Computational Investigations of Structure and Dynamics at the Interface

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Abstract

Interfaces are systems that may contain two or more condensed phases existing together, which makes the study of such systems challenging. However, the study of interfaces is critical in fields such as catalysis, energy storage, separations, drug discovery etc. Therefore the atomistic investigations of these systems are important to understand and improve the uses and properties of such interface systems. Two systems namely, graphene oxide (GO)-liquid interface and biological lipid bilayer membranes have been investigated in these studies. Nanosheets of graphene with oxygenated defects, termed as GO, have recently gained traction due to a number of exciting applications including water purification, proton conduction membranes etc. In this study one of the focuses is to gain molecular level understanding on the interfacial water of the GO-aqueous system using molecular simulations. The results from Born-Oppenheimer molecular dynamics (BOMD) simulations are compared to classical molecular dynamics (MD) simulations with a conventional non-polarizable force field (OPLSAA), which is used often in the literature. The orientation of water molecules and the local structure of water at different regions of the interface has been examined and compared with different force-fields/functionals. Our results indicate that the interfacial waters are much less ordered in the BOMD case, while the classical simulations show significant structuring at the interface. As the second interfacial system the lipid bilayer-liquid interface system was studied. This study focused on the adsorption of two different organic dye molecules through two different membrane-liquid interface systems. The free energies of the adsorption processes were determined through classical MD simulations with enhanced sampling methods. The orientations and the dipole moment of the dye molecules were evaluated to evaluate the determining factors for the adsorption. The results of these studies can be used to optimize the favorability of a drug molecule transporting across or adsorbing onto a liposome membrane. The results of these studies will be presented and discussed.

Introduction
GO – Liquid Interface

- GO sheets - Graphene modified oxygen containing functional groups (hydroxyl, epoxy, carboxyl, etc)

- Contain hydrophilic & hydrophobic domains

- Identity & degree of oxygen groups can be tuned

- Applications
  Water purification[1], gas separation[2], proton conducting membranes[3] etc.

Figure 1: a)Single GO sheet & b)Stacked GO sheets with –OH, -COOH, & epoxy defects

- Computational methods - ideal to study interactions, structure and dynamics of GO – liquid interface

Lipid Bilayer – Liquid Interface

Liposomes
- Spherical vesicles with phospholipid bilayer membranes
- Used in the delivery of drug molecules

Lipid Bilayer
- Composed of phospholipid molecules and embedded proteins
- Phospholipids (Amphiphilic)
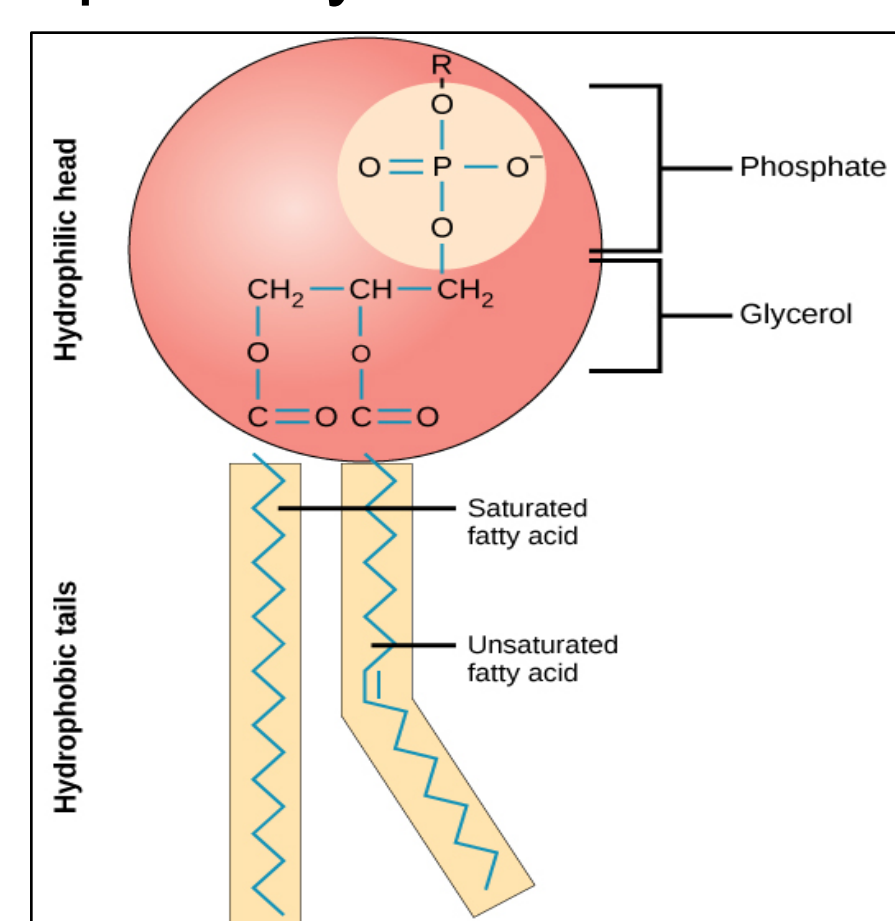 Polar head : Hydrophilic
  Non-polar tail : Hydrophobic

Figure 2: Structure of a phospholipid molecule

Methods & Results
GO – Liquid Interface

- Model system
  GO (-OH groups), Solvent (water)

- Molecular dynamics simulations (MD)
  LAMMPS software package
  OPLS-AA force-field, SPC/E water model

- Born-Oppenheimer MD simulations (BOMD)
  CP2K software package
  BLYP-D2 and revPBE-D3 functionals with Grimme dispersions
  Gaussian (DZVP- MOLOPT-SR-GTH) & plane wave basis set

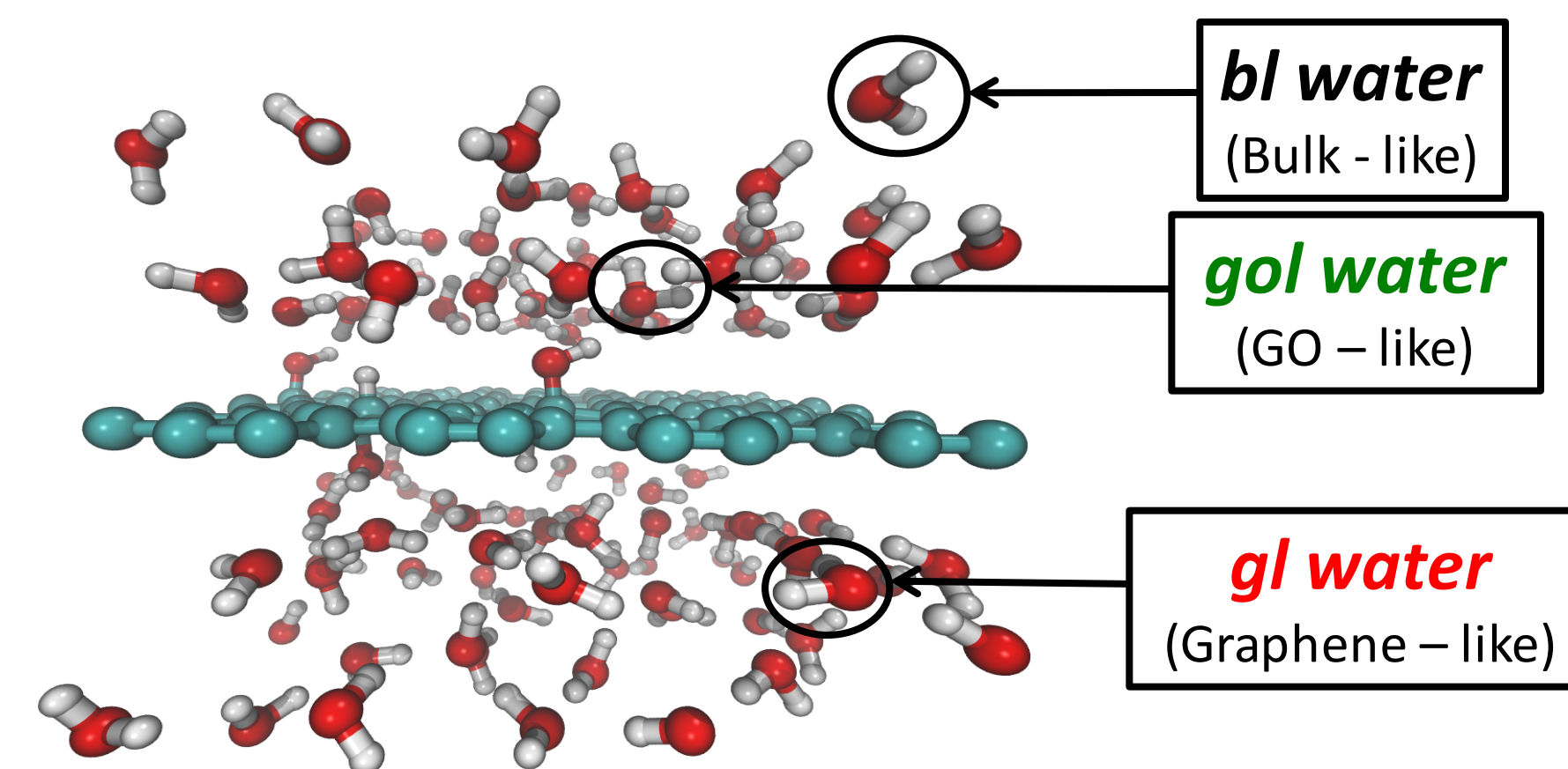- SAPT2+ calculations & orbital analysis with smaller coronene – water clusters

bl water
(Bulk - like)

gol water
(GO – like)

gl water
(Graphene – like)

Figure 3: The system under study and different types of water

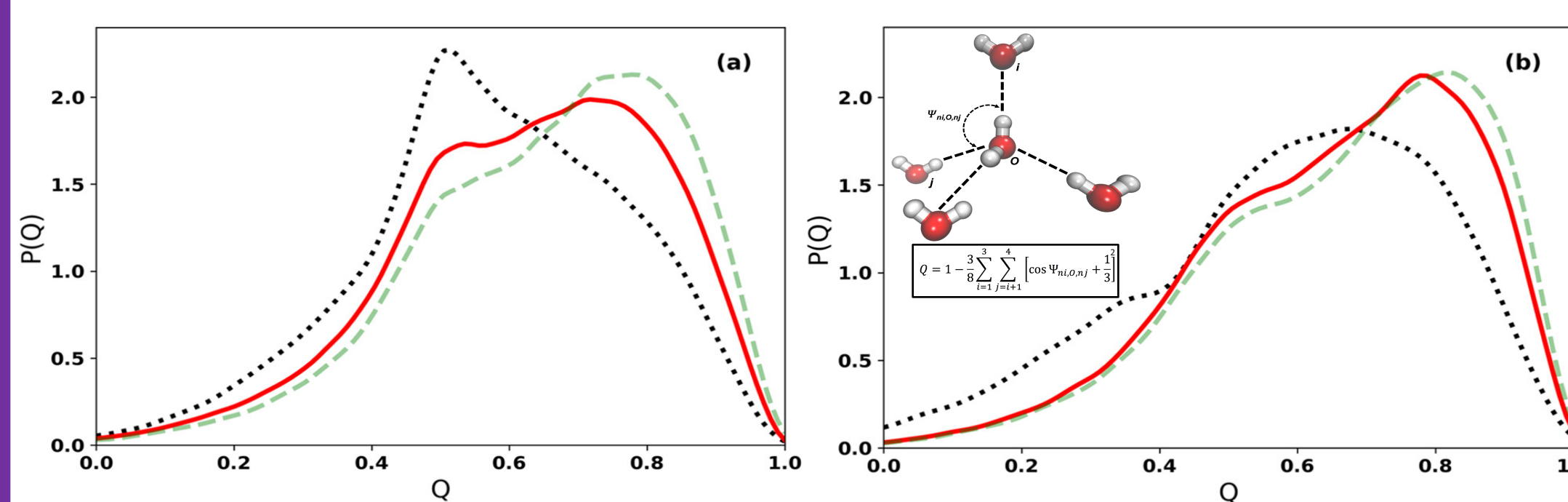### Orientational Tetrahedral Order Parameter (Q)

Figure 4: Probability distribution $P(Q)$ of Q. Black (dotted) and red (solid) lines correspond, respectively, to the gol/gl water and to the bl water. The green (dashed) line represents the distribution for water in a pure water box. (a) OPLS-AA. (b) BLYP-D2.
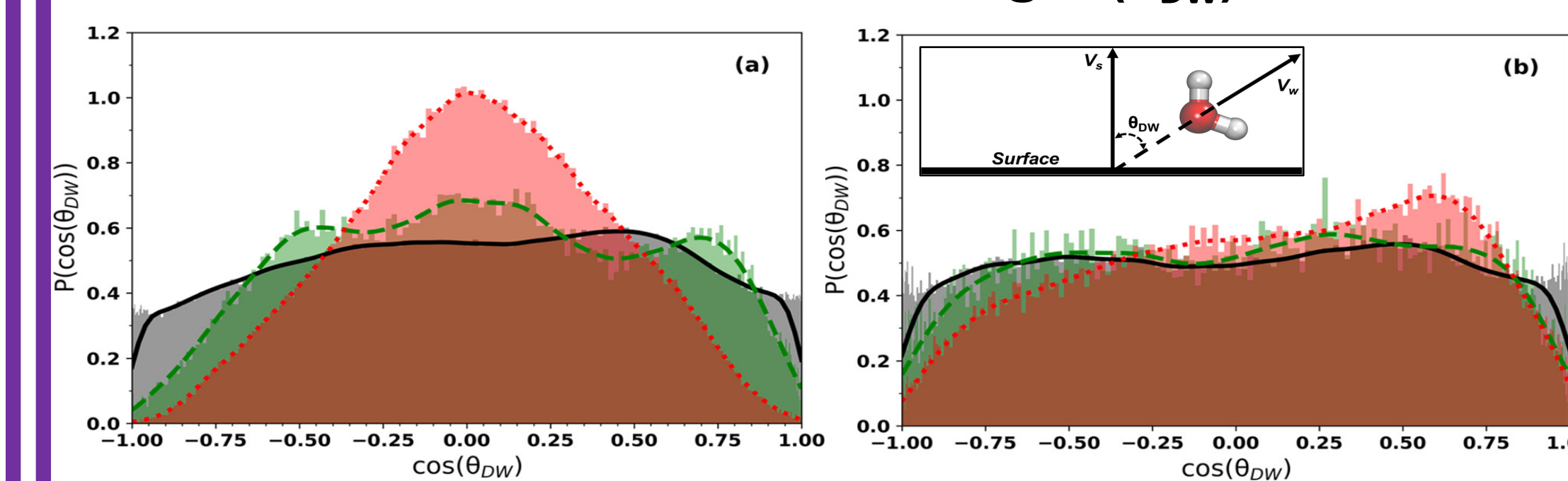
Water Orientation Angle (θ_{DW})

Figure 5: The probability distribution of θ_{DW} a) OPLS-AA b) BYLP-D2
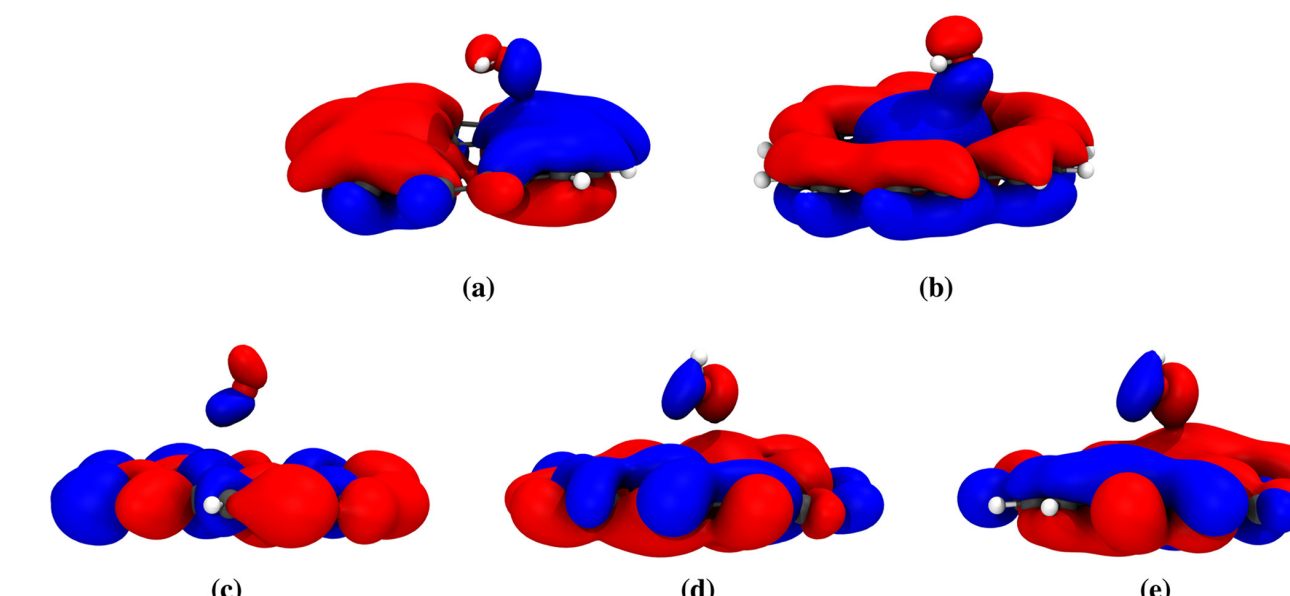

Figure 6: Interacting orbitals for the coronene-water system with an angle θ_{DW} of 90° (top, (a, b)) and with an angle θ_{DW} of 65° (bottom, (c–e))

Lipid Bilayer – Liquid Interface

- Two phospholipid bilayers
  DOPC - 1,2-dioleoyl-sn-glycero-3phosphocholine
  DOPG - 1,2-dioleoyl-sn-glycero-3phospho-(1'rac-glycerol)x

- Two dye molecules
  MG - Malachite green
  MGITC - Malachite green isothiocyanate

- Four systems
  1) MG in DOPC
  2) MGITC in DOPC
  3) MG in DOPG
  4) MGITC in DOPG

Figure 7: The chemical structures of phospholipid molecules a) DOPC b) DOPG & dye molecules c) MG d) MGITC

- Molecular dynamics simulations (MD)
  LAMMPS software package
  All-atom general AMBER force field (GAFF), SPC/E water model, 303 K

- Free energy Calculation
  Umbrella sampling & weighted histogram analysis (WHAM) method
  Collective variable - The z-distance between the center of mass (COM) of the lipid bilayer and the COM of the dye molecule
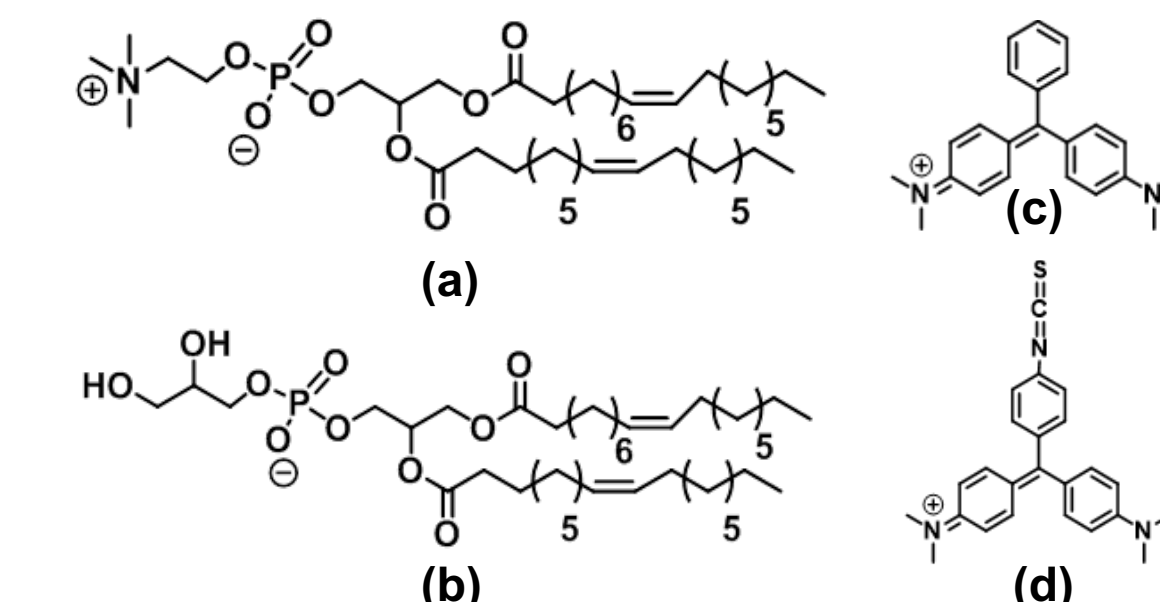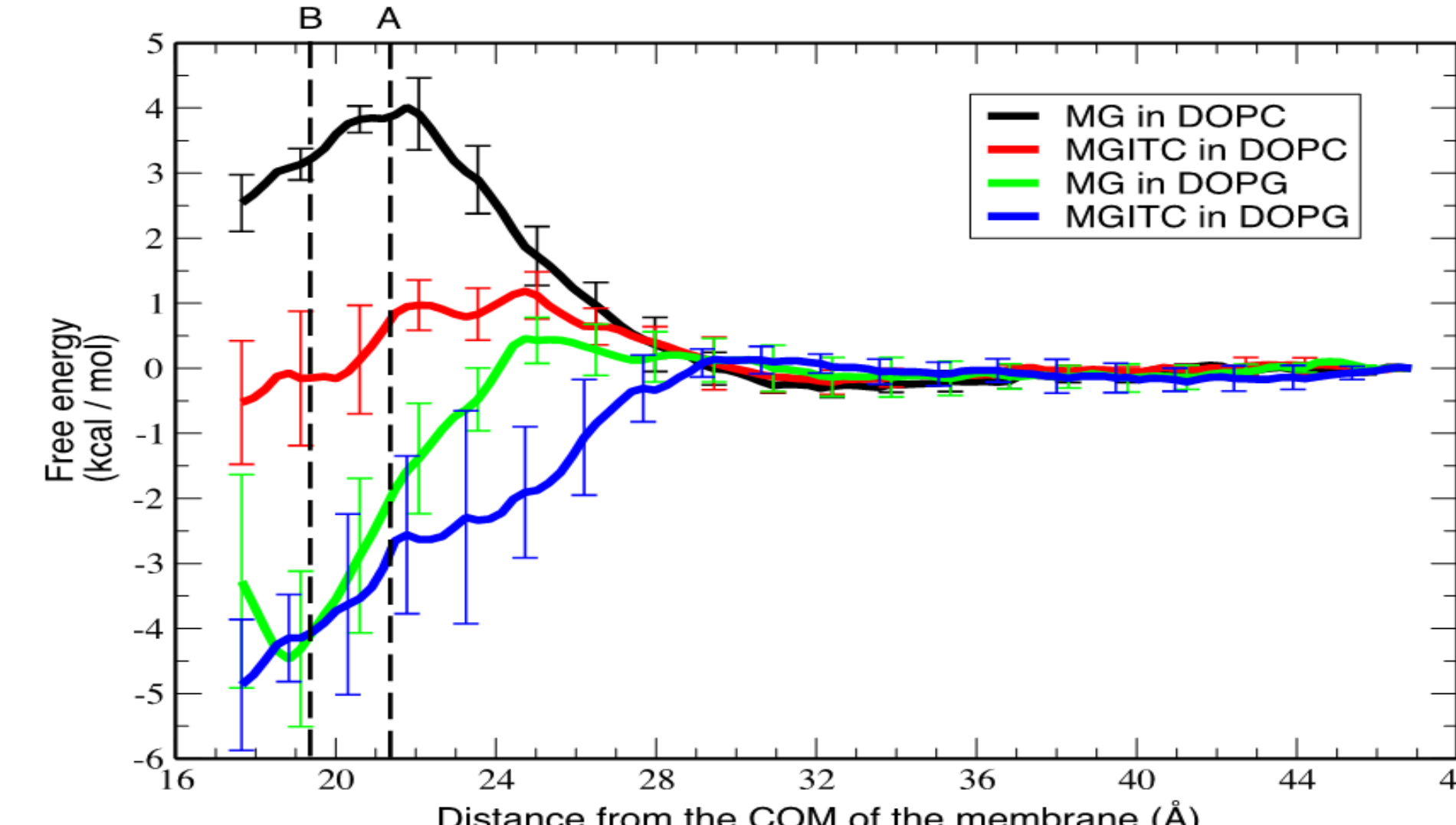

Figure 8: Potential mean force curves for the adsorption processes of MG & MGITC molecules in DOPC and DOPG lipid bilayers. The vertical dotted black lines represent the average interface for (A) DOPC and (B) DOPG lipid bilayers
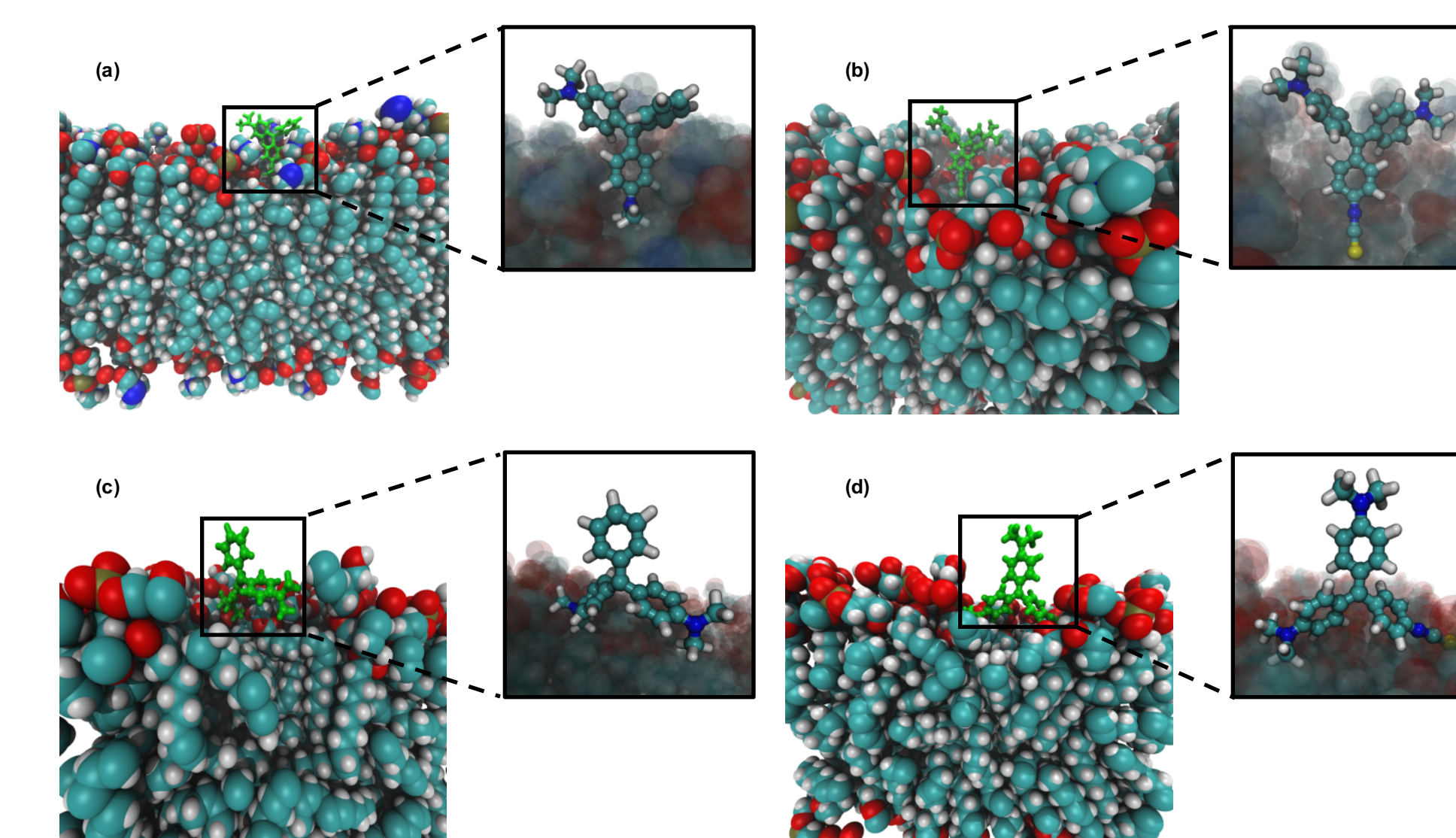

Figure 9: Snapshots showing the most probable orientation of the dye molecules at the surface of each lipid bilayer and a zoomed-in view (a) MG in DOPC, (b) MGITC in DOPC, (c) MG in DOPG, and (d) MGITC in DOPG. The atoms of C are represented in cyan, O in red, S in yellow, N in blue, and H in white

Dipole moment (Calculcated with Gaussian 09)
MG : 2.2758 Debye   MGITC : 10.5867 Debye

Conclusions & Future Work
GO – Liquid Interface

- OPLS – AA : Strong interfacial ordering[4]

- BOMD : Broad range of orientations of waters at the interface[4]

- Existing force-field can not capture subtle interactions (Induction) between the solvent & the GO sheet

➢ Develop a non–reactive force-field for GO – liquid system
  - Variational force – matching algorithm & many body terms

Lipid Bilayer – Liquid Interface

- MGITC & MG adsorbs more rapidly to DOPG than DOPC

- Stronger dipole moment of MGITC (by MGITC's isothiocyanate functional group) cause the favorable adsorption process
➢ Study the effect of temperature on the adsorption processes

References

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3. Feng, M.; Huang, Y.; Cheng, T.; Liu, X., International Journal of Hydrogen Energy 2017, 42 (12), 8224-8232.
4. Subasinghege Don, V.; David, R.; Du, Pu.; Milet, A.; Kumar, R., J. Phys. Chem. B 2019, 123(7), 1636-1649

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