The Thermodynamic and Dynamic Behavior of Supercooled Water

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Introduction

Water is ubiquitous and people are familiarized with the fact that water manifests itself in its solid, liquid, and gas forms in nature. However, the dynamics and thermodynamics behind the entire phase diagram of water (Figure 1) is not fully understood. Water supercooled below 0 °C or 273 K can still remain as a liquid and exhibit two distinct phases: as a low-density liquid (LDL) and as a high-density liquid (HDL). As we cool down the water from high to low temperatures, its dynamics transition from Arrhenius (fragile) behavior to non-Arrhenius (strong) behavior. This transition is known as the fragile-to-strong crossover. My computational study uses the TIP4P-2005 model of water and follows the simulation path shown by the arrow in Figure 1. We set all of our runs at fixed 1 atmospheric pressure and we perform trials from 290 K down to 195 K. Previous research at Starr's Lab adopted the ST2 model of water and performed experiments under 100 atmospheric pressure. Data from the TIP4P-2005 and the ST2 models validate our findings for the thermodynamic and dynamic behavior of supercooled water during the fragile-to-strong crossover.

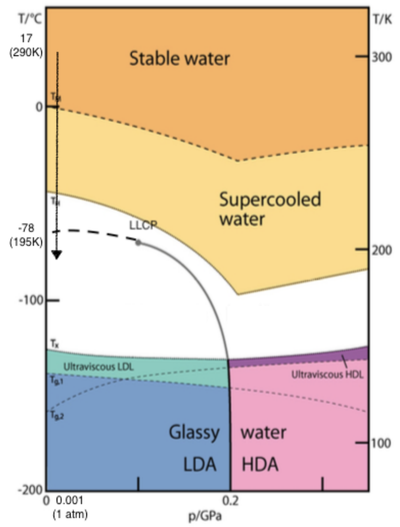


Figure 1: Phase Diagram of Water and Our Simulation Path. LDL: low-density liquid, HDL: high-density liquid, LDA: low-density amorphous ice, HDA: high-density amorphous ice
Adapted from Chem. Rev. 2016, 116, 7463−7500

Models: TIP4P-2005 and ST2

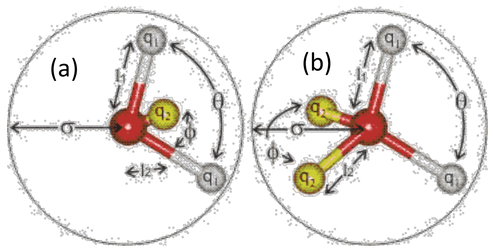


Figure 2: (a) A representation of the TIP4P-2005 of water as a four-site model (b) ST2 as a five-site model
Adapted from http://sites.science.oregonstate.edu/~hetheriw/astro/rt/info/water/water_models.html

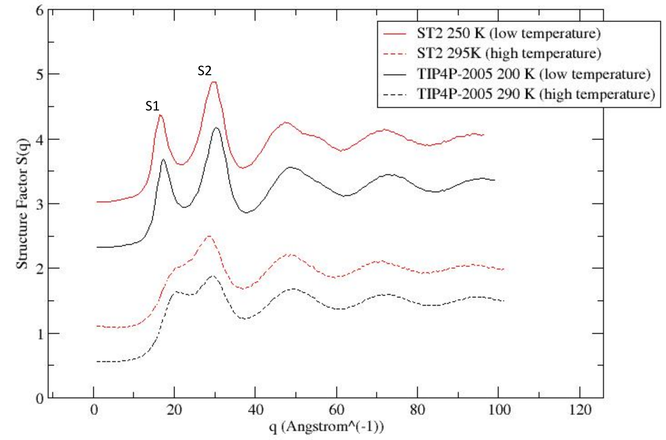
Both the TIP4P-2005 and the ST2 models are imperfect representations of the quantitative behavior of water over the entire range of temperatures and pressures. Their characterizations of water also differ from each other. Each model has its own strengths and weaknesses:

TIP4P-2005	ST2
-A rigid four-site water model (two lone-pair electrons grouped together)	-A 5-site model (two lone-pair electrons separated)
-Better representative of H_2O	-Emphasizes the anomalies from hydrogen bonding

Thermodynamic Signature: Structure Factor S(q)

Under high temperatures (marked by dotted lines in Figure 4), structure factor S(q) for both TIP4P-2005 and ST2 does not show a significant pre-peak. As temperature decreases, S(q) maximum splits into two-identifiable peaks S1 and S2. Low- and high- temperatures correspond to different values for the two systems. To show a similar change in thermodynamic behavior, ST2 decreases by 45 K (295 K -> 250 K) while TIP4P-2005 shows a 90 K drop (290 K -> 200 K). This finding is consistent with the fact that ST2's emphasis on hydrogen bonding makes its thermodynamic behavior more responsive to a change in temperature.

Figure 4: TIP4P-2005 and ST2 structure factor S(q) for low and high temperatures (Data shifted for clarity)



Changes in Dynamics: χ_4

Four-Point Susceptibility Function (χ_4) quantifies the root-mean-square fluctuations in displacement over a length scale determined by q.

$$M(t) = \frac{1}{N}\sum_{i=1}^{N} |\vec{r}_i(t) - \vec{r}_i(0)|^2 \quad \text{(a)}$$

$$\chi_4 = \frac{\beta V}{\langle M(t)\rangle^2}[\langle M^2(t)\rangle - \langle M(t)\rangle^2]. \quad \text{(b)}$$

Formula (a): Mean square displacement *M*(t)
Formula (b): Four-Point Susceptibility Function χ_4

χ_4 gives us information about the structural heterogeneity of molecular displacement. We can see from Figure 5 that as the temperature cools down (following the arrow directions), for both systems, the maximum of each χ_4 curve first increases up until a transition point (250 K for ST2 and 205 K for TIP4P-2005). Below this point, the dynamics become more uniform and less heterogeneous.

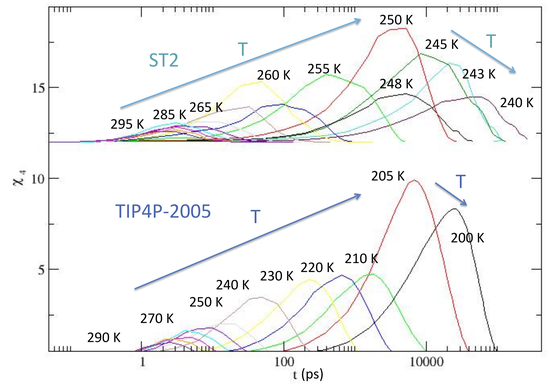


Figure 5: χ_4 for multiple temperatures at q = 30 nm^{-1} (Data shifted for clarity)

Thermodynamic Signature: Isobaric Heat Capacity

For simple liquids, potential energy (U) decreases as temperature decreases. During the fragile-to-strong crossover, however, the potential energy of water stops decreasing even when temperature decreases. Previous findings from the ST2 model show that the potential energy of water reaches a plateau at around 260 K. We also know that specific heat capacity at constant pressure, $C_p = dU/dT|_p + PdV/dT|_p$. We find the values of C_p by computing the centered difference of water's potential energy-temperature graph. For both the TIP4P-2005 and the ST2 systems, we observe a change in the behavior of C_p during the same regime. The transition moment is marked by a C_p maximum: 260 K for the ST2 system and 215 K for the TIP4P-2005 system.

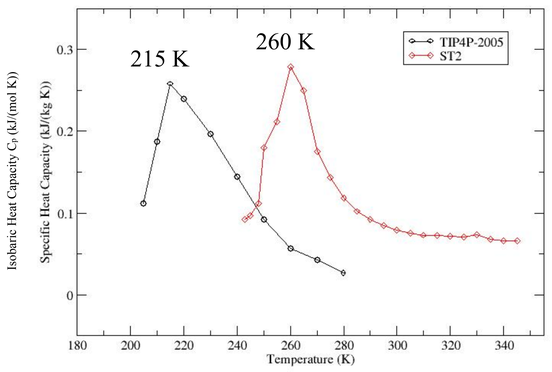


Figure 3: Isobaric Heat Capacity C_p of Water as a function of temperature (Data shifted for clarity)

Conclusion

This poster summarizes our findings in the thermodynamic and dynamic behavior of water during the fragile-to-strong crossover. From our thermodynamic data of the isobaric heat capacity (C_p) and structure factor (S(q)), I first identified the thermodynamics signature of the crossover. Due to the different features that the ST2 model and the TIP4P-2005 model focus on, the specific temperatures where the transition occurs are different. Nonetheless, we see a match in the general behavior of the two systems during the same regime. The decrease in dynamic heterogeneity below a peak temperature value (250 K for ST2, 205 K for TIP4P-2005) is consistent with our hypothesis that the crossover is a consequence of the water structure reaching an energetically stable random tetrahedral network as temperature decreases.

Bibliography

1. P. Gallo, et al. "Water: A Tale of Two Liquids" Chem. Rev. **2016**, 116, 7463−7500
2. M. Chaplin. "Water Structure and Behavior" (2007). URL: http://sites.science.oregonstate.edu/~hetheriw/astro/rt/info/water/water_models.html
3. C. Thorburn. "The Fragile-to-Strong Crossover in the Heterogeneous Dynamics of Supercooled Water" (2020).

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