Chapter 1
Introduction

1.1 The Evolution of Cluster Science

In the last thirty years, cluster science has become a rapidly expanding field of interdisciplinary study as experimental and theoretical techniques have advanced and computational power has increased. Clusters are finite aggregates of atoms or molecules that are bound by forces which may be metallic, covalent, ionic, hydrogen-bonded or Van der Waals in character and can contain from a few to tens of thousands of atoms.

Clusters can be prepared in a number of ways. A large proportion of experimental studies are now performed on clusters that are produced in molecular beams by free-jet expansion. The discovery of this technique was one of the most important factors in the growth of cluster studies. The resulting clusters can then be mass-selected and subjected to many types of high-resolution spectroscopies. However, although this technique allows very detailed and sensitive studies to be performed, it is not so suitable for producing large quantities of (size-selected) clusters—a likely requirement for industrial applications—and it is hard to make direct measurements of structure. One alternative that circumvents the latter problem is to deposit the clusters on a surface, where their structure can then be probed by techniques such as high resolution electron microscopy[1], and scanning tunneling microscopy[2,3]. However, the effects of the surface on the cluster have then to be taken into account.

The oldest route for the preparation of clusters is by colloidal chemistry: back in 1856 Faraday famously investigated the optical properties of gold colloids[4]. Typically, clusters produced by this method are stabilized by the addition of a passivating layer, as compared to the naked clusters produced in molecular beams. One of the main advantages of this method is that large quantities of clusters can be produced. Furthermore, significant advances have now been made in controlling the size, shape and structure of these particles[5–7].

But why are so many people interested in studying clusters? If you look back into the early cluster literature three motivations are particularly common. Firstly, clusters provide a bridge between the limits of isolated atoms and molecules and bulk matter, and so much interest has focussed on the evolution of properties with size[8], particularly those, such as phase transitions, which have no counterpart in atomic physics, and which must therefore emerge as collective behaviour becomes possible. The hope is that such knowledge will provide a new perspective on and an increased understanding of the behaviour that occurs at the more familiar limits. This motivation is still a fundamental driving force for cluster science and this thesis will touch upon some aspects of the size evolution of cluster properties.

A second motivation to study clusters, particularly from the theoretical viewpoint, is to try to understand nucleation at an atomistic level, rather than by the continuum theories of classical nucleation theory[9]. Whenever a new phase is forming the initial nuclei will be within the cluster regime. Much of the early work on the thermodynamics of clusters had this as its goal[10–12]. However, these ambitions have never been fully realized; this task is a far more difficult problem than perhaps was originally conceived. Most of the current work in this area is now no longer directed at clusters as as a model of a (critical) nucleus, but instead at clusters as an environment in which nucleation can occur on fast time scales[13] and for which only a single nucleation event is required to transform the cluster[14].

Thirdly, much work has been, and still is, driven by the prospect that a fundamental understanding of the properties, particularly the chemical reactivity, of metal clusters could have far-reaching consequences for catalysis. Small metal particles and clusters (supported, for instance, within a zeolite) could provide both a large surface area to volume ration and properties, such as activity and selectivity, that have been tailored to catalyse a specific reaction[15,16].

In recent years, though, the ambitions and breadth of cluster science have expanded greatly as the numbers of types of clusters that have been studied has grown, and as it has been realized that clusters can provide a new environment to study many of the phenomena of chemical physics. Here, we just provide some illustrative examples of the range of the recent work.

Insights into the nature of hydrogen bonding have been obtained from water clusters by the coupling of high-resolution laser spectroscopy with theoretical calculations[17] to identify in detail the structure of the clusters[18] and the rearrangement dynamics of the hydrogen-bond network[19]. By studying heteroclusters detailed microscopic information on the nature of solvation can be obtained[20], such as the number of species required for the formation of a complete solvent shell[21], and the effects of this solvent shell on the chemical reactions dynamics[22–24]. Helium, because of its superfluid properties, can be a particular gentle solvent. Consequently, helium clusters probably a suitable environment for ultra-cold high-resolution spectroscopy of Van der Waals complexes[25,26].

The collision of clusters with solid surfaces at high speeds can give rise to short-lived, but particularly extreme conditions of temperature and pressure[27]. It has been shown that these impact-heated clusters provide an environment in which chemical reactions can be induced[28]—it has even been suggested that they could lead to the burning of 'air' (binary N_2 and O_2 clusters)[29]. Energetic cluster impact also has the potential for technological application in the formation of particularly dense and coherent metal[30,31] and semiconductor[32] thin films. However, if clusters instead collide with surfaces covered by liquid layers, the clusters can be 'soft landed' onto the surface[33].

These latter examples touch on one of the more recent reasons for the increased interest in clusters: nanotechnology—the fabrication of structures and devices on the nanometer scale. In this regard, semiconductor clusters have been the focus of particular attention since size control could provide a means of tailoring their electronic and optical properties to a particular application[34,35]. One of the dreams of researchers is to produce quantum dot lasers whose frequency can be fine-tuned by variation of the cluster size[32]. Such hopes have led to a major efforts to improve fabrication techniques and methods are now available for making structurally well-defined monodisperse passivated clusters which can then be formed into orientationally-ordered superlattices[7,36]. Assemblies of nanoparticles have even been constructed using the base pairings of DNA as connections[37,38].

1.2 Thesis Overview

The work described in this thesis is theoretical and its aim is to help provide a fundamental understanding of three of the most important properties of clusters, their structure, thermodynamics, and dynamics. Rather than attempting to model accurately a specific substance, I choose to study homogeneous atomic clusters for which the interactions are described by simple potentials. Only with this simplicity does the main theme of the thesis—the relationship between the form of the potential and the behaviour of the cluster—become tractable. To attempt this task I focus on the potential energy surface (PES), because it allows the elucidation of this relationship to be broken down into two steps: firstly, how the potential determines the topographical features of the PES, and then how these in turn determine the behaviour of the cluster. In the analyses of the PES performed here, the stationary points (at which $\nabla V = 0$ where V is the potential energy) will be particularly important, since the minima on the PES represent locally stable structures, and the transition states characterize the possible rearrangement paths between minima.

The thesis progresses in the following way. In Chapter 2, I show how the range of attraction of the potential affects the structures of the global minima. In Chapter 3, I extend a statistical method to incorporate anharmonicity so that the thermodynamic properties of clusters can be accurately calculated from a representative sample of minima. In Chapter 4, I attempt to provide a microscopic explanation of the range-dependence of the stability of the liquid phase. In Chapter 5, by examining model PES's I seek to elucidate the topographical features which significantly affect relaxation to the global minimum. In Chapter 6, I outline and apply methods by which to characterize the topology of the PES, particularly the network of connections between the minima, in order to provide insights into the dynamics. Finally, in the conclusion I attempt to summarize the achievements of the work described in this thesis, and suggest some possible future directions. Comprehensive introductions into each area will be given at the beginning of each chapter.

As I hope the interdependence of the chapters in this thesis will illustrate, structure, thermodynamics and dynamics are intimately connected. For example, only once liquid structure is characterized can the range-dependence of the liquid phase thermodynamics be explained. Furthermore, to be able to predict whether a cluster is likely to adopt the structure of the global minimum, one must first know whether the minimum is kinetically accessible, which in turn depends on whether there are free energy barriers to this relaxation process.

Although the approach of this work is unashamedly fundamental, throughout the thesis I shall attempt to relate the findings to experiment and other more specific theoretical calculations. Indeed, the hope is that the results for these simple systems can begin to provide a framework for understanding the diverse behaviour of real clusters.