

1. Introduction to Clusters

1.1 The Field of Clusters

Atomic clusters are aggregates of atoms containing from few to a few thousand atoms. Due to their small size, the properties of the clusters are, in general, different from those of the corresponding material in the macroscopic bulk phase. The differences result from the fact that the number of atoms forming the surface is a substantial fraction of the number of atoms forming the cluster, while this fraction is negligible in the case of a macroscopic solid (of course the surface of a solid is relevant in itself, giving rise to the technologically important field of surface science). Many of the differences between clusters and bulk can also be viewed as arising from the small volume of the potential well confining the electrons in the clusters. In this case the electrons fill discrete levels, instead of having the continuous distribution (bands) characteristic of the solid. Of course the two views are inter-related. By studying the properties of clusters, scientists expect to obtain information on the early stages of growth of matter, and on the evolution of the properties towards the bulk. An interesting question which still lacks a convincing answer in many cases is the following: how many atoms are required for a cluster to show the properties of the bulk material? To make affairs more complicated, sometimes different properties of a given type of clusters appear to converge at a different rate. But, even more important, is knowing the precise behavior of a given property, like the cluster geometry, or the values of the ionisation potential, as the number of atoms increases one by one. These questions have motivated the development of experimental techniques for producing small clusters, as well as a series of experimental and theoretical studies of their structure and properties. The existence of especially stable clusters is sometimes advocated to construct models of amorphous materials.

Two discoveries, nearly simultaneous in time, stand at the top of the field of clusters, and have added strong impetus for its development. The first one, reported by Knight and coworkers in 1984, is the discovery of magic numbers in the abundance of clusters of the alkali metals [1]. These magic numbers are interpreted as reflecting an electronic structure characterized by the formation of discrete electronic shells separated by energy gaps, like electrons in atoms or nucleons in nuclei. In short, clusters with filled electronic shells are more stable and less reactive than clusters with open shells. This parallels the behavior of atoms across the Periodic Table: the inert gas atoms He, Ne, Ar, Kr, Xe and Rn have filled electronic shells, and consequently they are chemically unreactive. Also, some particular nuclei are specially stable because the nucleons (protons and neutrons) have a structure of closed shells in those nuclei. In summary, this is a general property of fermions moving in a common potential well of finite size. In fact, the shape of the potential well confining the electrons in the alkali metal clusters (smooth and nearly constant inside the cluster and rising abruptly at the surface) is qualitatively more similar to the potential well binding the nucleons in the nuclei as opposed to the potential that the electrons feel in the atom, where the strong Coulombic attraction of the highly charged point nucleus, screened of course by the core electrons, dominates. The electronic shell effects become reflected in many properties of clusters of the simple metals (with *sp* electrons) and many examples are discussed throughout this monograph. The second key work was the discovery by Kroto *et al.* [2] of the C_{60} fullerene in 1985 and the proposal of its peculiar cage structure. Those two discoveries were made possible by the efforts in many laboratories in developing experimental methods to produce clusters in the gas phase as molecular beams. Those experimental methods are described in Chapter 2. It is also worth noting that the experimental confirmation of the structure proposed for the fullerene was achieved five years after the discovery of C_{60} , when a method was developed [3] to purify and separate C_{60} in quantities large enough to allow spectroscopic studies to be performed.

Close in importance to these two key discoveries are other findings that will be discussed at length in this volume: like the formation of shells of atoms in the clusters of the inert gases [4], the excitation of collective modes similar to the giant dipole excitation of nuclei, *etc.* The spatial arrangement of the atoms, that is, the geometrical structure, is the

source of the differences between the properties of clusters of similar sizes; sizes that can differ by just one atom. In contrast to bulk solids, the structure of clusters is difficult to assign. Even more, several (or many) low lying isomers (for a given cluster size) often exist with binding energies differing very little from that of the ground state. This means that different isomers may be populated under typical experimental conditions. On the other hand, the existence of many isomers makes the theoretical identification of the ground state difficult, even if one uses sophisticated computational methods based on first principles theory.

1.2 Types of Clusters

The clusters can be classified according to the type of chemical bonding between the atoms forming the aggregate. The types of clusters that are considered in this monograph are now briefly introduced. The list is broad but it may not be comprehensive, since it reflects the personal selection of the author, motivated by reasons like his own interest and experience. For the same reasons, a selection of examples, taken from the abundant literature, has been made for the different types of clusters, but it is hoped that the selection reflects faithfully the relevant characteristics and properties of each type.

1.2.1 *Van der Waals clusters*

The interactions between inert gas atoms are weak and can be described accurately by central pair forces. The origin of the short-range repulsive part of the interaction is the quantum mechanical repulsion between cores with closed shell electronic configurations, and the attractive part is due mainly to the induced-dipole dispersion force. The strength of the binding is about 0.3 eV per atom or less. Due to the simple central force the most stable clusters are those with high atomic density, that is, with a close-packing of atoms. The weak binding leads to low melting and boiling points, and have made these clusters attractive to experimentalists. The simplicity of the interatomic forces makes them equally popular between theorists, who have used molecular dynamics techniques to simulate and enlighten the difficult problem of the solid to

liquid phase transition in systems with a small number of atoms. Van der Waals clusters are treated in Chapter 3. Molecular clusters, formed as aggregates of closed shell molecules, like $(I_2)_N$, $(N_2)_N$, $(CO_2)_N$, $(SF_6)_N$ also belong to this class. Aggregates of inert gas atoms also form in cavities in metals during ion beam mixing experiments [5]. In those experiments, inert gas ions with high kinetic energies are used to induce the mixing of metallic multilayers to produce amorphous alloys.

1.2.2 Metal clusters

The interatomic forces in metals are not simple. Many metals have non close-packed structures because the interatomic forces are partially directional. One can distinguish between simple metals, like Na or Al, with valence electrons of *sp* character, and transition metals, like Fe or Co, where the localized *d* electrons play an important role. Some polyvalent nontransition elements like Pb form a group inbetween. The clusters reflect these characteristics. The strength of the binding in metallic clusters ranges from moderate to strong, say from 0.5 to 3 eV per atom.

The main property of the clusters of the simple *sp* elements is the existence of electronic shell effects [1], discussed in detail in Chapter 4. There is a close connection between geometrical and electronic structure at the beginning of the growth staircase, when the addition of each new atom changes the properties of the system substantially. The simplicity of the *sp* clusters captured the attention of theorists and experimentalists, and a lot of progress has been made in the understanding of their electronic properties, which is reported in Chapter 5. In particular, the delocalized character of the electronic states allows for the occurrence of collective electronic excitations at relatively low energies. The induced fragmentation of these clusters, reviewed in Chapter 6, is also influenced by electronic shell effects. The solid to liquid phase transition, also considered in Chapter 6, is still an open problem. The observed trends are complex and the theoretical studies encounter two main difficulties. First, the interatomic potential is complex; strictly speaking it is a many-atom interaction as opposed to the simple two-body force of the Van der Waals clusters, and this makes designing potentials that could be used with confidence in molecular dynamics simulations a very difficult task. Of course, accurate first principles techniques are now available, but these become computationally very demanding as the cluster size

increases. Since the surface atoms represent a substantial fraction of the cluster, it is not surprising that the simulations seem to indicate the occurrence of steps in the melting transition.

The variety of bulk metallic alloys is enormous because many different elements can be combined, and for a given A–B pair, there is an additional variable, the relative concentration of the two components. Similarly, many A_nB_m mixed bimetallic clusters have been produced and their variety is also enormous: the nature of the elements and their relative compositions are again the relevant variables. The properties of alloy clusters are studied in Chapter 7. Mixing two elements in the adequate proportion may be a way to produce highly stable clusters that could form the building blocks of future cluster assembled new materials.

The d electrons present in the transition metals make the corresponding clusters substantially more complex than the clusters of the sp elements. Their structure and electronic properties are considered in Chapter 8. Part of the interest in these clusters comes from their potential use in catalysis, and in fact, their reactivity with different molecular species has been studied. Another topic of great interest deals with the magnetic properties, especially the nature of the magnetic ordering and its evolution with the size of the cluster. Chapter 9 presents a discussion of the trends in this evolution.

1.2.3 Clusters of ionic materials

Ionic materials are composed of closed shell ions, for instance Na^+ cations and Cl^- anions in the NaCl salt. In general these materials are formed from electropositive metals on the left side of the Periodic Table and electronegative elements on the right side. The cohesion in $(\text{NaCl})_N$ and similar clusters can be described by potentials composed of an attractive part due to electrostatic monopole forces and a repulsive part from the quantum mechanical overlap of the electronic clouds of ions with filled electronic shells. The bonding is strong: 2–4 eV/atom. The structures of many of these clusters, described in Chapter 10, can be interpreted as having the shape of rectangular nanocrystals cut from the solid. This is in accordance with the brittle character of the bulk crystals. Some computer simulations of the assembling of clusters to form new materials suggest that it may be possible to assemble solids formed by

large anionic clusters separated by cations, with a structure similar to that of the typical ionic crystals. In fact, this is also the structure of some natural alloys.

1.2.4 Network clusters

Covalent bonding leads to the formation of atomic networks in clusters of materials like Si, Ge and C. Networks also form in the corresponding solid crystals and in the amorphous forms of those elements. Since many atoms in small clusters are on the cluster surface, these surface atoms have dangling bonds and important structural reconstruction is expected, as in the case of the solid surfaces. The binding energy in network clusters is strong, typically between 1 and 4 eV per atom or more. Network clusters are studied in Chapter 11, taking as representative examples first carbon clusters, since the popular C_{60} fullerene belongs to this class, and then the so called metcars, formed by carbon and transition metal atoms.

1.2.5 Cluster assembled solids

The possibility of building highly stable and symmetrical nanostructures makes the class of network clusters the most promising one for the purposes of cluster assembling. In fact the self-assembling of C_{60} clusters to form the fullerite solid provides the best example [3], as discussed in Chapter 12. This chapter discusses the idea and the possibilities of building new materials by assembling very stable clusters.

References

1. Knight, W. D., Clemenger, K., de Heer, W. A., Saunders, W. A., Chou, M. Y., and Cohen, M. L., *Phys. Rev. Lett.*, **52**, 2141 (1984).
2. Kroto, H. W., Heath, J. R., O'Brian, S. C., Curl, R. F., and Smalley, R. E., *Nature*, **318**, 162, (1985).
3. Krätschmer, W., Lamb, L. D., Fostiropoulos, K., Huffman, D. R., *Nature* **347**, 354, (1990).
4. Echt, O., Sattler, K., and Rehnagel, E., *Phys. Rev. Lett.*, **47**, 1121 (1981).
5. Mitchell, D. R. G., Donnelly, S. E., and Evans, J. H., *Phil. Mag. A* , **61**, 53 (1990).