Dynamic crossovers in hydration water at 252 and 181 K from experiments, theory and simulations

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Abstract:

We study the dynamics of the hydrogen bond (HB) network of a percolating layer of water molecules and compare the measurements of a hydrated globular protein with the results of a many-body water model for a hydration monolayer. Using dielectric spectroscopy, we measure the temperature dependence of the relaxation time of proton charge fluctuations. These fluctuations are associated with the dynamics of the HB network of water molecules adsorbed on the protein surface. Using mean-field calculations and simulations, we study the dynamics and thermodynamics of the model. Both experimental and model analyses show two dynamic crossovers, (i) at approximately 252 K and (ii) at approximately 181 K. We show that the two crossovers are a consequence of two specific heat maxima. The first is caused by fluctuations in the HB formation, and the second, occurring at a lower temperature that corresponds to the Widom line, is due to the cooperative reordering of the HB network. We show also how our results allows to reconcile the apparently mismatching results about the specific heat of experiments and simulations.