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Anomalies in Supercooled Water at ~ 230 K Arise from a 1D Polymer to 2D Network Topological Transformation

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ABSTRACT

Puzzling anomalous properties of water are drastically enhanced in the supercooled region. But the nature of these anomalies is not known. We report here molecular dynamics simulations using the RexPoN force field from 298K to 200K along the 1 atm density curve. At 298K there are 2.1 strong hydrogen bonds (SHB), leading to a dynamic branched one-dimensional (1D) polymer. Water remains 1D down to 240K but at and below 230K the number of SHB becomes 3.0, leading to a two-dimensional (2D) network that persists to 200K. We propose that this 1D-to-2D topological transition, accounts for the anomalous properties of supercooled water. Near 230K, the power spectra show dramatic increases in the angular vibrational frequency modes while the diffusivity decreases dramatically, both arising from the 1D-to-2D transformation. This transition is not first order since free energy changes uniformly but fluctuations in the entropy near 230K suggest a possible second order transition.

TOC GRAPHICS

Water is a most important liquid, playing a crucial role in nearly all chemical, biological, and geological processes. It has many striking anomalous properties at ambient pressure¹⁻⁴ which are drastically enhanced in the supercooled region well below the freezing point⁵⁻⁶. In particular, the power-law divergence in thermodynamic properties with a possible singularity at $T_s \sim 228$ K⁷⁻⁸ has led to many discussions about the origin of the water anomalies. Direct experiments (exp.) on bulk water are limited to 10 to 20 K above T_s ⁷⁻⁹, because T_s is in the region of phase diagram (“no man’s land”) where liquid water transforms homogeneously to ice ($T_H \approx 232$ K)⁷⁻⁸. This has resulted in a variety of hypotheses^{2, 10-14}, the most popular one describes the anomalies at 228 K due to existence of a liquid-liquid critical point with most suggesting that this occurs at higher pressures¹⁴⁻¹⁷. Indeed, the LLCPP, which suggests coexistence of a high- and low-density liquids below the homogeneous nucleation line, has been studied extensively. Several experiments have avoided crystallization at T_H by using confining surfaces⁹, nanoscopic volumes of water¹⁸, and pulsed-laser-heating technique¹⁹, but these may not represent bulk water exactly. Recently, Kim *et al.*²⁰ performed the first direct measurements in supercooled region using femtosecond x-ray laser pulse technique on micron water droplets, reporting maxima in the thermodynamic response functions at ~ 229 K, but disagreements about their analysis have been expressed²¹. Thus, despite numerous experimental and theoretical studies, there remain considerable uncertainties about the origin of the anomalies in liquid water¹⁰.

In addition to direct and indirect experimental methods, molecular dynamics (MD) simulations have been very helpful in increasing our knowledge about the structural properties of water. Until recently the force fields (FF) on which the MD is based were very approximate, involving parameterization against two or three experimentally known properties of water. This has led to considerable uncertainties in whether the accuracy is sufficient to explain anomalous properties of liquid water.

The situation changed with the recent development of the RexPoN FF²², which is based on highly accurate quantum mechanics (QM) data at the coupled-cluster single-double triple *ab-initio* level²³. RexPoN led to the very accurate properties for water, even though no empirical data was used. Thus, at 298 K RexPoN predicts²²: heat of vaporization 10.36 kcal/mol (exp. = 10.52), density 0.9965 g/cm³ (exp. = 0.9965), entropy 68.4 J/mol/K (exp.=69.9), dielectric constant 76.1 (exp.=78.4), and melting point 273.3 K (exp. 273.15). Most important, RexPoN reproduces very accurately the oxygen-oxygen radial distribution (g_{OO}) of the first coordination shell from neutron and x-ray scattering. Indeed, even DFT calculations do not reproduce this description of the first coordination shell of water.

Earlier this year, we reported²⁴ that MD simulations using the RexPoN reactive FF²² at 298 K finds an average of 2.1 Strong Hydrogen Bonds (SHB) with an average lifetime of $\tau_{SHB}=90.3$ femtoseconds (fs). The SHB analysis was performed using 2.93 Å cutoff distance, the equilibrium distance for water dimer with bonding energy of 4.98 kcal/mol.

We also reported that connecting these SHBs leads to a 1D polymer with occasional branches to sidechains. This established the revolutionary new DynPol paradigm for the structure of water as a dynamic polydisperse branched polymer, leading to an average cluster size of 151 at 298 K that decreases to 36 at 400 K. The average ΣSHB decreases from 2.1 down to 1.6 at 400 K, while τ_{SHB} decreases from 90 to 68 fs.

This heterogeneity (i.e. polydispersity) of the HB in liquid water has been confirmed in experiments using 2D Raman-terahertz (THz) technique,²⁵ which has the ability to distinguish between the homogeneous and inhomogeneous broadening. Indeed, the 2D Raman-THz of Berger *et al.*²⁵ found the HB lifetime of H₂O to be in the range of 75 to 95 fs for the temperature range of 298 to 276 K which agrees well with the range of SHB lifetimes predicted independently by RexPoN FF, 90 to 100 fs, confirming the heterogeneity of the SHB network predicted by RexPoN.²⁴

Here, we use RexPoN MD to predict the properties of water as it is cooled from 298 K to 200 K while changing the density slowly along the 1 atm density curve.

Figure 1a shows the distribution of Σ SHB as a function of temperature. We find that Σ SHB increases continuously from 2.1 at 298 K to 2.5 at 240 K. Thus the water polymer chains have increased branches, while retaining the 1D polymer character from 298 K to 240 K. However, at 230 K Σ SHB reaches to 3.0, remaining at 3.0 down to 200 K. Simultaneously, Figure 1b shows that τ_{SHB} increases uniformly from 90 fs at 298 K to 126 fs at 228 K and then with a noticeable change in the slope increases to 133 fs at 220 K. Below 220 K, the τ_{SHB} stays almost constant down to 200 K.

This structure of water at 230 K with an average of 3.0 SHB leads to a network of connected small rings having 5, 6, and 7 water molecules. See Supplementary Information (SI) for the details of ring analysis. Figure 1c shows the population of ring sizes as the temperature is decreased, showing a dramatic jump at 230 K in number of 5-, 6-, and 7-membered rings. Indeed, the maximum population changes from 5-membered rings at 240 K to 6-membered rings at 230 K and remains there at lower temperatures.

Figure 1. Structural analysis of supercooled water. a) The percent population of the number of strong hydrogen bonds (Σ SHB) from 200 to 298 K. The maximum in Σ SHB is ≤ 2.5 for 240 K and higher. But this number jumps to 3.0 at 230 K (shown by arrow) and remains there for lower temperatures. **b)** The SHB lifetime (τ_{SHB}) from 200 to 298 K. The rate of increase in τ_{SHB} jumps between 228 K and 220 K. The inset shows the slope change around 228 K more clearly. **c)** The number of primitive rings versus the size from 200 to 298 K. The jump from 240 K to 230 K is due to 1D polymer to 2D network transformation.

To understand how these numbers map into the topology of water, Figure 2 shows the 6-membered rings (blue color) at 298 K, 240 K, 230 K, and 220 K together with other water molecules (red color) in the simulations cells (see Fig. S3 and Fig. S5 for other temperatures and ring sizes). To demonstrate the layout of the rings better, the mapping of them onto a 2D surface is provided for 240 K and 220 K, before and after the topological transformation. This shows a 2D network of

connected rings at 230 K and below while at 240 K and above such rings are few, sparse and not connected. The number of molecules in 5, 6, and 7-membered rings increases from 19% (with respect to all molecules in the cell) at 298 K to 42% at 240 K, 52% at 230 K and then accelerates to 66% at 220 K (see Table S1 in SI). This shows the higher tendency of water molecules to adjust in the 2D network for temperatures below 230 K. The lifetime of the 5, 6, and 7-membered rings (τ_{RS}) increases slightly as the temperature is decreased, but it stays between 20 fs to 40 fs at all temperatures (see Table S2 in SI).

Here, we should emphasize on the meaning of τ_{SHB} and τ_{RS} . They relate to the lifetime of an individual pair of water molecules (τ_{SHB}) or an individual ring (τ_{RS}). For example, $\tau_{SHB} = 100$ fs means that a particular SHB survives for 100 consecutive steps (1 step = 1 fs) without breaking at any step during this interval. This is different than relaxation time of the entire 2D network which may happen on much longer time scale. It is possible that for the 2D network there could be a pattern in which the internal parts of the network have longer lifetimes than the edges of the network.

Figure 2. Topology transformation in supercooled water. The three dimensional structure of the 6-membered rings (blue color) are shown for 298 K, 240 K, 230 K, and 220 K in the simulation cells. The rest of the molecules are shown with transparent red color. The mapping of the rings on the surface before and after 1D to 2D transformation is shown on right for 240 K and 220 K. The dominance of the 2D structure is clear for 230 K and 220 K. For each of the above frames duplicates of simulation cells were made along x-, y-, and z-directions to show the connectivity of the bonds and rings to the periodic images.

To provide a better understanding about the nature of this topological transformation, we computed the density of vibrational states (DoS) for the temperature range of 298 to 200 K. The DoS function was computed using two-phase thermodynamics (2PT) methodology²⁶⁻²⁷ based on the Fourier transform of the velocity autocorrelation function, for a time period of 20 ps averaged over 5 cycles. The results are shown in Figure 3. Figure 3A shows the total DoS for each temperature. This can be partitioned in terms of hindered translation and rotation vibration modes through velocity decomposition as shown in Figure 3B for 298 K. Here, the total DoS contains translational and rotational modes, $\text{DoS}(v)_{\text{tran}}$ and $\text{DoS}(v)_{\text{rot}}$, but no internal OH or HOH modes since we kept the water structure rigid. The dashed line in Figure 3A separates the translational and rotational modes at each temperature. Thus, the first two peaks (40 and 200 cm^{-1}) belong to the translational librations of water molecules and the third peak (400 to 600 cm^{-1}) involves the rotational librations. We see here a substantial increase in the higher frequency rotational modes as the temperature decreases from 298 to 200 K, showing the effect of increased branching. In particular the integral of DoS, $\text{IntS}(v)$, in Figure 3C shows a substantial transfer of the low-frequency 200 to 300 cm^{-1} modes to 500 to 800 cm^{-1} high-frequency modes. Here, $\text{IntS}(v)$ increased almost linearly for temperatures above 240 K but at 230 K it forms an inflection point in the 220 to 380 cm^{-1} range above which it accelerates and increases substantially. This transition from low to high frequency angular modes shows that the water molecules are considerably less mobile at temperatures below 230 K, because they are in a 2D network in contrast to 240 K and above where the one-dimensional nature provides less constraints to rotation.

Figure 3D shows the change in vibrational frequencies between 200 K and 230 K or 240 K as the structure goes from 2D network to 1D polymer. The big increase above 400 cm^{-1} reflects the increased rigidity of water molecules in the 2D network.

Figure 3. Vibrational frequency modes in supercooled water. A) DoS(ν) of supercooled water computed between 298 K and 200 K. The hindered translational and hindered rotational modes are separated by the dashed black line. The first two peaks (40 and 200 cm^{-1}) belong to the hindered translational motions and the third peak (400 to 800 cm^{-1}) corresponds to hindered rotational modes. B) Partition of DoS(ν) into hindered translational and rotational vibrational modes. C) The integral of DoS(ν) given in A. The vibrational angular modes exhibit an inflection point in the 220 to 380 cm^{-1} . D) Difference between DoS(ν) at 200 K and that of 230 K and 240 K. The positive difference ($>400 \text{ cm}^{-1}$) reflects the increased number of water molecules in the 2D network.

Figure 4 shows the free energy (A) and absolute entropy (S^0) as a function of temperature from 298 K to 200 K, extracted from the MD trajectories using the 2PT technique²⁶⁻²⁷. The uniform and continuous change of A with no discontinuity or sharp change in S^0 show that there is no first-order phase transition along the 1 atm curve. However, the topological transformation leads to fluctuations in S^0 around 228 K to 235 K, which may indicate a second-order phase transition.

Figure 4. Thermodynamic properties of supercooled water. Free energy (A) (right) and absolute entropy (S^0) (left) were computed as a function of temperature using 2PT. The free energy is continuous with temperature, showing that the topological transition is *not* first order (i.e. there is only one liquid phase). The entropy shows fluctuations near 228 K suggesting a possible second order transition. The inset provides a closer view of S^0 and A change around 230 K.

Another dramatic change induced by this topological transformation is in the diffusivity. Figure 5 compares the computed and experimental diffusivity as a function of temperature on both linear and semi-log scales, to provide a better understanding of the behavior of diffusivity as a function of temperature.

Figure 5a shows that the predicted diffusivity decreases linearly from 298 K to 240 K in agreement with experiment Price *et al.*²⁸. Then the calculated value fluctuates rapidly in a transition region

between 240 and 220 K, and then the diffusivity becomes very small and flat for 220 K to 200 K. Indeed, this low temperature behavior is verified *qualitatively* by experiments from Xu *et al.*¹⁹, who used a pulse laser-laser-heating technique to measure the crystalline-ice growth rate from which they extracted the liquid-water diffusivity. The experiment and theory agree on the very low diffusivity between 200 K and 220 K. But the experiment finds a smooth curve with a noticeable change in the slope at ~230 K, the theory leads to big fluctuations between 225 K and 235 K. We attribute the large fluctuations in this region as a symptom of the topological transition with rapid fluctuations in the topology leading to larger short scale motions that give an apparently larger diffusivity. Probably we need a larger unit cell to accommodate all these fluctuations within one cell. We also performed longer simulations for the temperatures in the range of 220 to 240 K to compute the diffusivity using mean-squared displacements (MSD). The computed diffusivity by MSD (Figure S12 in SI) follows a similar trend as the diffusivity using 2PT methodology but with smaller fluctuations. These results suggest that the fluctuations arise because of 1D to 2D transformation.

We believe that the difference between the magnitudes of computed and measured diffusivity at 220 K and lower is mainly due the nuclear quantum effects (NQE).

In addition, the difference might arise because the RexPoN calculations were performed for pure bulk water whereas the experiment uses a smart setup consisting of a thin film of amorphous solid water deposited on top of a thin layer of polycrystalline ice. The diffusivity is then calculated by measuring the growth rate of polycrystalline ice layer at the ice-water interface via the pulsed-laser-heating technique. These differences between experiment and simulation might be responsible for some of the discrepancies below 220 K.

The semi-log plot in Figure 5b helps to qualitatively understand the results in terms of Arrhenius behavior and activation energy barriers. This shows that from 298 K to 240 K the effective activation barrier for RexPoN is in good agreement with experiment. However, below 235 K experiment finds a much increased activation energy. RexPoN leads to a higher activation energy close to experiment for 225 K to 210 K. But for 210 K to 200 K and 235 K to 225 K the effective barriers are low compare to experiment. We attribute the low barrier for 235 K to 225 K as due to fluctuations between 1D and 2D topology, probably requiring a much larger cell for a proper description. We suspect that the lower barrier below 210 K may arise from the classical description of the dynamics requiring increased nuclear quantum corrections. Also, it is possible that at 200 K even larger time scales are needed to fully equilibrate the 2D networks.

Figure 5. Computed and experimental diffusivity as a function of temperature. a) The data are plotted using a linear scale. The computed diffusivity by RexPoN FF decreases linearly from 298 K to 240 K and then becomes very small and flat for 220 K to 200 K, in agreement with experiments. The fluctuations in the computed diffusivity from 235 K to 225 K arise from the topological transformation from 1D polymer to 2D network. The inset provides a closer view for the changes around 230 K. b) The data are plotted using a semi-log scale. This shows that RexPoN and experiment lead to the same activation barrier from 298 K to 240 K. From 235 K to 225 K the effective barrier is too low compared to experiment, which we attribute to fluctuations as the system is changing from 1D and 2D topology. From 220 K to 210 K the predicted barrier is similar to experiment, but clearly the barrier is too low below 210 K. We suspect that the main issues here are NQE and perhaps the cell is too small.

In 2014, Sellberg *et al.*²⁹ used a liquid jet to explore the structure of micron-sized water droplets in vacuum over the temperature range of 258 K to 227 K, which they analyzed with femtosecond x-ray laser pulses to extract the structure factor profile as a function of temperature. They noticed that the separation between the first peak (S1 at $q \approx 2 \text{ \AA}^{-1}$) and the second peak (S2 at $q \approx 3 \text{ \AA}^{-1}$) increases as temperature decreases. The increasing separation between S1 and S2 is a direct experimental indication that the structural ordering of supercooled water increases when the temperature is decreased.

Similarly, we computed the position (q) and the splitting (Δq) between S1 and S2 peaks as a function of temperature using RexPoN (see Methods). The computed splitting between S1 and S2 by RexPoN is compared with experimental data in Figure 6a. Clearly, RexPoN is in good agreement with experiment. By decreasing the temperature, the computed position of the peaks by RexPoN approach the characteristic values of low density amorphous (LDA) ice and hexagonal ice. These results show that RexPoN is able to capture the correct directional HB behavior of bulk water.

We interpret the close similarity with the experimental S1 and S2 splitting data as an additional validation of the transformation from a 1D polymer into a 2D network at $\sim 230 \text{ K}$. Sellberg *et al.*²⁹ find fluctuations from 232 K to 228 K similar to the RexPoN results in this region. They considered the results in this region to be artificial, but we believe it might arise from an induction period over which the 1D polymer chains adjust themselves into the 2D network.

In addition, the height of the second peak (g_2) in the oxygen-oxygen radial distribution function also provides useful information regarding the structural ordering of the water. Sellberg *et al* used an indirect method to extract the g_2 values from structure factor data. The used TIP4P/2005 water model³⁰ to create a mapping of the height of g_2 versus Δq and then used this mapping to estimate the height of g_2 from their splitting measurement. Therefore, their experimental g_2 values are affected by the accuracy of TIP4P/2005 model. On the other hand, RexPoN provides a good agreement for the splitting (Δq) and position of S1 and S2 compare to experiment. This shows that RexPoN can be used to provide a reliable mapping of g_2 and Δq data at different temperatures. Figure 6b compares the experimental (based on TIP4P/2005) and computed RexPoN g_2 curves. The computed g_2 from RexPoN increases linearly from 298 K to 240 K, then rises more steeply to 232 K, dips at 230 K then rises fast to 220 K. This increased g_2 from 230 K to 220 K indicates a narrower distribution of water molecules in the second coordination shell, which implies an increase in structural ordering.

Our predicted g_2 becomes nearly flat from 220 K to 200 K, which we interpret to indicate that the 2D network is already formed. Interestingly, extrapolating the RexPoN value from 200 K to 140 K would meet the experimental g_2 for low-density amorphous ice (LDA) from Finney *et al*³¹.

The above results show that experimental data strongly support the RexPoN results of a 2D topological transition at ~ 230 K.

Figure 6. Structural ordering in supercooled water. a) Temperature dependence of the first (S1) and second (S2) peaks positions of the structure factor computed by RexPoN (see SI) and compared with experimental data of Sellberg *et al.*²⁹, Ice Ih cluster²⁹, and low density amorphous (LDA) ice³². The positions of the S1 and S2 peaks from RexPoN and experiment agree, both of which indicate an increasing ordering as the temperature decreases. Interestingly, both move toward the characteristic values of low density amorphous (LDA) ice and Ice Ih cluster. **b)** The height of the second peak in g_{oo} (g_2) from RexPoN (red dots and line) compared to experiment (black circles) as a function of temperature. We have added the value for low-density amorphous ice (LDA) at ~ 140 K³¹. The blue line is a least-squares fit by Hestand and Skinner¹⁰ to experimental data extrapolated to LDA. The RexPoN g_2 curve follows the extrapolation line to 200 K suggesting

that it may end up at LDA. This suggests that the RexPoN description may remain amorphous down to ~ 140 K leading to the LDA phase.

One might wonder if the 6-membered rings we find at 200-230 K belong to a crystalline hexagonal ice phase. We consider that these rings belong to liquid phase for two reasons. First, the free energy and entropy curves show no first order behavior during the topological transformation, which means the liquid phase of water does not change upon the topological transformation. Second, the Σ SHB remains at 3.0 over the 230 K to 200 K range and does not tend toward the 4.0 SHB expected for formation of tetrahedral hexagonal ice phase. Indeed, Figure 2 shows that the connected 6-membered rings have little of the orientational correlation of ice.

It is important to emphasize here that we did nothing special in explaining the phenomena near 230 K in water. We simply started with the new RexPoN FF for water (fitted to very accurate QM calculations and leading to unprecedented accuracy in the properties, despite eschewing experimental data) and followed the changes with temperature at 1 atm.

We believe that the main reason that other water models did not predict the topological transition ~ 230 K is that all these models were developed based on the assumption that liquid water has nearly a tetrahedral structure, similar to ice. Thus, none were able to capture the first shall behavior implied by goo.

Our simulations in this study were performed along the experimental 1 atm density line explain that the anomalous behavior of water at 1 atm are related to changes in the topology of water, showing no evidence of the LLCP at 1 atm as expected. However, we cannot claim that there is not a critical point for some other pressures of the phase diagram.

All the phenomena described here involve time scales of ~ 100 fs. Thus, experiments at these time scales of 1 fs, 10 fs, and 100 fs, versus 1 ps time scales should be useful in characterizing the role of these fluctuating polymeric and 2D network structures on properties. The behavior of τ_{SHB} (Fig. 1b) and dramatic change in the diffusivity below 220 K should motivate many additional studies (theory and experiment) of the 2D network for lower temperatures.

Associated Content

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Author Contributions

S.N. and W.A.G. designed research; S.N. performed research; S.N. and W.A.G. analyzed data; and S.N. and W.A.G. wrote the paper.

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Supporting Information Available: It includes descriptions of Methods, Primitive Ring Analysis, Ring Structures of Supercooled Water at Different Temperatures, Number of Rings of Supercooled Water at Different Temperatures, Structural Ordering as a Function of Temperature, Structural Analysis of Supercooled Water at 140 K, Diffusivity Calculations for Supercooled Water, Hydrogen Bond Lifetime Using Empirical Models, Population Analysis of Different Ring Sizes, and Lifetime of Different Ring Sizes.

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