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Clusters in Nature

Clusters, also called nanoparticles, are special molecules. They are composed from the same building blocks, atoms or small molecules, stacked in any desired amount. This is similar to a bulk crystal. In fact, one may view clusters as small pieces of bulk material. It has only been within the past few decades that clusters have come into the focus of intense investigations. During these few decades, cluster science has developed into an extremely rich and promising field of research. As often in science, technological applications of clusters existed before they were identified and understood. One of the most famous and oldest examples of the application of clusters in technology is the coloring of glass by immersing small gold clusters into the glass itself. The process allowed for some tuning of colors depending on the inclusions' size. This technology dates back to Roman times, where there is evidence craftsmen had perfectly mastered this versatile technique. In scientific terms, such a phenomenon just reflects the size dependence of the optical response (that is, the color) of gold clusters in a glass matrix (although that prosaic formulation certainly does not give sufficient credit to the marvelous impressions attained that way). Another example of early applications is found in traditional photography which started about two centuries ago. The emulsion of a photographic film contains a dense distribution of AgCl (later AgBr) clusters whose special optical properties allowed to store information from light impulses and to visualize it later by chemical reduction. Progress in sensitivity and resolution was tightly bound in properly handling the cluster properties, where for a long time photographers did not even know that they were dealing, in fact, with clusters.

Figure 1.1 exemplifies clusters with an ancient and with a modern view. Figure 1.1a shows a church window from the St. Etienne cathedral in Bourges (France), whose impressive colors (not visible here, but which can be appreciated from the book cover) were fabricated to a large extent by Au clusters embedded in glass. Figure 1.1b was recorded with the most modern achievements of scanning tunneling microscopes (STM). It shows in detail Ag nanoparticles sitting on a highly oriented pyrolytic graphite (HOPG) surface. From the given length scale, we read off for this case cluster sizes in the range of a few nanometers, which corresponds to system sizes of about 100–10 000 Au atoms. As we will see, the combination of these quickly developing methods of nanoanalysis with nanoparticles, called clusters, constitutes a powerful tool for fundamental and applied physics.

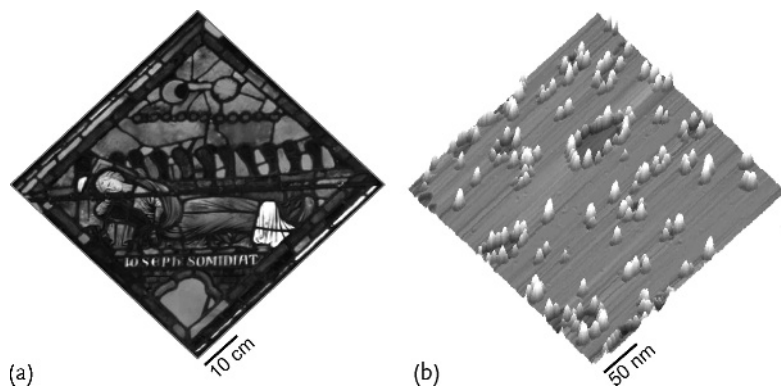


Figure 1.1 (a) Glass window of the St. Etienne cathedral in Bourges, France. Colors of church windows reflect their content in metallic particles. (b) Topography of silver nanoparticles deposited on (HOPG), recorded with an *in situ* scanning tunneling microscope (STM), from [2].

A first theoretical study which these days plays a basic role in cluster physics goes back to G. Mie in the early twentieth century [3]. Mie considered the question of the response of small metal particles to light, and how this optical response might depend on the size of the considered particle. It is interesting to quote Mie who turned out to develop a remarkable intuition of the future of cluster science: “Because gold atoms surely differ in their optical properties from small gold spheres”, it would “probably be very interesting to study the absorption of solutions with the smallest submicroscopic particles; thus, in a way, one could investigate by optical means how gold particles are composed of atoms.” This apparently simple and “reasonable” statement actually covers a large fraction of today’s activities in cluster science as the interaction with light is a key tool for the investigation of cluster structure and dynamics.

In spite of Mie’s intuition, the study of clusters as physical individual objects remained rather limited for the subsequent decades. Most investigations concerned clusters in contact with an environment (embedded or deposited). This limitation was due to the difficulty to create isolated clusters in a controlled manner. During the last quarter of the twentieth century, the capability of producing free clusters from dedicated sources finally triggered the emergence of cluster science on a systematic basis. The identification of the remarkable C_{60} clusters, the famous fullerenes [4], and the first systematic investigations of metal clusters [5] were impressive boosters. From then on, cluster science rapidly grew to an independent, although cross-disciplinary, field among the well-defined branches of physics and chemistry, ranging from fundamental research to applications in the context of nanotechnology.

Grossly speaking, clusters can be considered as large molecules or small pieces of bulk material. Their properties thus can be understood to some extent by methods from molecular and solid-state physics. Nonetheless, clusters represent a species of their own. One of the possibly most specific aspects of clusters is the fact that one can deliberately vary cluster size. Clusters are, so to say, “scalable” objects which

bridge the gap between atoms/molecules and bulk material. This makes them useful testing grounds for the many-body problems, for example, to understand the path to bulk matter. They are true multidisciplinary objects staying in contact with many areas of science. This includes even such a remote field as astrophysics where clusters play a role in the formation mechanisms and the properties of cosmic dust. But the interest in clusters is not purely fundamental. We have already mentioned their early technological use in photography and artwork. Cluster research has meanwhile triggered a wide field of further applications. In chemistry, for example, scalability allows to play with the tunable surface to volume ratio which governs reactivity and may thus find key applications for catalysis. In material science, the discovery of fullerenes and nanotubes opened up new ways to design new materials [6] making carbon, and more recently “nano” science, an emerging field *per se*.

Cluster science with its many achievements now belongs to one of the most active fields in physics and chemistry, and offers, in particular through related fields, one of the fastest developing areas in applied as well as in fundamental science. One single and short book on cluster science can certainly not cover all aspects. We therefore confine ourselves to present key cluster properties and tools of investigation in a compact manner. The aim here is to give the reader a basic understanding and a motivation for further detailed readings. To reach this double goal (basics and motivation), we split our book in two major parts. The first half provides the essential concepts. The introductory Chapter 1 gives a first overview of the field. Chapter 2 introduces major experimental concepts, discussing cluster production and tools for the analysis of cluster properties. The subsequent Chapter 3 describes basic theoretical tools used in cluster science. These three first chapters, roughly representing half of the book, lay ground for all further reading. The second part tries to present selected examples superficially covering both, current cluster science and closely related fields. Chapter 4 presents in a compact manner some key properties of free clusters, both static and dynamic. It serves as a first application of the concepts introduced before. Chapter 5 concerns applications of clusters mostly in relation to material science. Finally Chapter 6 covers relations of cluster science to close domains such as astrophysics and biology. In the last two chapters, and to a lesser extent in Chapter 4, the topics to be covered are so vast that an extensive review is impossible in such a short book. We have thus chosen to select illustrative test cases which we discuss in some detail. We believe that such a strategy is more motivating and easier to grasp, though the selection may be somewhat subjective.

1.1

Atoms, Molecules and Bulk

Clusters have this remarkable and unique property to interpolate between individual atoms/molecules and bulk matter. Their size, in particular, can be deliberately chosen, so that this interpolation can be followed step by step if necessary. By being “in between” individuals and bulk, one could naively consider them as simple ag-

gregates of individuals and/or finite pieces of bulk material. It turns out that they are neither the former nor the latter, and possess specific properties of their own. On the other side remain close relations with the extremes (atom/bulk). It is this subtle balance between specificity and connections with other systems that we first want to explore in this section. This provides a first overview of cluster science.

1.1.1

Scales of Matter Down to Atoms

We recall here a few basic scales of matter down to atoms and simple molecules, which in the following will constitute the building blocks of clusters. We focus on distances, energies and times. Figure 1.2 summarizes the following discussion in a compact and schematic manner indicating, in the time-distance plane, typical systems and observables of interest. The reader can also find a list at the beginning of this book summarizing the various units which are commonly used in atomic, molecular, cluster, and laser physics.

In bulk material, there is no clear macroscopic distance scale. We shall thus directly refer to the typical interconstituent distances, which lie in the nanometer and Å range. This also corresponds to the typical bond lengths in molecules. Atoms can be characterized by the typical radius of the electron cloud in the Å range. In the following, we shall thus use typical distances in the range 1 Å to 1 nm, and use as a standard unit Bohr's radius (hydrogen atom "radius") abbreviated as a_0 with $1 a_0 \simeq 0.529 \text{ Å}$.

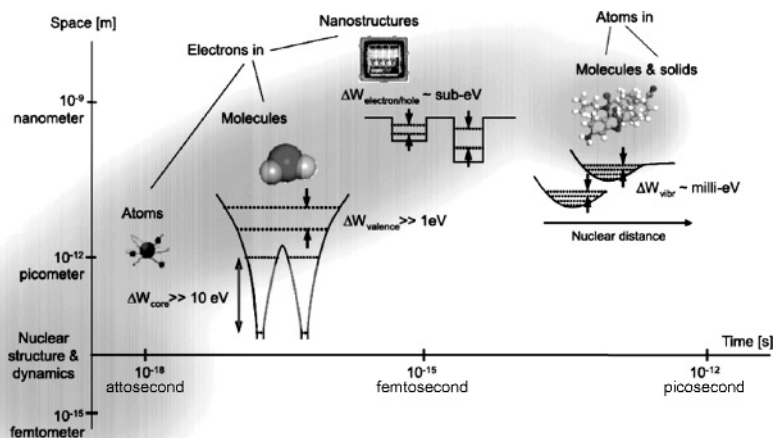


Figure 1.2 Schematic representation of typical time (abscissa) and length (ordinate) scales. We also indicate representative systems and components thereof, and associated energy scales for completeness. Today's investiga-

tions allow to access a wide range of distances and times in electronic systems including clusters, both from an experimental and a theoretical point of view. From [7].

Energies of interest span a much wider range with variations of six orders of magnitude. We shall take as a reference unit the electronvolt ($1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$). It provides an appropriate unit for characterizing the binding of a valence electron (least bound electrons) to the system, often called the ionization potential (IP). The IP is typically a few eV varying, of course, from one system to the other, but within at most a factor of 10. The eV also roughly corresponds to the typical dissociation energy of a molecule or cohesive energy of a solid. Much lower energies, in the meV range, are associated to vibrational motion (atomic vibrations) in bulk and molecules. The meV is the typical energy range of rotational motion in molecules as well. This range of energies, though, is directly connected to atomic masses and nature of bonding. It thus shows larger variations reflecting the large span of atomic masses and electronic binding. On the side of higher energies, the binding of deeply bound electrons in atoms (and thus in molecules and bulk) ranges up to the keV domain. In most low-energy situations, such electrons remain safely bound to their parent nucleus. We shall therefore denote by “ion” the nucleus and the core electrons, to distinguish the latter ones from valence electrons. There however exist high-energy processes where core electrons can be excited, such as irradiation by high intensity laser fields or high-frequency photons (X-rays).

The above range of energies fixes a range of associated time scales on the basis of the energy-time uncertainty relation. The eV is closely related to the femtosecond (10^{-15} s) which appears as the natural time scale of valence electron motion in atoms, molecules and bulk. The meV range in turn is associated to the picosecond domain, characteristics of atomic motion. On the other extreme, keV electrons are typically associated to attoseconds (10^{-18} s). This very short time scale was not accessible until very recently. The advent of new light sources now allows to produce light pulses with durations down to a few tens of attoseconds. Such short pulses suffice to directly excite low lying, deeply bound electrons. In a way similar to energies, accessible time scales today thus span several orders of magnitude in the domain of interest of cluster science.

1.1.2

More on Time Scales

Figure 1.2 provides a very general overview of typical time scales of cluster properties, cluster dynamics, and excitation mechanisms. Clusters are built of atoms and thus naturally cover the various time scales associated both to individual atoms and assemblies thereof. Furthermore, as already mentioned in Figure 1.1, the possible contact with an environment (surface, matrix, solvent, ...) may introduce more time scales to the picture. Finally, it is interesting to detail a bit the typical times scales associated to lasers, which, as we shall see at several places throughout the book, constitute a basic tool of investigation of cluster properties. We thus present in Figure 1.3 a schematic but more detailed overview of times related to electronic and ionic motion, lifetimes for relaxation processes, and laser characteristics. Numbers are given in the case of metal clusters because specifying the cluster type allows to be more specific on time scales. Changing the nature of the cluster would

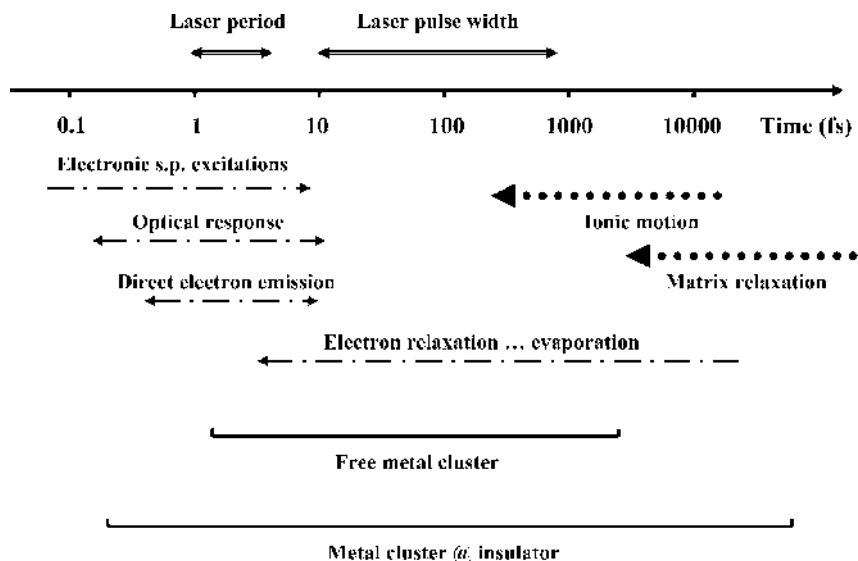


Figure 1.3 Typical time scales for the various dynamical processes in a cluster, here for the example of free sodium clusters, and clusters in contact with an inert, insulating substrate.

probably alter the detailed numbers, but not the qualitative relations between the various time scales. The fastest cluster time scales are related to electronic motion. Core electrons have cycle times of 0.1 fs and faster (depending on the element). The Mie plasmon period, see Eq. (2.6), most important for metal clusters, is on the order of femtosecond, see Section 2.2.3. In the same range, but with wider span from subfemtosecond to several femtosecond, are cycle times for other single-particle excitations and direct electron escape, that is single-particle excitation directly into the continuum. Somewhat slower is the plasmon decay due to Landau damping, a mechanism which is well known from plasma physics [8], see also the discussion of Figure 4.7. The most widely varying electronic times are related to damping from electron–electron collisions and thermal electron evaporation. Both strongly depend on the internal excitation energy of the cluster. They are long for low and moderate excitations, as indicated in Figure 1.3. Ionic motion spans a wide range of slow time scales. Vibrations, which may be measured by Raman scattering, typically in the meV regime, have cycle times of order 100 fs to 1 ps. Strong laser irradiation can lead to Coulomb explosion of the cluster where ionic motion becomes somewhat faster. Besides the ionization effects, the thermal relaxation between electrons and ions takes much longer, up to the nanosecond range. Ionic relaxation processes are even slower, for example thermal emission of a monomer can easily last μ s. As indicated in Figure 1.3, the pulse duration of optical lasers may be varied over a wide range and extends in principle from fs (even some hundreds of attoseconds) to ps or even ns.

The above discussion reveals that cluster dynamics comprises a huge span of time scales which are extremely hard to treat at the same level of refinement. A

most basic and widely used approximation is to treat nuclei, or ionic cores, respectively, as classical particles while the electrons remain quantum mechanical particles. We will come back to that aspect in more detail in Chapter 3.

1.1.3

Binding in Atoms, Molecules and Bulk

Atoms, molecules and solids are all made from the same constituents, namely nuclei and electrons. And yet, matter provides a great variety of properties. The reason is that electron binding shows up in very different manners, depending on the elements involved and the composition thereof. In this section, we will briefly discuss the different mechanisms of electron binding.

1.1.3.1 Atoms

Atoms consist, as is well known, of a nucleus at the center surrounded by a cloud of electrons. They interact with each other and with the central nucleus mainly through Coulomb interaction. The immense attraction provided by the positively charged nucleus suffices to counterweight the repulsion between electrons themselves. The basic theory is known as the central field approach [9]. Each electron independently moves in a common mean field, the central field, which consists of the Coulomb field of the central nucleus augmented by the screening field from the other electrons. The predominantly spherical shape of the central field leads to a pronounced bunching of the single-electron spectrum into shells, each one containing a couple of degenerated states. The Pauli principle determines the filling of these shells with increasing electron number. This simple shell model picture provides the key to a first sorting of atomic structure. Particularly important are shell closures which arise for those electron numbers where the occupied shells are all exactly filled. In the Mendeleev classification, this situation corresponds to the rare gas atoms He, Ne, Ar, Kr, Xe, and Rn. These are particularly inert in chemical reactions. In general, the amount of shell filling determines the chemical properties. Extreme cases are those next to shell closure. The alkalines Li, Na, K, Rb, Cs, and Fr, have one single electron on top of a closed shell and are considered as simple metals. At the other side of shell filling are the halogens F, Cl, Br, I, and At which have an almost complete shell, missing just one electron. Both these groups are particularly reactive. One can go stepwise further, two additional electrons or two missing electrons, and so forth. The properties of some transitional atoms may require to watch not only the shell of least bound electrons but also the next lower shell. This is, for example, the case for the transition metals Cu, Ag, and Au. All in all, the ensemble of these “active” electrons constitute what one usually calls the valence electrons, namely those which determine binding structure and low-energy dynamical properties.

The calculated shell structure of two typical metals is depicted in Figure 1.4. The states are labeled in standard atomic physics notation. The letters denote the orbital angular momentum l with the series s, p, d, f, g, ... corresponding to $l =$



line. Occupied states are indicated by filled circles and unoccupied ones by open circles. Deeply lying states are not shown. All results have been computed by density functional theory (see Section 3.2.4).

Quantitative indicators of the chemical properties of an atom are the binding energies of the lowest unoccupied molecular orbital (LUMO) and of least bound electrons known as highest occupied molecular orbitals (HOMO). The latter energy is directly measurable as the ionization potential (IP), that is the energy which is needed to singly ionize the atom. For example, rare gas atoms are associated with particularly large IP which indicate a high resistance against ionization (and chemical reactions in general). The binding energy of the LUMO is related to the electron

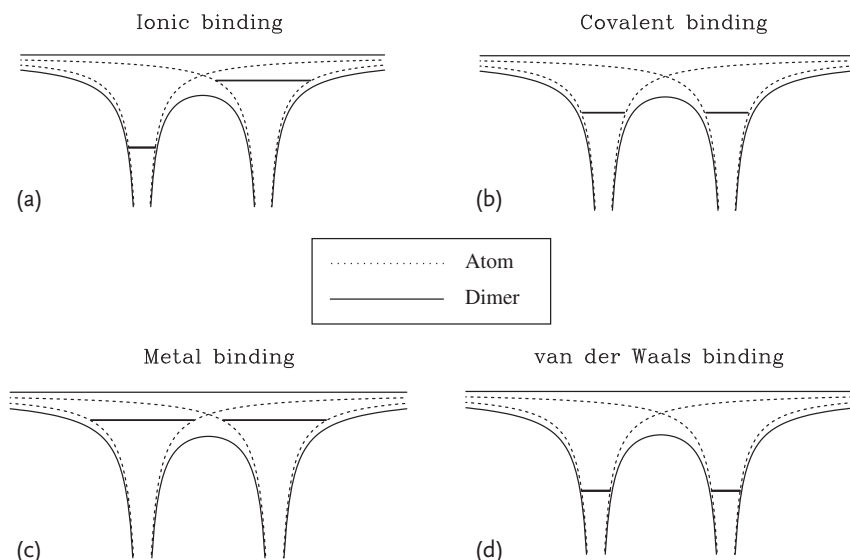


Figure 1.5 Schematic view of potentials and valence levels in dimers with the four basic types of binding as indicated (a–d). The potential seen by an electron in the molecule is

drawn with solid lines, while those originating from single atoms are represented by dashes. The valence levels are indicated by horizontal straight lines.

affinity which determines whether an atom is an electron donor (e.g., alkalines) or acceptor (e.g., halogens).

1.1.3.2 Simple Molecules

Because chemical binding is by nature a low-energy phenomenon, involving at most a few eV energy, the properties of the valence electrons mainly determine how atoms bind together. The Mendeleev classification thus provides a gross map of which atom may possibly bind with another one. We first discuss the dimer molecule which is the simplest conceivable case. The question is how electrons will rearrange themselves between both atoms. The answer is to a large extent related to electronic energies. Strongly bound electrons will tend to remain on their parent atom, while loosely bound ones will have a tendency to leave it. Depending on the partner atom, this leads to different situations, as sketched in Figure 1.5.

In the case of ionic binding (Figure 1.5a), one loosely bound electron is transferred from its parent atom to a host atom offering an empty, more deeply bound level. The transfer is all the easier the smaller the IP of the parent atom and the higher the electron affinity of the host. The electron then predominantly localizes on the host atom: the donor atom becomes positively charged and the host one negatively, leading to a robust binding between the two such formed ions. Typical examples of ionic binding are realized between alkaline (electron donor) and halogen (electron acceptor) atoms such as, for example, in NaCl, NaI, or LiF.

Ionic binding is all the more likely when the energy difference between the valence shells of the two atoms is large. In other cases, electron transfer becomes unfavorable and electrons tend to remain closer to their parent atoms. Binding then stems from charge sharing rather than charge transfer: the valence electrons tend to form a common electronic cloud establishing the binding of the two atoms together. Such a picture traditionally leads to two kinds of binding, depending on the actual strength of binding of each electron on its parent atom. If the valence electrons are weakly bound and if the atoms become sufficiently close to each other, the electronic wave functions become delocalized and fill the space all around the two atoms leading to a so-called metallic bond (Figure 1.5c). Alkalines are the typical elements which establish metallic bonds between each other. Metallic binding is especially simple in alkalines as it involves only one loosely bound electron per atom, hence the notion of “simple” metals to characterize these systems. Metallic binding is also observed in more complicated metals such as, for example, Cu, Ag, Au, or Pt. The shell below the HOMO is taking part in the binding. In this case, it is the d shell energetically close to the valence s shell (see Figure 1.4a). The energetic neighborhood of the d shell adds strong polarization effects with impact on binding and dynamical properties.

When electrons are initially more strongly bound to their parent atom, electrons rather gather in the region of smallest potential energy, that is between the two partner atoms, instead of fully delocalizing themselves. This leads to the so-called covalent bond realized between atoms like C or Si (Figure 1.5b). However, it should be noted that covalent and metallic bonds as described above are idealized situations. There is a smooth transition between these extremes. In addition, it is usually hard to disentangle these two types in small molecules. The distinction becomes better defined in bulk material.

In the extreme case where valence electrons are too deeply bound in the atom, as in rare gas atoms, neither charge transfer nor charge sharing are possible between the two atoms. Electrons remain basically localized to their parent atom. Still, the electronic cloud of each atom is influenced by the partner atom by mutual polarization. This polarization of the electronic clouds has to be understood as a dynamical correlation effect, with constantly fluctuating dipoles, rather than as a mere static polarization. It results in mutual dipole–dipole interactions between the two atoms, which finally establishes a binding of the system. Although the resulting binding is much weaker than the previous ionic, metallic or covalent bonds, it suffices for the binding of rare gas molecules up to possibly large compounds. This type of binding is known as van der Waals (or molecular) binding, in reference to the interactions between two neutral atoms or molecules (Figure 1.5d). It primarily concerns binding between rare gas atoms but will also be useful to describe binding between small molecules such as CO₂, because well-bound molecules as such represent also closed shell situations.

Simple energetic considerations for HOMO and LUMO thus allow one to identify four major types of bonding between atoms, as schematically represented in Figure 1.5. These energetic considerations are directly linked to the degree of localization of the electrons binding the two atoms: the more bound the electrons,

the more localized their wave functions. As already pointed out, there is no clear separation between the various binding mechanisms, but rather a continuous path between them. Still, the sorting in four classes provides useful guidelines for understanding the binding of most molecular systems. As a final remark, one should note that some other “classes” of binding are sometimes introduced such as the separation between van der Waals (for rare gas) and molecular (for molecules), and that between covalent (generic one) and hydrogen binding (specific to covalent binding involving hydrogen atoms). Such fine distinctions do not basically alter our global classification scheme and we shall thus ignore such details in the following.

1.1.3.3 Bulk

We have classified binding on the basis of binding energies of the valence electrons. Although bulk spectra differ by nature from the discrete atomic spectra, it turns out that binding proceeds in a similar way and finally allows a similar classification.

In a solid, the infinity of connected atoms smears discrete energy levels into bands of continuous energy levels. These bands are separated from each other by energy gaps. Band structure is related to the width of the gaps, that of the bands, and where they are located in the energy spectrum. One distinguishes between two extremes, conductors and insulators. In the former ones, the valence bands containing the least occupied electronic states overlaps with the conduction band of empty electronic states so that electrons can switch empty conductance levels at no energetic cost. Such a system is ideally represented by simple metals such as alkaline metals in which, again, electronic wave functions delocalize over the whole system. The other extreme are insulators in which valence and conduction bands are separated from each other by a finite, mostly large, energy gap. There is, of course, a continuous path between these two extremes depending on the size of the energy gap. The transitional cases (small gaps) are known as semiconductors where conductivity can be easily induced by thermal agitation or dedicated doping [10].

Similar as in molecules, bonding in non-metals, that is insulators, covers different forms, essentially reflecting the degree of localization of electrons around their parent atom. In covalent crystals, electrons are semilocalized, gathering along the lines joining atoms together. The typical example of such a binding is the case of diamond. The last two classes of insulators leave electrons fully localized on atomic sites. In van der Waals crystals such as a solid noble gas, electrons basically remain bound to the original atom they were attached to. Just as in simple molecules, they are bound by polarization effects. Finally, ionic crystals are composed of pronounced donor atoms (metals) and pronounced acceptors (for example halogens) in a regular manner. This leads to ionic bonds where the electrons are localized on atomic sites thus producing an interlaced lattice of cations and anions. Typical examples are alkaline-halogen compounds again, such as NaCl, NaF, or LiF.

It is not surprising that the classification of bonding in solid-state physics matches that of molecular physics. And again, one should emphasize that the four types of bonding are idealizations and that reality often resides in between. Clusters pro-

vide the unique opportunity to map a continuous path from atom to bulk as we will discuss in the next section. One of the interesting aspects consists in finding situations where the nature of bonding changes with system size.

1.2

A New State of Matter?

1.2.1

From Atom to Bulk, Small and Large Clusters

By construction, clusters are aggregates of atoms or molecules with arbitrarily scalable repetition of a basic building block and with an intermediate size between atoms and bulk. It corresponds to a chemical formula of the form X_n , where $3 \lesssim n \lesssim 10^{5-7}$ and X stands for an atom or a simple molecule as, for example, H_2O . The actual upper limit in size is given by experimental conditions. The size at which bulk-like behavior appears depends on the considered observable.

One is tempted to argue that clusters are “nothing else” than “big” molecules or “small” pieces of bulk. This is not the whole story. Indeed, clusters can develop properties of their own which differ from molecules and bulk. In order to illustrate that point, let us give a few typical examples. One of the characteristics of clusters is the usually huge number of isomers they possess, even in a small energy window. Already for such a small cluster as Ar_{13} , one can find hundreds of isomers. Metal clusters are also swamped by isomers, because of the softness of their binding. This behavior differs from the molecular case where the number of isomers is usually small, of order a few units at most. This exorbitant isomerism results from the homogeneous constitution of clusters. In other words, the ground-state potential energy surface (or Born–Oppenheimer surface, see Section 3.1.2) is in general very flat, which makes it very hard to figure out the actual ground-state structure of the system. It is therefore very hard to assess which is the most stable structure, in measurements as well as in numerical calculations. Standard quantum chemistry techniques are well adapted to molecules with few isomers, but are here often at a loss. The point is even more dramatic as clusters are usually formed at finite temperature (see Section 2.1.1). In this case, a given cluster covers a huge variety of isomers (thus shapes) in its equilibrium ensemble (see Section 4.2.3).

We now have seen that clusters are not simply large molecules. They are not finite pieces of bulk either. This is, of course, particularly true for small clusters (some tens of atoms) for which the “bulk” limit is obviously far away. But this remains also true for clusters containing several thousands of atoms. There are various features which distinguish a small piece of bulk from bulk itself. A basic difference lies in the electronic level structure which exhibits bands in bulk but discrete levels in finite systems. The path from a fully discrete molecular level scheme to continuous bands is a smooth process, as sketched in Figure 1.6. Figure 1.6b provides a schematic picture of the evolution of electron levels with cluster size, introducing some basic terminology from molecular and solid-state physics.

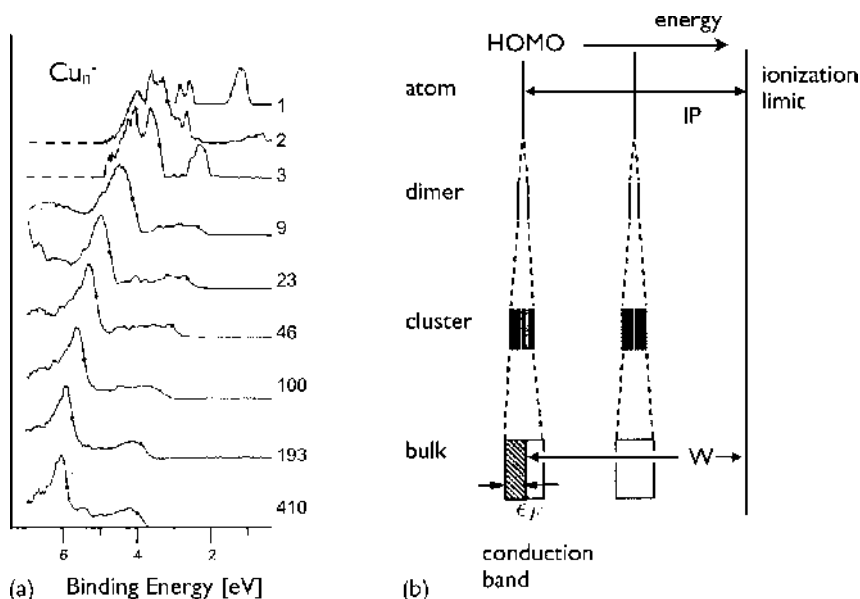


Figure 1.6 (a) Evolution of single-electron spectra with system size for a series of Cu_n^- cluster anions. The spectra are deduced from photoelectron spectroscopy (see Section 2.3.4). The upper atomic level in Cu is the 4s state and the lower one the 3d, see

also Figure 1.4. One can track down how the corresponding bands develop out of the atomic states. The points in the spectra for larger clusters indicate the upper band edge. (b) Schematic view of the development of bulk bands out from atomic levels. After [11].

The ionization potential (IP) becomes the work function (W) in solids. Up to a sign, the IP is the energy of the HOMO. The energy difference between HOMO and LUMO (see Section 1.1.3.1) becomes the “energy gap” in solids. The scheme nicely illustrates how the density of electron states (DOS) quickly increases with increasing system size. The view is complemented by the experimental example in Figure 1.6a showing the spectral distribution of occupied states in a series of anionic Cu_n^- clusters. The measurements [11] were performed using photoelectron spectroscopy which will be discussed in Sections 2.3.4, 3.4.5.2, and 4.3. For small clusters, one can still resolve fine peaks representing single states. The patterns are quickly smoothed for heavier clusters. There are also small, but systematic energy shifts on the way to bulk. Note that energy bands in solids are not necessarily gathering around the atomic levels where they originate from.

A way to quantify finite size effect characteristics of clusters (hence at variance with molecules and bulk) is the surface to volume ratio. Most clusters are indeed large enough that one can distinguish a surface zone, and yet, they remain sufficiently small such that a sizable fraction of the constituents lie on the surface of the system, at variance with bulk. For example, the Ar_{55} cluster has 32 atoms on its surface which leads to a ratio of surface atoms to total is thus $32/55 \sim 0.6$. On the other side, a cubic piece of bulk material of 1 mm^3 volume contains about $(10^{-3}/10^{-10})^3 \sim 10^{21}$ atoms, out of which about $(10^{21})^{2/3} \sim 10^{14}$ lie at the bound-

Table 1.1 Schematic classification of clusters according to the number n of atoms: diameter d for Na clusters (second row), estimate of the ratio of surface to volume atoms f (surface fraction, in third row). After [12].

Observable	Very small clusters	Small clusters	Large clusters
Number of atoms n	$2 \leq n \leq 20$	$20 \leq n \leq 500$	$500 \leq n \leq 10^7$
Diameter d	$d \leq 1 \text{ nm}$	$1 \text{ nm} \leq d \leq 3 \text{ nm}$	$3 \text{ nm} \leq d \leq 100 \text{ nm}$
Surface fraction f	Undefined	$0.9 \gtrsim f \gtrsim 0.5$	$f \leq 0.5$

aries, hence a surface to volume ratio of 10^{-7} . Taking a sample in the micrometer range increases the ratio to about 10^{-6} . It is only for typical cluster sizes in the nanometer range that one recovers ratios of order unity. Size is thus obviously a key parameter in cluster science and a classification in terms of the fraction of surface atoms to volume as illustrated in Table 1.1. Of course, this classification is schematic, and there are no strict boundaries between the various classes of clusters. But the scheme helps to sort the sizes and to specify the terms “small” or “large” clusters used in the following.

Another way to visualize how clusters connect between atoms/molecules and bulk is to plot a given observable as a function of cluster size n . We shall see examples of such trends at several places in the book, see, for example, for magnetic moments in Figure 2.6, for IP in Figure 4.1, or for X-ray yield in Figure 2.8. Figure 1.7 shows the evolution of the cohesive energy per atom for alkaline clusters. The cohesive energy of a cluster with n atoms is composed of the sum of dissociation energies from the atom up to the given n [13]. This definition merges for very large n into the cohesive energy of the corresponding bulk system [10]. The trends towards bulk are best visualized when plotting versus $n^{-1/3}$, which is proportional to the inverse cluster radius. The point at $n^{-1/3} = 0$ shows the bulk value. Average trends of almost any observable $X(n)$ having a finite bulk value X_0 can be expanded as $X(n) \approx X_0 + X_1 n^{-1/3} + X_2 (n^{-1/3})^2 + \dots$ where X_1 stems from planar surface effects, while X_2 is associated with curvature. Quantum shell effects may produce fluctuations about these smooth average trends. The straight lines in the insets indicate the lowest order trend for the cohesive energy $E_n \approx E_{\text{vol}} + E_{\text{surf}} n^{-1/3}$. Neutral clusters follow soon this line with only small fluctuations about it. Cluster cations approach this line only for larger system sizes. The example of Figure 1.7 demonstrates the trends towards bulk for the cohesive energy in alkalines. Actual convergence to bulk depends on the observable, on the material, and on the resolution of a measurement. For example, the experimental resolution of photoelectron spectra place the transition from well-separated discrete electron levels to quasi-continuous bands at about $n \approx 100$ in Cu_n^- , see Figure 1.6. Electronic shell effects, as for example HOMO-LUMO gaps at shell closures, proportionally shrink to $n^{-1/3}$. And yet, their importance has triggered large efforts to resolve them up to the range of $n \approx 3000$, while atomic shell effects have been resolved up to $n \approx 10\,000$ (see Section 4.1.1). The peak frequency of optical response also converges towards its

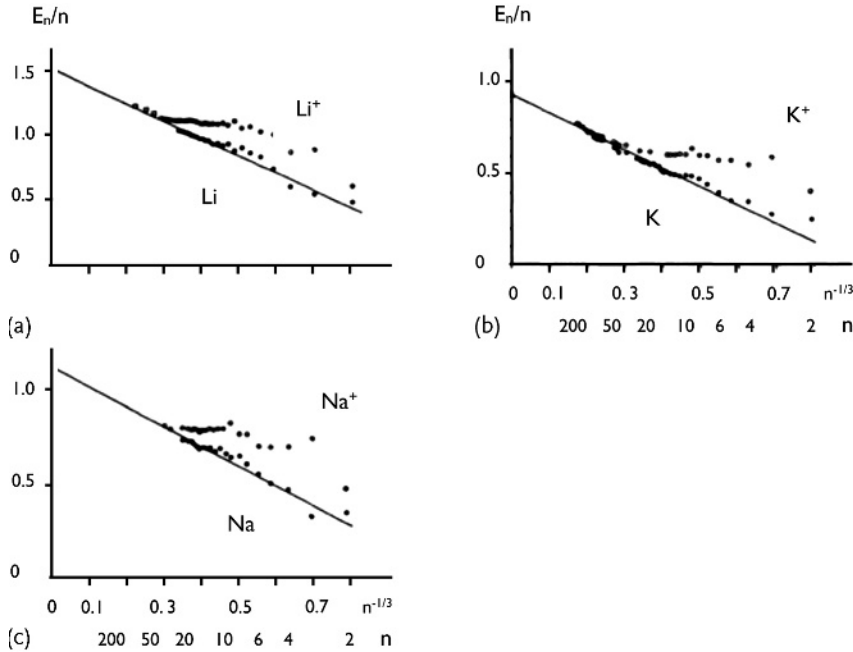


Figure 1.7 Cohesive energy per atom for neutral and cationic clusters of Li (a), K (b), and Na (c) drawn versus $n^{-1/3}$ where n is the number of ions in the cluster. The neutral

clusters are approaching nicely a straight line from which one can read off the volume energy (intercept at $n^{-1/3} = 0$) and surface energy (slope). Adapted from [13].

bulk value with a linear term in $n^{-1/3}$. This means that colors keep drifting with size up to very large clusters in the range above 10 000. Tuning cluster size was, in fact, the mechanism to tune colors in Roman and medieval glass technology, see Figure 1.1.

Altogether, we see that clusters are distinguished from molecules and bulk by a couple of finite size effects: influence of surface and its curvature, atomic shells, and quantum effects from electronic shells. More examples will be found throughout the rest of the book.

1.2.2

Cluster Types

We have seen above that there are four major classes of binding: metallic, covalent, ionic, and van der Waals (or molecular). They exist much similar in molecules and bulk. Accordingly, we identify the same four types of binding in clusters. Figure 1.8 gathers typical examples of these four classes of clusters. The famous C_{60} fullerene (Figure 1.8d) provides a beautiful example of covalent bonding in clusters. The cluster exhibits here a well-defined atomic structure with electrons localized along the various links between the atoms. Covalent binding is typical in clusters made of

atoms belonging to the carbon group (carbon and silicon in particular). The case of Ar_{13} (Figure 1.8c) provides an example of a van der Waals cluster, as it is found for all rare gas clusters. This particular example Ar_{13} corresponds to a closed atomic shell (see Section 4.1.1). The atomic structure of rare gas clusters can be computed rather simply by effective atom–atom potentials [10]. Here, we show the result of a quantum mechanical calculation to also illustrate the electronic structure. Each atom clearly carries its own electron cloud which has little overlap with the electrons from other sites. Binding is dominated by long-range van der Waals forces. An example of ionic binding is the Na_4F_4 cluster (Figure 1.8b). It is an especially simple case associating “ideal” partners (alkaline + halogen) in an almost stoichiometric manner. Four electrons move from Na to F. This yields four Na^+ cations without valence electrons and four F^- anions with rather well-localized electron charge. The binding is dominated here by the Coulomb interaction between positive and negative charges. It is worth noting that a regular structure already appears in such a small cluster. Finally, metallic bonding is illustrated on the example of Na_8 (Figure 1.8a). The electronic density extends more or less smoothly over the entire system. It is typical for metals that the valence electrons belong to the system as a whole and become independent from single ions. This makes them the ideal testing ground for electronic shell effects, see Section 4.1.1 for magic numbers, and Section 4.1.2 for deformation driven by the electron cloud. Note that the figure is drawn using the same scale for all four clusters. This gives an impression of the relative sizes. The binding in rare gas clusters is particularly weak, leading to soft and extended clusters. The opposite situation of very compact binding is found in ionic clusters as here the case of Na_4F_4 . Covalent binding is still rather compact (note that the C_{60} embraces more atoms than the other examples in Figure 1.8). Metallic binding tends to be slightly softer.

A summary of the four classes of bonding and some consequences thereof is presented in Table 1.2. The least bound clusters are van der Waals (or molecular) clusters. They can be considered as a collection of weakly interacting atoms. On the contrary, the strongest binding is usually attained in ionic clusters. Covalent clusters may bind almost as strongly. Metal clusters are generally a softer bond than covalent ones, thus constituting an intermediate class between the almost unbound van der Waals clusters and the tightly bound ionic (or covalent) clusters. A word of caution is necessary here. Such sorting schemes rely on idealizations and reality often falls in between the categories. One can even find examples where the type of binding depends on the cluster size, as for example in Hg_n^- . Indeed photoelectron spectra measurements indicate that these clusters are rather covalent for $n \leq 13$, then that they exhibit semiconductor-like densities of states for intermediate sizes, and a closure of the band gap for $n \geq 300$ and thus a metallic behavior.

Before concluding this section, it is interesting to make a remark on scales. Whatever the bonding type, binding energies lie in the eV range and elementary bond lengths take values in the few a_0 range, which perfectly matches our initial energy and distance scale (see Section 1.1.1). Complementary to this is that it is interesting to also evaluate a typical force in a cluster. This allows to compare with external fields probing the system (laser or colliding projectile) and so, to estimate regimes

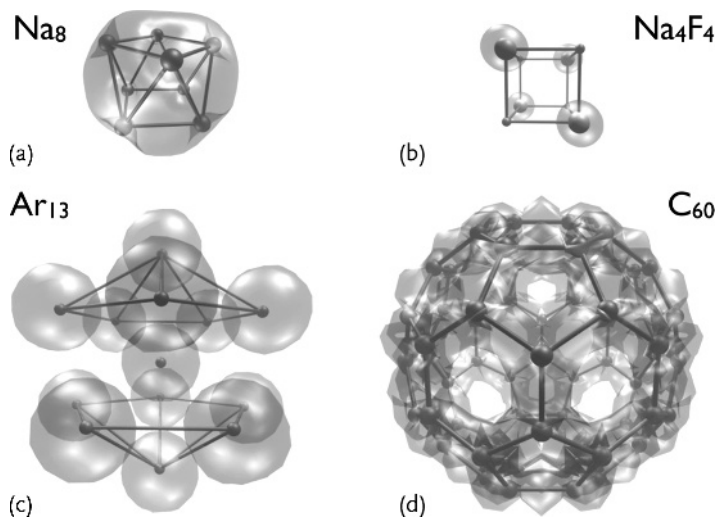


Figure 1.8 Examples of the four cluster types according to binding. Ions are indicated by small balls and the electron cloud by transparent gray. Nearest atoms are connected by bars to better visualize the atomic structure. All four clusters are plotted with the same scale, allowing a direct comparison of sizes. Metallic binding for the example Na_8 (a). Ionic binding for the example Na_4F_4 , where Na atoms are denoted by small spheres and F atoms by larger spheres (b). Van der Waals binding for the example Ar_{13} cluster computed with effective atom–atom potentials (c). Covalent binding for the example C_{60} (d).

Table 1.2 Classification of the four types of binding in clusters: examples of clusters (second column), nature (third column) and typical binding energies (last column). After [14].

Type	Examples	Nature of binding	Binding energy
Ionic clusters	$(\text{NaCl})_n$, $\text{Na}_n\text{F}_{n-1}$	Ionic bonds	
		Strong binding	$\sim 2\text{--}4\text{ eV}$
Covalent clusters	C_{60} , S_n	Covalent bonding	
		Strong binding	$\sim 1\text{--}4\text{ eV}$
Metal clusters	Na_n , Al_n , Ag_n	Metallic bond	
		Moderate to strong binding	$\sim 0.5\text{--}3\text{ eV}$
Van der Waals	Rare gas clusters Ar_n , Xe_n	Polarization effects	
		Weak binding	$\lesssim 0.3\text{ eV}$

of cluster dynamics. We take as an example the metal cluster Na_9^+ which exhibits a binding of intermediate strength. It has a radius of about $R \sim 8 a_0$ and charge $q = 1$. The typical electric field at the surface is $E_0 \sim q^2/R^2 \sim 3.4\text{ eV}/a_0$. This corresponds to the field strength of a laser with intensity $I \approx 10^{13\text{--}14}\text{ W/cm}^2$ (see Section 2.2.2). This means that nondestructive analysis of clusters by light must use laser intensities much below this value. In turn, laser intensities of this order

or larger will directly and quickly detach electrons and most probably destroy the cluster.

1.2.3

Cluster Science

1.2.3.1 A New Science

Cluster science is a young field which emerged as an independent scientific domain only a few decades ago. Indeed it has only been since then that one has been able to produce and control free clusters, that is in the gas phase, while embedded clusters have been used in technological applications for much longer. Their proper identification and analysis, again, lived up only recently with the steady improvement of measuring tools as, for example, the scanning tunneling microscope (STM). Still, within a relatively short period of a few decades, cluster science has gathered an impressive amount of insight and has also inspired many other areas of science. There are probably few scientific domains which experienced such a rapid development. This was certainly favored by the many relations of cluster science with other fields such as atomic, molecular physics, and chemistry on the one side, and solid-state physics on the other. They deal with “similar” systems, and yet clusters are different, as we have seen above, which make comparisons interesting and fruitful. As an emerging domain, it also has the spice of interdisciplinarity. Cluster science has gathered scientists with backgrounds from several longer established domains, all bringing their own, specific scientific and technological knowledge, thus creating a marvelous learning environment for all of them.

Cluster science even goes beyond these close related fields, as it also finds many applications in other apparently remote scientific domains such as biology or astrophysics. This is, if needed, another beautiful justification for the interest in studying clusters, even if they may represent key systems in other domains. Looking at those remote fields inspires cluster physics once more, as a complete understanding of clusters, for example, for astrophysical or biological applications, brings up new questions for cluster research.

These few general ideas lay out the guidelines we have tried to follow throughout this book. We develop them a bit further in this last section before attacking more specific aspects in the next chapters.

1.2.3.2 A Quantum Mechanical Playground

Quantum mechanics is crucial for understanding cluster properties as it is in molecular, solid-state physics, or chemistry. In this respect, cluster science might just appear as another playground for quantum mechanics. This would overlook a key aspect, which we already outlined in Section 1.2.1, namely scalability. Clusters are one of the few, if not the sole, system which can interpolate between atom and bulk, and which can thus provide a unique class of systems for understanding how matter is formed of atoms.

As is well known, the quantum many-body problem is very demanding and has known solutions only for rather a few cases. The systems with very few constituents (the helium atom or a few dimer molecules with one or two electrons, ...) allow highly elaborate approaches and can be treated almost exactly. On the other extreme, bulk matter with a lot of symmetries again permits very detailed computations as, for example, for the homogeneous electron gas if the ionic background is simplified to homogeneous jellium. These (almost) exact solutions play an essential role in the many-body problem as benchmarks of the test of approximations and inspiration for the development of further approximations. In between these two extremes, in terms of size and symmetry, one is bound to develop approximate and more or less elaborate theoretical schemes. This holds for molecules as well as for solids. Clusters interpolating between the two extremes allow, in particular, to test modeling continuously at all scales.

There is a further interesting aspect in relation to the quantum many-body problem. Clusters belong to the large class of finite fermionic systems, in which one can include atoms, molecules, quantum dots and nuclei. As we shall see in Section 6.1, there are indeed strong similarities between all these systems which as such are useful to collect. Moreover, they can often be treated with similar approaches and methods. Comparing the performance of these methods in the various fields helps to find out the limitations and to subsequently improve the methods.

1.2.3.3 Interactions with Related Fields

As mentioned above, clusters find applications in many domains of science, in obviously closely related fields as well as in apparently more remote areas. We will address selected examples in Section 5.3 and Chapter 6. Here, we briefly summarize and preview some examples.

Cluster science has direct and “natural” connections with material science. The developing capabilities to manipulate materials at the nanoscale is a typical example. The many principle studies led on embedded or deposited clusters (see, for example, [15]) may for example find direct applications in dedicated shaping of nanodevices, see, for example, [16]. Small Au clusters on surfaces serve as efficient catalysts, metal clusters are considered as nanojunctions in electrical circuitry, and the coupling to light is exploited in producing an enhanced photocurrent by depositing Au clusters on a semiconductor surface.

There are also many applications of clusters science in biology and medicine (see Section 6.4). One typical example is the use of coated metal clusters in treatment and medical imaging, thanks to their optical properties and their remarkable ability to easily couple to an external electromagnetic field.

More surprising are astrophysical applications. The understanding of the composition of the interstellar medium is a key issue in astrophysics, for example, for the transmission of electromagnetic signals emitted by stars. It turns out that the interstellar medium contains a sizable amount of carbon structures, known as polycyclic aromatic hydrocarbon (PAH) ones which might play a key role in light

absorption. The study of this class of clusters has become an important issue in astrophysics over the past few years, see Section 6.2.

Clusters are also of great importance in climate issues since aerosol particles, that is submicron particles, turn to play a key role in the formation of clouds, and also in the modification of their reflecting properties. Therefore a deeper understanding of the formation and growth of such nm objects will certainly help to better predict the radiative balance of the Earth's atmosphere. Key aspects will be addressed in Section 6.3.

Looking back at these examples demonstrates, again, the double use of cluster physics. On the one hand, there is a great variety of clusters important for applications. On the other hand, clusters are interesting as objects *per se* and provide ample testing ground for basic physics.