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

Supplementary Material

for

Hydrogen-bond dynamics at the bio-water interface in hydrated proteins: a molecular-dynamics study

Prithwish K. Nandi[a], Niall J. English[a], Zdenek Futera[a] , and Antonio Benedetto[b,c]

[a]School of Chemical and Bioprocess Engineering, University College Dublin, Belfield, Dublin 4, Ireland
[b]School of Physics, University College Dublin, Belfield, Dublin 4, Ireland.
[c]Neutron-Scattering and Imaging Laboratory, Paul Scherrer Institute, Villigen, Switzerland.

Table S1 Hydrogen-bond formation for all 129 HEWL residues ranging from 190 to 390 K. Only those residues have been highlighted which form hydrogen bonds with an overall occupation time exceeding 20% of the entire simulation time. The number specified corresponds to the number of active hydrogen-bond-forming-sites of each residue

Residue	190 K	210 K	230 K	250 K	270 K	310 K	350 K	390 K
Lys1	4	5	2	2				
Val2	1	1	1					
Phe3								
Gly4								
Arg5	9	6	4	3				
Cys6	1	1						
Glu7	2	1						
Leu8								
Ala9								
Ala10								
Ala11	1							
Met12								
Lys13	2	2	1					
Arg14	5	5	2					
His15	1							
Gly16								
Leu17								
Asp18								
Asn19	4							
Tyr20		1						1
Arg21	7	5	1	1				
Gly22								
Tyr23	1	2		1				
Ser24	4	2	2					
Leu25	1	1	1	1	1			
Gly26	1	1	1	1	1			
Asn27			1					
Trp28								1
Val29								
Cys30								
Ala31								
Ala32								
Lys33	3	2						
Phe34	1	1	1	1	1	1		

Glu35	1	1	1	1	1	1	1	
Ser36	2	2	2	2	2	2	2	
Asn37	4	1						
Phe38								
Asn39	2	2						
Thr40	1	1	1	1	1			
Gln41	3	2	1	1				
Ala42								
Thr43	1	1						
Asn44	2	1	1					
Arg45	7	6	4		1			
Asn46	1	1						
Thr47	2	2						
Asp48								
Gly49								
Ser50								
Thr51					1			
Asp52								
Tyr53	2	1	1	1				
Gly54								
Ile55						1	1	
Leu56	1	1	1	1	1	1	1	
Gln57	1	1	1	1	1	1		
Ile58								
Asn59	1	1		1	1			
Ser60								
Arg61	4	4	2	2	1			
Trp62	2	2	2	1	1	1	1	
Trp63	3	2	2	2	2		1	
Cys64								
Asn65	2	2	1					
Asp66	1	1						
Gly67	2	1						
Arg68	6	5	3		2			
Thr69								
Pro70								
Gly71		1						
Ser72	3				1			1
Arg73	5	4	3	3	3	2		1
Asn74	5	5	2	2	1	1		
Leu75								
Cys76								1
Asn77	2	2						1
Ile78								
Pro79								
Cys80		1						
Ser81	1	1	2					
Ala82								
Leu83								
Leu84								
Ser85								

Ser86	3	2						
Asp87	1							
Ile88	1							
Thr89	2	1	1					
Ala90	1	1	1	1	1	1		
Ser91	4	3	3	4	4	3		
Val92								
Asn93	1	1						
Cys94								
Ala95								
Lys96	2	3						
Lys97	3	3						
Ile98								
Val99								
Ser100								
Asp101								
Gly102	1	1			1			
Asn103	3	3	1			2		
Gly104	1	1	1		1	1		
Met105								
Asn106	4	3						
Ala107								
Trp108	1	1	1	1	1			
Val109		2	1					
Ala110	1	1	1					
Trp111								
Arg112	5	4	2	1				
Asn113	2	1	1					
Arg114	6	6	4					
Cys115								
Lys116	2	3						
Gly117	1	1	1					
Thr118	1							
Asp119		1	1					
Val120								
Gln121	2	3	3	1				
Ala122								
Trp123	1	1	1	1	1	1		
Ile124								
Arg125	3	3	2					
Gly126	1	1						
Cys127								
Arg128	7	4						
Leu129	1							

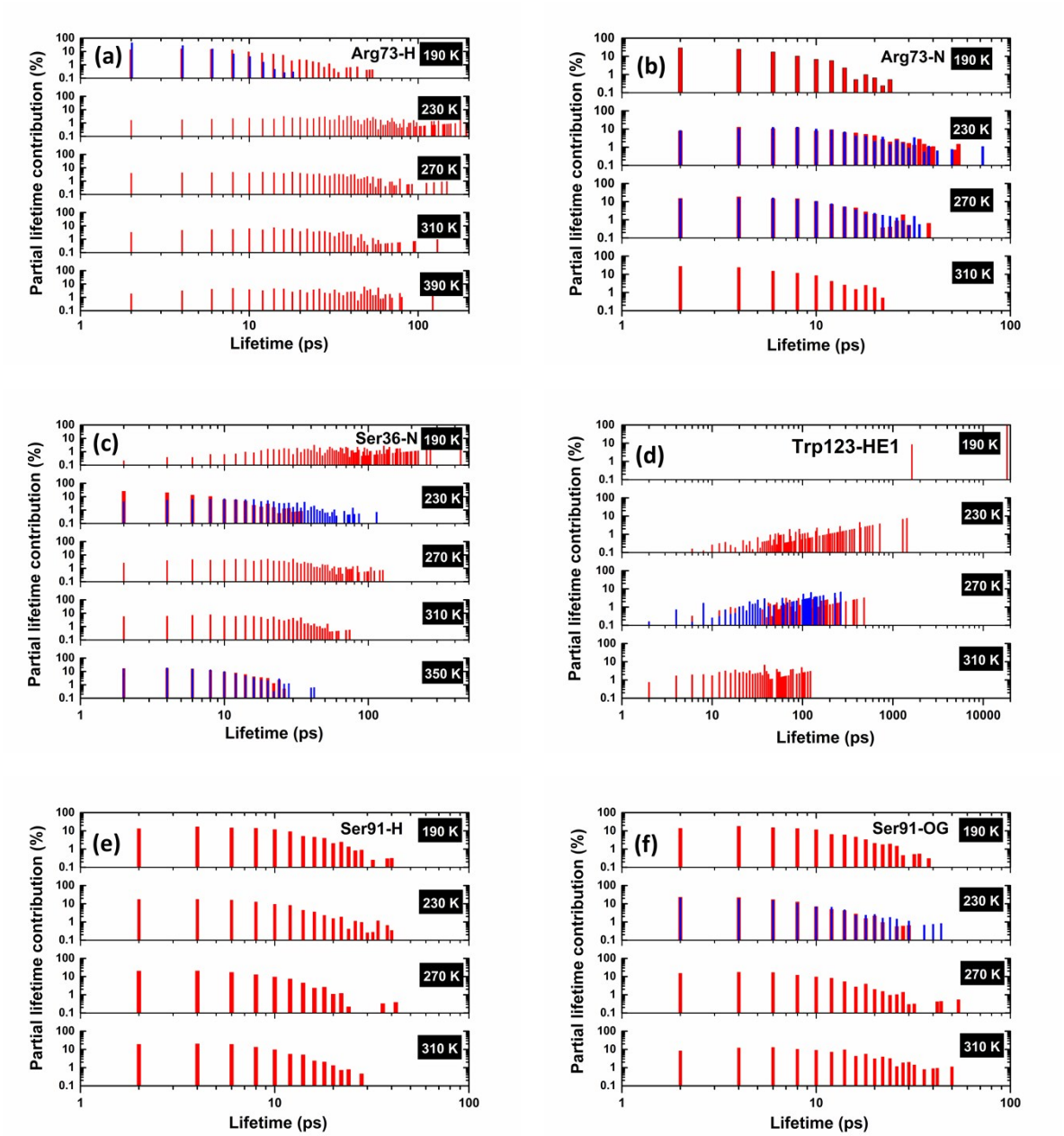

Figure S1. Partial lifetime contribution (PLC) for (a,b) Arg73, (c) Ser36, (d) Trp123, and (e,f) Ser91. Partial lifetime contribution is defined as *the proportion of time it contributes to the occupation time of that particular hydrogen bond (in percentage terms).*

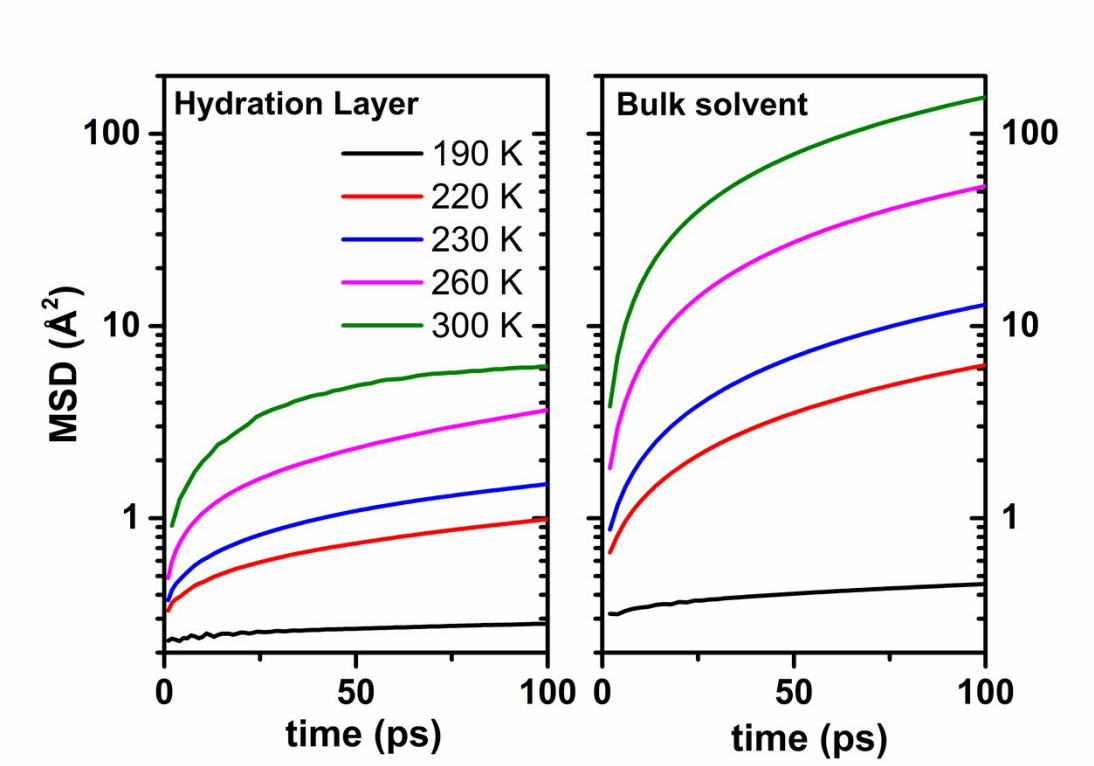

Figure S2. Comparison of mean square displacements of water in the hydration layer (left panel) and water consisting the rest bulk part of the solvent (right panel). It is quite evident that hydration layer MSDs are almost one order in magnitude less than the bulk. It clearly indicates that the water in the hydration layer are subject to spatial confinement.

Calculation of probability density associated to hydrogen bond lifetime (in Fig. 6):

The horizontal axes in Fig. 6, representing hydrogen-bond lifetime, is divided into '*N*' number of bins with a fixed '*binwidth*' (in *ps*). Here, each bin represents a particular value of lifetime for which the associated probability density, for the ith bin, is given by the following:

$$probality\ density\ (i) = prefactor \times bincount(i) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where,

$$prefector = \frac{total\ probability}{\sum_{i=1}^{N} (bincount(i) \times binwidth)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

In this work, we choose to express the total probability as the occupation time expressed in percentage proportion of the total simulation time. If '*OccpTime*' is the occupation time of a hydrogen bond, and '*SimlTime*' be the total length of the simulation, then the total probability is expressed as follows:

$$total\ probability = (OccpTime/SimlTime) \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$