Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

SUPPLEMENTARY INFORMATION

for

Yet Another Criticality of Water

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Estimation of spinodal and coexistence temperatures via polynomial fitting of Landau free energy functional

Here we describe the method to estimate the spinodal and coexistence temperatures at a given pressure by fitting the Landau free energy functional with a 6th order even polynomial, which is defined as a functional of the order parameter φ as follows:

$$g(\phi) = r'\phi^2 + u_4'\phi^4 + u_6\phi^6$$

$$= u_6(r'\phi^2/u_6 + u_4'\phi^4/u_6 + \phi^6)$$

$$= u_6(r\phi^2 + u_4\phi^4 + \phi^6), \qquad [S1]$$

where we redefine the coefficients as $r = r'/u_6$ and $u_4 = u_4'/u_6$. We assume u_6 is always positive by stability condition. When $u_4 < 0$, this polynomial has three minima at $\varphi = 0$ and at two non-zero φ values with different sign. Differentiation of this polynomial readily tells us that the coexistence of the three states, i.e., the condition where the values at three minima are the same, occurs when $r = u_4^2/4$, and the spinodal points correspond to the condition where the number of minima changes, which occurs when $r = 0$ or $r = u_4^2/3$.

Therefore, when the values $r - u_4^2/4$, r, and $r - u_4^2/3$ are plotted against temperature, their intersection points with the x axis (temperature axis) correspond to the unbiased estimates of the coexistence and two spinodal temperatures, respectively. With the real data obtained by the simulation, these values change almost linearly against temperature in the vicinity of the phase boundary and therefore we can estimate the intersection points fairly precisely. Fig. S1 illustrates the actual process of estimating these temperatures.

When r changes linearly and u_4 is constant against temperature, we obtain a simple relation between coexistence temperature T_c and lower and higher spinodal temperatures T_0 and T_1, that is

$$T_c - T_0 = 3\,(T_1 - T_c). \qquad [S2]$$

Actually, one can see this relation approximately holds at the pressures between 10 and 12 GPa in Fig. 1(b). We therefore also make use of this relation to estimate the coexistence temperature from two spinodal temperatures below 10 GPa where determination of coexistence temperature by direct molecular dynamics simulation is difficult.

Comparison with experimental data

Shown in Fig. S2 are the phase boundaries between ice VII and supercritical fluid water determined by experiments [1–8] and by computer simulations [9,10]. Note that the phase boundaries obtained by Takii et al. [9] and by Aragones et al. [10] by computer simulations have two branches corresponding to fluid-plastic and plastic-VII transitions.

Movie Legends

Movie S1 | Motion of water molecules in ice VII is picturized. Molecules are chessboard-painted in order to clarify their rotational motion and gradated from blue to red according to their bond order parameter values range between –1 and +1. Temperature and pressure are 455 K and 5 GPa, respectively. Frame rate is 30 frames per second and one frame corresponds to 10 fs. (HimotoSuppVideo1.mp4, 6.3 MB, mpeg4 format)

Movie S2 | Motion of water molecules in plastic ice is picturized in the same way as Video 1. Temperature and pressure are 456 K and 5 GPa, respectively. (HimotoSuppVideo2.mp4, 7.5 MB, mpeg4 format)

Movie S3 | Spatial distribution of bond order parameter in ice VII is visualized by contours gradated from blue to red according to the bond order parameter values range between –1 and +1. Molecules are not drawn. Temperature and pressure are 455 K and 5 GPa, respectively. Frame rate is 30 frames per second and one frame corresponds to 10 fs. (HimotoSuppVideo3.mp4, 9.0 MB, mpeg4 format)

Movie S4 | Spatial distribution of bond order parameter in plastic ice is visualized in the same way as Video 3. Temperature and pressure are 456 K and 5 GPa, respectively. (HimotoSuppVideo4.mp4, 8.7 MB, mpeg4 format)

Movie S5 | Spatial distribution of bond order parameter at the critical point is visualized in the same way as Video 3. Temperature and pressure are 745.5 K and 18 GPa, respectively. Note that one frame corresponds to 10 ps, which is different from other movies. (HimotoSuppVideo5.mp4, 4.3 MB, mpeg4 format)

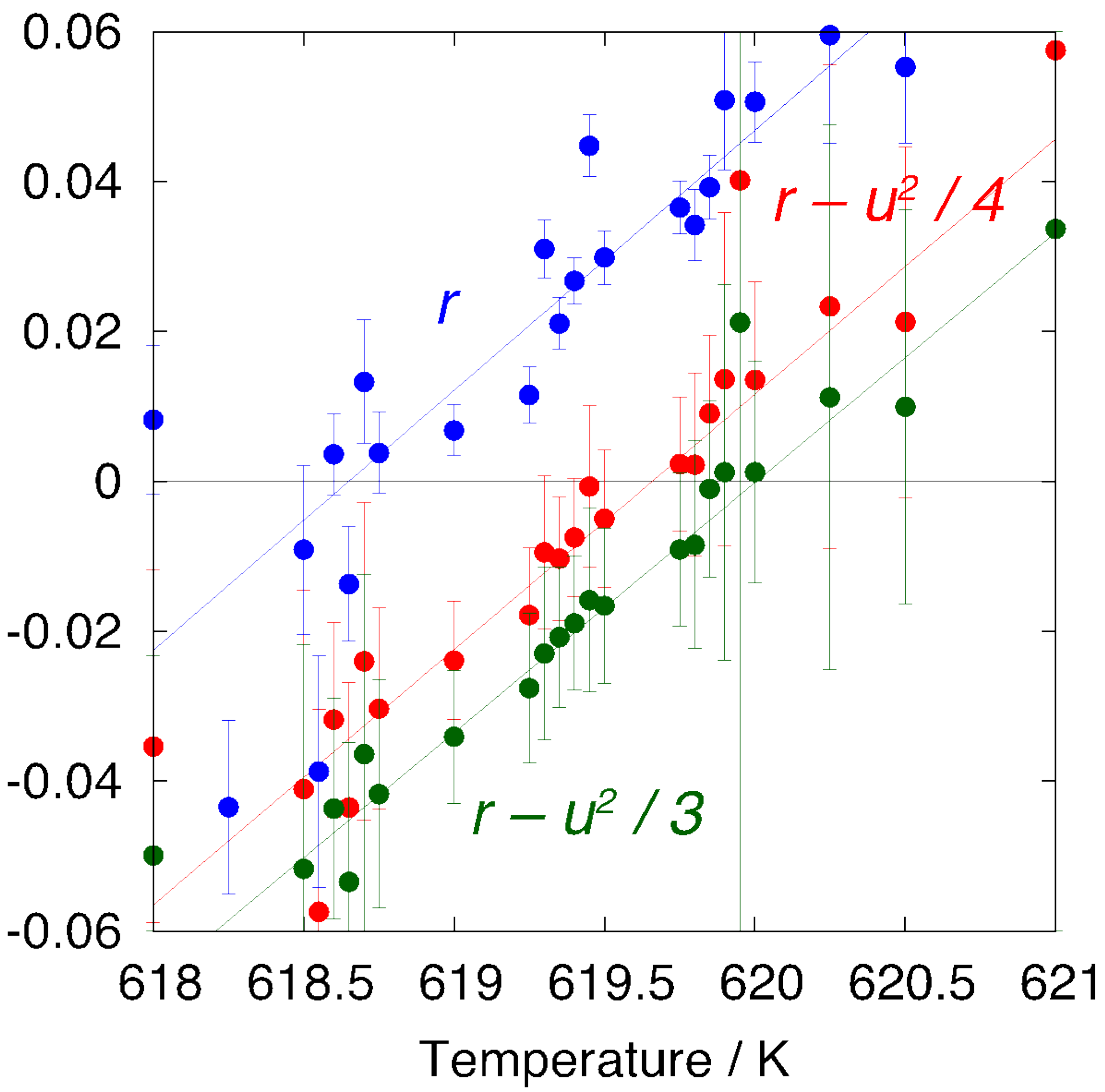

Figure S1 | Blue, red, and green points are values r , $r - u_4^2/4$, and $r - u_4^2/3$ obtained by fitting the Landau free energy functional with 6th order even polynomial, respectively. Intersection points of the linear fitting lines of them with the abscissa axis give the unbiased estimates of spinodal and coexistence temperatures. Pressure is 11 GPa.

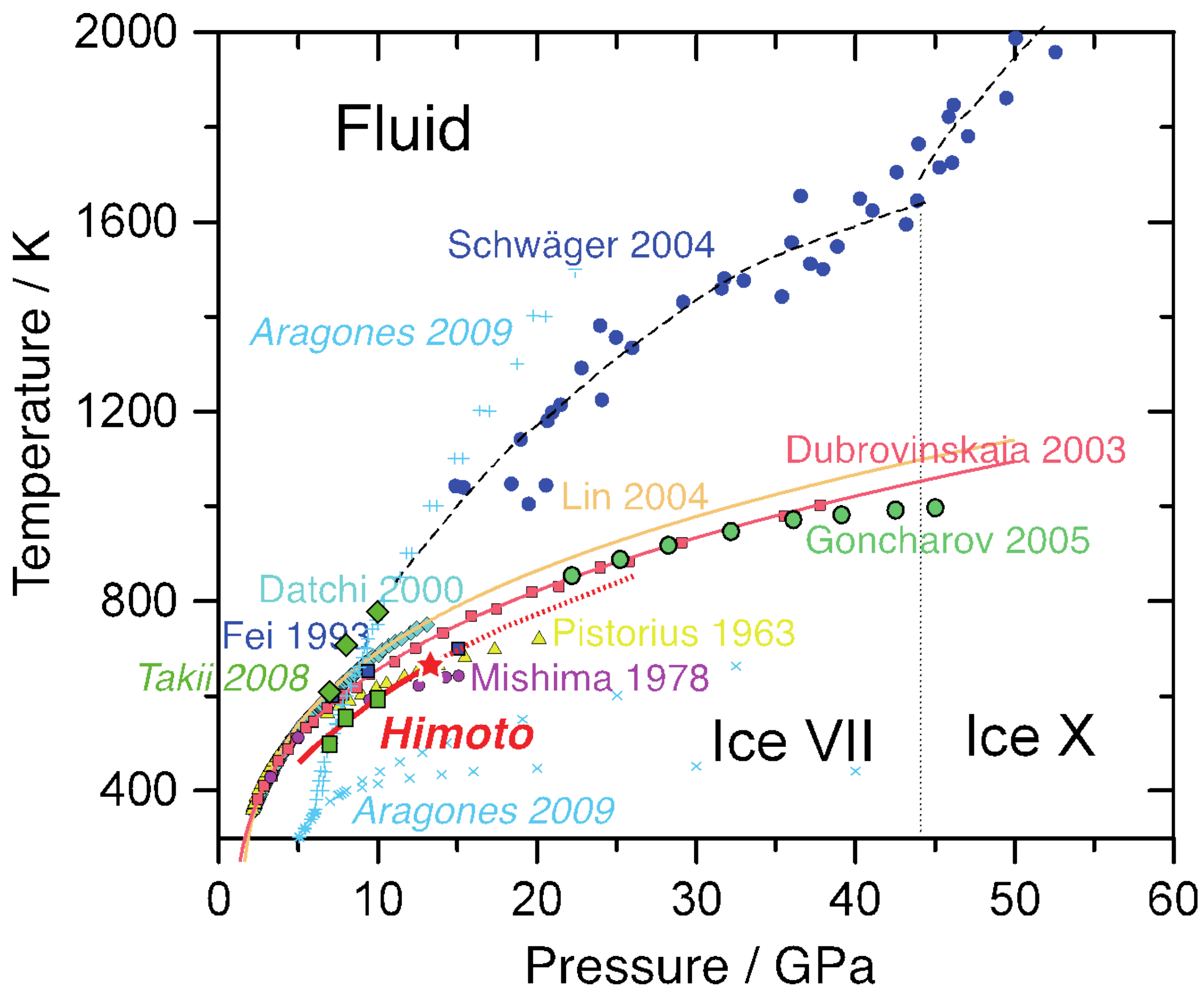

Figure S2 | Phase boundaries between ice VII and supercritical fluid water. Takii [9], Aragones [10], and Himoto's data (the present work) are obtained by computer simulations; other data are by experiments[1-8]. A red star in Himoto's series indicates the pressure and temperature of the tricritical point discovered in the present work.

References for Supplementary Information

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