[C1. J.M. Zanotti] Evidence that interfacial water is the driving force behind protein dynamics

The atomic scale behaviour of water as a monolayer on a porous silica glass is the result of a subtle coupling of local rotational and long range translational dynamics. We have been able to discriminate between these two contributions to shows that interfacial water experiences a glass transition at 165 K and a liquid-liquid transition at 240 K from a low-density to a high density-liquid. This unusual behaviour, compared to the bulk, is due to a strong weakening of the hydrogen-bond strength when water molecule lay in a 2D situation.

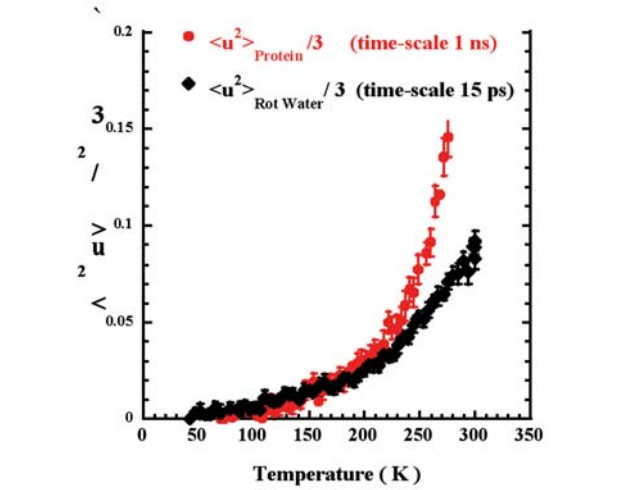


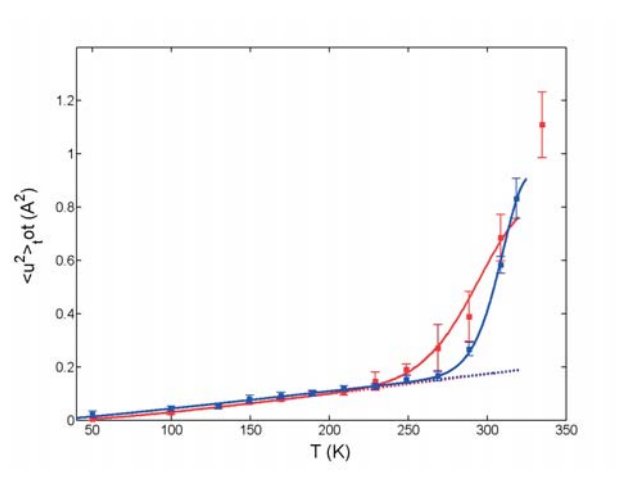
Figure 1. The atomic scale behaviour of water is the result of a subtle coupling of local rotational and long range translational dynamics. Here we show the temperature dependence of (i) $\langle u^2 \rangle_{\text{Rot Water}}$ the short time scale (15 ps, i.e. 80 μeV) rotational mean-square displacements of interfacial water and (ii) $\langle u^2 \rangle_{\text{Protein}}$ the hydrogen atom mean-square displacement of lysozyme hydrated with a monolayer of D_2O. We observe a strong correlation between the local reorientational transition in interfacial water at 220K and the onset of the long time (1 ns i.e. 1 μeV) large amplitude over-damped motions responsible for the $\langle u^2 \rangle_{\text{Protein}}$ to increase above 220K. The observed correlation suggests that water dynamics is the driving force governing the protein-function-relevant slow, long range, protein internal motion.

The well-known protein dynamical transition is clearly visible at about 220 K (Fig.1) and is strongly correlated, to the onset of short time-scale reorientational fluctuations that initiate structural rearrangements within the transient H-bond network of interfacial water surrounding the protein. This result seems to be the first experimental evidence supporting a possible mechanism controlling protein dynamics. Within the framework of this model, the protein external side-chain short time motions, induced by fast water reorientational motion ($\langle u^2 \rangle_{\text{Rot water}}$ Fig.1), propagate in a hierarchical way, along the protein structure from the residue side chains down to the protein core to induce the longer timescale protein backbone motion necessary for its function.

[Collaboration : J.M. Zanotti, M.C. Bellissent-Funel (LLB), Chen (MIT) and Kolesnikov (ANL/IPNS), J. Phys.: Condens. Matter 18 S2299–S2304 (2006)].

[C2. S. Combet] Influence of hydration solvent on the dynamic transition of phycocyanin

Phycocyanin (PC) is a light-harvesting protein present in the antenna of cyanobacteria, where it is involved in the first steps of photosynthesis. This protein, which can be fully deuteriated, has been used as a model to study hydration water dynamics at protein surface by neutron scattering. The aim of the present study was to compare the influence of hydration solvent (H_2O and D_2O) on the dynamics of PC by elastic neutron scattering. Samples of hydrogenated PC powder have been hydrated in H_2O (0.4 g/g PC) or D_2O (0.46 g/g PC) to obtain one similar monolayer of water molecules at the protein surface. Neutron elastic scattering spectra have been analysed by the double well-model. Evolution of the mean square displacements, as well as of associated thermodynamics values, was significantly different along the entire temperature range (20-320 K) between PC hydrated in H_2O and PC hydrated in D_2O. Dynamic transition temperatures between harmonic and anharmonic modes were, respectively, 220 ± 10 K and 270 ± 20 K for PC in H_2O and PC in D_2O. Differential microcalorimetry measurements confirmed these data with different slopes and vitreous transition temperatures between PC hydrated in H_2O (220 K) and PC hydrated in D_2O (235 K).



Mean square displacements of PC hydrated with 0.4 g H_2O/g PC (red) and PC hydrated with 0.46 g D_2O/g PC (blue).

[Collaboration: S. Combet, G. Gibrat, M.-C. Bellissent-Funel, LLB; M. Tehei, ILL].