

Supplemental Information: Configurational Disorder of Water Hydrogen Bond Network at the Protein Dynamical Transition

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MSD

The convergence of our results is probed by considering the extension of the MD trajectories up to 100 ns for a few selected temperatures, 200, 240, 260 K, respectively. The MSD was computed for three independent blocks of length 10 ns, and separated along these long trajectories. The computed values are reported in the Table S1.

Table S1: Mean square displacement $\langle u^2 \rangle$ computed for independent blocks along the 100 ns trajectories. Error bars on the last digit are reported in parenthesis.

T (K)	$\langle u^2 \rangle$ (\AA^2) [0-10 ns]	$\langle u^2 \rangle$ (\AA^2) [40-50 ns]	$\langle u^2 \rangle$ (\AA^2) [90-100 ns]
200	0.366(6)	0.369(3)	0.371(5)
240	0.597(15)	0.606(11)	0.598(5)
260	0.798(20)	0.777(14)	0.771(13)

In order to individuate the protein dynamical transition we have calculated the derivative of the MSD from the simulations as a function of the temperature, as estimated by using simple centered finite difference method. The data are reported in Fig. S1.

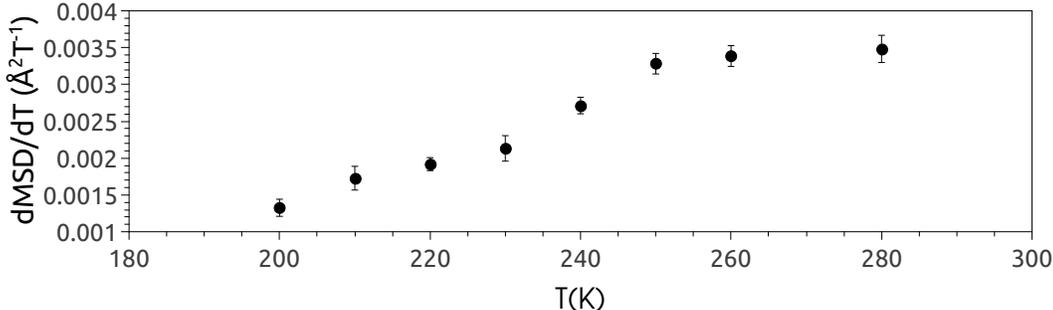


Figure S1: Derivative of the MSD as a function of temperature.

The effect of thermal excitation on the MSD of individual hydrogen is estimated for each protein in the system by computing the difference between the values at $T = 260 K$ and at $T = 230 K$. The results are reported for each chain in the Figure S2. The eight proteins are referred to according to their chain label, A to H.

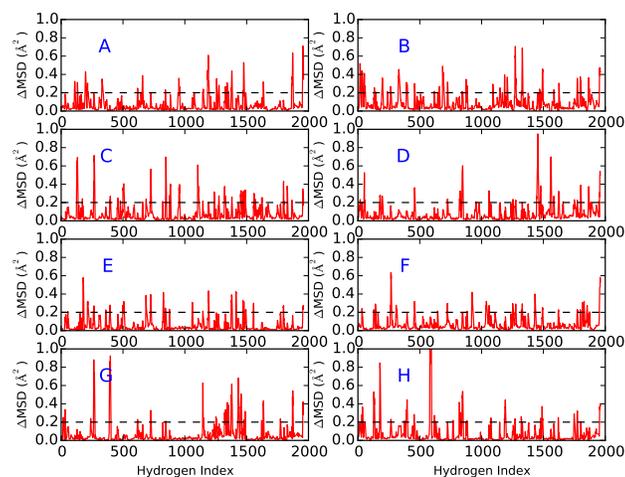


Figure S2: Difference between MSD values at temperatures 260 K and 230 K for individual hydrogen along the protein sequences.

Water Reorientation Dynamics

The time correlation function $P_2(t)$ of the water dipole $\vec{\mu}$ was calculated along the trajectory and fitted using two exponential functions and a constant term, $n_\alpha * e^{-t/\tau_\alpha} + n_\beta * e^{-t/\tau_\beta} + n_\infty$.

The set of parameters obtained are reported in the Table S2.

Table S2: Parameters describing the decay of the time correlation function $P_2(t)$.

T (K)	n_α	τ_α (ps)	n_β	τ_β (ps)	n_∞
200	0.04	15.2	0.1	276.0	0.86
210	0.05	15.8	0.11	229.0	0.84
220	0.08	20.7	0.2	272.0	0.72
230	0.10	19.0	0.26	237.0	0.64
240	0.15	16.3	0.33	197.0	0.52
260	0.25	14.2	0.33	142.0	0.42
280	0.38	11.0	0.32	120.0	0.30
300	0.48	9.0	0.28	116.0	0.24

HB Networks and Clustering

We have constructed ideal connectivity states of a network of 20 entities. The spectrum of the associated symmetric normalized Laplacian has been calculated so to provide a reference for the characterisation of the spectra obtained in the real case of hydration water, see Figure S3. Fully, or largely connected structures, are associated to a bimodal distribution. Depending on bipartite character of connected structure the spectrum is more or less symmetric. For ideal disconnected structures the spectrum peak at the eigenvalue $\lambda = 0$.

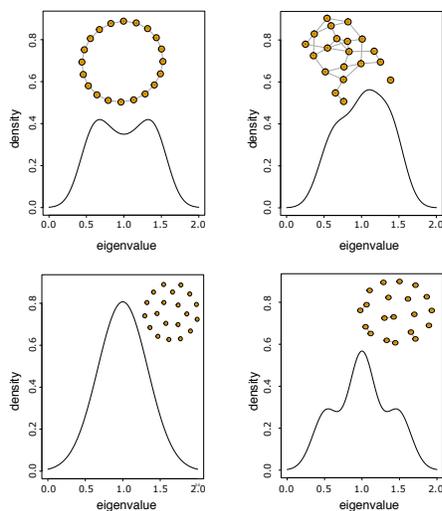


Figure S3: Spectra of the symmetric normalized Laplacian matrix for ideal connectivity states represented as connected yellow nodes in each panel.

The effect of the cut-off value is monitored for value of $J_c = 0.05, 0.075, 0.1$. When scaled with respect to the number of HB network configuration detected at the lowest temperature (n_0) the data nicely scale one on top of the others, see Figure S4.

For the value of the cut-off $J_c = 0.05$ a kinetic clustering is performed so to cast together network states that quickly interconvert one with each others and so single out the network configurations that are separated by high kinetic barrier. The temperature variation of the kinetic clusters is similar to the changes visible by considering all the networks states, see Figure S5.

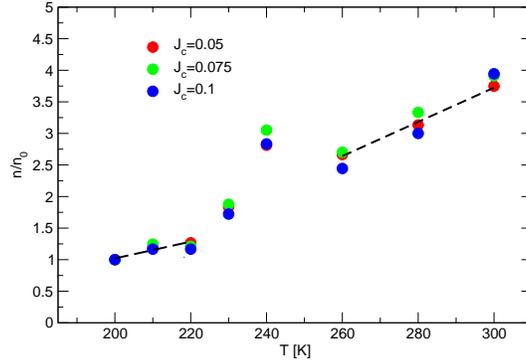


Figure S4: Number of HB network configurations as a function of temperature for different value of the cut-off J_c .

Volumetric analysis

The volume of water molecules in the powder system is calculated by using the Voronoi tessellation based on heavy atoms. In the top panel of Figure S6 we report the thermal change of the per molecule volume v_w of water while in the bottom panel we report the probability distribution of the per molecule volume $P(v_w)$ for selected temperatures. The derived density $\rho(T)$ is compared to the density obtained for a pure water system, see Figure S7

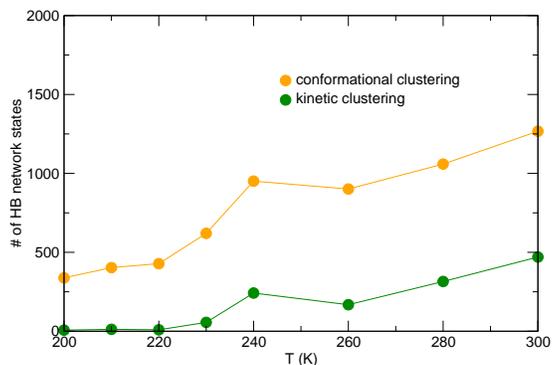


Figure S5: Number of HB network configurations detected via conformational and kinetic clustering as a function of temperature for the cut-off $J_c = 0.05$.

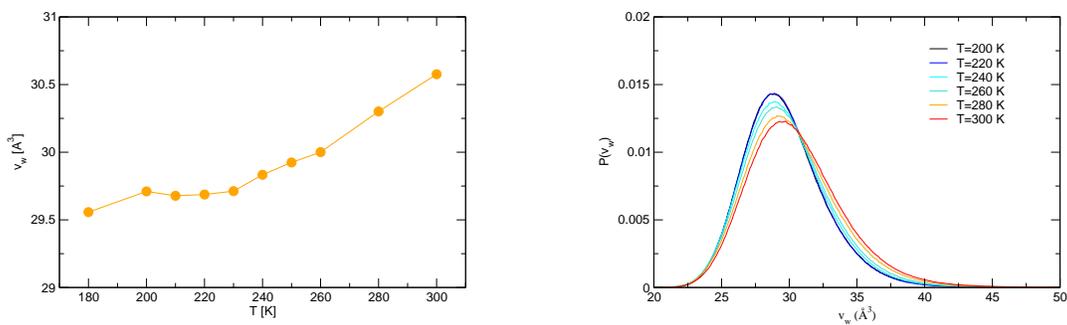


Figure S6: Top Panel: average value of the volume of a water molecule v_w in the powder system as a function of temperature. Bottom Panel: Probability distribution of the water volume v_w for selected temperature.

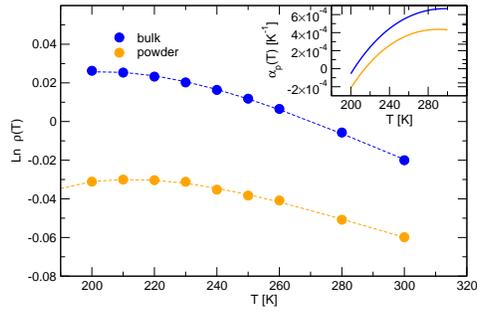


Figure S7: Water density as a function of temperature for the protein powder system (orange circles) and for a pure aqueous solution (blue circles). The solid lines indicate a polynomial fit of the data. The derived isobaric thermal expansion coefficient α_P for the two systems is reported in the inset graph of the figure.