Supporting Information: Structural and Dynamical Heterogeneities at Glutamine-Water Interfaces

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1 Comparison of CHARMM-TIP3P and OPLSAA-TIP4P for S1 Surface

In the main text, we showed that one of the surfaces is characterized by very slow dynamics involving water molecules getting incorporated into the crystal structure. These water molecules feature relaxation times on the order of several 10s of nanoseconds. This is observed using the TIP4P[1, 2] water model with the OPLSAA[3] force field. In order to assess the sensitivity of this result to the choice of the force field, we repeated the simulations for the S1 surface using CHARMM[4] and TIP3P[1]. Fig 1 illustrates the survival probability of water molecules residing in the hydration shell of the S1 surface. The number of the trapped water molecules obtained with CHARMM is 28 after $5ns$, while it was 31 with the OPLSAA force field and TIP4P water model. Thus the long-lived trapped water molecules at the interface appears to be a generic feature.

2 Rotational Relaxation Time

In the main text, we showed the rotational relaxation of water near each of the three surfaces for those water molecules that reside 100% of the time during some chosen time window. Fig 2 highlights the decay of rotational correlation function $P_1(t)$ as a function of water residence time. Different populations of water molecules with 100% , 50% and 25% residence time were taken within 10 Ådistance from the GDI of each system. It is clear from the figure that the

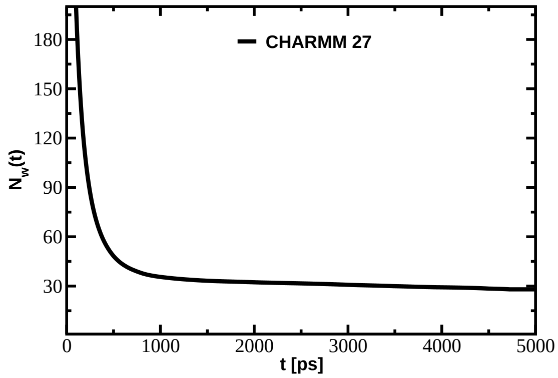

Figure 1: The residence time of water molecules in the hydration shell of S1 surface is shown. The simulations were done by using the CHARMM force field with the TIP3P water model.

water dynamics undergoes faster rotational relaxation as more exchange events are allowed.

3 Fraction of Water Molecules Exhibiting Slow Dynamics and Residence Times as a Function of Concentration

In Table 1, we report the fraction of water molecules that remain within 5 Åfrom the GDI of each surface for 100% , 50% and 25% of the total simulation time. It is clear that for both the 0.5 and 1ns time window, the fraction of water molecules experiencing a slow down

In Fig. 3 residence time of water is plotted for surface S1 as function of glutamine concentration in the solvent varying from 0-1M. The time for this analysis was chosen after 200 ns where most of the glutanime residues already migrated to the surface. The population of the solutes makes a rough jelly like surface. The hydration water get trapped and its exchanged dynamics get slowdown as compared to the pristine surface.

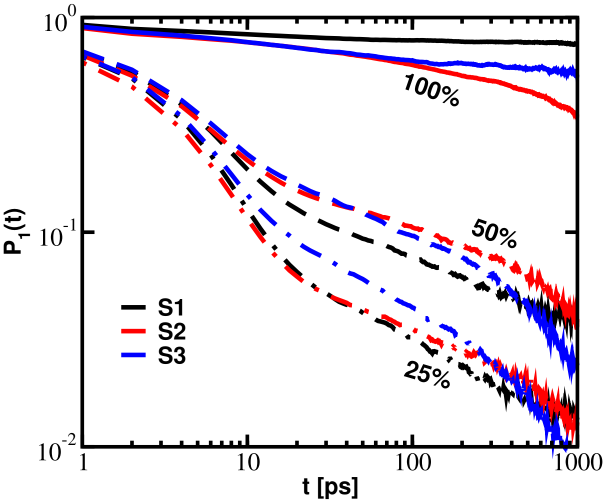

Figure 2: First rank rotational correlation function of the three surfaces plotted as function of water residence time: 100% , 50% and 25% within the hydration shell of width 10 Åfrom the interface.

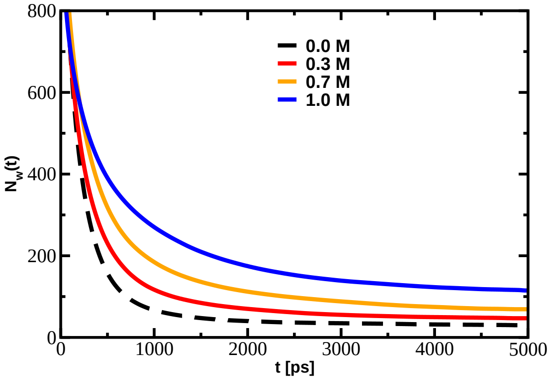

Figure 3: The residence time of water molecules in the hydration shell of S1 surface is plotted as a function of varying concentration of the solvent from 0M to 1M.

Table 1: **The number of water molecules residing in the hydration shell of width 0.5 nm from GDI of each system.**

	$0.5ns$			$1ns$		
Systems	100%	50%	25%	100%	50%	25%
S1	5%	35%	78%	3%	23%	80%
S2	7%	27%	68%	5%	18%	72%
S3	5%	31%	70%	1%	22%	68%

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