Microscopic Origin of Hysteresis in Water Sorption on Protein Matrices

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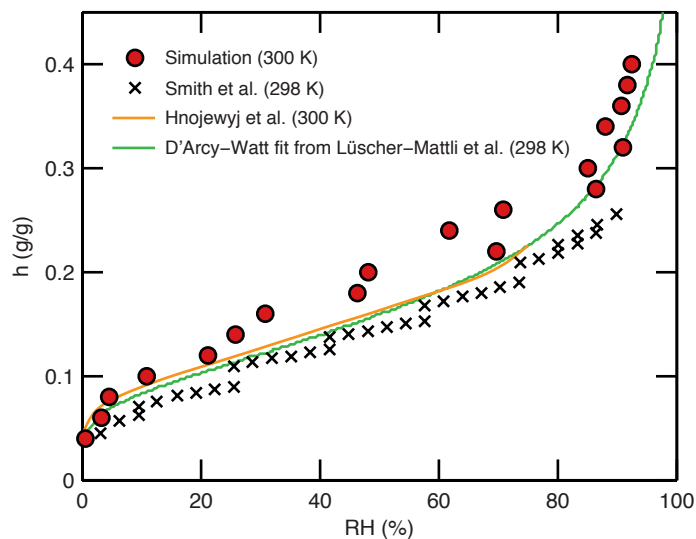*Corresponding author: pdebene@princeton.edu

Figure S1. Comparison of the water adsorption isotherms of lysozyme computed by simulation and experiment (Smith *et al.*,[1] Hnojewyj et al.,[2] and Lűscher-Mattli et al.[3]). Since the experimental measurement starts at 0 g/g hydration level at the relative humidity of 0%, the experimental isotherms were shifted upward by 0.04 g/g to account for the residual water remaining even in the dehydrated protein powder.
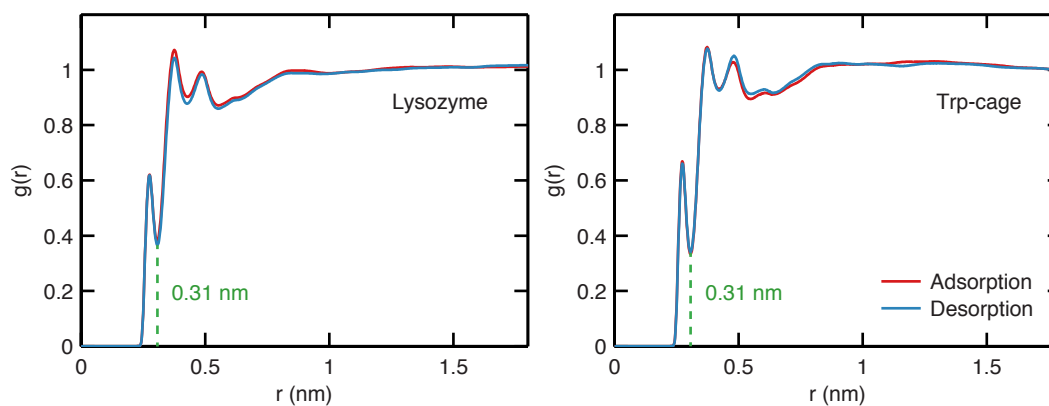

Figure S2. The radial distribution function between protein heavy atoms and water oxygen atoms, for the lysozyme (left) and Trp-cage (right) powders. The minimum after the first peak, which is located at 0.31 nm (green, dashed line), was determined to be the cutoff for determining the first hydration shell of the protein.

Water Sorption Simulation Method

The water sorption simulation was performed based on the method described by Kim et al.[4] During an adsorption simulation, water molecules are inserted in a "continuous" rather than "discrete" manner, where during an insertion of single water molecule, the interaction of the new water molecule is gradually increased from no interaction (ideal gas limit) to a full interaction. The potential energy (U) of the system during each insertion of water molecule is represented by the following equation:

$$U(\lambda) = U_{rest} + [\lambda(t) \times U_{inserted}(\lambda)]$$

where λ is the coupling parameter ranging from 0 (no interaction) to 1 (full interaction). First, a water molecule is inserted at a random position in the simulation box that is not overlapping with any of the existing atoms. At this point, the water molecule does not interact with the rest of the system ($\lambda = 0$). Then 400 ps of NPT MD simulation is performed, during which the interaction of the new water molecule is gradually increased until the full interaction limit ($\lambda = 1$) at the end of the MD run. This allows an efficient equilibration of the system because the very weak interaction at the beginning of the MD run allows the new water molecule to bypass any diffusion barriers or steric interference while during the later of the MD run the system can still relax at the full interaction of the water molecule. This procedure is repeated until a desired hydration level is reached. For the desorption simulation, the same procedure is used except that this time the interaction of a randomly selected water molecule is gradually turned off.

References

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