UNIVERSITY OF CAMBRIDGE
DEPARTMENT OF CHEMISTRY

# The Structure, Thermodynamics and Dynamics of Atomic Clusters

A dissertation submitted to the University of Cambridge in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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## Declaration

The work described in this dissertation was carried out by the author in the department of Theoretical Chemistry at the Univerisity of Cambridge from October 1993 to September 1996. The contents are the original work of the author except where indicated otherwise and have not been previously submitted for any other degree or qualification at any academic institution.

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*To*
*'David'*

# Abstract

The potential energy surface determines the structure, thermodynamics and dynamics of a cluster. In this thesis, I investigate for simple atomic clusters both the nature of this relationship, and how the form of the potential affects the potential energy surface and consequently the behaviour of the cluster.

The solid-like structure of a cluster is given by the global minimum on the potential energy surface. Using a Morse potential to describe the interatomic forces, I have investigated how the structure depends upon the range of attraction of the potential. This model exhibits a diverse range of structural behaviour, which is relevant to a wide variety of systems from sodium and rare gas clusters, to clusters of $C_{60}$ molecules. A short-ranged potential favours face-centred-cubic and decahedral structures, as opposed to those based upon the icosahedron.

The melting of clusters is associated with a transition from the low potential energy solid-like minima to the numerous high potential energy liquid-like minima. Here, I have developed a method to accurately describe the thermodynamics of this transition using a representative sample of minima on the potential energy surface.

By investigating the dependence of the topography of the potential energy surface on the range of the potential for both clusters and bulk, I have provided a microscopic explanation of the destabilization of the liquid phase that occurs for short-ranged potentials. Furthermore, this study shows that clusters can develop bulk-like liquid structure at small sizes, and also provides an explanation of the transition from electronic to geometric magic numbers that is seen in mass spectroscopic studies of sodium clusters.

If all the minima and transition states on the potential energy surface are known, the dynamics of a system can be obtained by solving a master equation. This method is applied to model potential energy surfaces to investigate the factors affecting relaxation to the global minimum. The results are not only relevant to clusters, but also to disciplines such as protein folding and glass formation. Finally, I investigate some ways of characterizing cluster potential energy surfaces which can give insight into their dynamics.

# Contents

# List of Abbreviations

| | |
|---|---|
| DSD | diamond-square-diamond |
| fcc | face-centred cubic |
| hcp | hexagonal close-packed |
| LJ | Lennard-Jones |
| M | Morse |
| MC | Monte Carlo |
| MD | molecular dynamics |
| PES | potential energy surface |
| PG | point group |
| RRKM | Rice-Ramsperger-Kassel-Marcus |
| STA | short time averaged |