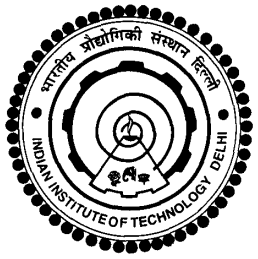
SOLVATION AND SELF-ASSEMBLY OF NANOPARTICLES: A COMPUTATIONAL STUDY

HARI OM SHARANAM YADAV



DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

FEBRUARY 2018

SOLVATION AND SELF-ASSEMBLY OF NANOPARTICLES: A COMPUTATIONAL STUDY

by

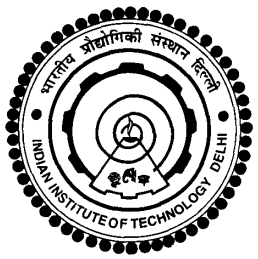
HARI OM SHARANAM YADAV

DEPARTMENT OF CHEMISTRY

Submitted

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

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

FEBRUARY 2018

To My Parents

and

our beloved Charu Ma'am
(Prof. Charusita Chakravarty)

Certificate

This is to certify that the thesis titled **"SOLVATION AND SELF-ASSEMBLY OF NANOPARTICLES: A COMPUTATIONAL STUDY"** is being submitted by **Mr. Hari Om Sharanam Yadav** 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 3 January, 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.

Date:

Hari Om Sharanam Yadav
(2010CYZ8802)

Dr. Ramakrishna Ramaswamy
Professor
School of Physical Sciences
Jawaharlal Nehru University
New Delhi - 110 067, India.

Dr. Sameer Sapra
Associate Professor
Department of Chemistry
Indian Institute of Technology Delhi
New Delhi - 110 016, India.

ACKNOWLEDGMENTS

I would like to express my earnest gratitude to all the people who contributed to this thesis with their constant guidance, encouragement and overwhelming support.

First and foremost, I would like to express my heartfelt gratitude and regards to my supervisor, (Late) Prof. Charusita Chakravarty, who enlightened my path for research with her excellent thoughts, knowledge and experiences. It is a result of her guidance and supervision that I have been able to complete this PhD research work successfully. It wouldn't be wrong to say that whatever knowledge I have in the area of computational chemistry and statistical mechanics is simply because of her excellent teaching, consistent support, and continuous encouragement. Her hardwork, determination and dedication towards work have been truly inspiring. She was always compassionate, encouraging and generous with her advice. Apart from teaching me about research, she also set a remarkable example of living life with optimism and hope, which will always serve as a secure anchor for me during my hard times in future. I am deeply grateful to her for all contributions and feel blessed, proud and honored to be her student.

I would like to thank my current supervisor Dr. Sameer Sapra for his timely guidance and cooperation to complete this thesis. I extend my sincere regards to my co-supervisor Prof. Ramakrishna Ramaswamy for his generous advice, fruitful discussions and suggestions, which helped me a lot to compile this research work. I thank both of them for being a great support during my hard times. I would also like to thank Prof. Sanat K. Kumar, Department of Chemical Engineering, Columbia University, New York, for his useful suggestions and comments, which assisted me in the preparation of manuscripts.

I thank my Research Committee members- Prof. A. Ramanan (Department of Chemistry), Dr. Hemant K. Kashyap (Department of Chemistry), Prof. B. R. Mehta (Department of Physics) for their timely evaluation, valuable comments, and useful suggestions during my Comprehensive and Synopsis viva which made me

think beyond my work and helped me improve. A special thanks to Prof. N. D. Kurur (Department of Chemistry) and Dr. Pramit K. Chowdhury (Department of Chemistry) for timely helping me to solve some research problems. I thank DRC Chairman Prof. Anil J. Elias, and all the other faculty members of the Department of Chemistry for their help and support during the tenure of my PhD. A special thanks to Prof. Pragya Jain (CSC, IIT Delhi) for always being generous to extend her help in solving the issues related to the computational resources.

I thank Computer Services Center, IIT Delhi for providing the computational facilities and good support, without which the work of this thesis would not have been possible. My sincere thanks to IIT Delhi Library for giving me access to books and journals, which have always been useful during the research and in writing this thesis. I also would like to express my gratitude to the office staff of Department of Chemistry and all the other staff members of IIT Delhi, especially the staff of Aravali hostel for their support. I acknowledge Council of Scientific and Industrial Research (CSIR, New Delhi) and IRD IIT Delhi for providing the financial assistance for the research.

I am indebted to my group members for providing a stimulating and amusing environment, where I never felt the loads of work. I thank Dr. Ruchi Sharma (Ruchi Didi) for helping to learn the basics of molecular simulations during my initial period of PhD. My special thanks to Dr. Manish Agarwal for sharing skills to efficiently use computational resources, taking part in discussions and helping in solving the problems. I would like to thank Dr. Murari Singh, Dr. B. Shadrack Jabes, Dr. Divya Nayar, who have always been very supportive and discussed my queries with interest. I thank to my lovable junior labmates Saurav, Madhulika, Gaurav for their timely help and kind cooperation during the course of research work. My special thanks to Debdas Dhabal (Debu) for help and useful discussions.

I owe a deep sense of gratitude to my friends, Dr. Sushil Kumar (University of Delhi), Adish Tyagi (BARC), Dinesh Sir, Jay Pandey, Amit Pandey, Manish, and Pankaj for their constant moral support and encouragement. A special thanks to Snehal with whom I cherished a lot of fond memories at Aravali hostel and enjoyed this entire journey of academic life. I also thank Anuushka Pal (Annu), who always

supported me with her inspirational words and good wishes during my difficult times.

Above all, I am deeply indebted to my family members for their unwavering love and countless support which cannot be expressed in words. My deep love and affection to my parents, Shri Durga Prasad Yadav and Smt. Janaki Yadav, for their constant support, sacrifice, and continual blessings without which perhaps I could not have been able to complete this thesis. I would like to thank my wife, Dr. Ritika Chauhan (Ritu), who has not only given her relentless support, encouragement, love and care but also assisted me in research. Thank you Ritu for all your contributions and being the strength and pillar of my life. I would like to convey my heartfelt gratitude to my elder brothers, sisters, and sister-in-laws for their support and good wishes. A special thanks to my eldest Brother, R. N Yadav, whose ambition and support have helped me to reach this position. I thank my in-laws, Mr. Surinder Singh and Mrs. Renu Chauhan for their kind support and motivation. My earnest gratitude to Mr. Narendar Kumar Saini, Mrs. Veena Saini, Mrs. Jyotika Saini, Mr. Pradeep Saini, Varun, Vrishti, and Pranav for their good wishes. I also would like to take this opportunity to acknowledge the kids in my family, Dilip, Saroj, Shradha, Aalok, and Teshu, whose smiling faces and sweet phone calls always bring me happiness, inner strength, and positivity towards life.

I thank to Almighty God for making this thesis possible !

Hari Om Sharanam Yadav

Abstract

In this thesis, molecular dynamics (MD) simulations are employed to understand two important aspects of nanoparticle self-assembly: the first aspect is examining the structure and solvation thermodynamics of single passivated nanoparticle, hence the dispersion stability of nanoparticles, and the second is computing the effective pair interactions between nanoparticles as a route for understanding self-assembly. The gold (Au) and semiconductor (CdSe) nanocrystals passivated with alkanethiol and alkylamine ligands respectively are taken as systems of interest. The near-critical fluids (ethane and propane) and liquid hydrocarbons (C_6-C_{12}), which are commonly used in most experiments, are chosen as the solvents for these nanoparticles. The solvation thermodynamics at the single nanoparticle level is studied following the Ben-Naim's formulation of statistical mechanics of solvation. The entropic changes associated with the ligand shell and solvent reorganizations are explicitly calculated using the structural metrics frequently exercised in biomolecular hydrations. The Helmholtz free energy of solvation is estimated by combining the change in entropy with the solvation energy, which is estimated from the pair interactions between the solvent molecules and the nanoparticle. The effective interactions (i.e., the pair potential of mean forces, PMFs) of nanoparticles at two- and three-particle level are computed employing the constrained MD simulations, in which both the isotropic and anisotropic interactions are characterized. Anisotropy arises from instantaneous fluctuation of ligands, which introduces directional characteristic in the interparticle interactions. The role of various factors affecting the assembly process such as solvent density, temperature, nanocrystal size, ligand chain length, and surface coverage on both the aspects are thoroughly examined. Implications of generating coarse-grained potentials for understanding the single-component superlattices (SLs) and binary nanocrystal superlattices (BNSLs) are discussed. Both the solvation and interaction results are found consistent with experiment, suggesting the approach used in work as a good route of obtaining the structural insights into solvation thermodynamics and the effective interactions that could be useful for understanding the dispersion stability and self-assembly of passivated nanoparticles.

सार

इस शोध में, मॉलिक्यूलर डायनामिक्स (MD) सिम्युलेशन्स का प्रयोग करके नैनोपार्टिकल सेल्फ-असेंबली के दो महत्वपूर्ण पहलुओं को समझा गया है: पहला पहलू एकल नैनोकणों की संरचना और सॉलवेशन थर्मोडायनामिक्स का परीक्षण करना है, अर्थात् नैनोकणों के डिस्पर्शन स्थायित्व को समझना है, और दूसरा, सेल्फ-असेंबली को समझने के लिए एक मार्ग के रूप में दो नैनोकणों के बीच प्रभावी इंटरेक्शन्स की संगणना करना है । अल्केनथायोल और एल्काइलअमीन्स लिगैंड्स से निष्क्रियित गोल्ड (Au) और सेमीकंडक्टर (CdSe) नैनोक्रीस्टल्स इस शोध के प्रमुख अंग हैं । प्राय: प्रयोगों में प्रयुक्त् किये जाने वाले नियर-क्रिटिकल फ्लूयिडस् (एथेन और प्रोपेन) और लिक्विड हाइड्रोकार्बन्स (C_6-C_{12}) को इन नैनोपार्टिकल्स के लिए सॉल्वेंट्स के रूप में चुना गया है। एकल-नैनोपार्टिकल स्तर पर सॉलवेशन थर्मोडायनामिक्स का अध्यन बेन-नैम के द्वारा विकसित स्टैटिस्टिकल मेकैनिक्स पर आधारित सूत्र का प्रयोग करके किया गया है। लिगैंड शेल और विलायक के पुनर्गठन के साथ जुड़े एंट्रोपिक परिवर्तनों की गणना बायोमॉलिक्यूलर हाइड्रेशन में प्रयुक्त् किए जाने वाले संरचनात्मक मेट्रिक्स का उपयोग करके करते हैं। सॉलवेशन की हेल्महोल्ट्ज़ मुक्त ऊर्जा, एंट्रोपिक परिवर्तन को सॉलवेशन ऊर्जा के साथ संयुक्त करके प्राप्त किया जाता है, जिसे नैनोपार्टिकल और विलायक अणुओं के बीच इंटरेक्शन्स से आंका जाता है। दो और तीन नैनोपार्टिकल स्तर पर प्रभावी युग्म इंटरेक्शन्स (अर्थात, पोटेनशियल ऑफ मीन फोर्सस, PMFs) का आक़लन, कन्स्ट्रेंड MD सिम्युलेशन्स से किया गया है, जिसमे हम आइसोट्रोपिक और अनिसोट्रोपिक इंटरेक्शन्स को पृथक रूप से कंप्यूट करते हैं। अनिसोट्रोपी लिगैंड्स के तात्कालिक फ्लक्चुयेशन्स से आता है, जो दो नैनोपार्टिकलों के इंटरेक्शन में दिशात्मक प्रवृति को जन्म देता है। सेल्फ-असेंबली प्रक्रिया को प्रभावित करने वाले विभिन्न कारकों, जैसे कि विलायक के घनत्व, तापमान, नैनोक्रीस्टल्स के आकार, लिगैंड्स की लंबाई और सतह कवरेज की भूमिका का विस्तृत अध्यन किया गया है। सिंगल-कॉम्पोनेन्ट सुपरलैटिसेस (SLs) और बाइनरी नैनोक्रिस्टल सुपरलैटिसेस (BNSLs) को समझने के लिए कोर्स-ग्रेन्ड पोटेनशियल को विकसित करने के निहितार्थ की चर्चा गयी है। दोनों सॉल्वेशन और इंटरेक्शन्स के परिणाम प्रयोगों के अनुरूप हैं, जो इस बात का सुझाव देते हैं, कि इस अध्यन में प्रयुक्त किया जाने वाला दृष्टिकोण, सॉल्वेशन थर्मोडायनामिक्स और इंटरेक्शन्स में संरचनात्मक अंतर्दृष्टि प्राप्त करने का एक अच्छा मार्ग है, और ये नैनोपार्टिकलों के डिस्पर्शन स्थायित्व और सेल्फ-असेंबली को समझने के लिए बहुत उपयोगी हो सकता है।

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 as on Date of Submission of Thesis

1. Divya Nayar, **Hari O. S. Yadav**, B. Shadrack Jabes and Charusita Chakravarty, "Relating Structure, Entropy and Energy of Solvation of Passivated Metal Nanoparticles", *J. Phys. Chem. B.* **116**, 13124-13132 (2012).

2. B. Shadrack Jabes, **Hari O. S. Yadav**, Sanat K. Kumar and Charusita Chakravarty, "Fluctuation-Driven anisotropy in effective pair interactions between nanoparticles: Thiolated gold nanoparticles in ethane", *J. Chem. Phys.* **141**, 154904, (2014).

3. **Hari O. S. Yadav**, Gourav Shrivastav, Manish Agarwal and Charusita Chakravarty, "Effective interactions between nanoparticles: Creating temperature-independent solvation environments for self-assembly", *J. Chem. Phys.* **144**, 244901, (2016).

4. **Hari O. S. Yadav** and Charusita Chakravarty, "Thiolated gold nanoparticle solvation in near-critical fluids: The role of density, temperature, and topology", *J. Chem. Phys.* **146**, 174902, (2017).

Contents

List of Figures

List of Tables