POTENTIAL ENERGY LANDSCAPES AND PROPERTIES OF SIMPLE LIQUIDS

BY

POOJA SHAH
DEPARTMENT OF CHEMISTRY

Submitted

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

to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI
INDIA
NOVEMBER 2002

Certificate

This is to certify that the thesis titled **"Potential Energy Landscapes and Properties of Simple Liquids"** is being submitted by **Ms. Pooja Shah** 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 her 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.

Charusita
Chakravarty

Dr. C. Chakravarty
Associate Professor
Department of Chemistry
Indian Institute of Technology
New Delhi - 110 016

To my parents

Acknowledgements

It is by God's grace that I had an invaluable chance to work with **Dr. Charusita Chakravarty**, my friend, mentor and guide. "Mam", as she is respectfully called, has been a source of constant encouragement and inspiration throughout the tenure of my research, guiding me both professionally and personally at every step. Mam has led the way and showed me the path in the exciting World of Computational Chemistry. This work would have been incomplete without her tireless efforts, insightful knowledge and constructive criticism. I am inspired by the beautiful shloka in the Geeta describing the qualities of a Guru (one who leads and shows the light):

Chaitanyam Shashwatham Shantam Vyomaateetam Niranjanam
Nadabindu-Kalateetam Tasmai Shree Guruve Namah

I bow to my teacher who is the supreme spirit, who is eternal and benign; who is beyond sound, line and art. Salutations to thee !

My sincere thanks to Prof. H. M. Chawla, Head, Department of Chemistry, for providing the necessary facilities and to all faculty members especially Dr. N. D. Kurur, Prof. A. K. Singh, Dr. A. K. Ganguly and Dr. A. Ramanan for their valuable advice and co-operation. I must record my acknowledgement to the Council for Scientific and Industrial Research for financial support and the Computer Services Centre of I.I.T-Delhi for access to their computational resources. I am grateful to IIT Librarians and staff especially Shree Raghubir Singhji for their cooperation. I also extend my thanks to JNU authorities for allowing me to use their library facilities.

Prof. S. Banerjee and his group members particularly Mohan Raj Gupta and Saumyadeb Mitra, Department of Computer Science, and Achintya Das, Department of Chemistry, have been very helpful in resolving computers related issues. I am grateful to Prof. Anurag Sharma, IIT-Delhi , Prof. Subhir Sarkar, JNU and Dr. Sushmita Choudhary, Gargi College , DU.

I would like to express my deep sense of gratitude and respect to Prof. R. Ramaswamy, Dean, School of Physical Sciences, JNU, for his valuable suggestions . It was a great oppurtunity for me to discuss my work with his research group.

The pleasant lunches and dinners shared with Dr. Sudeshna Kar and Shweta Sharma are unforgettable. My M.Sc. collaborators, Piyalee Chakrabarti and Sharani Roy are thanked for their contributions to this work. The exciting tea sessions with my labmates Anirban, Nilanjan and Somendra would be remembered.

I am grateful to my colleagues and friends especially Bimlesh, Madhulika, Meenu, Prasun and Pooja Kumar. I will cherish your friendship throughout my life. Neelima, your caring and helping attitude and those late night discussions made my stay in Hostel a memorable one.

I owe a great deal to **my parents** who worked hard to give me the best education and inherting in me social values and respect for elders. This thesis is dedicated to them. It was constant endearment of my parents-in-law, Bhaiya, Bhabhi, Nidhi Didi, Deepak Jijaji, Rakhi Didi, Ranjeet Jijaji, Nanhi, Chotti, Cheeku, Shreya, Nikki and Shaurya. It gives me an immense pleasure to thank my younger brother, **Vivek**, who was always there whenever I needed him. Rahul, my cousin, has always boosted me to do hard work.

I have no words to express my thanks to my husband, **Manish**, for being supportive, understanding and always encouraging me especially during the crisis time. Thanks for your sacrifices and changing my attitude towards life.

Last but not the least, I bow down to **Almighty** whose invisible hands inspired and encouraged me. I prostrate with all my heart, to every person who has taught me anything in life.

New Delhi

Pooja Shah

Abstract

This thesis employs classical Metropolis Monte Carlo simulations to understand the connection between the topography of the potential energy surface and properties of simple liquids bound by Lennard-Jones or Morse pair interactions.

The first chapter provides an introduction to certain aspects of the liquid-phase relevant to this thesis. It summarises the key features of one-component phase diagrams, specially with reference to the region of liquid phase stability. Simulation studies of specific systems that are of importance for correlating generic features of the pair potential with properties of the bulk system are described. A brief overview of potential energy landscape approaches for understanding phase transitions and collective dynamics is given. The concluding section of this chapter discusses the motivation for the present work and the organisation of the thesis.

Chapter 2 summarises Monte Carlo simulation results for bulk liquids bound by Morse, Lennard-Jones and shifted Lennard-Jones interactions in the constant temperature and pressure (NPT) ensemble. The structural and thermodynamic properties are mapped out as a function of the range of the pair potential by constructing isobars going from the low-temperature, solid phase region into the liquid region. This allows one to obtain the properties of the pure phases as well as to locate the metastability limit of solid, T_k^*, which is higher than the true thermodynamic melting temperature. The results show that decreasing range of the Morse potential is correlated with increasing melting temperatures and with increasing density, enthalpy and internal energy changes on melting. For example, at a given pressure, the maximum temperature at which the solid phase is observed increases with decreasing range of the Morse potentials. The fractional changes in density vary from approximately 5% for metallic systems to approximately 15% for van der Waals systems.

The properties of the softer, longer-ranged bulk Morse systems are most susceptible to change with increasing variations in temperature and pressure.

Chapter 3 discusses the application of instantaneous normal mode (INM) analysis to Morse liquids with a view to understanding the changes in liquid-state dynamics that take place as the range and curvature of the pair potential are varied. The fraction of imaginary frequency modes is shown to rise with increasing temperature and decreasing range. In contrast, the Einstein frequency, which is a measure of the curvature of the effective potential well that traps a tagged particle in the liquid state, shows a non-monotonic behaviour with range. A participation ratio analysis of the INM spectra is used to demonstrate the transition of the Morse fluid phase from a liquid-like regime, dominated by collective rearrangements, to a gas-like regime dominated by binary collisions as the range of the pair interaction decreases. Key INM spectral features are shown to undergo discontinuous changes on melting.

Chapter 4 presents an extensive statistical analysis of the stationary points of several simple liquids with a view to understanding the physical significance of the inherent saddles. Since stationary point analysis is a relatively new approach, a couple of important computational issues connected with the location of quasi-saddles of liquids are initially discussed. The first concerned the applicability and accuracy of gradient-based minimisation algorithms to bulk systems with a finite spherical cut-off radius for the pair interactions. The second involved the possibility of distinguishing between true saddles and inflexion points when multi-dimensional minimisations are carried out with finite precision. A detailed analysis of the bulk Lennard-Jones liquid is then made comparing the properties of inherent minima, inherent saddles and instantaneous configurations. The final section of the chapter studies the correlation between properties of the stationary points and the range parameter of Morse liquids. The configurational energy of saddle configurations is shown to depend linearly on the index density of saddles with a slope that is proportional to the range of the potential. The relative values of ensemble-averaged energies of saddles, minima and instantaneous configuration are shown to have qualitatively different temperature-dependent behaviour for short, intermediate and long range Morse systems.

Chapter 5 focuses on the finite-size analogue of the melting transition seen in Morse clusters. Interesting similarities and differences between bulk and cluster melting are brought out by comparing the results of Chapter 2 with simulations of 55-atom Morse clusters. The finite size analogue of melting in Morse clusters shows a range-dependent behaviour similar to the increasing strength of the first-order melting transition with decreasing range seen in the bulk. In addition, the width of the solid-liquid coexistence regime for clusters is shown to increase with increasing values of the range parameter of the Morse interaction. Unlike bulk systems, melting in clusters shows very interesting qualitative changes with range due to the relative ease with which defects can be created in a finite cluster with a free surface.

Chapter 6 presents the final conclusions of this thesis regarding the relationship between properties and potential energy landscapes of Morse systems.

Contents