Dynamical Heterogeneity of Interface Water upon Membrane Phase Transitions

A Thesis submitted by
Sheeba Malik

in partial fulfillment of the requirements for the award of the degree of
Doctor of Philosophy



Indian Institute of Technology Jodhpur
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Declaration

I hereby declare that the work presented in this thesis titled *Dynamical Heterogeneity of Interface Water upon Membrane Phase Transitions* submitted to the Indian Institute of Technology Jodhpur in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy, is a bonafide record of the research work carried out under the supervision of Dr. Ananya Debnath. The contents of this thesis in full or in parts, have not been submitted to, and will not be submitted by me to, any other Institute or University in India or abroad for the award of any degree or diploma

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Certificate

This is to certify that the thesis titled *Dynamical Heterogeneity of Interface Water upon Membrane Phase Transitions* submitted by *Sheeba Malik (P17CY002)* to the Indian Institute of Technology Jodhpur for the award of the degree of *Doctor of Philosophy*, is a bonafide record of the research work done by her under my supervision. To the best of my knowledge, the contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Dr. Ananya Debnath
Ph.D. Thesis Supervisor

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List of Symbols

Symbol	Description
C_p	Specific head capacity
κ_T	Isothermal compressibility
α_P	Coefficient of thermal expansion
$\partial^2 r_i$	Second order derivative of displacement
F_i	Force on ith particle
∂V	Potential on ith particle
Δt	Time step
K	Kinetic energy
τ_T	Time constant associated with temperature coupling
P_0	Reference pressure
P	Pressure generated during simulation
τ_P	Time constant associated with pressure coupling
S_{CD}	Deuterium order parameter
θ	Angle between C-D vector and bilayer normal
$S(t)$	Survival probability
$\sum_{i=1}^{N}$	Summation over N molecules
$\prod_{t_k=t_0}^{t_0+t}$	Product of probabilities of water molecule residing in a specific region
$P_i^d t(k)$	Probability of water molecules residing in a layer d for time t$_k$
$\left\langle \right\rangle$	Averaging over time origins
A_f	Coefficient associated with fast residence time
A_s	Coefficient associated with slow residence time

τ_f	Fast residence time
τ_s	Slow residence time
ρ_N	Particle density
α	Anomalous diffusion exponent
D_L	Lateral diffusion coefficient
$\alpha_2(t)$	Non Gaussian parameter
$\Delta r(t)$	Displacement of the molecule
$C_{HB}(t)$	Hydrogen bonding auto correlation function
τ_{HB}	Hydrogen bond lifetime
τ_α	α-relaxation time
τ_i	Intermediate time relaxation
τ_l	Long time relaxation
τ_s	Short time relaxation
k	Forward rate constant
K_B	Boltzmann constant
h	Planck's constant
T	Temperature
δ	Dirac-delta function

List of Abbreviations

Abbreviation	Full Form
AMBER	Assisted Model Building and Energy Refinement
BW	Bulk Water
Carb	Carbonyl
CC	Correlation Coefficient
CHARMM	Chemistry at Harvard Macromolecular Mechanics
COM	Centre Of Mass
CPK	Corey Pauling Koltun
DMPC	1,2-DiMyristoyl-sn-glycero-3-Phospho Choline
DOPC	Dioleoylphosphatidylcholine
DPPC	1,2-DiPalmitoyl-sn-glycero-3-Phospho Choline
DLS	Dynamic Light Scattering
DSC	Differential Scanning Calorimetry
FF	Force Fields
FFT	Fast Fourier Transform
FTIR	Fourier Transform Infrared Spectroscopy
Glyc	Glycerol
GROMACS	Groningen Machine for Chemical Simulation
GROMOS	Groningen Molecular Simulation package
HB	Hydrogen Bonding
HBACF	Hydrogen Bond Auto Correlation Function
HDA	High Density Amorphous

HG	Head Group
IR	Infra Red
IW	Interface Water
KWW	Kohlrausch Williams Watts
L-BFGS	Limited memory Broyden Fletcher Goldfarb Shanno
LDA	Low Density Amorphous
LJ	Lennard Jones
LINCS	Linear Constraint Solver
MC	onte Carlo
MCT	Mode Coupling Theory
MD	Molecular Dynamics
MSD	Mean Square Displacement
N	Nitrogen
NGP	Non Gaussian Parameter
nm	Nano Meter
NMR	Nuclear Magnetic Resonance
NPT	Constant number of particles, pressure and temperature
NVT	Constant number of particles, volume and temperature
ns	Nano Second
ODNP	Overhauser Dynamic Nuclear Polarization
P	Phosphorus
PBC	Periodic Boundary Conditions
PC	Phosphatidyl Choline
PDT	Protein Dynamical Transition
PME	Particle Mesh Ewald
PO	Phosphate

POPC	1-Palmitoyl-2-Oleoyl-sn-glycero-3-Phospho Choline
POPE	1-Palmitoyl-2-Oleoyl-sn-glycero-3-Phospho Ethanolamine
ps	Pico Second
QENS	Quasi Elastic Neutron Scattering
RACF	Reorientational Auto Correlation Function
RDF	Radial Distribution Function
RF	Retardation Factor
SISF	Self Intermediate Scattering Function
SPC	Simple Point Charge
SPC/E	Simple Point Charge / Extended
TIP3P	Transferable Intermolecular Potential 3 Point
TIP4P/2005	Transferable Intermolecular Potential 4 Point
TIP5P	Transferable Intermolecular Potential 5 Point
VACF	Velocity Auto Correlation Function
VDW	van der Waals
VRT	Vibration Rotation Tunneling
VSFG	Vibrational Sum Frequency Generation
WC	Without Constraints