Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Fast and Slow Dynamics and Local Structure of Liquid and Supercooled Water next to a Hydrophobic Amino Acid

Supporting Information

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Tables

Table 1 – Density and mean number of waters for the different water populations.

T/K	ρ/g·cm^{-3}	N_{Bulk}	N_{HSh}	N_{4WN}	N_{L4WN}
234	0.9872	233.7±0.2	22.7±0.1	12.0±0.1	10.7±0.1
249	1.001	232.5±0.2	22.7±0.1	11.7±0.1	11.05±0.09
261	1.003	232.47±0.07	22.55±0.09	11.34±0.07	11.21±0.07
271	1.004	232.6±0.1	22.34±0.09	11.1±0.07	11.2±0.1
286	1.002	233.12±0.04	22.10±0.05	10.70±0.03	11.40±0.04
301	0.9982	233.86±0.04	21.79±0.03	10.36±0.09	11.4±0.1
328	0.9883	235.44±0.04	21.22±0.08	9.72±0.07	11.5±0.1
365	0.9615	239.38±0.09	20.22±0.06	8.86±0.05	11.35±0.02

Figures

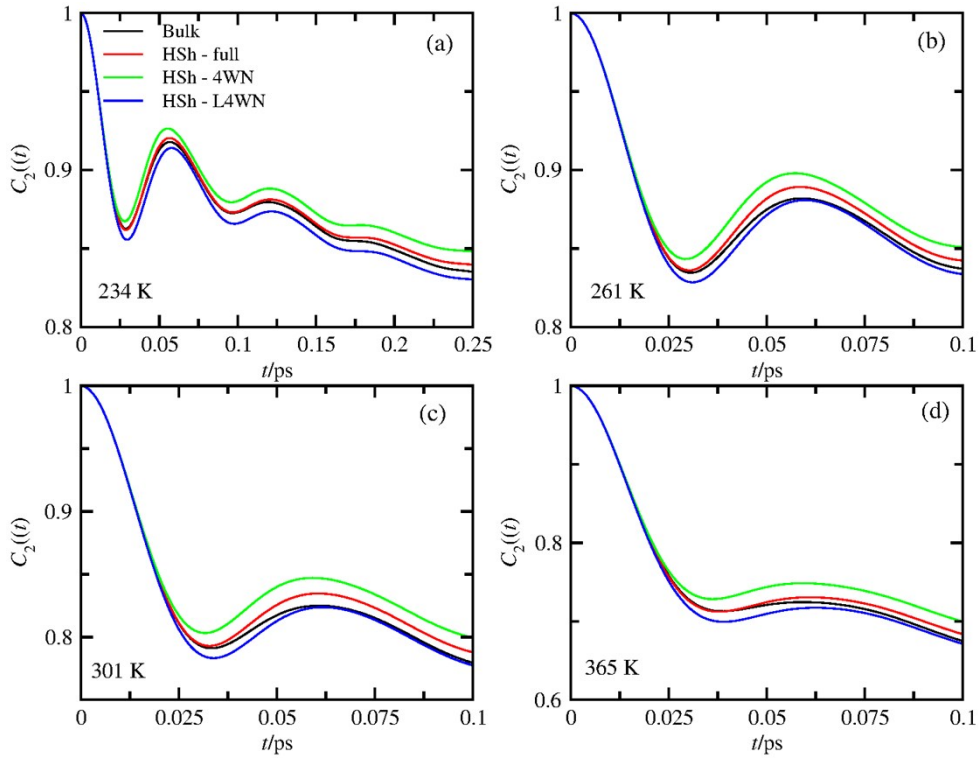

Figure 1-SI – Orientational time correlation functions at short times for four different temperatures. The plots show that the librational dynamics of waters with L4WN in the Val (C_β) hydration shell (HSh) is faster than in bulk water, opposite to waters with 4WN.

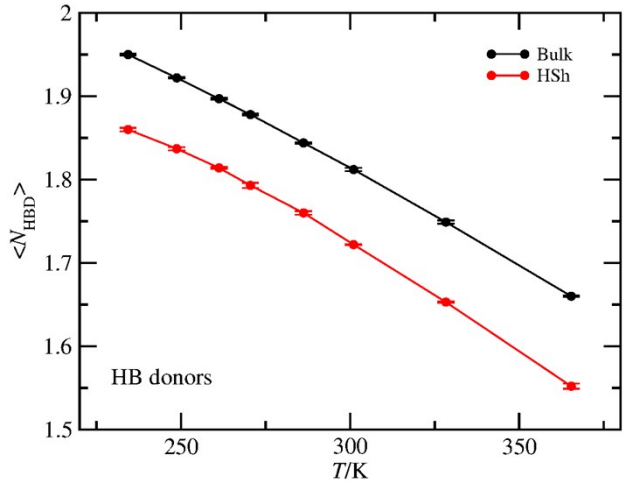

Figure 2-SI – Mean number of HB donors in the bulk and in Val (C_β) hydration shell (HSh).

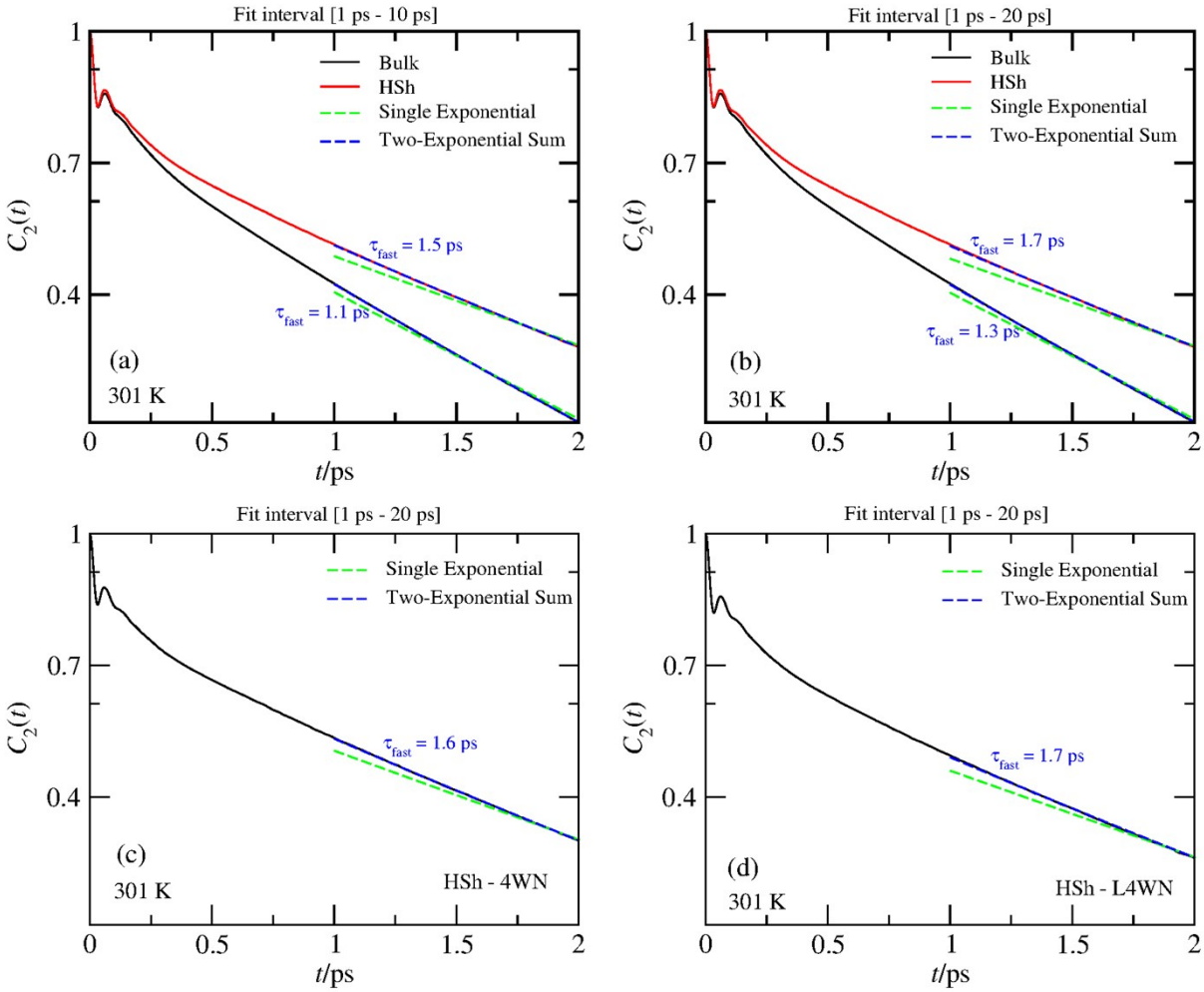

Figure 3-SI – Single and two-exponential sum fits of the OTCFs at short times for bulk and shell water, (a) and (b), and for 4WN (c) and L4WN (d) shell water populations. Deviations from a single exponential at short times can be observed for bulk and shell water while a good fit is observed with a two-exponential sum for every population.

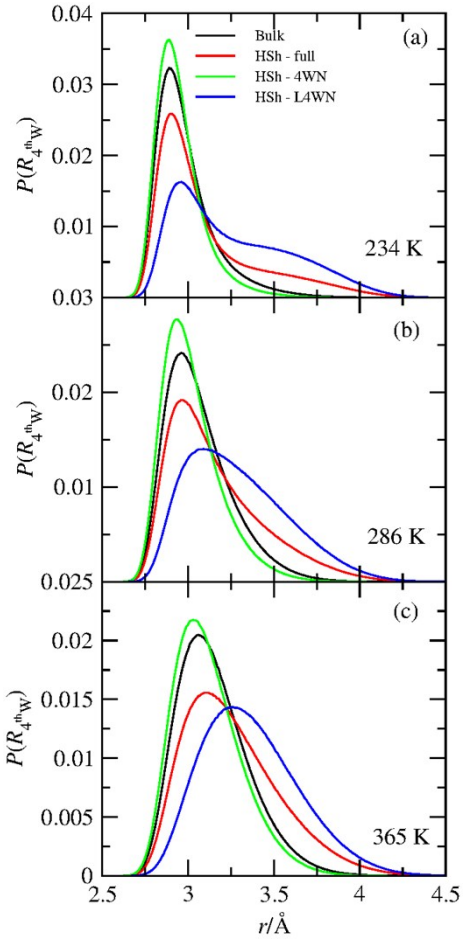

Figure 4-SI – Distribution of the fourth nearest water neighbor at three distinct temperatures. A narrowing and a shift of the distributions to lower distances can be observed at every temperature for the 4WN population. The fraction of neighbors at $r \leq 3.5$ Å in the bulk, hydration shell (HSh), HSh-4WN, and HSh-L4WN are respectively: 234 K (98%, 88%, 99%, and 75%); 286 K (97%, 88%, 99%, and 78%) and 365 K (94%, 82%, 96%, and 74%).

Fig. 4-SI shows that ~75% of the waters with L4WN have a fourth water neighbor in the first hydration layer ($r \leq 3.5$ A), although at a distance larger than the nearest atom of Val. We note that if instead of the solute heavy atoms the fourth water is considered, an even lower tetrahedrality is found. Thus, the proximity to the solute induces a distortion of the tetrahedral geometry.