Network structure and dynamics of hydration water at zwitterionic lipid membrane surfaces

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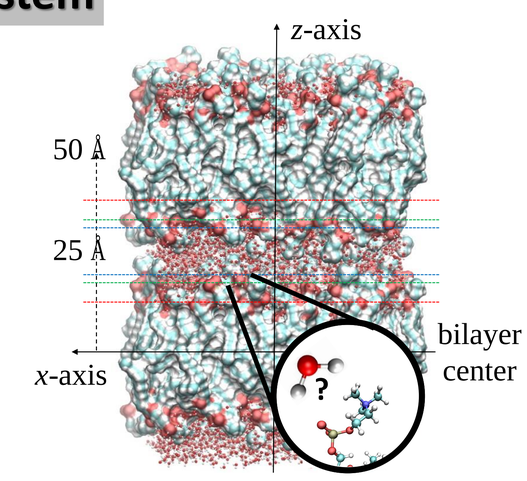
Abstract

Lipid bilayer is an excellent model system for investigating membrane structures and its hydration water. These membrane and hydration water have been studied by various experiments and computational studies. To observe detailed interactions between lipid head groups and their hydration water, we performed molecular dynamics (MD) simulation for the lipid multi-bilayer. From hydrogen bond number analysis, radial distribution, and orientational distribution of hydration water, we checked a strong interaction between phosphate group and water molecule, even to the second hydration shell. In contrast, a choline-associated water shows weak interaction with choline group. And, results from orientational relaxation and FT-IR spectroscopy for the hydration water revealed slow water dynamics and red-shifted absorption spectrum induced by the phosphate group, indicating the strong interaction between the phosphate group and its hydration water consistently. In this study, our results are in good agreement with experimental results and give insight into the interfacial water research at the lipid membrane surfaces.

System



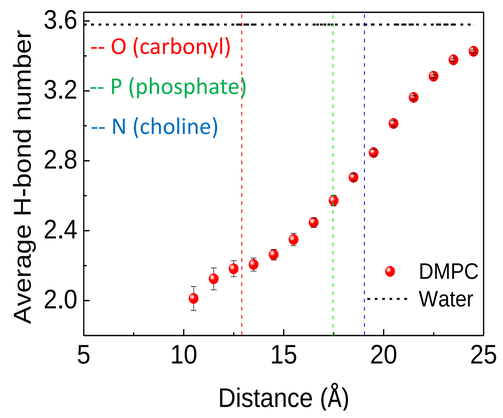
Components
128 DMPC lipids+2048 TIP3P water molecules in the periodic box
(Experimental condition)

System building
using the CHARMM membrane builder GUI
→ AMBER lipid 14 force field

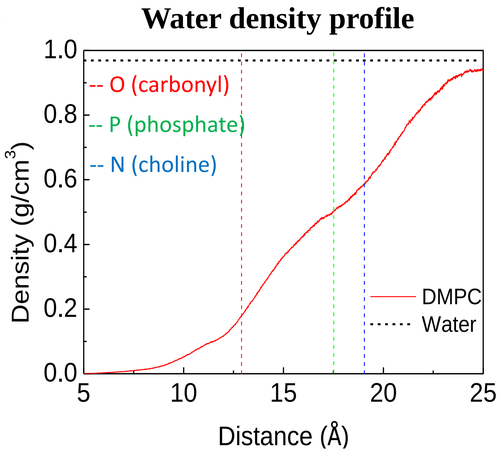
Production MD run
300 ps *NVT* MD simulation * 5 times
(trajectories are saved every 10 fs)
at T=318 K & p=1 atm

Interfacial water

Average H-bond number/water molecule



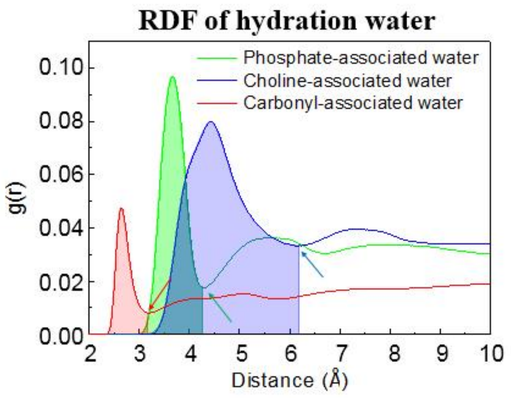
Water density profile



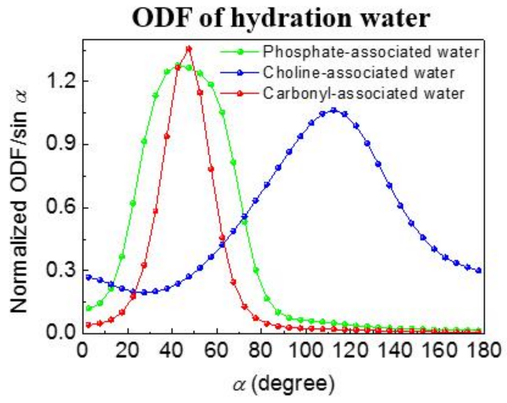
Whole water molecules in DMPC lipid bilayer system are the interfacial water
(H-bond number & density in DMPC < H-bond number & density in liquid water)

Network structure of hydration water

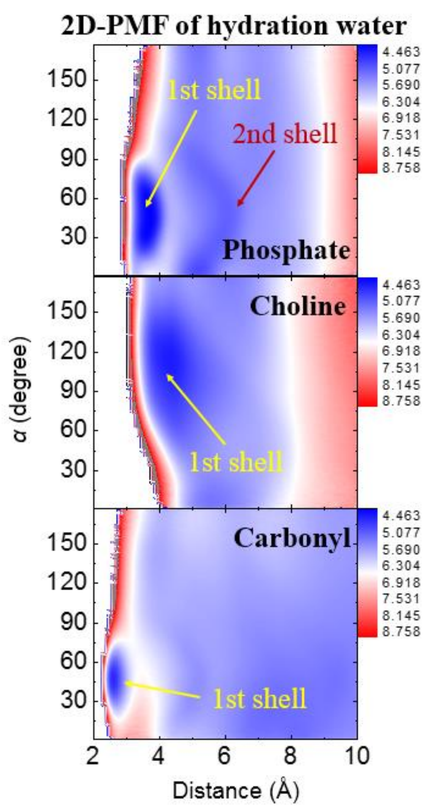
RDF of hydration water

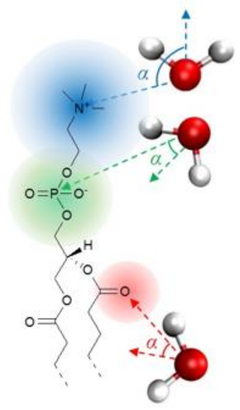


ODF of hydration water

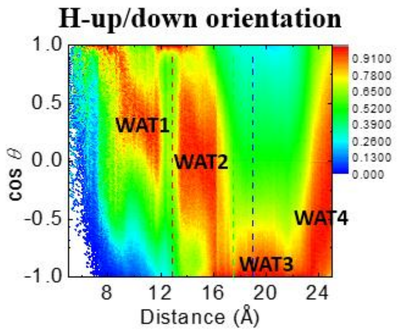


2D-PMF of hydration water





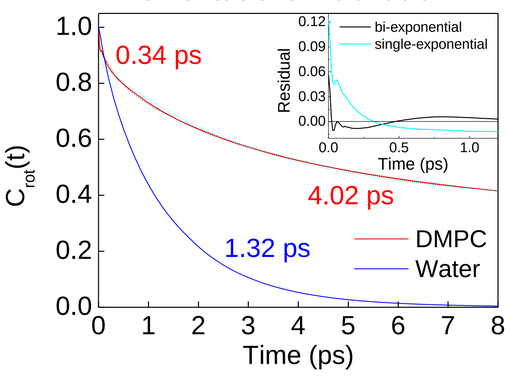
H-up/down orientation



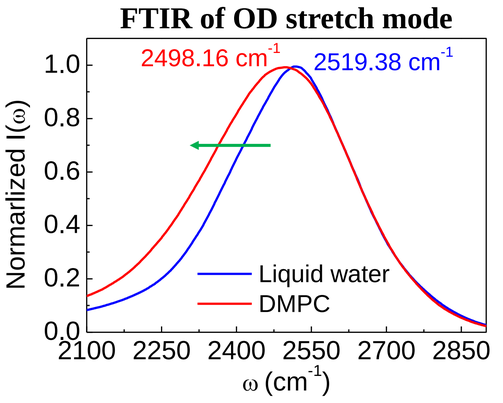
■ Narrow radial and orientational distribution of phosphate-/carbonyl-associated water
→ Strong interaction with phosphate and carbonyl groups // Weak interaction with choline group
■ Distribution of phosphate-/carbonyl-associated water in low angle regions
→ H atoms of water point towards phosphate and carbonyl groups // O atom of water points towards choline group
■ Presence of the second hydration shell of phosphate group
→ Strong interaction between phosphate group and water molecules

Dynamics of hydration water (Direct comparison with Experiment)

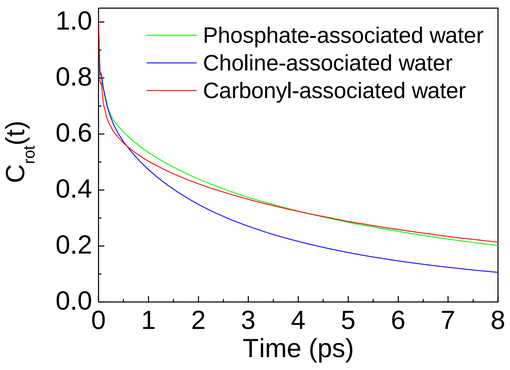
Orientational relaxation



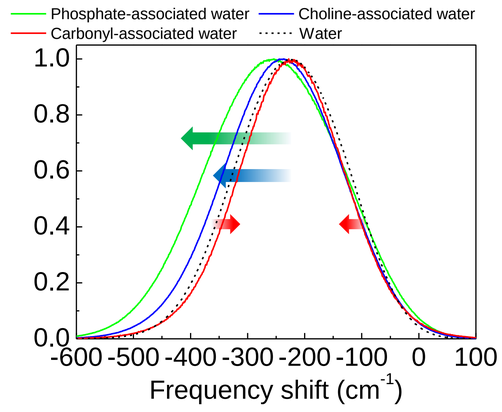
FTIR of OD stretch mode



Orientational Relaxation of hydration water (68 ps)



Instantaneuous frequency shift



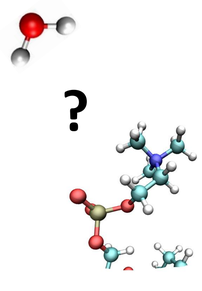
Experiment (IR pump-probe)
Relaxation time in liquid water=**1.7** ps
Relaxation time in DMTAP* lipid system=**1.8** ps
Relaxation time in DMPG* lipid system=**0.4** and **4.2** ps
*DMTAP(only choline in head), DMPG(only phosphate in head)

Experiment (FT-IR)
Red-shifted OD stretch mode of HOD
Peak shape broadening

■ Slow rotational dynamics and red-shift of water in DMPC lipid bilayer system
→ Strong interaction with phosphate group inhibits the motion of water

Summary

"Strong interaction between phosphate group and water molecules"



	Phosphate-associated water	Choline-associated water	Carbonyl-associated water
Quantity			Very small
Radial distribution	Narrow, even to second shell	Broad	Narrow
Orientational distribution	Narrow, low angle	Broad, high angle	Narrow, low angle
Rotational dynamics	Slower than bulk	Similar to bulk	Slower than bulk
OD stretch mode of HOD	Red-shifted and broad	Slightly red-shifted and broad	Narrow
Environment	Heterogeneous	Heterogeneous	Homogeneous
Contribution to total water	**Dominant**	**Weak**	Weak

References

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