Supplementary information for "Quantification of spatio-temporal scales of dynamical heterogeneity of water near lipid membranes above supercooling†"

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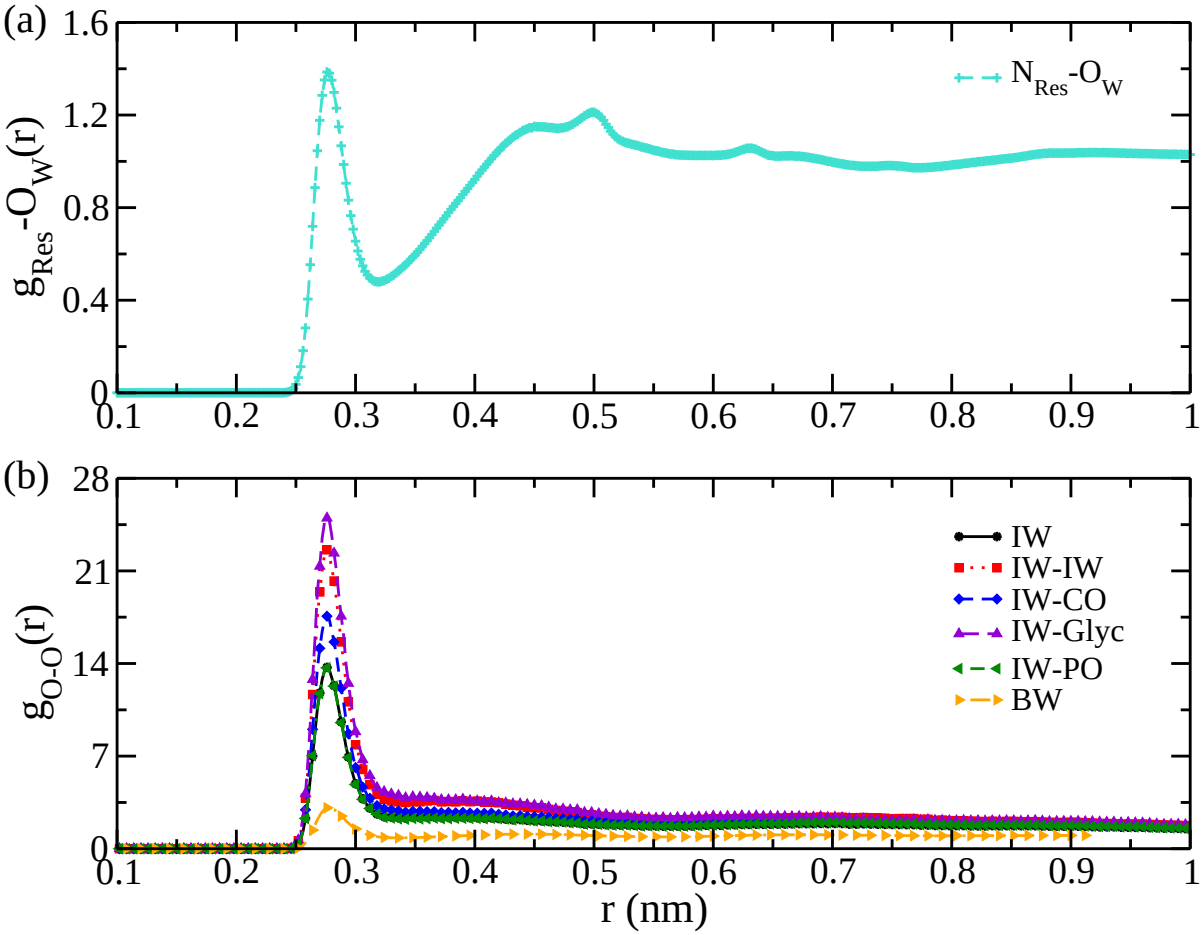

Figure S1: RDF for different classes of IW between a) oxygen-nitrogen of lipid heads and b) oxygen-oxygen of IW.

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0.1 Survival probability

Survival probability is an important quantity governing relaxation dynamics of water. Survival probability (P_i^d) is defined as the probability (which can be either 0 or 1) of i^{th} water molecule residing in a given layer d for a time duration t. P_i^d is calculated using following equation,

$$S(t) = \sum_{i=1}^{N} \left\langle \prod_{t_k=t_0}^{t_0+t} P_i^d(t_k) \right\rangle \tag{1}$$

where, N denotes total number of molecules, angular bracket denotes averaging over time origins t_0. P_i^d is calculated for water residing in vicinity of the headgroup of DMPC for 1 ns time window. The

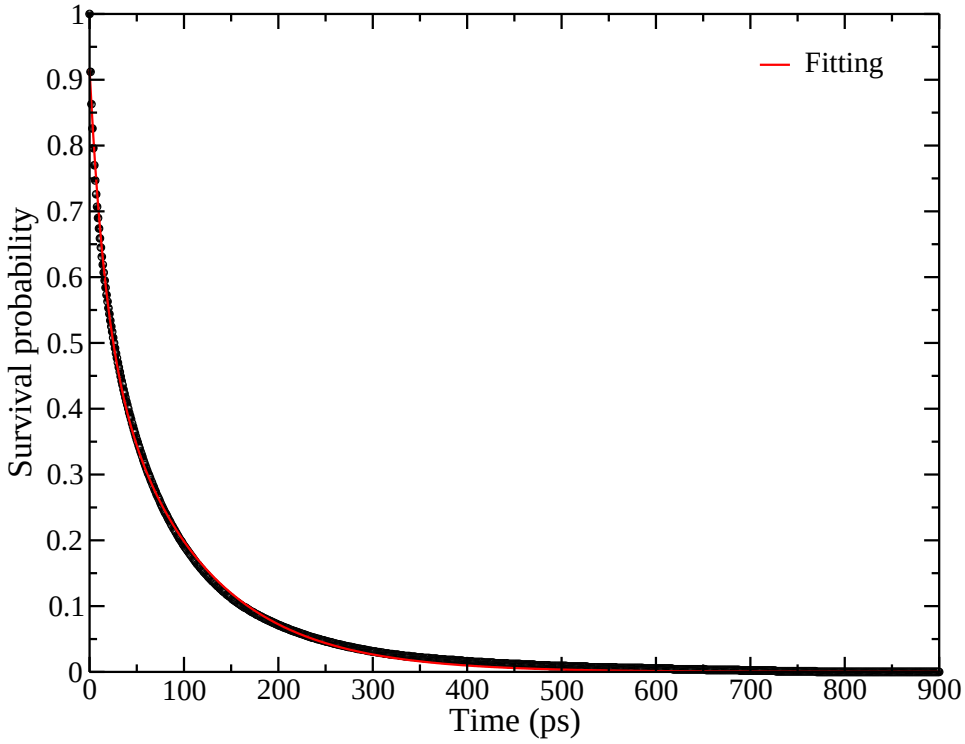

Figure S2: Survival probability of water analyzed over 1 ns time window. Solid red line show bi-exponential fitting.

residence time scales for water are quantified by fitting the survival probability to bi-exponential function given by equation 2.

$$y = A_f exp\left(-\frac{t}{\tau_f}\right) + A_s exp\left(-\frac{t}{\tau_s}\right) \tag{2}$$

Table S1: Residence time scales for water analyzed over 1 ns time window. Correlation coefficient is >0.99 .

A_f	τ_f (ps)	A_s	τ_s (ps)
0.38	16.40	0.54	99.56

where, τ_f and τ_s denote fast and slow residence time scales, A_f and A_s show coefficients associated with fast and slow time scales respectively.

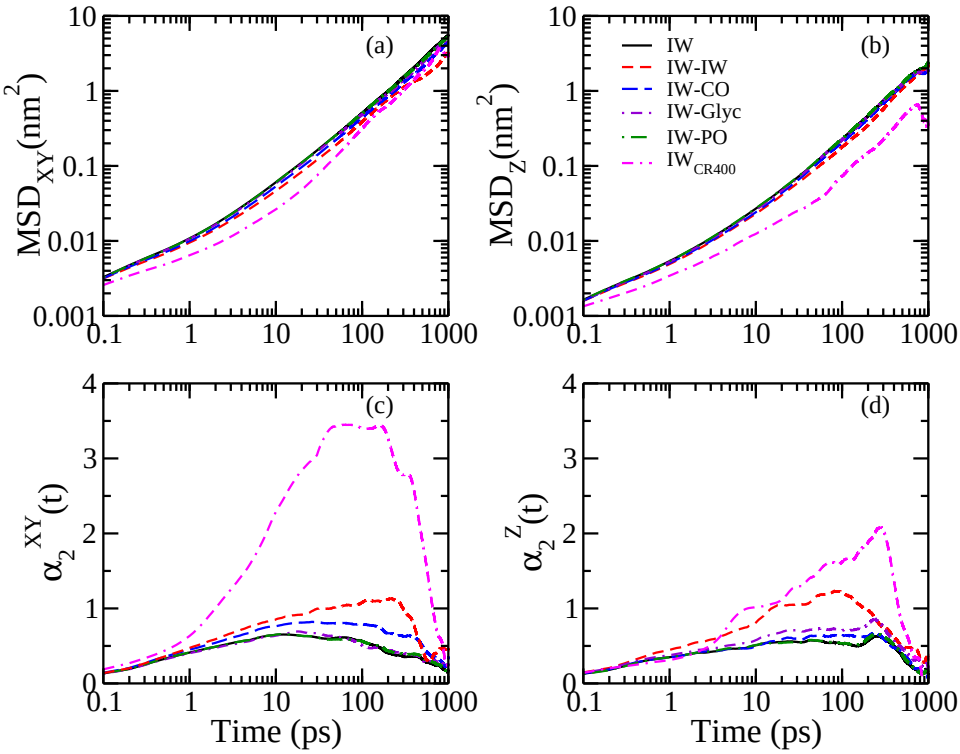

Figure S3: Translational mean square displacement for all classes of IW molecules along a) xy, b) z. NGP for all classes of IW molecules along c) xy and d) z.

0.2 Reorientational auto-correlation function (RACF)

For quantifying rotational dynamics, we computed reorientatinal auto-correlation function of lipid head, tail and IW. RACF is characterized by l^{th} order Legendre polynomial given by the following equation,

$$C_{vl}(t) = \frac{< \sum_{i=1}^{N} P_l[e_i{}^v(t).e_i{}^v(0)] >}{< \sum_{i=1}^{N} P_l[e_i{}^v(0).e_i{}^v(0)] >} \tag{3}$$

where, $e_i{}^v(t)$ is the vector for which RACF is calculated and P_l is the l^{th} order Legendre polynomial. We calculated RACF for IW and atoms of DMPC lipids. For IW, RACF is calcualted for the vector normal to the plane of OHH. For DMPC lipids, RACF is calculated for carbonyl moeity which is averaged for both alkyl chains and for atoms of sn-1 and sn-2 chain averaged over both chains. RACF ($\hat{n}$) for all cases is shown in figure S4. For extracting the time scale, RACF is fitted with bi-exponential function as,

$$y = A_f exp\Big(-\frac{t}{\tau_f}\Big) + A_s exp\Big(-\frac{t}{\tau_s}\Big) \tag{4}$$

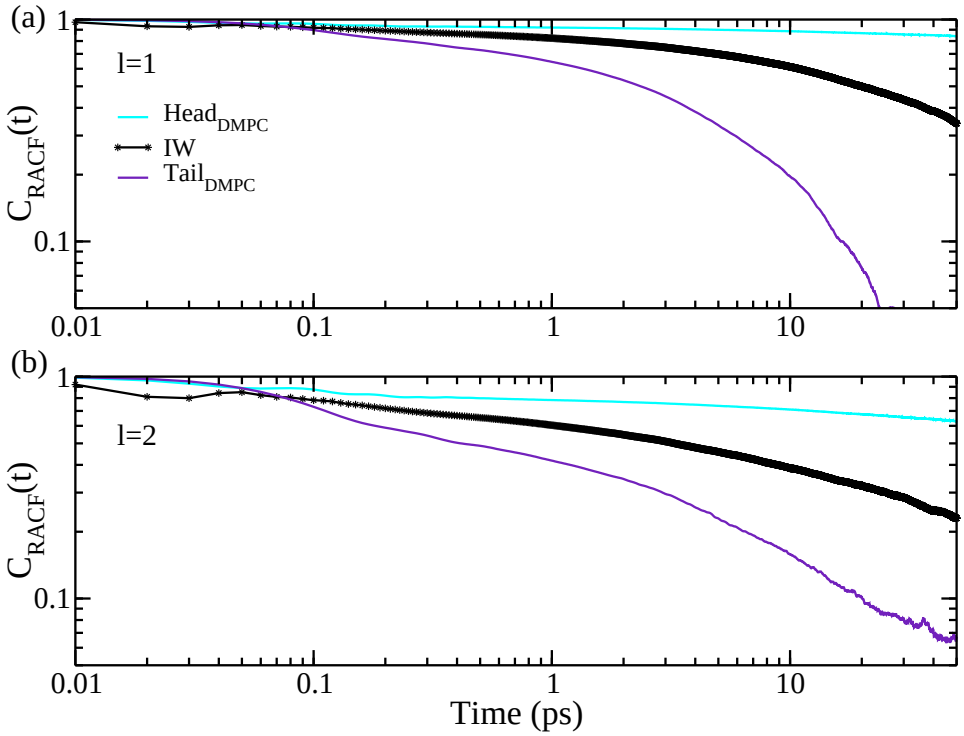

Figure S4: Reorientational auto correlation function (RACF) for a) first and b) second order Legendre polynomial for headgroup, tail and centere of mass of DMPC and IW.

Table S2: Reorientation correlation relaxation time for head and tail of DMPC lipids. All correlation coefficients are >0.99.

	Region	A_f	τ_f (ps)	A_s	τ_s (ps)
l=1	$Head_{DMPC}$	0.09	50	0.90	637.07
l=2		0.10	50	0.75	252.06
l=1	$Tail_{DMPC}$	0.48	2.75	0.36	14.32
l=2		0.25	1.01	0.40	11.94
l=1	IW	0.25	6.51	0.62	83.26
l=2		0.29	3.05	0.42	77.83

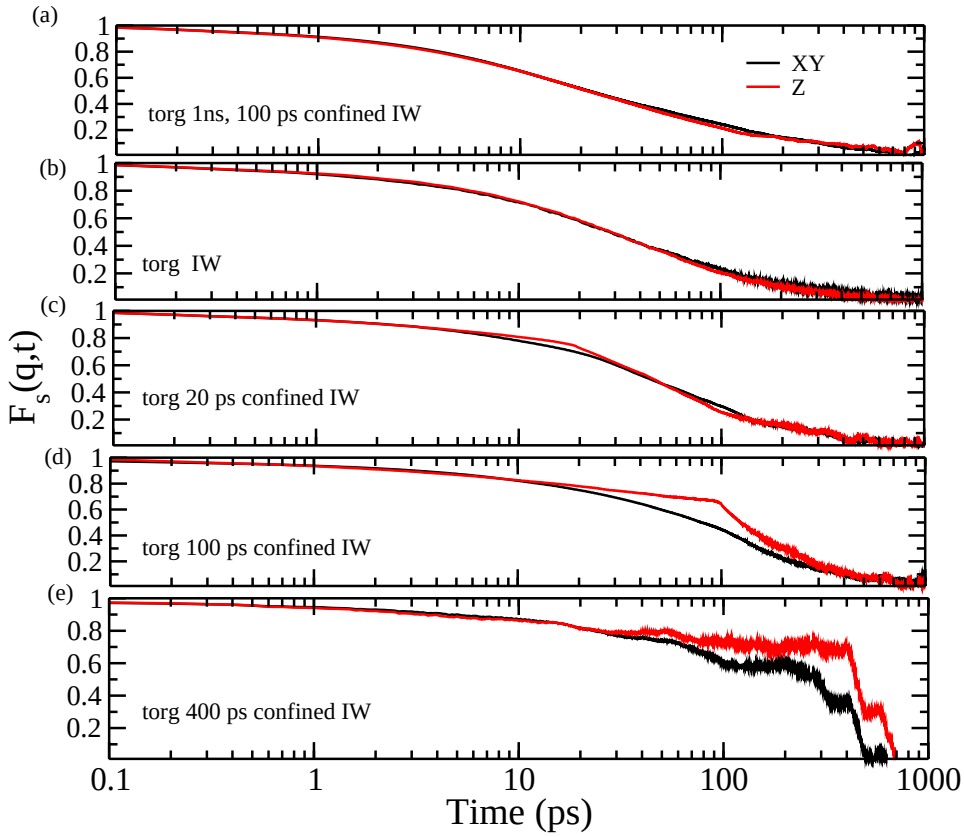

Figure S5: $F_s(\mathbf{q}, t)$ of IW calculated along xy and z at = 1 nm. Time origins (torg) are averaged in two ways. a) torg over entire 1 ns runlength for continously residing IW for 100 ps . b)-e) torg over confinement time. b) IW for any frame, c) continuously residing IW for 20 ps , d) continuously residing IW for 100 ps, e) continuously residing IW for 400 ps.

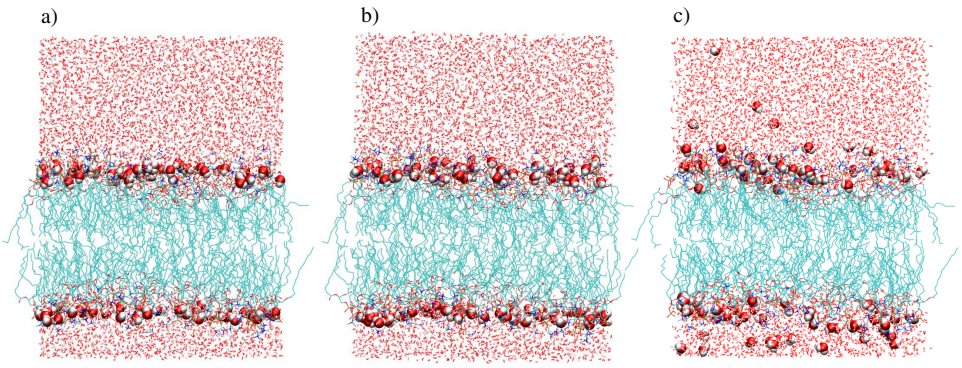

Figure S6: Snapshot of the DMPC bilayer at a) 50 ps, b) 100 ps, c) 150 ps. IW: CPK representation in red and white, DMPC lipids: line representations in cyan blue, remaining water: red dots.