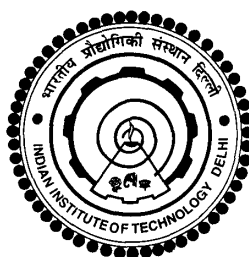


COMPUTER SIMULATIONS OF AQUEOUS SOLUTIONS AND NANOPARTICLE DISPERSIONS

SAURAV PRASAD



DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
OCTOBER 2017

COMPUTER SIMULATIONS OF AQUEOUS SOLUTIONS AND NANOPARTICLE DISPERSIONS

by

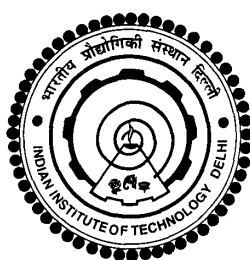
SAURAV PRASAD

DEPARTMENT OF CHEMISTRY

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

OCTOBER 2017

Dedicated To My Parents and
(Late) Prof. Charusita Chakravarty

Certificate

This is to certify that the thesis titled "**COMPUTER SIMULATIONS OF AQUEOUS SOLUTIONS AND NANOPARTICLE DISPERSIONS**" is being submitted by **Mr. Saurav Prasad** to the Department of Chemistry, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**. This thesis is a record of bona-fide research work carried out by him under the supervision of (Late) Prof. Charusita Chakravarty from 21 July, 2011 to 29 March, 2016 and subsequently under our guidance. In our opinion, the thesis has reached the standards fulfilling the requirements of the regulations relating to the degree.

The results contained in this thesis have not been submitted to any other university or institute for the award of any degree or diploma.

Prof. Ramakrishna Ramaswamy

Professor

School of Physical Sciences

Jawaharlal Nehru University

New Delhi-110 067, India

Dr. Hemant K. Kashyap

Assistant Professor

Department of Chemistry

Indian Institute of Technology Delhi

New Delhi-110 016, India

ACKNOWLEDGEMENTS

I would like to express my heartfelt gratitude to God and all the people who have contributed to this thesis with their words of continuous encouragement and unfailing support.

First and foremost, I would like to thank my supervisor and mentor (Late) Prof. Charusita Chakravarty who has always steered my research in the right direction. She was an excellent teacher and her patience, determination and wealth of knowledge has constantly inspired me to achieve new horizons in life. She was an exceptional guide who always brought out the best in me as a person and as a researcher. I would like to acknowledge her immense strength and determination to work despite of tough times. Her valuable guidance and consistent efforts to make me realize my strengths and objectives is the epitome of this thesis. I cannot thank her enough for her contributions and support in all these years of Ph.D. life.

My special thanks to Dr. Hemant K. Kashyap and Prof. Ramakrishna Ramaswamy for guiding and supporting me during rough times and in clinching this thesis. I thank my Senior Research Committee (SRC) members Prof. A. K. Singh (Chairperson, SRC), Dr. Sameer Sapra (Internal expert) and Dr. Gourav Goel (External expert) for their timely evaluation and discussions. I would also like to thank Prof. Ravi Shankar (Head, Department of Chemistry), Prof. N. D. Kurur (DRC Chairman, Chemistry) as well as the entire staff and faculty of Chemistry Department. A very special thanks to Prof. A. Ramanan for his inspirational words and help in arranging financial support. I thank IIT Delhi for instituting the best in me. I would also like to thank HPC facility at IIT Delhi for computational resources as well as CSC staff.

I would like to thank my seniors, Dr. Manish, Dr. Shadrack, Dr. Murari and Dr. Divya for fruitful discussions. I also extend my thanks to my current group members, for providing an amicable work environment. I thank all my friends at IIT especially Mahabir and my Bengali gang, Tanmoy, Debdas, Sanjib and Sandeep

for accompanying me during food and tea times and ordering fish and chicken for a change from the monotonous menu of the hostel. Thanks to my M.Sc. friends, J.P., Santosh, Sumit, Anshu and Vikas for enjoyable and encouraging chats. The contributions of my B.Sc.B.Ed. friends; Mangal, Sushant, Debasis, Jena, Jpr, Pabitra, Samir and Santosh have been tremendous and are truly treasured. I thank them for being in constant touch and providing a change during my busy Ph.D. schedule. I would like to extend my thanks to all my juniors and seniors during my bachelor's and master's degree.

A stupendous and an underpinning role in nurturing my Ph.D. years have been played by my best buddies. I begin by thanking Madhulika for her constant support in all my endeavours. She always stood by my side and provided solace despite of often bearing my wrath. My special thanks to Mangal for constantly pinging me on all social sites and on phone when I project myself as busy and for always telling me "Tu accha karega". My heartfelt thanks to Pramod and Sourabh bhaiya; for acting like two big brothers and inviting me to their house for chicken as well as in other parties held at IITD. An important role has been played by my local guardians; Mousaji, Mousiji, Pranshu and Vagisha for providing me a homely atmosphere. I would also like to thank Madhulika's Mom and Ritika for providing me a second home in Delhi, delicious food and for engulfing me in talks other than my research.

Above all, I would like to thank my family members for endowing me with internal strength and acting as a shadow to my problems, which made this day possible. My utmost gratitude to my Mom and Dad who have played a pivotal role in my life. I whole-heartedly admire their yearn to understand and help my research work despite of not belonging to this field. Their sacrifices, blessings, support and motivation have bolstered this thesis. I would like to extend my thanks to sister; Subhala didi and Rajiv jijaji for constantly encouraging me. I am grateful to my brothers; Parmeshwar da and Sanatan da and bhabhis, Piyali bhabhi and Preeti bhabhi for instilling me with confidence and providing a moral support. A special thanks to my siblings, Advika (Palak), Shagun (Meethi) and Ira for their beautiful smiles and lovely talks.

Saurav Prasad

Date

Abstract

This thesis presents molecular dynamics simulations of two types of complex fluids: liquids with varying degrees of tetrahedrality and nanoparticle dispersions. The relationships between structure, entropy and transport properties are examined for (a) modified hybrid water models, (b) LiCl aqueous solutions in water and modified hybrid waters and (c) bulk water at very high pressures. Simulations of modified hybrid water models provide explanation for thermodynamic scaling observed in RTIL's and hydrogen-bonded systems and also demonstrate that the Rosenfeld scaling does not depend on the degree of configurational energy virial correlation. LiCl appears to be better solvated in liquid with high hydrogen bond strength than SPC/E water, which is in contrast to NaCl solvation as revealed from solvation of constant concentration of LiCl in liquids with varying hydrogen bond strengths. The effects of LiCl concentration on local order, entropy, mobility and their relation with the experimental phase diagram and the glass forming region of aqueous LiCl solutions at 1 atm pressure are examined. The tetrahedral structure of water breaks with increasing LiCl concentration and it is linearly correlated with the pair entropy in the region where the aqueous solution is in contact with ice I_h . The Nernst-Einstein deviation shows pronounced negative deviation in the glass forming region. One-to-one mapping of pressure values of water to the composition values of aqueous LiCl solutions is shown for pair entropy, diffusivity and viscosity. In bulk water, with increase in pressure, orientational disorder increases, whereas in aqueous LiCl solutions with increase in concentration the structure of the liquid shifts from tetrahedral to close-packed structure. The second category of complex liquids studied here are the nanoparticle dispersions of end group functionalized gold nanoparticles in modified hybrid water models and decane solvent. All the pair potentials of mean force between identical nanoparticles show attractive well depths. The well depths and the degree of anisotropy are significantly dependent on the solvent and ligand chemistry.

PERMISSIONS

Permissions have been taken from the respective journals for the publications related to work presented in this thesis.

List of Publications Related to Work Presented in this Thesis

1. **S. Prasad** and C. Chakravarty*, Onset of Simple Liquid Behaviour in Modified Water models, *J. Chem. Phys.*, **140**, 164501 (2014).
2. **S. Prasad*** and C. Chakravarty, Tuning the Tetrahedrality of the Hydrogen-bonded Network of Water: Comparison of the Effects of Pressure and Added Salts, *J. Chem. Phys.*, **144**, 234509 (2016).
3. **S. Prasad**, C. Chakravarty and H. K. Kashyap*, Concentration-dependent Structure and Dynamics of Aqueous LiCl Solutions: A Molecular Dynamics Study, *J. Mol. Liq.*, **225**, 240-250 (2017).
4. **S. Prasad*** and C. Chakravarty, Solvation of LiCl in Model Liquids with High to Low Hydrogen Bond Strengths, *J. Chem. Phys.*, **146**, 184503 (2017).
5. **S. Prasad***, M. Gupta, Hari O. S. Yadav and C. Chakravarty, Gold Nanoparticles Passivated with Functionalized Alkylthiols: Simulations of Solvation in the Infinite Dilution Limit, *Phys. Chem. Chem. Phys.*, (Submitted).

*Corresponding author

Contents

Certificate	i
Acknowledgements	iii
Abstract	v
Permissions	vii
Table of Contents	ix
List of Figures	xv
List of Tables	xxvii
1 Introduction	1
1.1 Simple Liquids	3
1.1.1 Alternate Definition of Simple Liquids	7
1.2 Water: An Anomalous Liquid	8
1.2.1 General Characteristics of Water	8
1.2.2 Water Phase Diagram	10
1.2.3 Water-like Anomalies	12
1.3 Systems of Variable Tetrahedrality	15
1.3.1 Water and Modified Hybrid Water Models	15
1.3.2 Stillinger-Weber Model	17
1.3.3 Aqueous Solutions	17
1.4 Hydration of Hydrophobic and Hydrophilic Solutes	19
1.5 Structural Order and Entropy	20

1.5.1	Structural Order Metrics	20
1.5.2	Multiparticle Correlation Expansions of the Liquid-state En- tropy	24
1.5.3	Excess Entropy using Thermodynamic Integration	28
1.6	Transport Properties	29
1.7	Thermodynamic Scaling and Excess Entropy Scaling of Transport Properties	34
1.7.1	Thermodynamic Scaling	34
1.7.2	Excess Entropy Scaling of Transport Properties	35
1.8	Omega-functionalized Ligand Passivated Gold Nanoparticles in Water	38
1.9	Motivation and Organization of the Thesis	40
2	Onset of Simple Liquid Behaviour in Modified Water Models	43
2.1	Computational Details	47
2.2	Results	49
2.2.1	Configurational Energy-Virial Correlations	49
2.2.2	Diffusivities	51
2.2.3	Thermodynamic Scaling	53
2.2.4	Temperature Scaling of the Excess Entropies	56
2.2.5	Excess Entropy Scaling of Diffusivities	56
2.2.6	Competing Structural Effects due to Repulsion-Dispersion and Electrostatic Effects	59
2.2.7	State-point Dependence of Configurational Energy-Virial Cor- relations	61
2.3	Conclusions	62
3	Solvation of LiCl in Model Liquids with High to Low Hydrogen Bond Strengths	67
3.1	Computational Details	69
3.1.1	Potential Energy Surface	69
3.1.2	Simulation Details	70
3.2	Results	71

3.2.1	Radial Distribution Functions	71
3.2.2	Angular Distribution Functions	74
3.2.3	Triplet Correlation Functions	77
3.2.4	Tetrahedral Order and Pair Entropy	79
3.2.5	Configurational Energy - Virial Correlation	82
3.2.6	Transport Properties	83
3.3	Conclusions	86
4	Concentration-dependent Structure and Dynamics of Aqueous LiCl Solutions	91
4.1	Computational Details	95
4.1.1	Intermolecular Potential	95
4.1.2	Simulation Details	95
4.1.3	Thermodynamic and Transport Properties of Aqueous Lithium Chloride	98
4.2	Results	99
4.2.1	Diffusivity, Viscosity and the Stokes-Einstein Relation	99
4.2.2	Ionic Conductivity and the Nernst-Einstein Relation	102
4.2.3	Radial Distribution Functions and Pair Entropy	106
4.2.4	Tetrahedral Order	110
4.2.5	Rosenfeld Scaling of Oxygen and Ionic Diffusivities	112
4.2.6	Angular Distribution and Triplet Correlation Functions	113
4.3	Conclusions	116
5	Tuning the Tetrahedrality of the Hydrogen-bonded Network of Water: Comparison of the Effects of Pressure and Added Salts	121
5.1	Computational Details	124
5.1.1	Intermolecular Potential	124
5.1.2	Molecular Dynamics Simulations	124
5.1.2.1	Aqueous Lithium Chloride	124
5.1.2.2	Water	125
5.1.3	Evaluation of Transport Properties	126

5.1.4	Thermodynamic and Transport Properties of Bulk H ₂ O	127
5.2	Results and Discussion	130
5.2.1	Pair Entropy Scaling of Transport Properties	130
5.2.2	Understanding the Equivalence of Pressure and Salt Effect on Crystallization Kinetics in Dilute Aqueous Solutions	132
5.2.3	Local Structure at Equivalent State Points	136
5.2.3.1	Radial Distribution Functions	136
5.2.3.2	Tetrahedral Order	137
5.2.3.3	Triplet Correlation Functions	140
5.3	Conclusions	141
6	Gold Nanoparticles Passivated with Functionalized Alkylthiols:	
	Simulations of Solvation in the Infinite Dilution Limit	145
6.1	Solvation Structure and Thermodynamics	148
6.1.1	Entropy of the Ligand Shell	149
6.1.2	Entropy due to Solvent Reorganization	150
6.1.3	Potentials of Mean Force	151
6.2	Computational Details	153
6.2.1	Potential Energy Surface	153
6.2.1.1	Modified Hybrid Water Models	153
6.2.1.2	Decane, Gold-core and Ligands	153
6.2.2	Molecular Dynamics Simulation Details	157
6.2.2.1	Passivation of Au ₁₄₀ Core in Vacuum	158
6.2.2.2	Solvation of a Passivated Nanoparticle	158
6.2.2.3	Potentials of Mean Force in Vacuum and Water . . .	159
6.3	Results	160
6.3.1	Bulk Solvent: Structure, Thermodynamics and Transport Properties	160
6.3.2	Solvation of a Single Nanoparticle	163
6.3.2.1	Effect of Solvent Reorganization	163
6.3.2.2	Effect of Ligand Reorganization	170

6.3.3	Effective Interactions Between a Pair of Nanoparticles	175
6.4	Conclusions	180
7	Conclusions and Future Research Problems	185
	Bibliography	190
	Biodata of the Candidate	

List of Figures

1.1	Phase diagram of hard–sphere system in the pressure–volume fraction plane. The phase diagram is reproduced from Ref. [24] with permission.	5
1.2	Phase diagram of argon in the pressure–temperature (PT) plane. Reproduced from Ref. [28].	6
1.3	Metastable phase diagram of water. The disputed LLCP is denoted by the red dot. The dotted line represents the Widom line. The figure is taken from Ref. [22].	11
1.4	Non-monotonic variation in density of water with temperature at atmospheric pressure. Reproduced from Ref. [13] with permission.	13
1.5	Variation of (a) isothermal compressibility (κ_T), (b) isobaric heat capacity (C_p) and thermal expansion coefficient (α_P) with temperature. Solid and dashed lines represent water and a typical simple liquid. Reproduced from Ref. [103].	14
1.6	Pair correlation function of an atomic liquid with organization of atoms in neighbor shells.	21
1.7	Formation of diamond-like crystals from organization of two oppositely charged nanoparticles in solution. Reproduced from Ref. [264] with permission.	39
2.1	Comparison of the oxygen-oxygen pair correlation functions at 300 K and 1 g cm ^{−3} for hybrid water models with $\lambda = 1.00, 1.56, 3.00$ and 4.00.	50
2.2	Comparison of probability distributions, $P(q_{tet})$, for tetrahedral order at 300 K and 1 g cm ^{−3} for hybrid water models with $\lambda = 1.00, 1.56, 3.00$ and 4.00.	51

2.3	Arrhenius plots for the diffusivities of modified hybrid water models: (a) $\lambda = 1.00$ (H1.00) (b) $\lambda = 1.56$ (H1.56) and (c) $\lambda = 3.00$ (H3.00) . Diffusivities are in units of $m^2 s^{-1}$. For each hybrid model, the $1/T$ dependence along different isochores is shown.	52
2.4	Test of thermodynamic scaling of diffusivities for modified hybrid wa- ter models with: (a) $\lambda = 1.00$ (H1.00) (b) $\lambda = 1.56$ (H1.56) and (c) $\lambda = 3.00$ (H3.00). The dimensionless diffusivities, D^* , are obtained us- ing: $D^* = D\rho^{1/3}/(k_B T/m)^{1/2}$. The variable ρ_{UW}^γ/T uses the reduced density (ρ^*) and temperature (T^*) with γ_{UW} derived from the simu- lation at 300 K, 1 g cm $^{-3}$. Data for different isotherms are shown.	54
2.5	Test of thermodynamic scaling of excess entropies (S_e) for hybrid modified water models with: (a) $\lambda = 1.00$ (H1.00) (b) $\lambda = 1.56$ (H1.56) and (c) $\lambda = 3.00$ (H3.00). Excess entropy per particle is given in units of k_B . Data are labeled according to the isotherms.	55
2.6	Test of Rosenfeld-Tarazona scaling of excess entropies for hybrid mod- ified water models with: (a) $\lambda = 1.00$ (H1.00) (b) $\lambda = 1.56$ (H1.56) and (c) $\lambda = 3.00$ (H3.00). Excess entropy (S_e) per particle is given in units of k_B and temperatures (T) are in Kelvin. Data are labeled according to isochores.	57
2.7	Correlation of reduced diffusivity with excess entropy (S_e) for (a) $\lambda = 1.00$ (H1.00) (b) $\lambda = 1.56$ (H1.56) (c) $\lambda = 3.00$ (H3.00). The dimensionless diffusivities, D^* , are obtained using: $D^* =$ $D\rho^{1/3}/(k_B T/m)^{1/2}$. Excess entropy per particle is given in units of k_B and temperatures are in Kelvin. Data are labeled according to isochores.	58
2.8	Structural changes along the 1.15 g cm $^{-3}$ isochore of the $\lambda = 3.00$ (H3.00) hybrid modified water model: (a) oxygen-oxygen pair correla- tion function ($g_{OO}(r)$) and (b) tetrahedral order distributions ($P(q_{tet})$).	60

2.9	Variation of (a) configurational energy-virial correlation coefficient (R) and (b) inverse power law exponent (γ_{UW}) along the 0.85, 1.15 and 1.30 g cm ⁻³ isochores of the $\lambda=1.56$ (H1.56) hybrid modified water model. Temperatures (T) are given in units of Kelvin.	62
2.10	Variation of (a) configurational energy-virial correlation coefficient (R) and (b) inverse power law exponent (γ_{UW}) along the 0.85, 1.15 and 1.30 g cm ⁻³ isochores of the $\lambda=3.00$ (H3.00) hybrid modified water model. Temperatures (T) are given in units of Kelvin.	63
3.1	Radial distribution functions of (a) O-O and (b) O-H atom pairs in pure modified hybrid water solvents at 300 K and 1 atm.	72
3.2	Radial distribution functions of (a) Li-O, (b) Cl-O, (c) Li-Cl, (d) Li-Li and (d) Cl-Cl atom pairs in LiCl-modified hybrid water solutions at 300 K and 1 atm. In part (a) and (b), the change in first peak height with λ has been shown in inset for λ around 1.00.	74
3.3	Normalized probability distributions of (a) O $\cdots$ O $\cdots$ O, (b) O $\cdots$ H-O and (c) H $\cdots$ O-H angles for modified hybrid water models at 300 K and 1 atm with $\lambda = 0.60$ to 6.00.	75
3.4	Normalized probability distributions of (a) O $\cdots$ Li $\cdots$ O and (b) O $\cdots$ Cl $\cdots$ O angles for LiCl-modified hybrid water solutions at 300 K and 1 atm with $\lambda = 0.60$ to 6.00.	77
3.5	(a) Triplet correlation functions, $g_{OOO}^{(3)}(r, r, r)$ and (b) irreducible triplet correlation functions, $\delta g_{OOO}^{(3)}(r, r, r)$, for equilateral triangle configurations for modified hybrid water solvents at 300 K and 1 atm. The horizontal cyan colored line indicates $\delta g_{OOO}^{(3)}(r, r, r) = 1.00$	78
3.6	Contour plots showing triplet correlation functions, $g_{OOO}^{(3)}(r, r, s)$, for isosceles triangle configurations as a function of the distance r and angle θ for modified hybrid water models at 300 K and 1 atm with $\lambda = 0.60, 0.80, 1.00, 1.56, 2.00, 3.00, 4.00$ and 6.00.	80

3.7	Comparison of probability distributions, $P(q_{tet})$, for tetrahedral order at 300 K and 1 atm for modified hybrid water models with $\lambda = 0.60$ to 6.00.	81
3.8	Variation of tetrahedral order and pair entropy with different values of the hybrid potential parameter λ at 300 K and 1 atm. Solid lines with circular points are for pure solvents and dashed lines with square points are for LiCl-modified hybrid water solutions at $X_{LiCl}=0.025$. .	82
3.9	Variation of configurational energy - virial correlation coefficient (R) and IPL exponent (γ_{UW}) with different values of the hybrid potential parameter λ at 300 K and 1 atm. Solid lines with circular points are for pure solvents and dashed lines with square points are for LiCl-modified hybrid water solutions at $X_{LiCl}=0.025$. Black solid line indicates $R = 0.90$	83
3.10	Variation of (a) oxygen diffusivity (D_O) and viscosity (η) and (b) ion diffusivity (D_{Li} and D_{Cl}) and ionic conductivity with different values of the hybrid potential parameter λ at 300 K and 1 atm. Solid lines with circular points are for pure solvents and dashed lines with square points are for LiCl-modified hybrid water solutions at $X_{LiCl}=0.025$. .	85
3.11	Variation of (a) inverse of hydrodynamic radii of oxygen, lithium and chloride ion and (b) Nernst-Einstein deviation parameter with different values of the hybrid potential parameter λ at 300 K and 1 atm. Solid lines with circular points are for pure solvents and dashed lines with square points are for LiCl-modified hybrid water solutions at $X_{LiCl}=0.025$	87
4.1	Experimental phase diagram of: (a) LiCl-H ₂ O at 1 atm pressure with eutectic at $E = (X_{LiCl} \approx 0.135, 200 \text{ K}, 0.0001 \text{ GPa})$ [52–54], (b) LiF-BeF ₂ system [64,311,312]. The light yellow and light blue region indicate strong glass forming ability(GFA) in LiCl-H ₂ O and LiF-BeF ₂ system, respectively [52,53,312]. Lin in part(a) refers to the hydrate including n water molecules [54].	92

4.2	Variation of transport properties with composition (X_{LiCl}) for LiCl-H ₂ O system: (a) H ₂ O (D_{OW}) diffusivity, (b) lithium ion (D_{Li}) diffusivity, (c) chloride ion (D_{Cl}) diffusivity and (d) viscosity. The yellow region indicates high glass forming ability(GFA) and the vertical line shows the experimental eutectic at $X_{LiCl} \approx 0.135$. Data obtained using DS parameters are shown using solid line-points, whereas dashed lines are used for data obtained using KBFF parameters.	101
4.3	Testing of Stokes-Einstein relation using: (a) variation of inverse of hydrodynamic radius of oxygen with composition (X_{LiCl}), (b) correlation between cation(Li^+) and anion(Cl^-) diffusivities and (c) logarithm of cationic diffusivities, $\ln D_{Li}$, as a function of T/η . The magenta line in part (b) indicates $D_{Li}=0.98D_{Cl}$, whereas the straight line in part (c) is $\ln D_{Li} = 0.91 \ln(T/\eta) + \ln(k_B/4\pi r_{Li})$. Data obtained using DS parameters are shown using solid points, whereas data obtained using KBFF parameters are shown by dashed lines in part (a) and open points in parts (b) and (c).	103
4.4	Testing of Stokes-Einstein relation using variation of inverse of hydrodynamic radius of (a) lithium ion and (b) chloride ion with composition (X_{LiCl}). Data obtained using DS parameters are shown using solid line points, whereas data obtained using KBFF parameters are shown by dashed lines. The yellow region indicates high glass forming ability(GFA) and the vertical line shows the experimental eutectic at $X_{LiCl} \approx 0.135$	104
4.5	Variation with composition (X_{LiCl}) of: (a) ionic conductivity (σ) and (b) Nernst-Einstein deviation parameter. The yellow region indicates high glass forming ability(GFA) and the vertical line shows the experimental eutectic at $X_{LiCl} \approx 0.135$. Data obtained using DS parameters are shown using solid line-points, whereas dashed lines are used for data obtained using KBFF parameters.	105

4.6	Radial distribution function, for various compositions at 275 K: (a) O-O, (b) Li-O, (c) Cl-O and (d) Li-Cl. Data obtained using DS parameters have only been shown.	107
4.7	Coordination number of: (a) lithium ion w.r.t. oxygen atom, (b) Chloride ion w.r.t. oxygen atom and (c) lithium ion w.r.t. chloride ion along various isotherms as a function of X_{LiCl} . The curves were generated by Bezier smoothing of the data. Solid and dashed lines are used for data obtained using DS and KBFF parameters, respectively.	108
4.8	Pair entropy (S_2) as a function X_{LiCl} along various isotherms. The yellow region indicates high glass forming ability(GFA) and the vertical line shows the experimental eutectic at $X_{LiCl} \approx 0.135$. Data obtained using DS parameters are shown using solid line-points, whereas dashed lines are used for data obtained using KBFF parameters.	109
4.9	Tetrahedral order parameter distribution, $P(q_{tet})$, for various compositions at 275 K. For comparison, $P(q_{tet})$ for bulk water at $P = 1$ atm, $T = 275$ K is also shown. Data obtained using DS parameters have only been shown.	110
4.10	Ensemble averaged tetrahedral order ($\langle q_{tet} \rangle$) as a function of X_{LiCl} along various isotherms. The yellow region indicates high glass forming ability(GFA) and the vertical line shows the experimental eutectic at $X_{LiCl} \approx 0.135$. Data obtained using DS parameters are shown using solid line-points, whereas dashed lines are used for data obtained using KBFF parameters.	111
4.11	Correlation of ensemble-averaged tetrahedral order, $\langle q_{tet} \rangle$, with the pair entropy along different isotherms for compositions with $X_{LiCl} < 0.175$. Solid and dashed lines are used for data obtained using DS and KBFF parameters, respectively.	112
4.12	Rosenfeld plot showing correlation of oxygen and ionic diffusivities ($D_{OW/Li^+/Cl^-}^*$) with pair correlation entropy S_2 for the LiCl-H ₂ O system.	112
4.13	Normalized probability distribution of (a) O-O-O, (b) O-Li-O and (c) O-Cl-O angles for aqueous LiCl-H ₂ O solution at 275 K.	114

4.14	Triplet correlation functions: (a) $g_{OOO}^{(3)}(r,r,r)$, (b) $g_{OLiO}^{(3)}(r,r,r)$ and (c) $g_{OCIO}^{(3)}(r,r,r)$ for equilateral triangle configurations for LiCl-H ₂ O system at 275 K.	115
4.15	Contour plot showing triplet correlation functions: (a),(b),(c) $g_{OOO}^{(3)}(r,r,s)$; (d),(e),(f) $g_{OLiO}^{(3)}(r,r,s)$ and (g),(h),(i) $g_{OCIO}^{(3)}(r,r,s)$ for isosceles triangle configurations as a function of the distance r and angle θ for aqueous LiCl-H ₂ O solution at 275 K.	117
5.1	Experimental phase diagram of H ₂ O with eutectic point at $S = (0.2 \text{ GPa}, 250 \text{ K})$ [330]. The blue region shows the experimental pressure regime where quenching of water or compression of ice leads to high density amorphous (HDA) ice [13, 121]. Circles show simulated state points. Different colours indicate different isotherms.	122
5.2	Variation of equilibrium density for three temperatures (225 K, 275 K and 350 K) with concentration of LiCl-H ₂ O and pressure of bulk H ₂ O. Data for LiCl-H ₂ O and bulk H ₂ O are labelled by X and P, respectively. Shaded region represents the high GFA region. Vertical turquoise line denotes eutectic of LiCl-H ₂ O system. Pressures and temperatures are given in GPa and Kelvin, respectively.	128
5.3	Rosenfeld-scaling plot between pair entropy (S_2) and: (a) reduced oxygen diffusivity (D_O^*) (b) reduced viscosity (η^*). Data for the LiCl-H ₂ O and high pressure H ₂ O systems are labeled by X and P, respectively, with lines fitted for state points with $T \geq 275K$. The violet and blue lines show S_2 values at onset of caging dynamics in LiCl-H ₂ O and H ₂ O, respectively. The change in the exponential scaling parameter (α and α') at $S_2 \approx -3.4k_B$ is marked by the orange line.	131

5.4	Variation with composition (X_{LiCl}) for LiCl-H ₂ O (labelled X) and with pressure for bulk H ₂ O (labelled P) of: (a) pair entropy (S_2/Nk_B) (b) H ₂ O diffusivity (D_O) (c) shear viscosity (η) and (d) Maxwell time (τ_M). Vertical line shows the experimental eutectic at $X_{LiCl} \approx 0.135$ for LiCl-H ₂ O and the corresponding pressure $P \approx 3.19$ GPa. The light yellow region indicates strong glass forming ability (GFA) in LiCl-H ₂ O system. Solid lines are used for salt-water, whereas dotted-lines with open symbols are used for bulk water.	133
5.5	Correlation between different entropic contributions ($X_\alpha X_\beta S_{\alpha\beta}/Nk_B$) and the pair entropy (S_2/Nk_B) at 275 K for (a) bulk water and (b) LiCl-H ₂ O mixture. The light blue region in part (a) shows the experimental pressure regime where quenching of water or compression of ice leads to high density amorphous (HDA) ice. The light yellow region in part (b) indicates strong glass forming ability (GFA) in LiCl-H ₂ O system.	135
5.6	Comparison of radial distribution functions for four equivalent points, shown in identical colours at 275K : (a) $g_{OO}(r)$ and (b) $g_{HH}(r)$. Dotted lines are for bulk water, whereas solid lines are for salt-water at state points where the pair entropy and transport properties are in good agreement. Pressures are given in units of GPa.	138
5.7	Variation of $\langle q_{tet} \rangle$ with concentration of LiCl-H ₂ O and pressure of bulk H ₂ O. Data for LiCl-H ₂ O and bulk H ₂ O are labelled by X and P, respectively. Vertical line denotes eutectic of LiCl-H ₂ O system. The light yellow region indicates strong glass forming ability (GFA) in LiCl-H ₂ O system. Pressures and temperatures are given in GPa and Kelvin, respectively.	139

5.8	Tetrahedral order parameter distribution, $P(q_{tet})$, for four equivalent points, shown in identical colours at 275 K. For comparison, $P(q_{tet})$ for bulk water at $P = 0.000101$ GPa, $T = 275$ K is also shown. Dotted lines are for bulk water, whereas solid lines are for salt-water mixture. Shift in peak positions with increasing salt concentration and pressure are indicated by the arrows. Pressures are given in units of GPa. . . .	139
5.9	Triplet correlation functions, $g_{OOO}^{(3)}(r, r, s)$, for isosceles triangle configurations for aqueous LiCl-H ₂ O solution and bulk water for pairs of equivalent state points at 275 K.	141
5.10	Normalized probability distribution of O-O-O angles for aqueous LiCl-H ₂ O solutions and bulk water for pairs of equivalent state points, shown in identical colours at 275 K.	142
6.1	Schematic diagram illustrating the mass dipole vector, $\vec{\Delta}$, and the orientation of the mass dipole vector with respect to the inter-nanoparticle separation vector ($\vec{r}$). The snapshot is for two Au ₁₄₀ (SC ₁₀) ₆₂ nanoparticles in vacuum at 300 K for the pair separation of 55 Å. The sulfur atoms are shown in yellow and carbon in cyan. Au_{COM} and $Ligand_{COM}$ represent the center of mass of the gold nano-core and ligand shell, respectively. The mass dipole vector, $\vec{\Delta}$, is defined as the vector connecting the Au_{COM} and $Ligand_{COM}$. θ is the angle between the $\vec{\Delta}$ and the inter-nanoparticle axis ($\vec{r}$), joining the center of masses of the two nanoparticles.	151
6.2	Fitting of torsional potential used in literature and multi-harmonic torsional potential used in this study for (a) CH ₂ -CH ₂ -CH ₂ -N and (b) CH ₂ -CH ₂ -N-H dihedrals.	156
6.3	Fitting of torsional potential used in literature and multi-harmonic torsional potential used in this study for (a) CH ₂ -C-O-H; (b) CH ₂ -CH ₂ -C=O and O=C-O-H dihedrals.	157
6.4	Schematic diagram illustrating the insertion of Au ₁₄₀ (SC ₉ NH ₂) ₆₂ nanoparticle in solvent box.	159

6.5	Comparison of the oxygen-oxygen radial distribution functions (RDFs) for modified hybrid water models with $\lambda = 1.00, 1.56$ and 3.00 at 300 K and 1 atm. The RDF of decane monomer units including bond, angle and dihedral peaks has also been shown at the same temperature and pressure.	161
6.6	Pair correlation function, $g_{ns}(r)$: (a) for different end groups functionalized nanoparticles in SPC/E water and decane, (b) for $\text{Au}_{140}(\text{SC}_9\text{COOH})_{62}$ nanoparticle in different solvents at 300 K and 1 atm.	164
6.7	Solvation properties of different end group functionalized nanoparticles in solvents with varying degrees of repulsion-dispersion and electrostatic interactions. (a) solvent excess number, n_s^E (b) partial molar volume at infinite dilution, $\bar{V}_{ns}^\infty$ (c) solvation pair entropy due to local ordering of solvents, $\Delta S_{ns}^{local}/k_B$ and (d) total entropy of solvation with local and long-range correction terms, $\Delta S_{ns}^{total}/k_B$. Solid and open points have been used for data at 300 and 275 K , respectively. The right panel gives the running integral of the solvation properties of different end group functionalized nanoparticles in water and decane at 300 K and 1 atm.	167
6.8	Comparison of average local tetrahedral order of waters, $q_{tet}(r)$, as a function of the distance from the center of mass of the Au_{140} nanocore in H1.00 or SPC/E and H3.00 at 275 K and 1 atm. Solid and dashed lines are used for nanoparticles solvated in H1.00 and H3.00 modified hybrid water model , respectively.	168
6.9	Conditional tetrahedral distributions, $P_r(q_{tet})$, calculated for water molecules lying within distances of $35\text{-}36 \text{ \AA}$, $19\text{-}20 \text{ \AA}$, and $15\text{-}16 \text{ \AA}$ from the center of mass of the gold core for (a) SPC/E and (b) H3.00 water at 275 K and 1 atm.	170

6.10	Radial density profiles, $\rho_L(r)$, of ligand chain monomers (for nine CH_2 groups only, which are common in all the end group functionalized nanoparticles) in (a) water and decane and (b) solvents of varying degrees of repulsion-dispersion and electrostatic interactions for $\text{Au}_{140}(\text{SC}_9\text{COOH})_{62}$ nanoparticle at 300 K and 1 atm.	171
6.11	(a) Radius of gyration between the center of mass of the gold nano-core and the SH, CH_2 groups of the passivating ligands and (b) $\langle\Delta\rangle$, where, Δ , denotes the magnitude of the vector connecting the center of mass of the gold nano-core and the SH, CH_2 groups of the ligand shell. The solid and open points are used for data at 300 and 275 K at 1 atm, respectively. The right panel gives the probability distribution, $P(\Delta)$: (c) for different functionalized nanoparticles in SPC/E water and decane at 300 K, 1 atm; (d) for COOH functionalized nanoparticle in various solvent media at 300 K, 1 atm.	173
6.12	Snapshots of different end group functionalized nanoparticles in solvents of varying interactions at 300 K and 1 atm. Solvent molecules are not shown for clarity. Sulfur atoms are shown in yellow, carbon in cyan, oxygen in red, nitrogen in blue and hydrogen in white.	174
6.13	Isotropic potential of mean force, $V_{PMF}(r)$, as a function of pair separation, r , between two identical end group functionalized nanoparticles in (a) vacuum, (b) H1.00 or SPC/E and (c) H3.00. Solid lines are for 300 K and dashed lines are for 275 K.	177
6.14	Anisotropy due to ligand shell disorder at different pair separations for the $\text{Au}_{140}(\text{SC}_9\text{COOH})_{62}$ nanoparticle in vacuum and SPC/E water at 300 K. The color coding is same as in Figure 6.12.	179
6.15	Fluctuation-driven anisotropy in passivated nanoparticles as a function of pair separation, r , at 300 K. The mean value of the magnitude of the mass dipole, $\langle\Delta\rangle$, and the mean angle between the mass dipole vector and the inter-nanoparticle axis, $\langle\cos \theta\rangle$, are shown in (a and a') vacuum, (b and b') H1.00 or SPC/E and (c and c') H3.00, respectively.	181

List of Tables

1.1	Relation between various transport properties studied, the corresponding gradients and phenomenological laws.	31
2.1	Potential energy parameters for modified water models. The Lennard-Jones site is associated with the energy (ϵ_{OO}) and length (σ_{OO}) parameters. The bond lengths and bond angles of the water molecules are denoted by r_{OH} and $\angle HOH(^{\circ})$. Partial charges on oxygen and hydrogen atoms are denoted by q_O and q_H respectively.	48
2.2	Comparison of modified water models with different values of the hybrid potential parameter λ at 300 K and 1.00 g cm ⁻³ . The configuration energy-virial correlation coefficient is R and the three IPL exponents are denoted by γ_{UW} , γ_W and γ_{W^2} . The contribution of the Lennard-Jones and electrostatic contributions to the configurational energy (λU_{LJ} and U_{ES} respectively) are given in units of kJ mol ⁻¹ . .	49
2.3	Comparison of T_{onset} and excess entropy (S_e) at T_{onset} for hybrid water models with $\lambda=1.00$, 1.56 and 3.00.	59
3.1	Potential energy parameters for Dang-Smith potential for aqueous LiCl. Lennard-Jones energy and size parameters are denoted by ϵ and σ , respectively [144–146].	70
4.1	Potential energy parameters for Kirkwood-Buff derived potentials for aqueous LiCl. Lennard-Jones energy and size parameters are denoted by ϵ and σ , respectively [321].	95

4.2	Computational details of molecular dynamics simulations of LiCl-H ₂ O system. The temperatures (T), mole fraction of LiCl (X_{LiCl}), no. of water molecules (N_{H_2O}), no. of LiCl molecules (N_{LiCl}), total no. of atoms (N_{Total}), Berendsen thermostat constants (τ_B), equilibration run lengths (t_{equil}) and production run lengths (t_{prod}) are specified.	96
4.3	Comparison of transport properties like oxygen diffusivities (D_O), viscosities (η) for 0.050 mole fraction of LiCl at 300 K with different Berendsen thermostat constants (τ_B). The average temperatures ($\langle T \rangle$) and configurational energies ($\langle U_{conf.} \rangle$) are also noted.	97
4.4	Properties of aqueous LiCl solution calculated at different mole fractions of LiCl (X_{LiCl}) at 275 K. The equilibrium densities (ρ), average configurational energies ($\langle U_{conf.} \rangle$), pair entropies (S_2/Nk_B), oxygen diffusivities (D_O) and viscosities (η) are noted. Standard errors are reported in parantheses, rounded upto four decimal places.	98
4.5	Comparison of transport properties like oxygen diffusivities (D_O) and viscosities (η) at 300 K for LiCl-H ₂ O at 0.050 and 0.200 X_{LiCl} with different choice of thermostat and barostat. The average temperatures ($\langle T \rangle$) and configurational energies ($\langle U_{conf.} \rangle$) are also noted.	99
4.6	For the highest molefraction of LiCl used ($X_{LiCl} = 0.300$), observables calculated in the NVE ensemble are reported. The average temperature ($\langle T \rangle$), average configurational energies ($\langle U_{conf.} \rangle$), pair entropies (S_2/Nk_B), oxygen diffusivities (D_O) and viscosities (η) are noted.	99
5.1	Computational details of molecular dynamics simulations of H ₂ O. The pressures (P), temperatures (T), Berendsen thermostat constants (τ_B), equilibration run lengths (t_{equil}) and production run lengths (t_{prod}) are specified.	126
5.2	Comparison of transport properties like oxygen diffusivities (D_O) and viscosities (η) at 300 K and 1.0133 GPa for H ₂ O with different Berendsen thermostat constants (τ_B). The average temperatures ($\langle T \rangle$) and configurational energies ($\langle U_{conf.} \rangle$) are also noted.	127

5.3	Properties of bulk H ₂ O calculated at different pressures (P) at 275 K. The equilibrium densities (ρ), average configurational energies ($\langle U_{conf.} \rangle$), pair entropies (S_2/Nk_B), oxygen diffusivities (D_O) and viscosities (η) are noted. Standard errors are reported in parentheses, rounded upto four or five decimal places.	128
5.4	Comparison of transport properties like oxygen diffusivities (D_O) and viscosities (η) at 300 K for H ₂ O at P= 1.0133 and 5.0663 GPa with different choice of thermostat and barostat. The average temperatures ($\langle T \rangle$) and configurational energies ($\langle U_{conf.} \rangle$) are also noted. . . .	129
5.5	For the highest pressure of bulk H ₂ O used ($P = 7.09$ GPa), observables calculated in the NVE ensemble are reported. The average temperature ($\langle T \rangle$), average configurational energies ($\langle U_{conf.} \rangle$), pair entropies (S_2/Nk_B), oxygen diffusivities (D_O) and viscosities (η) are noted.	129
6.1	Lennard-Jones and Coulomb potential parameters for non-bonded interactions for the ω -functionalized gold nanoparticles; $U_{ij}(r_{ij}) = 4\epsilon_{ij}[(\frac{\sigma_{ij}}{r_{ij}})^{12} - (\frac{\sigma_{ij}}{r_{ij}})^6] + \frac{1}{4\pi\epsilon_o} \frac{q_i q_j}{r_{ij}}$. The ϵ and σ are the energy and size parameters, respectively. Partial charges on different atoms are denoted by q . The letters in parentheses indicate the atom with which the particular site is bonded.	154
6.2	Harmonic stretching potential parameters for the ω -functionalized gold nanoparticles; $U(r) = \frac{1}{2}k_r(r - r_0)^2$ where, k_r is the force constant and r_0 is the equilibrium bond length. Same references were used as given in Table 6.1.	154
6.3	Harmonic bending potential parameters for the ω -functionalized gold nanoparticles; $U(\theta) = \frac{1}{2}k_\theta(\theta - \theta_0)^2$ where, k_θ is the force constant and θ_0 is the equilibrium bond angle. Same references were used as given in Table 6.1.	155

6.4	Triple cosine potential parameters for 1-4 torsional interaction in the ω -functionalized gold nanoparticles; $U(\phi) = \frac{1}{2}A_1(1+\cos(\phi)) + \frac{1}{2}A_2(1-\cos(2\phi)) + \frac{1}{2}A_3(1+\cos(3\phi))$ where A_1 , A_2 , and A_3 are constants. Same references were used as given in Table 6.1.	155
6.5	Multi-harmonic potential parameters for 1-4 torsional interaction in the ω -functionalized gold nanoparticles; $U(\phi) = \sum_{i=1}^5 C_i \cos^{i-1}(\phi)$ where, C_i 's are constants. Same references were used as given in Table 6.1.	156
6.6	The structure, thermodynamic and dynamic properties of all the solvents used in this study at 300 K and 1 atm. The number density (ρ_{liq}^*), correlation coefficient (R), slope of the correlation plot (γ_{UW}), isothermal compressibility (κ_τ), pair entropy (S_2/Nk_B) and diffusivity (oxygen of water/decane monomer unit) are tabulated.	163
6.7	Ligand shell configurational entropy, S_L ($J K^{-1} mol^{-1}$), due to reorganization of the ligands in the presence of different solvents at 300 K and 1 atm.	175
6.8	The summary of fitting parameters for V_{PMFs} at 300 K. The isotropic PMFs (V_{PMFs}) in vacuum as well as in solvents are fitted with Morse function, $D_e ((1 - \exp(-a(r - r_e)))^2 - 1)$, where $a = \alpha/r_e$, r_e is the equilibrium pair separation and D_e is the well depth at r_e	178