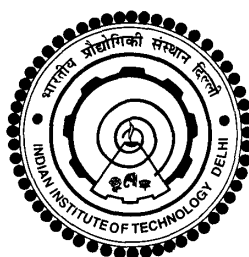


COMPUTER SIMULATIONS OF TETRAHEDRAL LIQUIDS AND NANOPARTICLE DISPERSIONS

B. SHADRACK JABES



DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
DECEMBER 2014

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by

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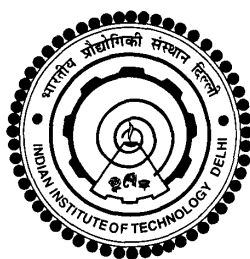
DEPARTMENT OF CHEMISTRY

Submitted

in fulfillment of the requirements of the degree of

Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

DECEMBER 2014

Certificate

This is to certify that the thesis titled "**COMPUTER SIMULATIONS OF TETRAHEDRAL LIQUIDS AND NANOPARTICLE DISPERSIONS**" is being submitted by **Mr. B. Shadrack Jabes** 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 my guidance and supervision. In my 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.

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ACKNOWLEDGMENTS

This PhD is not just another degree to me, but it is the most challenging experience in disciplining my life and a test of endurance. It was an adventure, in studying the things that were already pre-defined meticulously by someone. I am thankful and grateful to that Creator, who has sustained me with all His wisdom and perseverance which enabled me to complete this thesis.

I would like to express my deep sense of respect with gratitude to my supervisor and mentor Prof. Charusita Chakravarty, for her valuable precious time taken to guide and encourage me to carry and complete the research. I truly thank her amidst all her limitations (health) she was very patient and consistent in guiding me. Whenever I felt like I have achieved something in research, she is the one, who trained me to press on and run towards the perfection. I am really blessed to have her as my guide and I am proud to be her student. A special thanks to Prof. Ramakrishna Ramaswamy who has given many practical and innovative suggestions and ideas in my research during the Saturday talks at school of physical sciences, JNU.

"Where there is no counsel the plans fail, but with many advisers they succeed" Prov.15:22. I express my heartfelt gratitude to my Research Committee members Prof. A. K. Ganguli (Chairperson, SRC), Dr. Ravi Shankar (Convener DRC), Prof. A. K. Singh, Prof. Sameer Sapra, Prof. Bodh Raj Mehta (External expert, Department of Physics) for their evaluation and support in my work.

I thank all the IITD staff, who timely helped me in getting scholarship and funds for various trip to the conferences.

I was surrounded with an awesome group of people in IITD, who supported me in many ways. Heartily, I thank my seniors Ruchi di and Manish for helping me during my initial years of Ph.D. and teaching me the microscopic details of computers and related subjects. I would like to specially thank my two best friends Murari Singh (Muru bhai) and Divya Nayar (D) who made me special and sustained

me throughout this PhD life. Their presence has given me a joyful and healthy study atmosphere that enabled me to progress well in research. Again I would like to say my very special thanks Muru for introducing me to the outside world and opening my mind. His sense in music, at-least taught me how not to play music. My special thanks to Divya, who always inspired me with her interesting theories, beliefs, talents (drawing, music). I thank all my juniors friends Debdas dhabal (Debu, W) and Hari Om (Harry), Varun, Gaurav, Madhulika, Saurav, Sohona for their timely help. Again a very special thanks to Debu and Harry for being my partner in various projects in PhD.

I would like to also thank my church members at St.James church, Delhi and at Bethany House of Worship, Chennai and other Esteemed ones, whose company and prayer support strengthened me through many tough times during my PhD. Again I would like to say a very special thanks to my best friends in St.James church (Olivia, Mark, Aman, Monisha, Rachel, Oliver, Madhumita, Neha, Steven) who were always there for me and inspired me with their astonishing talents.

My deep love and affection to my parents, my brother B. Samuel Ebenezer, my sister in-law Ruth Beulah Samuel, all my cousins (Mama, Chitappa and their families), my grand parents for their support, encouragement and their continual prayers which spiritually nurtured me to sustain during my whole PhD years and to complete the thesis successfully.

B. Shadrack Jabes

Date

Abstract

This thesis presents molecular dynamics studies of two types of complex fluids: tetrahedral atomic liquids and nanoparticle dispersions. In the case of tetrahedral fluids, relationships between structural order, thermodynamics and transport properties are characterized, using as examples: (a) water, (b) single-component ionic melts (GeO_2 , SiO_2 , BeF_2), (c) liquid phases of Group IV elements (C, Si, Ge, and Sn) (d) binary ionic melts (LiF-BeF_2). Simulations of GeO_2 demonstrate structural, pair entropy and diffusional anomalies but no density anomaly, consistent with low degree of tetrahedrality predicted by the radius ratio rules. The transition from simple to tetrahedral liquid behavior is illustrated by the Stillinger-Weber (SW) potential, applicable to group IV elements and water. The density anomaly is observed only at intermediate tetrahedralities, while the heat capacity anomaly exists for all SW systems with a tetrahedral, crystalline ground state. Different tetrahedral liquids are compared with respect to order maps, nesting of anomalous regimes and the relationship between structural order and onset of the density anomaly. Systems with similar order maps in terms of the degree of correlation between tetrahedral and translational order also show similar tetrahedral order distributions at the onset temperature for the density anomaly. The degree of tetrahedrality is controlled by composition in the case of a binary fluid (e.g LiF-BeF_2). There is a clear correlation between pair entropy and local tetrahedral order as the fluoroberyllate network forms. Network formation is accompanied by qualitative changes in transport properties, such as breakdown of Rosenfeld-scaling between diffusivity and pair entropy as well as the Nernst-Einstein and Stokes-Einstein relationships. The second category of complex liquids studied here are nanoparticle dispersions of alkyl-thiolated gold clusters in ethane solvent. The pair potential of mean force is shown to have a significant degree of anisotropy due to ligand shell fluctuations that can cause deviations from simple liquid behaviour.

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