List of Figures

Figure	*Title*	*Page*
1.1	Temperature dependent density of liquid water at different pressures ranging from 1 bar to 200 bar. The figure is taken from [ToolBox, 2009].	2
1.2	a) Four coordinated and b) five coordinated structures of water.	2
1.3	Thermodynamic anomalies of water a) specific heat capacity, b) isothermal compressibility and c) coefficient of thermal expansion of water. For contrasting anomalous behavior of water simple liquids are also shown. Figure is taken from [Kumar, 2008].	3
1.4	Snapshot showing geometric criteria for hydrogen bond formation in water where the distance between donor and acceptor (R_{HOO}) $< 3.5\mathring{A}$ and the angle between $\vec{OO}$ and $\vec{OH}$ (θ_{HOO}) $< 30^o$.	5
1.5	Self intermediate scattering function (F_s(q,t)) for bulk water at room temperature showing β and α relaxation regions. The pictorial representation of β and α relaxations are demonstrated by particles in green and red circles representing trapped and escaping molecules from its respective cage. The image is taken from [Janssen, 2018].	8
2.1	Snapshot of a) single DMPC molecule and b) DMPC bilayer in presence of interfacial water shown in red. All water molecules are not shown for clarity.	20
2.2	Density profile of DMPC bilayer from Berger and CHARMM36 force fields hydrated with TIP3P and TIP4P/2005 water. Solid lines : Berger bilayer with TIP3P water model, Dashed lines: Berger bilayer with TIP4P/2005 water model and Dashed dot lines show CHARMM36 bilayer with TIP4P/2005 water model. For clarity, density distribution of Nitrogen (N) is multiplied by a factor of 10.	21
2.3	Snapshot showing the bilayer thickness (d) using VMD [Humphrey *et al.*, 1996]. Color code: blue nitrogen atoms of DMPC head-groups.	23
2.4	a) Snapshot of single DMPC molecule showing acyl chain beads for order deuterium order parameter calculation. Color code: green vdw methylene beads of acyl chains. H predicted hydrogen atoms for united atom force fields associated with the methylene group. b) Deuterium order parameter of the DMPC bilayer hydrated with TIP3P and TIP4P/2005 water models are reasonably consistent with each other.	24
2.5	Lateral mean square displacements of the DMPC bilayer hydrated with TIP3P and TIP4P/2005 water models. All three systems a), b) and c) mentioned in table 2.2 reach diffusive regimes within 100 ns.	24
2.6	Pair correlation function between nitrogen (N) atom of DMPC head and oxygen atom of water.	25
2.7	Survival probability of water residing at DMPC head-group surface.	26
2.8	Pair correlation functions between a) oxygen-oxygen of IW and BW, b) oxygen-hydrogen of IW and BW.	27
2.9	Anomalous diffusion exponent (α) as a function of time showing the type of diffusion for the IW and the BW for both water models. Fluctuations at longer times are not shown. Both TIP3P and TIP4P/2005 bulk water are diffusive where the IW are sub-diffusive in nature.	28
2.10	VACF of IW and BW using TIP3P and TIP4P/2005 water models (for IW in presence of Berger and CHARMM36 lipids). IW show deeper minima than the BW suggesting more back-scattering from the oscillations of IW cages formed by the neighboring molecules via hydrogen bonds.	29

2.11 NGP of IW and BW for both water models. NGP of BW of both models increase within a very short time and then asymptotically decay to zero showing underlying Fickian dynamics. NGP of IW show non-zero α_2(t) for all combinations of force-fields indicating the presence of dynamical heterogeneity. 30
2.12 Displacement map for a) $IW_{TIP3P\ (DMPC\text{-}Berger)}$, b) BW_{TIP3P}, c) $IW_{TIP4P/2005\ (DMPC\text{-}Berger)}$, d) $BW_{TIP4P/2005}$ and e) $IW_{TIP4P/2005\ (DMPC\text{-}CHARMM36)}$ at respective β-α relaxation time scales. The displacements are mapped on the bilayer surface. 31

3.1 Oxygen-oxygen RDF for different classes of water hydrogen bonded to another water. For the sake of clarity in the differences in amplitudes, the RDF of the interface water is not shown until they reach the values of bulk water. 38
3.2 Oxygen-oxygen RDF for different classes of water hydrogen bonded to lipid head groups (IW-Res). 38
3.3 Translational MSD for interfacial and bulk water where the BW has a diffusive regime and others follow a sub-diffusive behavior. **Inset**: MSD for interfacial waters showing slowest motion for IW-CO and the fastest motion for IW-IW. 39
3.4 RACF for interface and bulk water for l$= 1$ for a) $\hat{n}$, b) $\vec{OH}$, c) $\vec{HH}$ and d) $\vec{\mu}$. 41
3.5 RACF for interface and bulk water for l$= 2$ for a) $\hat{n}$, b) $\vec{OH}$, c) $\vec{HH}$ and d) $\vec{\mu}$. 41
3.6 Distribution of number of hydrogen bonds per water molecule for all classes of IW. 47
3.7 Distribution of number of hydrogen bonds per water molecule for BW. 47
3.8 Hydrogen bond auto-correlation function for interface and bulk water. 48
3.9 Number of hydrogen bonds per water molecule which remain *intact* for simulation time *t* are shown for interfacial water. **Inset**: bulk water 50
3.10 Snapshot of DMPC molecules hydrogen bonded to interfacial TIP$4P/2005$ water. DMPC and water are shown in licorice and Corey, Pauling and Koltun representations respectively. Hydrogen bonded oxygens of DMPC are shown in VDW representations. Color code: green-PO oxygen, violet-Glyc. oxygen, blue-CO oxygen, red-water oxygen. 50

4.1 Interface water continuously residing for 400 ps (IW_{CR400}) in the first hydration layer of DMPC. Color code: Blue vdw - carbonyl oxygen; Violet vdw - glycerol oxygen; water molecules were shown in CPK. DMPC bilayer shown in transparent in pink licorice representation. 56
4.2 Translational mean square displacement for all classes of IW and BW. All classes of IW follow sub-diffusive regime while BW obeys diffusive regime with diffusion exponent as $\alpha = 0.99$. 57
4.3 NGP (α_2(t)) for all classes of IW molecules and the BW molecules show a cross-over from β to α relaxation at the same time-scale when respective mean square displacements have transitions from sub-diffusive to diffusive region. 58
4.4 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. 58
4.5 Self part of translational radial van Hove correlation function for all classes of IW and BW. The existence of larger correlation length indicates structured network of IW than BW. 60
4.6 Self part of van Hove correlation function along x direction. Gaussian fitting for BW depicts Fickian dynamics while non-exponential tails for all classes of IW reveal deviations from Gaussian behavior. 60
4.7 SISF of IW_{CR400} at λ values ranging from 0.50 nm to 3.00 nm. 61
4.8 SISF of BW at λ values ranging from 0.50 nm to 3.00 nm. 62
4.9 log(τ) vs log(q) plot for BW, IW_{CR400} and IW. Solid lines: fitting. 62
4.10 SISF for all classes of IW and BW at $\lambda = 0.50$ nm. 63
4.11 RACF for a) first and b) second order Legendre polynomial for lipid head, tail and IW. 64
4.12 F_s(q,t) of IW calculated along xy and z at $\lambda = 1$ nm. Time origins (torg) are averaged in two ways : a) torg over entire 1 ns run length for continuously 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 at $\lambda = 1$ nm and $\lambda = 0.50$ nm and e) continuously residing IW for 400 ps. 65

4.13 Snapshot of the DMPC bilayer at a) 50 ps, b) 100 ps and c) 150 ps. IW: CPK representation in red and white, DMPC lipids : line representations in cyan blue, remaining water : red dots. 65
4.14 One dimensional van Hove correlation function for different coarse grained length scales. Solid blue line showed Gaussian fitting for coarse grained block area of 5.5×5.5 nm^2. 68
4.15 a) Top view of spectral intensity of DMPC tilt plotted on bilayer x-y plane showing emergence of peaks. x and y indicate the grids present on the surface and thus has no units. b) The spectral intensity t(q) vs q shows the q value with the highest intensity at 1.14 nm^{-1}. c) Side view of DMPC lipid bilayer showing the length scale of the local weak undulation of the lipid membrane. 69

5.1 Snapshot of a hydrated DMPC bilayer and a DMPC molecule in presence of IW^{HB} molecules hydrogen bonded to lipid moieties residing near N head-groups. 75
5.2 Hydrophilic and hydrophobic beads of a DMPC molecule for which dynamical calculations are performed. Color codes: VDW Ochre - Nitrogen (N_{Head}), Green - Phosphorus (P_{Head}), Orange - Oxygen atoms associated with phosphate group, Pink - Oxygen atoms of carbonyl moiety, Ice blue - Oxygen atoms of glycerol moiety, Violet - Carbon atoms of glycerol moiety ($Glyc_{Head}$), Blue - Carbon atoms of carbonyl moiety ($Carb_{Head}$), Silver - $B1_{Tail}$, Magenta - $B2_{tail}$ and Orange - $B3_{Tail}$. 76
5.3 Density profiles of DMPC lipids and all classes of IW^{HB} along the bilayer normal. Density profiles of all classes of IW^{HB} are averaged over a) 100 ps and b) 1 ns. 77
5.4 Two dimensional translational mean square displacement (MSD_{XY}) of all beads of DMPC, IW^{HB} and BW. 78
5.5 Two dimensional translational mean square displacement (MSD_{XY}) of all classes of IW^{HB} and BW. Inset: different classes of IW^{HB} show similar MSD_{XY}. 78
5.6 a) Retardation factor calculated for DMPC lipid moieties and IW^{HB} with respect to BW. Glyc beads show maximum retardation due to its buried nature in hydrophobic core. b) Ratio of RF showing retardation of lipids with respect to IW^{HB}. The ratio is maximum for Glyc moiety followed by a decrease from Carb to P to N. 79
5.7 One dimensional van Hove correlation function of DMPC beads and IW^{HB}. End beads of lipid tails have minimum deviations from Gaussianity. 81
5.8 One dimensional van Hove correlation function of all classes of IW^{HB}. IW-PO^{HB} close to the lipid-water interface have minimum deviations from Gaussianity. 81
5.9 Time evolution of P ($\log_{10}(r(t)/\sigma)$) of IW^{HB}, P (phosphate) and BW. The peak of BW at ~ 2.13 corresponds to Gaussianity. IW^{HB} molecules reveal a bimodal nature characterizing presence of intermittency at a time scale when Fickian dynamics is followed. 82
5.10 Trajectory of an atom of IW^{HB}, carbonyl carbon (Carb) and phosphorus (P) for 1 ns run length. $S1$, $S2$ and $S3$ represent three segments of the IW^{HB} trajectory showing three regions with consequent hopping from one region to the other. IW^{HB} remains hydrogen bonded to oxygens of Carb and P in these regions. 82
5.11 SISF of different beads of DMPC lipids for $\lambda = 0.60$ nm. Two ends of a lipid chain relax faster compared to the moieties situated in the middle. 84
5.12 SISF for all classes of IW^{HB} at $\lambda = 0.60$ nm. IW-Glyc^{HB} molecules buried deep in the hydrophobic core relax slowest. 85
5.13 a) Shortest relaxation time scales, τ_s, are compared for the lipid head moieties and the IW^{HB} hydrogen bonded to the respective lipid heads. The values of τ_s are obtained in table 5.3 and 5.4. b) Ratio of τ_s of the lipid moieties and the IW^{HB}. 86
5.14 a) τ_α are compared for the lipid moieties and the IW. The values of τ_α are obtained from table 5.3 and 5.4. τ_α of lipids is divided by 20 for the clarity. b) Ratio of τ_α of the lipid moieties and the respective IW decreases as moving towards outer water. 87
5.15 a) Slowest relaxation time scales are compared for lipid moieties (τ_α) and the IW^{HB} molecules (τ_l) hydrogen bonded to those lipid moieties. The time scales are obtained in table 5.3 and 5.4. b) Ratio of the slowest time-scales of the lipids and the IW obtained from SISF fitting and $\frac{1}{e}$ cut-off. τ_l of IW^{HB} obtained from $\frac{1}{e}$ is divided by 4. 87

5.16 Colormap of a snapshot of a lipid bilayer and the IW^{HB} in terms of a) fast and b) relaxations for SISF calculated at $\lambda = 0.6$ nm for both DMPC and IW^{HB}. The fast relaxations are obtained from τ_s values in table 5.3 and 5.4. The slow relaxations for lipids and IW^{HB} are obtained from their τ_α (table 5.3) and τ_l (table 5.4) values respectively. 88