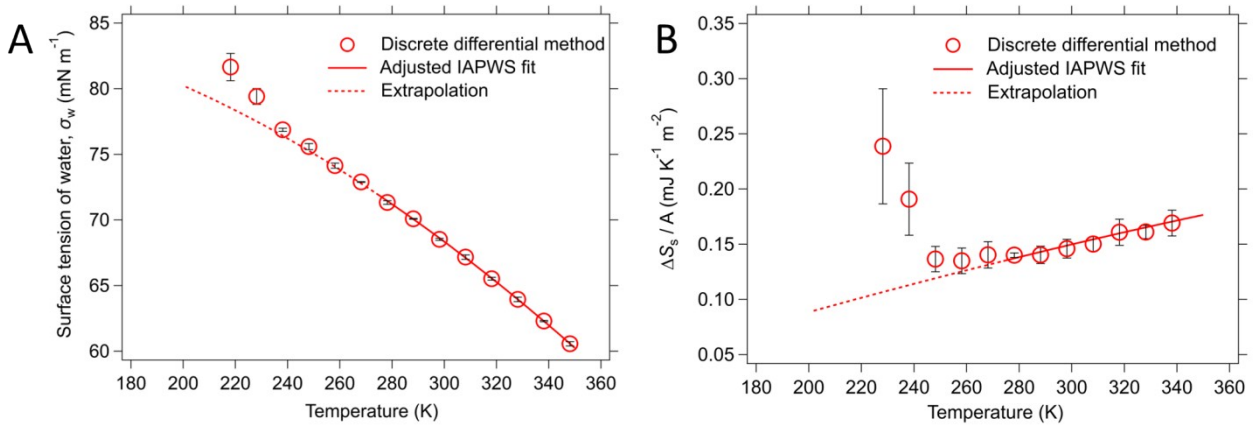

Fig. S4. Temperature dependence of surface tension of water (A) and surface excess entropy per unit of area (B) simulated with the TIP4P/2005 water model.

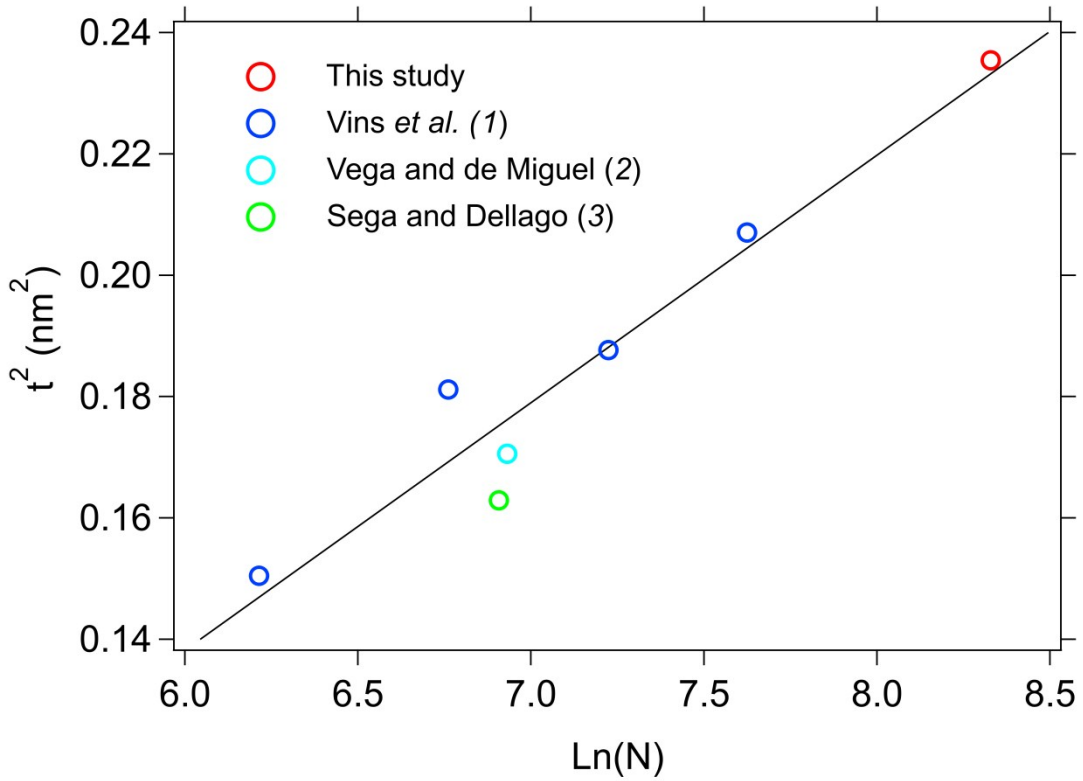

Fig. S5. The relationship between the natural logarithm of number of water molecules in simulations and the square of thickness of surface at ~350 K.

Notes and references

1. V. Vinš, D. Celný, B. Planková, T. Němec, M. Duška and J. Hrubý, *EPJ Web of Conferences*, 2016, **114**, 02136.
2. C. Vega and E. De Miguel, *J. Chem. Phys.*, 2007, **126**, 154707.
3. M. Sega and C. Dellago, *J. Phys. Chem. B*, 2017, **121**, 3798-3803.