# HANDBOOK OF NANOPHYSICS Clusters and Fullerenes



# Edited by Klaus D. Sattler





#### Handbook of Nanophysics

Handbook of Nanophysics: Principles and Methods Handbook of Nanophysics: Clusters and Fullerenes Handbook of Nanophysics: Nanoparticles and Quantum Dots Handbook of Nanophysics: Nanotubes and Nanowires Handbook of Nanophysics: Functional Nanomaterials Handbook of Nanophysics: Nanoelectronics and Nanophotonics Handbook of Nanophysics: Nanomedicine and Nanorobotics



# **Clusters and Fullerenes**

Edited by Klaus D. Sattler



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# Preface

The *Handbook of Nanophysics* is the first comprehensive reference to consider both fundamental and applied aspects of nanophysics. As a unique feature of this work, we requested contributions to be submitted in a tutorial style, which means that state-of-the-art scientific content is enriched with fundamental equations and illustrations in order to facilitate wider access to the material. In this way, the handbook should be of value to a broad readership, from scientifically interested general readers to students and professionals in materials science, solid-state physics, electrical engineering, mechanical engineering, computer science, chemistry, pharmaceutical science, biotechnology, molecular biology, biomedicine, metallurgy, and environmental engineering.

#### What Is Nanophysics?

Modern physical methods whose fundamentals are developed in physics laboratories have become critically important in nanoscience. Nanophysics brings together multiple disciplines, using theoretical and experimental methods to determine the physical properties of materials in the nanoscale size range (measured by millionths of a millimeter). Interesting properties include the structural, electronic, optical, and thermal behavior of nanomaterials; electrical and thermal conductivity; the forces between nanoscale objects; and the transition between classical and quantum behavior. Nanophysics has now become an independent branch of physics, simultaneously expanding into many new areas and playing a vital role in fields that were once the domain of engineering, chemical, or life sciences.

This handbook was initiated based on the idea that breakthroughs in nanotechnology require a firm grounding in the principles of nanophysics. It is intended to fulfill a dual purpose. On the one hand, it is designed to give an introduction to established fundamentals in the field of nanophysics. On the other hand, it leads the reader to the most significant recent developments in research. It provides a broad and in-depth coverage of the physics of nanoscale materials and applications. In each chapter, the aim is to offer a didactic treatment of the physics underlying the applications alongside detailed experimental results, rather than focusing on particular applications themselves.

The handbook also encourages communication across borders, aiming to connect scientists with disparate interests to begin interdisciplinary projects and incorporate the theory and methodology of other fields into their work. It is intended for readers from diverse backgrounds, from math and physics to chemistry, biology, and engineering.

The introduction to each chapter should be comprehensible to general readers. However, further reading may require familiarity with basic classical, atomic, and quantum physics. For students, there is no getting around the mathematical background necessary to learn nanophysics. You should know calculus, how to solve ordinary and partial differential equations, and have some exposure to matrices/linear algebra, complex variables, and vectors.

#### **External Review**

All chapters were extensively peer reviewed by senior scientists working in nanophysics and related areas of nanoscience. Specialists reviewed the scientific content and nonspecialists ensured that the contributions were at an appropriate technical level. For example, a physicist may have been asked to review a chapter on a biological application and a biochemist to review one on nanoelectronics.

#### Organization

The Handbook of Nanophysics consists of seven books. Chapters in the first four books (*Principles and Methods*, *Clusters and Fullerenes*, *Nanoparticles and Quantum Dots*, and *Nanotubes and Nanowires*) describe theory and methods as well as the fundamental physics of nanoscale materials and structures. Although some topics may appear somewhat specialized, they have been included given their potential to lead to better technologies. The last three books (*Functional Nanomaterials*, *Nanoelectronics and Nanophotonics*, and *Nanomedicine and Nanorobotics*) deal with the technological applications of nanophysics. The chapters are written by authors from various fields of nanoscience in order to encourage new ideas for future fundamental research.

After the first book, which covers the general principles of theory and measurements of nanoscale systems, the organization roughly follows the historical development of nanoscience. *Cluster* scientists pioneered the field in the 1980s, followed by extensive work on *fullerenes, nanoparticles*, and *quantum dots* in the 1990s. Research on *nanotubes* and *nanowires* intensified in subsequent years. After much basic research, the interest in applications such as the *functions of nanomaterials* has grown. Many bottom-up and top-down techniques for nanomaterial and nanostructure generation were developed and made possible the development of *nanoelectronics* and *nanophotonics*. In recent years, real applications for *nanomedicine* and *nanorobotics* have been discovered.

# Acknowledgments

Many people have contributed to this book. I would like to thank the authors whose research results and ideas are presented here. I am indebted to them for many fruitful and stimulating discussions. I would also like to thank individuals and publishers who have allowed the reproduction of their figures. For their critical reading, suggestions, and constructive criticism, I thank the referees. Many people have shared their expertise and have commented on the manuscript at various stages. I consider myself very fortunate to have been supported by Luna Han, senior editor of the Taylor & Francis Group, in the setup and progress of this work. I am also grateful to Jessica Vakili, Jill Jurgensen, Joette Lynch, and Glenon Butler for their patience and skill with handling technical issues related to publication. Finally, I would like to thank the many unnamed editorial and production staff members of Taylor & Francis for their expert work.

> Klaus D. Sattler Honolulu, Hawaii

# Editor

Klaus D. Sattler pursued his undergraduate and master's courses at the University of Karlsruhe in Germany. He received his PhD under the guidance of Professors G. Busch and H.C. Siegmann at the Swiss Federal Institute of Technology (ETH) in Zurich, where he was among the first to study spin-polarized photoelectron emission. In 1976, he began a group for atomic cluster research at the University of Konstanz in Germany, where he built the first source for atomic clusters and led his team to pioneering discoveries such as "magic numbers" and "Coulomb explosion." He was at the University of California, Berkeley, for three years as a Heisenberg Fellow, where he initiated the first studies of atomic clusters on surfaces with a scanning tunneling microscope.

Dr. Sattler accepted a position as professor of physics at the University of Hawaii, Honolulu, in 1988. There, he initiated a research group for nanophysics, which, using scanning probe microscopy, obtained the first atomic-scale images of carbon nanotubes directly confirming the graphene network. In 1994, his group produced the first carbon nanocones. He has also studied the formation of polycyclic aromatic hydrocarbons (PAHs) and nanoparticles in hydrocarbon flames in collaboration with ETH Zurich. Other research has involved the nanopatterning of nanoparticle films, charge density waves on rotated graphene sheets, band gap studies of quantum dots, and graphene foldings. His current work focuses on novel nanomaterials and solar photocatalysis with nanoparticles for the purification of water.

Among his many accomplishments, Dr. Sattler was awarded the prestigious Walter Schottky Prize from the German Physical Society in 1983. At the University of Hawaii, he teaches courses in general physics, solid-state physics, and quantum mechanics.

In his private time, he has worked as a musical director at an avant-garde theater in Zurich, composed music for theatrical plays, and conducted several critically acclaimed musicals. He has also studied the philosophy of Vedanta. He loves to play the piano (classical, rock, and jazz) and enjoys spending time at the ocean, and with his family.

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### **1.1 Introduction**

A number of chapters in this handbook refer to, or rest on, the control of nanocluster (NC) size and size distribution, i.e., the first and second moments of the NC population. In fact, the entire, detailed shape of the NC size distribution is often very important. Its effect has actually been used for thousands of years. The colors of ancient or medieval glasses are generally due to the semiconducting or metallic NCs that they contain, and the varying shades of beautiful colors that we marvel at are most often due to the empirical control obtained by glassmakers, via complex heat treatments, over NC sizes and size distributions. Today, these parameters are known to bear critically on such important properties as the optical emission linewidth or the magnetic anisotropy distribution. The obtention of narrow size distributions is also crucial to the fabrication of three-dimensional NC arrays in solar cells, photodetectors, or other photonic devices. Control over these parameters requires that we understand and monitor the physical processes that determine them. Our purpose in this chapter is to summarize the present status in this regard.

In order to predict and control the NC average size and size distributions, we would ideally need (1) a full description of nucleation processes and of growth processes; (2) criteria to avoid overlap of nucleation and growth, since this obviously broadens the size distribution; and (3) a full description of coarsening (mass transport from small particles to their larger counterparts), i.e., of the particle size distribution's time evolution from an arbitrary initial distribution. This ideal situation is almost fully realized in techniques based on colloidal chemistry (e.g., Pileni 2001, 2003, Park et al. 2004, Weiss et al. 2008), which have provided a broad range of metal and semiconductor NCs in solution, in a variety of shapes and sizes and with excellent control over the size distribution (at the 5% level or under). Studies of intrinsic NC properties, and a number of applications, benefit hugely from these techniques. Summarily, liquid-state chemistry is expected to provide more degrees of freedom in the NC synthesis process, and species diffusion does not limit interactions. However, most applications-notably involving inorganic solid matrices-require that the NCs be transferred from a solution to a solid host. This generally poses serious problems related to solubility, to possible reactions of the NC element(s) with host components, to clustering, or to coalescence. In solids, none of the requirements listed above are fully available for several reasons. The initiation of nucleation differs widely depending on the nature of the material in which the NCs are to be grown: e.g., in metals and many semiconductors, it usually depends on quasi-equilibrium thermodynamics and on diffusion, whereas in insulators and in some semiconductors, the primary aggregation process also depends on the charge state properties (i.e., the chemistry) of moving species, including electrons and holes. Growth processes are correspondingly also very different. As a result, except in the simplest cases, multiple mechanisms occur and interfere, a situation that generally leads, as we shall see, to difficulties in predicting how to control NC populations and narrow size distributions.

Our discussion starts with a short review of standard quasiequilibrium thermodynamics nucleation and growth, which provides us with some terms of reference. Although it is by no means ideal for obtaining narrow size distributions, it has the advantage of being predictive in simple cases. The best example is that of the late-stage coarsening process, very well described by a scaling approximation. We then scrutinize nucleation conditions in various cases, since they determine most of an NC's "short and midterm" future. We summarize a generalization of the quasi-equilibrium thermodynamics approach, given by Binder, in terms of coupled rate equations. This provides a useful framework to evaluate conditions for the control of an NC population's evolution. It allows us to discern whether a study of the NC population moments' time and/or temperature evolution, in some of the more common NC nucleation and growth cases, provides a framework to estimate the possibility of obtaining narrow size distributions from different classes of experimental synthesis techniques (near to, or far away from, equilibrium) as they are described elsewhere in this handbook.

Our topic involves many aspects of statistical physics, equilibrium, and nonequilibrium thermodynamics that cannot be covered in this chapter—detailed treatments are given in the references. The aim here is to provide a rather pragmatic guide to experimentalists interested in a critical view of the physics underlying attempts to control the synthesis of NCs.

#### 1.2 Mechanisms of Nanocluster Nucleation and Growth

#### 1.2.1 A Word on Precipitation

As is obvious from their very name, NCs are formed by progressively separating one or more constituents from a solid or a liquid solution or alloy, e.g., by cooling from the melt, modifying the system's pressure, or via the addition of a chemical reagent. The common term for this operation is "precipitation," a concept that covers a large variety of phenomena ranging from atmospheric rain droplet formation to solid-state nanoscale aggregation. Over more than a century, a rather general common description of all these occurrences has emerged, based on statistical physics and on the thermodynamics of phase transformation. Of course, there are limitations to the information derived from this description. From a theoretical viewpoint, precipitation is a highly nonlinear phenomenon, hence quite complex to formulate. Experimentally, material properties (e.g., rain versus second-phase nanoclustering) will obviously affect the behavior at some level of detail. In all instances, a major difficulty remains in discerning the initial nucleation stage, which is found to be crucial for control over precipitation. We will go into this later. First, we briefly review the more common physicochemical mechanisms of NC nucleation and growth, emphasizing those features that affect NC sizes and size distributions.

The essential driving force for precipitation of a new phase (e.g., ice from cooled water second-phase extraction from a liquid or a solid solution, etc.) is the lowering of the potential energy of a group of atoms (or molecules) when they bond together. Two rather different stages occur: nucleation and growth. Nucleation involves the formation of small clusters—it depends on an energy instability in the parent state, where lowering the temperature provides a driving force toward equilibrium, and this driving force increases as the temperature is *reduced*. On the other hand, in order to cluster atoms must meet, so diffusion is essential, and diffusion increases at *increasing* temperatures. We recognize here that thermodynamics determines whether nucleation is possible (tending to minimize the system's free energy), whereas kinetics determine the nucleation rate. The two have opposite temperature dependences, so their multiplication leads to a maximum in the nuclei density temperature dependence. There is also, as we will see shortly, a condition for the formed clusters to be stable. If it is satisfied, growth of these clusters is diffusion controlled (i.e., increases with temperature). The total rate of NC formation is then the product of the nucleation rate and the growth rate. Let us now briefly quantify this picture.

#### **1.2.2 Some Basic Thermodynamics**

Quench the simplest binary system A–B (Figure 1.1, upper part): it will end up in a metastable state below a critical temperature,  $T_c$  (Porter and Easterling 1981, Binder and Fratzl 2001, Wagner et al. 2001). The locus of the  $T_c$ 's for different compositions (coexistence line) defines a phase boundary. The evolution of a metastable system tends to minimize the Gibbs free energy,  $\Delta G = \Delta H - T\Delta S$ , where  $\Delta H$  is the enthalpy,  $\Delta S$  is the entropy, and T is the temperature. For an NC, the competition between



**FIGURE 1.1** Upper: Schematic binary A–B alloy phase diagram, showing the coexistence line and the spinodal line. The region in which unmixing—hence homogeneous nucleation—occurs lies between these two lines. The region below the spinodal line is the unstable decomposition region, where spinodal decomposition (rather than nucleation) occurs. Lower: The free energy's composition dependence for the same system at two different temperatures (see text).

the formation enthalpy  $\Delta H_{\rm f}^0$  (which is determined by the atomic interactions, hence size-dependent for small sizes) and the entropy term (also size-dependent) in the Gibbs free energy leads to a temperature (typically  $T_c = \Delta H_f^0 / 2R$ , where R is the perfect gas constant) below which B-rich domains may form. Quenching to lower temperatures, two possibilities occur depending on the composition- and temperature-dependent free energy of the system. The latter varies as shown for two temperatures in Figure 1.1 (lower part)-the locus of all the free energy curves' inflexion points is the so-called spinodal curve. Free energy fluctuations exist even at thermodynamic equilibrium. In both the metastable and unstable part of the phase diagram, some of these fluctuations can diverge and start growing. As seen by inspection of Figure 1.1 (lower), they have very different effects depending on the region of the phase diagram we consider. In the area under the spinodal (where the second derivative of the free energy is negative), any change in composition or temperature leads to an instability (there is no energy barrier and no phase transition at the spinodal line). If there is sufficient atomic mobility, the enhanced affinity of B for B, rather than for A, tends to form a solution with regions locally and randomly richer in B than in A. If kinetic blocking occurs (i.e., low temperatures freeze atomic movements in a region where typically  $T < 0.1T_c$ ), diffusion constants are very low and separation is limited. Theoretical treatments describing how concentration fluctuations, particularly in the spinodal decomposition regime, can lead to nucleation and growth are summarized elsewhere (Binder and Fratzl 2001, Ratke and vorhees 2002). For an excellent introduction to relevant phase transition theories, see Binder (2001).

Outside the spinodal region, between the spinodal and coexistence lines, the second derivative of the free energy is positive, so that the system gains energy if a true second-phase nucleates (*with an energy barrier*!) and grows. This is the metastable region, in which unmixing occurs, producing locally organized precipitates, i.e., NCs. NCs generally grow in the low solute concentration/volume fraction part of the phase diagram, where unmixing occurs by metastable decomposition. Clusters form because of solute species mobility and chemical affinity (bond energies); monomers eventually bond to each other and form small aggregates that can grow or dissolve depending on their free energy. Once the NCs have reached a critical size (see below), the thermodynamic driving force induces further growth by capture of surrounding monomers, and later at the expense of surrounding precipitates (coarsening).

Microscopically, the very first stage of phase separation is described by (1) near-neighbor bond energies and (2) differing energy barriers for B and A atomic jumps as they diffuse and interact. These parameters determine the crucial macroscopic quantities—the diffusion coefficients and the solubility. As the corresponding cluster grows from 2, 3,... to *n* atoms, its energy changes relative to the surrounding solution, modifying its stability and internal and interface structure. The thermodynamics of binary systems provides a rather good initial approach (experimentally verified in many simple metallic systems) to the origin and main parameters determining the unmixing phase evolution that leads to NC formation in solids as well as liquids or on surfaces.

Whereas the phase diagram is obtained from studies of bulk solids, surface effects must be taken into account when NCs are involved. This leads to changes in the position of the boundaries in the unmixing diagram of Figure 1.1. Microscopically, this is due to the fact that the NC (or, more generally the second-phase domain) exchanges atoms with the primary phase through the interface, which—the NC being small—is curved and comprises a large fraction of NC atoms. The exchange rates depend on the curvature, so that the equilibrium concentration at any point in the interface vicinity also depends on the local curvature (Figure 1.2). Chemical and structural equilibrium conditions lead to the so-called Gibbs– Thomson relation, relating the concentration of B in the vicinity of a planar interface to that around a single NC of radius *R*:

$$c_{\rm G-T}(R) = c_{\infty} \exp\left\{\frac{R_{\rm c}}{R}\right\}$$

where  $c_{\infty}$  is the impurity equilibrium concentration at a flat interface, the "capillary length"  $R_c = 2\beta V \sigma$  depends on the atomic volume *V* and the surface tension  $\sigma$ , and  $\beta = 1/kT$ . The smaller the NC, the higher the equilibrium concentration at the NC surface. This will therefore shift the phase boundary upward in the unmixing diagram. These effects are important in the 1-10 nm size range. The Gibbs-Thomson relation has a major effect on the entire NC population: it shows that when in thermodynamical equilibrium with their embedding medium, NCs of different sizes will undergo correlated evolution. Due to the concentration gradient, the smaller ones tend to dissolve and the larger ones grow correspondingly. This process, known as Ostwald ripening, is rather widespread (Ratke and Vorhees 2002). It is, in fact, the only feature of the NC population evolution that has been modeled analytically to a reasonable approximation (based on scaling, see below). It is also the only one that is predictive as regards changes in the average NC size and



**FIGURE 1.2** Schematic view of the solute concentration field in the host surrounding an NC with radius *R* and composition  $c_R$ , when in the unmixing regime. The NC is first shown in the initial, nucleation stage, then during growth, and lastly in its final, equilibrium state. The quantity  $c_s$  is the equilibrium concentration of the solute B in the host A. In the unstable spinodal regime, the progressively increasing concentration fluctuation amplitudes (with a characteristic wavelength) would ultimately—above a critical concentration—also lead to a precipitate structure. The long-term structures in both cases are essentially indistinguishable.

population, and which predicts a well-defined long-term size distribution.

A word on chemistry. As noted above, colloidal solution-based synthesis has met with huge success in those cases where the NCs produced may be manipulated and introduced into other media. Because the reacting system is liquid, it favors control over the way reagents are introduced as well as offers considerable versatility in exploring the influence of the environment. Chemical reagents are an excellent way to separate nucleation and growth (this approach is also used in glasses). Standard thermodynamics are at work here, and diffusion often plays a minor role as compared to chemical reaction rates. A popular analysis of the process is that of LaMer (LaMer and Dinegar 1950), often quoted by liquid solution chemists. It is a phenomenological description of the conditions required for obtaining narrow size distributions using a flash nucleation scheme-i.e., separating nucleation and growth. It has met with renewed interest because of the exciting properties of metallic and semiconducting NCs grown in solution. Transition probabilities are connected via the detailed balance condition, the free energies of the states involved in the transition are used, and the mass action law describes the chemical kinetics (implying proximity to thermodynamic equilibrium). This is essentially identical to the nucleation and growth model described below, with different notations.

#### 1.2.3 Kinetics and Nucleation

NC nucleation is generally by no means an irreversible process smoothly evolving from a diatom to a several hundred- or thousand-fold configuration. Subtle quasi-equilibrium thermodynamics nucleation theories (Cahn and Hilliard 1958, 1959, Cook 1970, Binder and Fratzl 2001, Wagner et al. 2001) provide an adequate description of how concentration fluctuations lead to incipient nucleation—as long as atoms are free to move. Hence the importance of kinetics combined with thermodynamics (Philibert 1991). This feature cannot be overestimated: the very first steps of NC nucleation, their composition and structure at this early stage, are crucial to their evolution, since they determine the NC free energy (i.e., stability) and reactivity with their surroundings.

In order to obtain, after growth, as narrow a size distribution as possible, the initial NC population size distribution should itself be narrow—ideally, all nuclei should be formed simultaneously. This obviously depends on the nucleation speed, hence on an adequate combination of fast NC component diffusion, a large NC formation enthalpy, and free energy (the latter determining its stability). The ultimate NC density and average size, as well as the size distribution, all depend on how well this criterion is met. Now the metastable precipitation mechanism described above depends on an energy barrier, so it is relatively slow. As a result, in quasi-equilibrium thermodynamics conditions, a significant fraction of NCs are still undergoing formation as others grow an effect that broadens the NC size distribution significantly. In some cases, such as growth of selected NCs in glasses (Borelli et al. 1987), this is circumvented by a two-stage anneal: first a low-temperature anneal to allow the slow nucleation process to develop, then—once the entire population of nuclei has been formed—a faster high-temperature anneal to induce growth. The efficiency of such procedures is limited by the phase diagram and diffusion properties. The effort to find tricks leading to a narrow, controlled initial NC population is one of the main reasons for developing techniques in which NCs are formed under far-from-thermodynamic equilibrium conditions.

What are the requirements for an NC to be stable? The primary one (notably in metals, many semiconductors, polymers, and liquids) is thermodynamical. In the binary system discussed above, for example, the volume term driving force for phase separation is the difference in B concentration between B-rich and B-poor domains: nucleation requires the existence of a steep concentration gradient. Forming these domains thus also leads to the formation of interfaces, hence to surface energetics terms. These constitute another crucial thermodynamic driving force responsible for the change of equilibrium concentration in an NC's vicinity (Gibbs-Thomson equation). This is schematized in Figure 1.3, which shows that the competition between the negative free energy volume term and the positive free energy surface (interface) term leads to a critical size below which the NC is unstable. There is an energy cost in constructing an interface; hence, above some free energy threshold, the system will tend to minimize the interfacial energy by increasing the NC size.

This greatly simplified presentation of the requirements for nucleation (Porter and Easterling 1981, Wagner et al. 2001) only considers the interplay between the surface and volume free energy terms in a binary system displaying homogeneous nucleation. Complications arise when aiming to synthesize compound NCs in the solid state. Clearly, working in a ternary or multielement phase diagram introduces new degrees of



**FIGURE 1.3** Competition between the negative free energy volume term and the positive free energy surface (interface) term for a coherent spherical precipitate in a host. The negative—energy-gaining—volume free energy is proportional to  $R^3$ . It includes a chemical driving force and an elastic coherence driving force. The surface term, proportional to the surface (or interfacial) energy and to  $R^2$ , is positive. Summing the two terms leads to a critical size  $R_c$  for growth.

freedom, such as the different diffusion coefficients of the individual species in the host or the competition between formation energies and stabilities of all possible compound NCs that may appear in the complex phase diagram, etc. The Gibbs-Thomson relation, for example, is substantially altered, involving diffusion of all alloy components and a competition between the chemical affinities of the components with different solubilities. There may also be strain- or defect-induced diffusion effects such as those observed, e.g., for transition metals in GaN or for chalcogenides in glass (e.g., see Espiau de Lamaestre et al. 2005). Similar or further complications arise when attempting to synthesize so-called core-shell NCs with differing compositions of the core volume and of near-surface layers. This has been very successful via colloidal chemistry or cluster beam deposition, but is far more difficult inside solid-state matrices. As discussed elsewhere in this volume, such structures are of considerable interest in order, e.g., to add a wide-gap semiconductor shell to a narrow-gap semiconductor core for exciton trapping (Hines and Guyot-Sionnest 1996, Peng et al. 1997), passivate semiconducting (Alivisatos 1998), or metallic (Skumryev et al. 2003, Morel et al. 2004) NCs by a surface oxide layer, e.g., to study magnetic exchange bias in NCs, or, by growing bimetallic NCs with different alloy compositions in the core and the shell, or to control the surface plasmon band emission wavelength (Mattei et al. 2009). But their nucleation and growth again require working in a multielement phase diagram that includes the host elements, with major difficulties in controlling NC evolution and size distribution. This is where nonequilibrium techniques become necessary.

Our discussion has largely remained so far within the realm of classical thermodynamics. As we have just indicated, however, other contributions to the energetics of an NC often come into play. These are quite diverse, as shown by two examples to which we return at the end of this chapter. (1) In a liquid or an insulator, the first stages of nucleation-typically involving just a few atoms-are largely a matter of chemistry. For a very small NC (say, well below a few hundred atoms), the free energy is a nonmonotonic function of its size and depends on charge equilibrium in the liquid or solid host. The stability and mobility of reactioninduced ionic charge states are then important factors (possibly overriding, if there are only a few atoms). Also, in the same initial stage, redox effects usually dominate dynamics (reaction paths) and ultimate equilibrium among species. (2) If nucleation occurs in a host containing, say, interface dislocations or artificially introduced surface defects, these act as traps for heterogeneous nucleation. In such cases, surface energetics (including straininduced diffusion) dominate the nucleation process, affecting the predictability and control of the growth process.

#### 1.3 Growth and Coarsening

The first feature of growth according to thermodynamics is the concentration gradient around an NC nucleus (modified by the effect of NC surface curvature, Gibbs–Thomson relation). An isolated nucleus, surrounded by such a concentration gradient, progressively accretes atoms from its surroundings, i.e., growth is diffusion controlled. This should lead to a parabolic growth law  $(R^2 \propto t)$ —a prediction that is rarely verified experimentally, since dilution is never infinite and other processes intervene. These are notably the birth of new nuclei while others grow and precipitate interaction (coarsening). Another important possibility is that growth not be diffusion limited, but interface limited, i.e., determined by the free energy gained by transferring an atom from the host to the NC, leading to a linear growth rate.

The growth law may be deduced in a very general way from a conservation equation for the NC size density distribution. Let f(R, t) be a population of NCs characterized by their size distribution. In size space, as long as there is no creation or destruction of NCs, the conservation of NC number around radius R (at time t) may be written as

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \left(\frac{\mathrm{d}R}{\mathrm{d}t} \cdot f\right)} = 0$$

The term in parentheses is the flux density in size space. Were the rate dR/dt of NC growth known, this continuity equation would predict the size distribution. Unfortunately, this is most often not the case: neither the number density nor the total NC mass are conserved, hence the difficulty in assessing how to control the size distribution.

If we now consider a population of grown NCs, it is clear that the system's total energy is enhanced by the existence of a large interfacial area. The largest relative contribution to the latter being provided by the smallest NCs, the total energy is reduced if the larger NCs grow at the expense of the smaller ones. This is the coarsening (Ostwald ripening) process involving competitive growth. An important, experimentally discovered feature of the process is the possibility of scaling: at sufficiently long times, the entire size distribution remains self-similar when normalized by an appropriate length scale such as the average NC size or the average interparticle distance. This has opened the way to the analytical treatment of Ostwald ripening (see below).

A similar treatment may be performed in the case of a related problem—that of coagulation. This concerns growth by aggregation, in the absence of mass transfer, of clusters whose sizes may be similar or different. This process often occurs in the case of NC diffusion on surfaces and dominates growth processes in polymers (e.g., those that encage metallic or semiconducting NCs).

Both coarsening and coagulation lead to an asymptotic size distribution; time and size scaling holds for both, so that an analytical treatment could be devised for the latter (Smoluchowski 1916) and for the former (Lifshitz and Slyozov 1961, Wagner 1961, commonly referred to as LSW). This was done in the framework of quasi-equilibrium thermodynamics, the evolution being due to a balance between thermodynamic and kinetic growth factors. We discuss these processes now, using the synthetic approach of Binder.

#### 1.4 A General Description of Phase Separation

An extensive, generalized description of the phase separation in a binary mixture was proposed by Binder (Binder 2001, Binder and Fratzl 2001, Wagner et al. 2001). This is a microscopic aggregation model involving attachment and detachment of clusters or monomers, quite analogous to the chemical reaction theory. The main result is an equation describing the cluster size distribution's evolution in size and time space. Both the coagulation and condensation regimes are derived as a limiting behavior from this equation.

Coagulation involves reactions between clusters of any size, occurring, for example, in liquid systems or at relatively high concentrations, as opposed to condensation dealing with aggregation steps between a monomer and a cluster of any size.

In the case of the coagulation regime, the equation reads

$$\frac{\partial n_{l}(t)}{\partial t}\Big|_{\text{coag}} = \frac{1}{2} \int_{l_{c}}^{l} dl' W(l-l',l') \frac{n_{l'}(t)}{n_{l'}^{\text{eq}}} \frac{n_{l-l'}(t)}{n_{l-l'}^{\text{eq}}} - \frac{n_{l}(t)}{n_{l'}^{\text{eq}}} \int_{l_{c}}^{\infty} dl' W(l,l') \frac{n_{l'}(t)}{n_{l'}^{\text{eq}}}$$

where

*W* are size-dependent kinetic factors  $n_l(t)$  is the population of *l*-size clusters at time *t* 

This equation then reduces to that of Smoluchowski (Smoluchowski 1916), except that the latter used a discrete representation.

In the condensation regime, the equation reads

$$\frac{\partial n_l(t)}{\partial t}\Big|_{\text{cond}} = \frac{\partial}{\partial l} \left[ R_l \frac{\partial}{\partial l} n_l(t) - \frac{\partial}{\partial l} \left( \frac{\Delta F_l}{k_{\text{B}} T} \right) R_l n_l(t) \right]$$

where

 $R_l$  are the kinetic factors  $\Delta F_l$  is the free energy of a *l*-size cluster

This equation has the form of a conservation equation

$$\frac{\mathrm{d}n_l(t)}{\mathrm{d}t} + \frac{\mathrm{d}}{\mathrm{d}l}J_l = 0$$

where the cluster current in the size representation consists of two terms

1. A thermodynamically driven drift component that leads the system toward its minimum free energy. This is

$$J_{\rm der} = -\frac{\partial}{\partial l} \left( \frac{\Delta F_l}{k_{\rm B} T} \right) R_l n_l(t)$$

2. A diffusion component describing the contribution of fluctuations to the nucleation and growth process. This contribution is

$$J_{\rm diff} = R_l \frac{\partial}{\partial l} n_l(t)$$

and always tends to broaden the size distribution.

The evolution of the size distribution is thus determined by a highly nonlinear set of coupled differential equations, among which various approximations allow us to identify the main contributions to either coagulation or condensation. For example, in a long-time approximation, the equation describing condensation provides the LSW expression for coarsening (late-stage growth):

$$f_{\rm LSW}(R,t) = n_0 \left(\frac{R_{\rm c0}}{R_{\rm c}}\right)^3 \frac{3^4 2^{-5/3} e}{R_{\rm c}} \left(\frac{R}{R_{\rm c}}\right)^2 \left(\frac{R}{R_{\rm c}} + 3\right)^{-7/3} \left(\frac{3}{2} - \frac{R}{R_{\rm c}}\right)^{-11/3} \\ \times \exp\left(\frac{1}{\frac{2R}{3R_{\rm c}} - 1}\right)$$

with

$$R_{\rm c}(t) = \left( R_{\rm c0}^3 + \frac{4}{9} \frac{2V_m \sigma D}{\left( x_{\rm B}^\beta \right)^2 k_{\rm B} T} t \right)^{1/3}$$

the average radius ( $R_{c0}$  the initial mean radius,  $n_0$  the initial cluster density,  $V_m$  the molar volume of the precipitates,  $\sigma$  the surface tension, D the diffusion constant, and  $x_B^{\beta}$  the fraction of B in the precipitate—usually close to 1). This expression is derived by assuming (see Section 1.4.2) an adequate scaling law for diffusion as well as mass conservation, the validity of the Gibbs–Thompson equation, and a very low cluster density, typically below 0.1 at%.

Binder's derivation is sufficiently general to account for a cluster growth mechanism that includes not only the number of constituent atoms but also, for example, the number of surface atoms or the NC ionic charge (if there is one); it may be extended to clusters including more than one chemical component, i.e., other contributions to their free energy. Unfortunately, due to the nonlinear nature of the problem, finding an analytical path to other than the long-term solution is difficult, hence the use of elaborate simulations (described in the references above). The fact that a general formulation of the nucleation, growth, and coarsening dynamics is obtained remains a significant advantage. In the latter two processes, the thermodynamical term dominates, whereas in the former, the diffusive term plays a crucial role in "igniting" the processes. We briefly review these two limiting cases.

#### 1.4.1 Short-Term Behavior: Nucleation

The equation given above describes homogeneous nucleation, i.e., nucleation initiated only by intrinsic fluctuations of the

system's free energy. Nucleation can also be initiated by external perturbations such as defects or impurities. We have seen that in order to obtain narrow size distributions, control over growth should attempt to carefully separate the nucleation and the growth stages: if all clusters start growing together, the resulting size distribution will be narrower than if new nuclei are continuously generated while older ones are growing.

Note that this rate equation approach is adequate for cluster precipitation in both liquid and solid-state matrices. In the former, it is often referred to as the method of LaMer (LaMer and Dinegar 1950, Park et al. 2007), in which reactants are rapidly introduced in the solvents to induce nucleation. We previously also mentioned the two-stage annealing technique (Borelli et al. 1987) well known to glass makers.

#### 1.4.2 Long-Term Behavior: Scaling

The long-term behavior of a precipitate system is far easier to observe than the nucleation and growth processes. Can we deduce any information from it as concerns the inception and evolution of the system's essential features? As mentioned above, during long-term growth (the coarsening regime), the system's main parameters (e.g., density of clusters and size distribution) are self-similar. One can therefore clearly distinguish the system's time evolution, well described by the time dependence of a typical size, and other normalized topological observables such as the NC spatial and size distributions.

In the long-term LSW size distribution (Lifshitz and Slyozov 1961, Wagner 1961), the mean radius  $R_c$  is the scaling length. When the radius is normalized by  $R_c$ , the size distribution's shape is invariant in time:

$$\tilde{f}(z) = 3^4 2^{-5/3} e z^2 (z+3)^{-7/3} ((3/2) - z)^{-11/3} \exp\left(\frac{1}{(2z/3) - 1}\right)$$

where

$$f_{\rm LSW}(R,t) = n(t) \left[ \frac{1}{R_{\rm c}} \tilde{f} \left( \frac{R}{R_{\rm c}} \right) \right]$$

This is referred to as the asymptotic form of the size distribution. It does contain some information about the system's precipitation physics. An example (Valentin et al. 2001) is shown in Figure 1.4. The entire nuclei population was first synthesized by ion irradiation (analogous to the first stage of the photographic process) and then all nuclei grew simultaneously under a thermal anneal. The conditions of this experiment were very close to LSW approximation conditions, and the resulting late-stage growth size distribution is in excellent agreement with the LSW prediction.

We have seen that the dynamics of  $R_c$  are determined by the diffusion constant, as expected, and also, more interestingly, by the surface tension that dominates coarsening in the LSW model. Note that  $R_c^3 \propto t$  (this is also found in the experiment of



**FIGURE 1.4** Comparison of the LSW distribution with an experiment in which all the nuclei of the very dilute NC population grew together after being simultaneously produced by an ion irradiation, whose effect is analogous to a photographic exposure, see text. (From Valentin, E. et al., *Phys. Rev. Lett.*, 86, 99, 2001.)

Figure 1.4). The influence of the microscopic mechanism is further illustrated by a comparison of the results above with those obtained when cluster condensation is no longer diffusion limited, but is limited by chemical reactions at the NC surface. This change in the microscopic conditions of aggregation leads to a broader size distribution (which still has a tail on the smallersize side, again due to the surface tension mechanism) with a growth law exponent ½ instead of ½.

These examples reveal an influence of microscopic mechanisms on the final size distribution shape and growth exponents. However, although this agreement validates the assumptions regarding the system's long-term evolution, can one work backward and say anything at all about the earlier nucleation and growth mechanisms from the post-coarsening size distribution? Clearly, this is at best very difficult. For example, the long-term LSW solution is obtained whether or not there is an energy barrier for nucleation (spinodal or metastable decomposition). Other cases are worse, as shown by a scrutiny of the observable quantities.

#### 1.4.2.1 Observable 1: Growth Time Exponent

Many experiments deal with the time-dependent growth law. However, its experimental determination is a very difficult task, requiring studies over several decades to obtain sufficient precision. When the experimental determination is based on a single decade, and since measurements are necessarily performed on small precipitate sizes, unequivocal results are unlikely. This difficulty is long known and needs to be carefully resolved in interpreting experiments. Worse still, agreement with a microscopic mechanism is sometimes claimed on the basis of a growth law exponent in contradiction to the observed size distribution shape. This illustrates the fact that a growth exponent is not unequivocally related to a growth mechanism. In fact, theoretical considerations show that there is a degree of universality in this exponent, i.e., it is representative of families of first order phase-separating systems (universality classes) rather than identifying a particular mechanism (Binder 1977).

#### 1.4.2.2 Observable 2: Size Distribution Shape

We have seen, in the case of the LSW distribution, that changes in the shape of the size distribution were related to differences in the aggregation process. This is by no means a general result, as demonstrated by the example of lognormal size distributions. The lognormal distribution function reads

$$f(r) = \frac{1}{r \ln(\sigma) \sqrt{2\pi}} \exp\left(-\frac{\ln^2(r/\mu)}{2 \ln^2(\sigma)}\right)$$

where

 $\boldsymbol{\sigma}$  is the geometric standard deviation

 $\mu$  is the geometric average

Both are dimensionless. Experimental results on NC size distributions after more or less complex, nonequilibrium synthesis techniques often display such shapes, which are usually noted by authors, but not discussed. Could they possibly provide any information on operative mechanisms?

Experiments on clusters provide evidence for lognormal distributions in very different nonequilibrium physical contexts (e.g., laser-, plasma-, or sputter-deposition, physical vapour deposition (PVD), ion implantation, etc.). For clusters synthesized by vacuum evaporation (Granqvist and Buhrman 1976), the observed lognormal shape originated in a single multiplicative stochastic process, i.e., the lognormal distribution of time spent by a nucleus in the region where growth occurred. Lognormal distributions were found in closed systems under coagulation of aerosols or colloids: Friedlander and Wang (1966) checked, by the approximate solution of the coagulation equation, that the asymptotic shape of the size distribution was close to the experimentally found lognormal shape. Note that, as in the case of the LSW distribution, this asymptotic size distribution shape is independent of the initial nucleation conditions. This was demonstrated theoretically (Hidy 1965). In fact, a perusal of the scientific literature shows that lognormal distributions are ubiquitous. For example, a lognormal distribution was even found when measuring the height distribution of British infantry soldiers in the late nineteenth century. It does not, apparently, tell us much about the birth and growth conditions of these young men.

#### 1.4.3 Amount of Information Contained in the Size Distribution Shape

These results illustrate the difficulty in relating the shape of the size distribution to the existence of one or another growth mechanism. In order to estimate whether any information is obtainable at all, we may approach the problem in terms of information theory. The amount of information on a distribution is usually given by its entropy, defined by

$$S = \int f \ln f$$

For example, the entropy of a normalized Gaussian is  $S_g = \ln(\sigma\sqrt{2\pi e})_l$ . The entropy increases with the size distribution width, confirming the intuition that the broader the distribution, the less controlled, or more disordered, the growth process.

This observation may be related to the example of LSW coarsening. We first note that the derivation of LSW is valid for the limit of a very low fraction of NCs. This assumption allows an analytic solution to the problem within a mean field approximation-clusters do not interact with one another, they are only subject to a mean solute concentration that fixes the rate of growth/dissolution with the help of the Gibbs-Thomson relation. If we now increase the volume fraction of NCs, they begin to interfere through dipole and higher order interactions. For a given NC, the rate of growth/dissolution differs depending on whether it is close to a large, or small, NC. The surroundings of a cluster are random because of the intrinsically random nature of nucleation, so the stochastic character of growth is enhanced. We then anticipate, from our initial comments to this section, a broadening of the size distribution. This is indeed the case, as confirmed by experiments and theory (Ardell 1972).

Information theory does help us to understand the significance of the lognormal shape. One of its principles (Jaynes 1957) is that entropy is maximized at equilibrium (the case here, since we consider long-term behavior) under a set of general constraints that can be written as

$$\int C_i(u)f(u)du = \langle C_i \rangle$$

As concerns nucleation and growth, these constraints are, for example, the matter conservation equation

$$\int_{0}^{\infty} ln_{l}(t)dl = cste$$

and the size distribution's evolution equation given above, which is a conservation equation in size space:

$$\frac{\mathrm{d}n_l(t)}{\mathrm{d}t} + \frac{\mathrm{d}}{\mathrm{d}l}J_l = 0$$

These two equations fully determine the system's evolution. Each of them contains a different amount of information on the growth process, and the entropy maximization principle allows determination of the main one. Specifically, it may be shown (Rosen 1984) that the distribution function obtained by using the sole constraint of matter conservation is simply

$$\tilde{n} = e_l^{-\nu}$$

This equation is actually a very close approximation to the largesize tail of the lognormal size distribution in the case of, e.g., Brownian coagulation studied by Rosen, as well as in the case



**FIGURE 1.5** Plot of *u*, the reduced volume's probability density. Crosses are experimental data for semiconductor PbS, PbSe, CdSe, and PbTe nanocrystals grown after sequential implantation of the components into pure silica and long-term annealing in quite different conditions. Despite their differences in preparation, average sizes, and depth distributions, all these data fall on the universal curve corresponding to the maximum entropy distribution,  $e^{-u}$ , determined by the sole constraint of volume conservation. The dashed line is the best fit of experimental data (u > 1) to the reduced lognormal distribution m = 1: it is seen that the latter only deviates from the former when the NC sizes are extremely small. The existence of a lognormal distribution thus provides no information at all on the NC evolution. (From Espiau de Lamaestre and Bernas, H., *Phys. Rev.*, B73, 125317, 2006.)

(Figure 1.5) of NC syntheses in which multiple growth mechanisms combine and interfere (Espiau de Lamaestre and Bernas 2006). It was also shown (Gmachowski 2001) that even the standard deviation of the lognormal distribution is a fairly universal quantity, independent of the growth process.

Whereas the shape after LSW ripening reflected at least partially some aspects due to the initial nanocrystal population and its evolution, the existence of a long-term lognormal size distribution in an NC population reveals that any memory of its evolution mechanisms is lost in a maze of different (possibly interfering) nucleation and growth processes. The lognormal shape of the distribution is simply due to the existence of matter conservation. Its occurrence in a particular process signals that the nucleation and growth are too complex to control, other than by clever empiricism.

# 1.5 Perspectives and Conclusion: How to Narrow Size Distributions?

This analysis leads to several general remarks regarding control over NC synthesis. (1) Conceptually, the procedure that consists in separating nucleation and growth may be viewed as a means to avoid the interference of two distinct processes. (2) The versatility

and theoretical understanding provided by late-stage growth conditions are, unfortunately, less crucial to NC control than the nucleation stage conditions. Long-term size distributions are systematically broader and, as detailed above, are mostly controlled by general constraints such as the growth space dimensionality, matter conservation, and basic thermodynamical (including entropy) contributions. (3) The properties of the late-stage NC ensemble generally lose memory of the system's initial stage, i.e., the nucleation conditions. This emphasizes the radically different origin of the size distributions that are obtained in the two limiting stages, nucleation versus coarsening. For example, using recently developed techniques, one might wish to prepare an artificial nanostructured system with inhomogeneous (local) supersaturation and ordered nucleation centers. The discussion above shows that the long-term coarsening stage of such a system would behave exactly as one in which nucleation centers were initially random-all efforts made to control NC position and size would be lost. (4) Control of the nucleation stage offers the best conditions for size distribution control. As long as we stay in its vicinity, artificial structuring methods that localize (heterogeneous) nucleation or/and early growth (inhomogeneous supersaturation) tend to limit the disorder (entropy) increase during precipitation, leading to narrower size distributions. The price to pay for this is in the limitation of the NCs' average sizes, typically below or around 10 nm. For optical quantum dots this is within the range of the exciton Bohr radii, hence is not a drastic problem.

These considerations justify the broad interest in far-fromequilibrium techniques described elsewhere in this book. They are quite successful experimentally, but theoretical treatments for them are still rudimentary or absent. Here are a few general comments on NC population control in some of these cases.

First, what do we mean by nonequilibrium conditions? Consider our initial phase diagram: once thermodynamical conditions (formation enthalpy, free energies, surface energies, etc.) required for precipitation are fulfilled, the system can relax to an equilibrium state, provided that some atomic mobility is introduced. Mobility can of course be due to temperatures high enough to overcome activation energy barriers. But external sources may have an overriding influence: species mobility may also be due to a nonequilibrium concentration of interstitials and vacancies produced in a crystalline solid by irradiation, to 3D bulk diffusion in glasses, to diffusion on surfaces or in grain boundaries, and to convection in a liquid. Some of these processes involve random, homogeneous, nucleation; others (e.g., nucleation on lattice defects or grain boundaries) involve heterogeneous nucleation. The latter is viewed as disadvantageous when nucleation sites or the resulting precipitate size distribution are uncontrolled. However, techniques have been developed to produce ordered arrays of NCs for applications to magnetism or optics, as discussed elsewhere in this handbook. In such instances, nucleation of small NCs at defects such as surface defects produced by a focused ion beam impact (Bardotti et al. 2002), or by an ordered array of dislocations after surface (interface) strain relaxation (Romanov et al. 1999) or by ordered step formation on a specially chosen crystalline facet (e.g., Weiss et al. 2005) often allow control over the NC density. All these methods are based on trapping by external forces (e.g., the introduction of a dislocation array) rather than on the internal evolution of the system. But since the latter is required in order to nucleate and grow the NCs themselves, successful size and size distribution control (generally via temperature-controlled diffusion) has been, so far, essentially dependent on trial and error. More generally, due to the impact of molecular beam deposition (MBE) methods, the extension of quasi-equilibrium thermodynamics to clustering (mediated by atomic-scale diffusion from a supersaturated solution) on surfaces has been a major area of activity, for which we refer to the literature (e.g., Villain and Pimpinelli 1998). As evidenced by the Stranski-Krastanov or van der Merwe growth modes, the NC surface energetics include large strain or stress contributions due to differing lattice cell parameters. This has a major influence on the kinetics of NC formation when surface diffusion dominates, and requires simulations (e.g., Amar and Family 1995) to predict. As mentioned previously, the surface's detailed structural properties are also crucial to surface diffusion as well as to the trapping efficiency for different elements.

In glasses, NC synthesis is of importance not only for stainedglass window applications, but also for nanophotonics. This field has been repeatedly revisited, and it has become increasingly clear that-just as in liquids-redox chemistry plays a crucial role in both thermodynamical and kinetic effects. Specifically, moving charged species play a crucial role in the clustering process. Their relative stability and interactions (among themselves and with electrons or holes), as well as their chemical affinity for glass matrix components, all determine the nature and stability of the NC to be formed. In other words, NC formation is essentially analogous to the photographic process (Belloni and Mostafavi 1999, Espiau de Lamaestre et al. 2007). This means that, as in photography, it is possible to induce simultaneous nucleation of all incipient clusters (e.g., by irradiation with UV light, electrons, ions, etc.) and then-separately!-induce (and control) growth by a short thermal anneal.

A trick to obtain a rather dense, ordered NC array with a narrow size distribution is the nucleation and growth of NCs in nonreacting "cages" that may be inorganic (e.g., zeolites) or organic (polymers, biological systems, colloidal systems, see Sun et al. 2000). The size of the cage and the corresponding external forces may sometimes limit the amount of accretion to the growing NC. In some cases, this leads to a very narrow size distribution reflecting that of the cages (determined in turn by the chemical processing). However, in other instances such attempts have led to the lognormal-like size distributions described above, a strong indication that control over growth during the process was then mediocre.

Finally, a word on far-from-equilibrium techniques such as plasma deposition of cluster beams and UV, electron, or ion irradiations. In cryogenic plasma or thermal evaporation systems, as well as in techniques combining selective evaporation with incipient aggregation in a He jet, growth largely depends on (1) the mean time that a nucleus (typically a cluster of 2 to several atoms) spends in the region where it can grow and (2) the physical parameters governing the coagulation rate such as the monomer source temperature or plasma gas pressure. We then deal with an open system in which aggregates can be extracted from the growing zone and projected on a substrate on which they might be unstable. Growth on the substrate occurs essentially via coagulation (Smoluchowski, Binder), and if surface diffusion is involved, requires elaborate simulations (Politi et al. 2000). Experimentally, size sorting (via an electric or magnetic field) of charged aggregates allows deposition of NCs with a highly nonequilibrium, narrow size distribution. Depending on the electronic properties of the matrix, UV or electron and Ion beam irradiations may assist in controlling nucleation and growth in different ways. In metals, for instance, electron or, more usually, ion irradiation induces or accelerates species diffusion by producing a supersaturation of vacancies or interstitials. Processes that-at quasi-equilibrium-would occur at high temperatures then are active at temperatures that may be typically 200° lower. Playing on nucleation and growth with the combination of temperature and deposited energy density due to irradiation is a means of "driving" (and enhancing control of) the alloy system in a context where theoretical work relating driven alloys to thermodynamics has progressed (Martin and Bellon 1997, Averback and Bellon 2009). The "photographic process" in insulators mentioned above, or the use of defect creation and control to stabilize NC formation into well-defined arrays, are successfully implemented experimental techniques, but they remain to be systematically included in a predictive approach. If the reader comes away with the impression that each new NC synthesis technique enhances the need for a critical eye (and more theoretical work) on the conditions for size distribution control, we will have reached our purpose.

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2

## Structure and Properties of Hydrogen Clusters

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### 2.1 Introduction

Hydrogen is expected to play an important role in the future as an alternative to the present fuels for the massive production of energy. The first pillar, which still looks far away, will be the production of electricity in nuclear fusion reactors, once the problem of sustaining and controlling the reactions is solved. The second pillar, which looks closer, is the production of electricity by means of hydrogen fuel cells, and its widespread application in cars as an alternative to gasoline. For these reasons, the study of hydrogen becomes an important subject from the technological point of view. The basic aspects of the physics and chemistry of hydrogen are also interesting. Under normal conditions of pressure and temperature, hydrogen is a gas formed by H<sub>2</sub> molecules. The binding energy of the two H atoms in the molecule is strong, 4.8 eV. In this molecule, which is the simplest and more abundant molecule in the universe, the two electrons form a closed shell. The molecule exists in two isomeric forms differing in their nuclear spin configuration. In the para-hydrogen isomer, the nuclear spins of the two nuclei are in an antiparallel configuration, that is, they point in opposite directions, while in the ortho-hydrogen isomer, the two nuclear spins are parallel, that is, they point in the same direction. When the gas condenses, it forms a molecular liquid or a molecular solid in which the H<sub>2</sub> molecules interact weakly by van der Waals forces. The intensity of the H<sub>2</sub>-H<sub>2</sub> interaction is intermediate between the He-He and Ar-Ar interactions. At low temperatures, the parahydrogen isomer, which is the isomer with lower energy, is in its

ground rotational state (J = 0) and thus the molecule behaves as a boson of zero spin.

The condensation of the gas can also be forced by molecular beam techniques allowing the production of clusters formed by a finite number of  $H_2$  molecules. In this chapter, clusters formed by *N* hydrogen molecules will be denoted as  $(H_2)_N$ . These clusters have attracted attention due to their peculiar properties, which arise from the coexistence of the strong intramolecular H–H bonding and weak  $H_2$ – $H_2$  intermolecular forces (Castleman et al. 1998, Alonso 2005). Part of the interest in para-hydrogen comes from the fact that it is considered to be the only natural species in addition to the He atom isotopes, which might exhibit superfluidity (Ginzburg and Sobyanin 1972).

Nuclear fusion reactions have been observed to occur by irradiating a dense molecular beam of large deuterium clusters (deuterium is an isotope of hydrogen with a nucleus formed by a proton and a neutron) with an ultra-fast high-intensity laser (Zweiback et al. 2000). The laser irradiation produces the ionization of the deuterium atoms and leads to a violent Coulombic explosion of the clusters; the nuclear fusion reactions occur in the collisions between the flying deuterium nuclei. Neutrons are produced in these nuclear reactions and tabletop neutron sources have been constructed based on this cluster beam technique. Many investigations of hydrogen clusters have focused on single-charged clusters of the family  $(H_2)_N H_3^+$  with N = 1, 2, ... The majority of the hydrogen clusters in the universe belongs to this family. On the other hand, these clusters are easily handled in the laboratory. In this chapter, a review is provided of
the structure and properties of hydrogen clusters. Topics treated are the experimental production of hydrogen clusters in the laboratory, the structure of neutral and charged clusters, free and confined in cages, phase transitions, Coulombic explosions induced by laser irradiation, clusters on surfaces, and finally the manifestation of quantum effects and its possible relation to superfluidity.

The theoretical treatment of the clusters using state-of-the-art methods is given strong emphasis in this chapter because these methods provide important insights into the structure and energetics of the clusters, but connection to experiment is made in all possible cases. It is expected that the topics selected will give an idea of the wide reach of this field.

#### 2.2 Production of Hydrogen Clusters in Cryogenic Jets

An efficient method to produce hydrogen clusters (Tejeda et al. 2004) consists in the expansion of extremely pure (99.9999%) H<sub>2</sub> gas, originally at a pressure  $P_0$  of 1 bar, through a small hole (called nozzle) of diameter  $D = 35-50\,\mu\text{m}$  into a second chamber at a lower pressure of 0.006 mbar. The first chamber is cooled by a helium refrigerator, which provides a source temperature  $T_0$  of 24–60 K, regulated to within ±1 K. The vapor exiting the hole expands adiabatically into the vacuum, and the density

and temperature of the jet rapidly decrease as the distance z to the orifice increases. The expansion produces an extremely cold molecular jet and small para-H2 clusters are formed by aggregation of the molecules in the jet. The analysis of the abundance of clusters of different sizes has been made applying Raman spectroscopy techniques using an Ar<sup>+</sup> laser. The spectrometer can be focused to different regions of the jet, that is, at different distances z from the expansion orifice. Figure 2.1a shows five Raman spectra measured at different reduced distances  $\xi = z/D$ along the center line of the expanding jet. The reduced distances go from  $\xi = 1$  to  $\xi = 24$ . The measuring time for each spectrum is between 4 and 15 min and it increases with z because the density of the jet is inversely proportional to  $\xi^2$  and varies between  $10^{20}$  and  $10^{16}$  molecules cm<sup>-3</sup>. The large peak at 4161.18 cm<sup>-1</sup> is the Q(0) line of the para-H<sub>2</sub> molecule, characterizing the vibration of the molecule, and the small peak at 4155.25 cm<sup>-1</sup>, marked by an asterisk, is due to the small amount (<1%) of ortho- $H_2$  in the jet. The interaction between the hydrogen molecules in the cluster shifts the Q(0) line of  $(H_2)_N$  clusters to lower wave numbers, and each of the peaks at the left of the para-H<sub>2</sub> monomer line can be assigned to clusters of specific size N. Dimers,  $(H_2)_2$ , can already be identified at  $\xi = 1$ , but not larger clusters. Trimers, tetramers, and pentamers are visible at  $\xi = 3$ . Then, for  $\xi = 5$ , a broad peak appears at  $4158 \text{ cm}^{-1}$ , which was assigned to N = 13. The intensity and the width of this peak suggest the formation



**FIGURE 2.1** Raman spectra of small para- $(H_2)_N$  clusters in a free jet as a function of the reduced distance  $\xi$  and the flow time *t* from the orifice.  $T_i$  is the estimated ambient temperature at each distance  $\xi$ . Source conditions: (a)  $T_0 = 46$  K,  $P_0 = 1$  bar, and  $D = 50 \mu$ m; (b)  $T_0 = 36.5$  K,  $P_0 = 2$  bar, and  $D = 35 \mu$ m. L indicates liquid and S solid. (Reproduced from Tejeda, G. et al., *Phys. Rev. Lett.*, 92, 223401-1, 2004. With permission.)

of a first layer of H<sub>2</sub> molecules and also indicate that completion of that shell makes the cluster highly stable. Sizes corresponding to very stable clusters are usually called magic numbers (Alonso 2005). Measuring the spectrum at larger distances from the nozzle hole gives time for the formation of larger clusters. So, at  $\xi = 24$ , with the distribution approaching a steady state, additional peaks appear around N = 33 and N = 55. A good estimate of the abundance of the (H<sub>2</sub>)<sub>N</sub> clusters relative to the monomers is obtained by dividing the area under each peak by *N*.

Using a lower source temperature and a higher pressure produces much larger clusters, as shown in Figure 2.1b. At  $\xi = 4.3$ , the maximum in the Raman spectrum is shifted to 4151.5 cm<sup>-1</sup>, very close to the line for liquid para-H<sub>2</sub> at 18 K, which is the dashed line in the figure. In addition to this liquid peak (L), at  $\xi = 7.1$ , a new peak (S) appears at 4150 cm<sup>-1</sup>, whose position agrees with the spectrum for the solid para-H<sub>2</sub> at 2 K. The intensity of the solid peak (S) grows at larger distances from the orifice, a feature that indicates that the cluster growth continues. The liquid peak is strongly shifted at large  $\xi$  toward the position of the solid peak. The coexistence of the two peaks suggests that the solid clusters have a significant liquid fraction, most likely located at the cluster surface.

#### 2.3 Atomic Structure and Growth of Neutral Clusters

The depth of the interaction potential between two hydrogen molecules is very small, about 3 meV, but still several times larger than the interaction between two He atoms. Accurate ab initio quantum chemical calculations have been performed for the smallest clusters  $(H_2)_2$ ,  $(H_2)_3$ , and  $(H_2)_4$  using the Möller–Plesset (MP2) and Coupled Cluster (CC) methods (Diep and Johnson 2000, Carmichael et al. 2004). Those methods treat accurately the correlations between the electrons. The dimer,  $(H_2)_2$ , has a T-shaped structure, that is, the axes of the two molecules lie in the same plane and are perpendicular to each other, and the separation between the two mass centers is 6.55 a.u. (the atomic unit of length is equal to 0.529 Å). The T shape optimizes the interaction between the permanent electric quadrupoles of the two molecules. The binding energy  $E_b$  of a cluster  $(H_2)_N$  can be defined as

$$E_{\rm b}(N) = NE({\rm H}_2) - E(({\rm H}_2)_N), \qquad (2.1)$$

where

 $E((H_2)_N)$  is the total energy of the cluster  $E(H_2)$  is the energy of an isolated hydrogen molecule

The energy of the cluster is smaller than the sum of the energies of the *N* separated molecules, and the binding energy measures the stabilization gained by the system when the molecules are brought together to form the cluster. The calculated binding energy of the dimer is between 4 and 5 meV. The potential energy surface of  $(H_2)_2$ , that is, the interaction potential as a function of

the relative orientation of the molecules, shows some anisotropy, but interconversion to some other structural forms is easy. The trimer,  $(H_2)_3$ , is planar and cyclic (with  $C_{3h}$  symmetry), with each pair of molecules slightly offset from the ideal T-shape orientation (Carmichael et al. 2004). The binding energy of the trimer is nearly equal to three times the  $H_2-H_2$  interaction; this means that three-body forces are very small. A structure of the tetramer,  $(H_2)_4$ , that preserves the T-shape arrangements for each pair of adjacent molecules can be formed as a square planar cluster, but this is not the structure of lowest energy. The ground state is a nonplanar, near tetrahedral structure in which the molecules still preserve to a large extent the T-shape arrangements among adjacent molecules (Carmichael et al. 2004). The stabilization gained by the nonplanarity is quite small. The binding energy of the tetramer is more than four times the H<sub>2</sub>-H<sub>2</sub> interaction energy, and this reflects the contribution from quadrupolequadrupole interactions between molecules on opposite corners of the structure.

For larger cluster sizes, the quantum chemical calculations become prohibitive, and only calculations employing less accurate methods have been performed. Carmichael et al. (2004) have used an empirical force field fitted to the ab initio results for the trimer and tetramer. The empirical total potential,  $V = V_{\text{elect}} + V_{6-12}$ , is the sum of a classical electrical interaction energy  $V_{\text{elect}}$  and a site–site term  $V_{6-12}$ . The site–site term is based on having a small number of selected sites distributed within the hydrogen molecule and a Lennard-Jones interaction

$$V_{ij} = \frac{C_{ij}}{r_{ij}^{12}} - \frac{D_{ij}}{r_{ij}^{6}}$$
(2.2)

between every pair of sites *i* and *j* located in different molecules.  $r_{ii}$  represent the distances between sites *i* and *j*, and the site-specific parameters  $C_{ij}$  and  $D_{ij}$  specify the potential. The first term in Equation 2.2 is repulsive and the second term is attractive. This piece collectively represents nonelectrical effects, that is, van der Waals dispersion forces, quantum mechanical exchange (which arises from the antisymmetry of the many-electron wave function), and overlap between the electronic orbitals of different molecules. The electrical interaction energy  $V_{\text{elect}}$  includes the quadrupole-quadrupole permanent moment interaction, plus direct (non-mutual) polarization effects. The polarization effects account for the interaction of the permanent quadrupole on a molecule with the induced dipoles and induced quadrupoles in other molecules. Because of these induction effects, in a cluster of more than two molecules, V<sub>elect</sub> implicitly includes three-body polarization effects. The calculations indicate that an increasing number of isomers with similar energies appear as the cluster size grows. The ground state of  $(H_2)_5$  is a four-sided pyramid, nearly flat tetramer with a molecule overhead.  $(H_2)_6$  is a bipyramid, that is, molecules are placed on both sides of the tetramer. Then, a pentagonal bipyramid is found for  $(H_2)_7$ . For larger clusters up to  $(H_2)_{13}$ , Carmichael et al. noticed the interesting trend that the energy of the ground state structure is close to the energies of many other local minima. The zero point energy reduces further the small binding energy of these clusters.

The observation of magic numbers (Tejeda et al. 2004) motivated a theoretical study of the structures of para-(H<sub>2</sub>)<sub>N</sub> clusters (Martínez et al. 2007) using the density functional theory (DFT) with the local density approximation (LDA) for electronic exchange and correlation effects (Parr and Yang 1989). The calculations are valid at T = 0 K. An intramolecular H-H bond length of 1.38 a.u., close to the experimental value of 1.40 a.u. for the isolated molecule, is obtained independent of the cluster size. In the optimized structure of  $(H_2)_2$  the two molecules are in a perpendicular configuration, a triangular structure is obtained for N = 3 and a bent rhombus for N = 4. Triangular, square, and pentagonal bipyramids are obtained for N = 5, N = 6, and N = 7, respectively. The optimized structures of these small clusters are similar, although not identical to the structures obtained with the ab initio MP2 and CC methods. Larger clusters grow following a pattern of icosahedral growth. The first icosahedron is completed for N = 13, where a central molecule is surrounded by other 12 molecules occupying the vertices of the icosahedron. This structure is characteristic of clusters formed by equal atoms (or molecules) with closed electronic shells, like the inert gases neon or argon (Alonso 2005). Due to this similarity, calculations for larger clusters were restricted to specific growth models. An icosahedron is formed by 20 triangular faces joined by 30 edges and 12 vertices. Molecules can then be added in two different ways to form a second shell. In a first type of decoration, molecules are added on top of edge (E) and vertex (V) positions. These provide a total of 42 sites (30 + 12), and a cluster with 55 molecules is obtained. This is called multilayer icosahedral (MIC) growth. Alternatively, the 12 V sites and the 20 sites at the center of the triangular faces (F sites) can be covered to obtain a cluster with 45 molecules. This second type of decoration is often called face-centered (FC) growth.

The calculated binding energies per molecule indicate that FC structures are more stable than MIC structures in  $(H_2)_N$  clusters from N = 14 up to about N = 27. Between N = 27 and N = 35 (the largest cluster studied), the two structures are almost degenerate, and this trend suggests an imminent transition to MIC structures after N = 35. A similar transition occurs for inert gas clusters, although a bit earlier, for N = 27-28 (Alonso 2005). The quantity

$$\Delta e_{\rm b}(N) = 2e_{\rm b}(N) - \left[e_{\rm b}(N+1) + e_{\rm b}(N-1)\right]$$
(2.3)

gives the relative stability of the  $(H_2)_N$  cluster with respect to clusters with sizes N + 1 and N - 1, and has been plotted in Figure 2.2 for the FC and MIC families. In this equation,  $e_b(N) = E_b(N)/N$  represents the binding energy per molecule of the cluster  $(H_2)_N$ . The peaks of  $\Delta e_b(N)$  indicate the most stable clusters. For *N* larger than 13, the peaks reveal the progressive formation of the second layer. For instance, the FC peak at  $(H_2)_{19}$  corresponds to the decoration of  $(H_2)_{13}$  with a cap of six molecules forming a pentagonal pyramid. One molecule sits on a V site and the other



**FIGURE 2.2** Stability function,  $\Delta e_b(N)$ , defined in Equation 2.3, from density functional calculations for MIC and FC growth models of  $(H_2)_N$  clusters. Peaks denote clusters with enhanced stability. Vertical lines indicate features observed in a Raman spectroscopy experiment. (Reproduced from Martínez, J.I. et al., *Eur. Phys. J. D*, 43, 61, 2007. With permission.)

five molecules sit on the surrounding F sites. This structure is usually known as the double icosahedron. Filling adjacent caps leads to the structures of  $(H_2)_{23}$ ,  $(H_2)_{26}$ , and so on. We notice that  $(H_2)_{32}$  is a stability peak in both the FC and MIC structures. Some of the features of Figure 2.2 appear consistent with the Raman experiments. Large cluster abundance was observed for  $N \approx 13$ , 32, and 55, and as discussed above the DFT calculations provide an interpretation of the first two. The DFT calculations also suggest that a transition from FC to MIC structures occurs soon after  $(H_2)_{35}$ . The observed large abundance of  $(H_2)_{55}$  is then trivially explained by the completion of the second icosahedral MIC shell.

The binding energy of  $(H_2)_2$  obtained by the MP2 and CC methods is  $E_{\rm b} = 4-5$  meV and the LDA calculation gives 16.5 meV. The LDA overestimation of binding energies is well known, but considering the tiny binding energies of the  $(H_2)_N$  clusters, the result can be considered acceptable and it is probably the most one can expect from a simple density functional. All clusters are subject to similar errors, and consequently trends in the binding energy as a function of N are more trustable than the absolute binding energies. Some recent implementations of van der Waals interactions in a DFT framework (Langreth et al. 2005) may improve matters. Zero point effects reduce substantially the binding energies. Accounting for anharmonicity in the zero point energy, a corrected value of  $E_{\rm b} = 2.75 \,\mathrm{meV}$  is obtained for  $(H_2)_2$  in the LDA, and similar reductions affect other clusters. Due to those small binding energies, hydrogen is a molecular gas except at very low temperatures and high pressures. The small binding energies have other important consequences, as we discuss below.

In the quantum chemical calculations mentioned above, including DFT, the intermolecular interactions are evaluated explicitly by a quantum mechanical treatment of the electrons for each configuration of the molecules in the cluster, but the dynamics of the nuclei is classical. Other calculations of the structure of the clusters have been performed in which the bosonic nature of the para-H<sub>2</sub> molecules is explicitly considered (Cuervo and Roy 2006, Guardiola and Navarro 2006, Khairallah et al. 2007). These calculations make use of quantum Monte Carlo (MC) methods and include quantum effects by solving the Schrödinger equation to calculate the wave function for the system of N identical bosonic particles. However, the disadvantage is that the  $H_2-H_2$  interactions are described by an effective two-body potential. In these quantum MC calculations, the H<sub>2</sub> molecules do not have precise positions in the cluster, and, as for any other system of quantum particles, one can only talk about probability distributions for finding the molecules in different regions of space. The quantum MC calculations of the structure at very low temperature of para-H2 clusters having up to about 50 molecules employed the isotropic pairwise  $H_2-H_2$  interactions modeled by Buck et al. (1983) and by Silvera and Goldman (1978). The chemical potential

$$\mu_N = E(N-1) - E(N)$$
 (2.4)

obtained from the ground state total energies of the clusters with N-1 and N molecules, is the energy required to remove a hydrogen molecule from the  $(H_2)_N$  cluster, and gives a sensitive measure of its stability. The calculated  $\mu_N$  shows a clear maximum for N = 13. This feature indicates the special stability of that cluster. The chemical potential shows a less pronounced maximum at N = 19, and Khairallah et al. (2007) also obtained features for clusters with N = 23, 26, 29, and 32. The density of particles reveals that the molecules arrange in shells with a shape close to spherical. The radial thickness of those shells is about 2Å. For clusters with sizes close to N = 13 and N = 50, the density of particles has a large peak near the center of mass of the cluster. This peak indicates that a molecule sits at the center of mass. More precisely, clusters with N between 7 and 16, and also with N between 43 and 50 have a molecule at the center, as indicated in Figure 2.3 (data for N larger than 50 was not reported). In contrast, for cluster sizes between N = 17 and N = 42, the molecules form two concentric spherical shells around an empty center. The radii of the shells and their population increase with increasing cluster size.

A comparison with the density functional results is not a simple task because of the intrinsic delocalization of the molecules in the quantum MC calculations. Nevertheless, similarities between the results of both methods can be established and are now discussed.  $(H_2)_{13}$  is the best example. In the DFT calculations, this cluster has a central molecule surrounded by 12 other molecules at equal distances from the center, forming a shell, in agreement with the quantum MC result. DFT clusters with sizes near N = 13 also have a molecule at the center, like the quantum MC clusters (see Figure 2.3). Near N = 19, the DFT calculations



**FIGURE 2.3** The number of molecules in each shell as a function of the size of the cluster obtained in quantum Monte Carlo calculations. Horizontal lines correspond to 1 and 12 molecules. (Reproduced from Guardiola, R. and Navarro, J., *Phys. Rev. A*, 74, 025201-1, 2006. With permission.)

predict structures with no central molecule, just like quantum MC. For instance, for N = 19, the DFT structure is the double icosahedron, a structure having an inner shell formed by two molecules. Near N = 55, the expected DFT structures are related to the icosahedron formed by a central molecule surrounded by two shells. The overall structural features in this size region are the same obtained in the quantum MC calculations, as shown in Figure 2.3. In summary, interesting similarities exist between the DFT and quantum MC structures. The similarities refer to the presence (of absence) of a molecule at the center of the cluster and to the number of shells surrounding that molecule (or empty center site), but these should not be overstated.

It is intriguing that a pattern of cluster growth similar to that of the quantum clusters in Figure 2.3 was found years ago for a simple cluster model, the SAPS (spherically averaged pseudopotential) model, applied to simple metallic clusters (Lammers et al. 1990). In the SAPS model, the total ionic pseudopotential acting on the electrons is spherically averaged around the cluster center. The model forces these clusters to be rather spherical, and the resulting structures calculated by minimizing the total cluster energy are formed by well-defined concentric shells of atoms, like shells in an onion. For instance, Cs<sub>N</sub> clusters with N smaller than 7 do not have an atom at the center of the cluster. Clusters with N between 7 and 18 have a central atom surrounded by a single shell whose radius increases as N grows. The cluster center is again empty between N = 19 and N = 39 and the cluster is formed by two shells. Between N = 40 and N = 62, two shells surround an atom placed at the cluster center, and so on. The similarity with the quantum MC structural features of Figure 2.3 is striking, although the two systems are physically different. In the case of the SAPS model, the structural pattern arises from the interplay between electron-electron, electron-ionic pseudopotential, and ion-ion interactions in a constrained geometry imposed by the spherically averaged ionic pseudopotential. For the H<sub>2</sub> clusters, we propose a tentative explanation. A hollow spherical shell geometry with the center empty appears to be consistent with a wave function representing a system of *N* identical bosonic particles. Then, as the size *N* grows, the increase of the surface energy associated to the increasing radius of the shell promotes the formation of a new shell in the inner region of the cluster, and so on.

The influence of thermal effects on the stability and abundance of clusters at finite temperature has been studied by Guardiola and Navarro (2008). They calculated cluster excitations with angular momentum from L = 0 to L = 13 for sizes N = 3, ..., 40. For each value of L (L is the angular momentum of the wave function of the N-particle system), the Schrödinger equation was solved using the diffusion Monte Carlo (DMC) method, describing the H<sub>2</sub>-H<sub>2</sub> interactions by the pair potential of Buck et al. (1983). Besides the excited states with angular momentum L, vibrational excitations characterized by a quantum number n were also considered. The excited states are then represented by the pair of quantum numbers (n, L), with energies  $E_n^{(L)}$ . After calculating the ground state energy  $E_0^{(0)}(N)$  and the excited state energies  $E_0^{(L)}(N)$  and  $E_1^{(0)}(N)$ , the excitation energies are defined as

$$\Delta E_L(N) = E_0^L(N) - E_0^{(0)}(N), \qquad (2.5)$$

$$\Delta E_0(N) = E_1^{(0)}(N) - E_0^{(0)}(N).$$
(2.6)

Comparison of the excitation energies with the chemical potential  $\mu(N) = E_0^{(0)}(N-1) - E_0^{(0)}(N)$  indicates which excited states are stable (those with energies smaller than  $\mu$ ; if the excitation energy is larger than  $\mu$ , then the cluster will dissociate). Stable excitations exhibit size thresholds, as shown in Figure 2.4. All clusters with  $N \ge 3$  exhibit stable excitations (n = 0, L = 2), (n = 0, L = 3), and (n = 1, L = 0). The excited level (n = 0, L = 4) starts to be bound at N = 4, and the excited levels with L = 5 and L = 1 appear at N = 6. Then, the next L levels appear at regularly increasing size thresholds. In the size range studied, the highest stable excited state is L = 13, which occurs for  $N \ge 31$ . The quadrupolar, L = 2, is the lowest excitation for most sizes, except at N = 26, 28, 30, and 37, for which the lowest excitation is the octupolar, L = 3. The vibrational excitation (n = 1, L = 0), not shown in the figure, displays a smooth behavior with N, and its energy lies in between the energies of the excited (n = 0, L) levels. Another useful observation from this figure is the local maximum of the chemical potential for  $(H_2)_{13}$  and a less pronounced maximum for  $(H_2)_{36}$ .

The knowledge of the excitation spectra allows for the analysis of thermal effects using the partition function  $F_N$  of statistical mechanics. In particular, the temperature-dependent energy of the cluster,  $E_N(T)$ , becomes (Guardiola and Navarro 2008)

$$E_N(T) = E_0^{(0)}(N) + \frac{1 + \sum_L (2L+1) \Delta E_L(N) e^{-\Delta E_L(N)/kT}}{1 + \sum_I (2L+1) e^{-\Delta E_L(N)/kT}},$$
 (2.7)

where *k* is Boltzmann's constant. Noticeable effects on the energy values begin to appear at temperatures close to the energy of the first excited state, L = 2. For instance, at T = 1 K the energy changes are minimal, with the exception of the clusters with  $N \approx 20$ , which is related to a minimum of  $\Delta E_2$  occurring at this size (see Figure 2.4).

The effect of the temperature on the mechanism of cluster formation in a free jet expansion is also interesting. We assume that cluster growth in the jet is dominated by the chemical equilibrium reaction

$$(H_2)_{N-1} + H_2 + X \Leftrightarrow (H_2)_N + X, \tag{2.8}$$



**FIGURE 2.4** Excitation energies (in K) of para-H<sub>2</sub> clusters as a function of the number *N* of molecules, for states (0, *L*) with L = 1-6, obtained from DMC calculations. The chemical potential  $\mu$  is also plotted to indicate the stability limit. (Reproduced from Guardiola, R. and Navarro, J., *J. Chem. Phys.*, 128, 144303-1, 2008. With permission.)

where X is a spectator particle needed for the conservation of energy and momentum. The equilibrium constant  $K_N$  for the reaction is obtained from the partition functions F as  $K_N = F_N/(F_{N-1} F_1)$  and  $K_N$  is dominated by the ratio

$$\frac{F_N}{F_{N-1}} = \left(\frac{N}{N-1}\right)^{3/2} e^{\mu(N)/kT} \frac{1 + \sum_L g_L e^{-\Delta E_L(N)/kT}}{1 + \sum_L g_L e^{-\Delta E_L(N-1)/kT}}, \quad (2.9)$$

where the degeneracy factor for the excited state *L* is given by  $g_L = 2L + 1$ . Evidently, the ratio  $F_N/F_{N-1}$  reflects the non-smooth behavior of the chemical potential and the excitation energies as a function of *N*. A plot (Guardiola and Navarro 2008) of  $F_N/F_{N-1}$  at several temperatures, lower than the source temperature of the experiments of Tejeda et al. (2004), exhibits peaks at N = 13, 31, and 36, and a less pronounced peak at N = 26 in rough correlation with the experimental abundance maxima at N = 13 and 33. This points out the influence of the excited states on the abundance of hydrogen clusters produced in free jet expansions of pressurized gas.

#### 2.4 Charged Clusters

Mass spectrometric experiments on positive cluster ions (Kirchner and Bowers 1987) have revealed that  $H_m^+$  clusters with an odd number of atoms, m = 3, 5, 7,... are much more abundant than those with even-number of atoms, m = 2, 4, 6, ... The ionization of a neutral  $(H_2)_N$  cluster occurs in two steps. First, a  $H_2$  molecule of the cluster is ionized, and the charged molecule reacts with a neighbor neutral molecule, producing a trimer carrying the positive charge and a neutral H atom

$$H_2^+ + H_2 \rightarrow H_3^+ + H.$$
 (2.10)

This reaction is exothermic and the energy released, 1.7 eV, is enough to eject the H atom out of the cluster. The  $\text{H}_3^+$  cation is stabilized by the surrounding  $\text{H}_2$  molecules, which form solvation shells around the charged trimer (Bokes et al. 2001; Chermette and Ymmud 2001; Prosmiti et al. 2003). The composition of the cluster cations can be viewed as  $\text{H}_3^+$  ( $\text{H}_2$ )<sub>N</sub>. The fact of being charged makes these clusters easier to handle experimentally (Farizon et al. 1998). These clusters can grow easily (Clampitt and Towland 1969). The gas-phase clustering reaction

$$H_3^+(H_2)_N + H_2 \to H_3^+(H_2)_{N+1}$$
 (2.11)

has been experimentally studied and the enthalpy  $\Delta H$  of the reaction has been determined (Hiraoka and Mori 1989). The measurements, shown in Figure 2.5, indicate a stepwise decrease in the enthalpies at particular sizes. The gain in binding energy by adding a H<sub>2</sub> molecule drops substantially after N = 3 and N = 6, and this indicates that H<sub>3</sub><sup>+</sup> (H<sub>2</sub>)<sub>3</sub> and H<sub>3</sub><sup>+</sup> (H<sub>2</sub>)<sub>6</sub> are specially stable clusters. This stability has been interpreted as indicating shell formation.



**FIGURE 2.5** Measured enthalpies for the gas phase reaction  $H_3^+(H_2)_{n-1} + H_2 \rightarrow H_3^+(H_2)_n$ . (Reproduced from Hiraoka, K. and Mori, T., *Chem. Phys. Lett.*, 157, 467, 1989. With permission.)

Charged hydrogen clusters are important active species in the stratosphere and in interstellar clouds. The charged trimer,  $H_3^+$ , and its deuterated variant  $D_3^+$  have attracted a lot of attention. The unusual nature of its bonding leads to an exceptional roto-vibrational spectrum (Kostin et al. 2003). Experiments and calculations (Tennyson and Miller 1994) have shed light on the electronic structure, the infrared photodissociation spectrum, and the classical and quantal behavior of the molecule at its dissociation limit.  $H_3^+$  is present in any environment where molecular hydrogen gas is ionized: It has been detected in the atmospheres of Jupiter, Saturn, and Uranus. It was also identified in the supernova SN1987A (Miller et al. 1992) and in the interstellar medium (McCall et al. 1998).  $H_3^+$  is, in fact, the main agent responsible for the formation of complex molecules in the reaction network of the interstellar medium.

The charge state has influence on the binding energy of the  $H_3^+$  ( $H_2$ )<sub>N</sub> clusters. Taking  $H_3^+$  ( $H_2$ )<sub>5</sub> as an example, the average binding energy of the  $H_2$  molecules in the cluster, which can be defined as

$$e_{\rm av}(\text{cation}) = \frac{E(H_3^+(H_2)_5) - E(H_3^+) - 5E(H_2)}{5}$$
 (2.12)

is equal to 60 meV in an LDA calculation. For comparison, the average binding energy of five  $H_2$  molecules attached to a sixth  $H_2$  molecule to form the neutral  $(H_2)_6$  cluster,

$$e_{\rm av}(\rm neutral) = \frac{E((H_2)_6) - 6E(H_2)}{5}$$
 (2.13)

is 25 meV. So, the effect of the charge localized at the cluster center is to increase the binding energy substantially. Zero-point corrections lower those binding energies.



**FIGURE 2.6** Structure of  $H_3^+$  ( $H_2$ )<sub>N</sub> clusters calculated by ab initio quantum chemical methods. (Reproduced from Bokes, P. et al., *Int. J. Quantum Chem.*, 83, 86, 2001. With permission.)

Accurate theoretical studies of the ground-state configuration and binding energies of the  $H_3^+$   $(H_2)_N$  clusters have been performed using different levels of theory. The results for N = 1-7obtained using ab initio quantum chemical methods (Bokes et al. 2001) are shown in Figure 2.6. In  $H_3^+$   $(H_2)$ ,  $H_3^+$   $(H_2)_2$ , and

 $H_3^+$  ( $H_2$ )<sub>3</sub>, each  $H_2$  molecule is chemically attached to one of the H atoms of H<sub>3</sub><sup>+</sup>. The center of mass of each of those H<sub>2</sub> molecules is in the plane of  $H_3^+$ , and the molecular axes are perpendicular to that plane. A first shell is completed at  $H_3^+$  ( $H_2$ )<sub>3</sub> with the three H<sub>2</sub> molecules forming an external triangle with the same form as that of the internal H<sub>3</sub><sup>+</sup> core. The experiments show that  $H_3^+$  ( $H_2$ )<sub>3</sub> is especially stable (notice the drop after N = 3 in Figure 2.5). Addition of more  $H_2$  molecules builds up a second shell with the molecules at a longer distance from H<sub>3</sub><sup>+</sup>. The binding of these molecules to H<sub>3</sub><sup>+</sup> is weaker compared to those in the first shell. Figure 2.6 shows the calculated structure for  $H_3^+$  $(H_2)_4$ ,  $H_3^+$   $(H_2)_5$ ,  $H_3^+$   $(H_2)_6$ , and  $H_3^+$   $(H_2)_7$ . There are small differences of detail among different calculations concerning the location of the added molecules (Bokes et al. 2001; Prosmiti et al. 2003; Seo et al. 2007), but the structures reported here are sufficiently representative. Those clusters show several isomers with similar energies (Seo et al. 2007). For instance, for  $H_3^+$  ( $H_2$ )<sub>4</sub>, Bokes et al. (2001) found six different isomers, three with the additional  $H_2$  molecule above the  $H_3^+$  molety and three with the molecule below. A second shell appears to be completed for H<sub>3</sub><sup>+</sup>  $(H_2)_6$ , as indicated by the measured drop of the binding energy of an additional molecule (see Figure 2.5), also reproduced by the calculations. The three molecules of the second shell are on the same side of the  $H_3^+$  plane in Figure 2.6, but in other calculations two molecules are on one side and one molecule on the other side (Seo et al. 2007). Although the enthalpy appears to indicate that a new shell is opened at  $H_3^+(H_2)_7$ , the distance from the last added molecule to the H<sub>3</sub><sup>+</sup> core is similar to those for the



**FIGURE 2.7** Potential energy surface of  $H_3^+$  ( $H_2$ )<sub>4</sub> calculated by the Hartree-Fock method. The insets in the upper part show the coordinates of the potential energy surface and the molecular motion along the minimum energy path connecting two neighboring minima (from minimum 1 to minimum 2 through the saddle point). (Reproduced from Bokes, P. et al., *Int. J. Quantum Chem.*, 83, 86, 2001. With permission.)

molecules in the second shell. Further work should be welcome to clarify if a shell is completed or not at  $H_3^+$  ( $H_2$ )<sub>6</sub>.

Because of the weak bonds in these clusters, thermal and quantum fluctuations can cause fluxional behavior of the system. As an example, we summarize the study of Bokes et al. (2001) of the behavior of the most weakly bound H<sub>2</sub> molecule in H<sub>3</sub><sup>+</sup> (H<sub>2</sub>)<sub>4</sub>. That molecule is the first one in the second shell around  $H_3^+$ . For this purpose, Figure 2.7 shows the potential energy surface of the system obtained by scanning the two angle parameters u and v defined in the inset of this figure. In calculating the energy for each (u, v) point, the rest of the structural parameters of the cluster are free to relax. The calculations were performed with the Hartree-Fock method. There are three equivalent minima above the H<sub>3</sub><sup>+</sup> plane and three below. The transition path with the lowest energy barrier connecting two neighboring minima corresponds to the H<sub>2</sub> molecule moving, as indicated in the inset of the figure (from minimum 1 to minimum 2 through the saddle point). The barrier height is  $\Delta E = 0.078 \text{ kcal mol}^{-1}$ , and a more accurate, coupled-cluster (CC) calculation gives a similar value,  $\Delta E = 0.084$  kcal mol<sup>-1</sup>. The lowest vibrational energy of the hydrogen molecule in the potential well is  $(1/2)\hbar\omega_{min} =$ 0.066 kcal mol<sup>-1</sup>, and the thermal energy at temperature T is kT = 0.0020T kcal mol<sup>-1</sup>. Therefore, we can expect that zeropoint motion fluctuations and temperature effects for T = 10 Kand higher will enable the outermost H<sub>2</sub> molecule to pass the barriers from one minimum of the potential energy surface to another, resulting in fluctional behavior. H<sub>2</sub> molecules in the successive coordination shells will be even more mobile.

#### 2.5 Liquid-to-Gas Phase Transition

A good identification of a first- or second-order phase transition in a cluster is provided by the specific shape of the caloric curve, that is, the thermodynamic temperature as a function of the total energy. The caloric curve of size-selected hydrogen clusters has been determined in high energy collision experiments (Gobet et al. 2001, 2002), and has been interpreted as indicating the transition from a bound cluster to the gas phase. In those experiments, the hydrogen clusters are first formed in a cryogenic cluster expansion source, then ionized using a high-performance electron ionizer and finally size-selected in an ion accelerator. The collisions between size-selected  $H_3^+$  ( $H_2$ )<sub>N</sub> clusters with N smaller or equal to 14, accelerated to kinetic energies of 60 keV amu<sup>-1</sup>, and a helium gas target were analyzed. Collisions lead to the fragmentation of the clusters

$$H_3^+(H_2)_N + He \rightarrow a H_3^+(H_2)_k + b H_3^+ + c H_2^+ + d H^+ + e H_2 + f H_3$$
 (2.14)

where a - f = 0, 1, ..., and for each collision event, a multidetector records simultaneously the number (multiplicity) of each massidentified fragment ion resulting from the reaction (neutral species larger than H<sub>2</sub> are absent). The construction of the caloric curve requires the simultaneous determination of the energy



**FIGURE 2.8** Caloric curves for hydrogen cluster fragmentation induced by collisions with helium. Reduced temperature  $T/T_0$  ( $T_0$  is the temperature in the plateau of the curve) is given as a function of the energy deposited on the clusters  $H_3^+$  ( $H_2$ )<sub>N</sub>, with N = 6 (open squares), N = 8 (open circles), N = 9 (triangles), N = 11 (diamonds), N = 12 (inverted triangles), and N = 14 (filled circles). (Reproduced from Gobet, F. et al., *Phys. Rev. Lett.*, 89, 183403, 2002. With permission.)

and the temperature of the system. The cluster energy, that is the energy deposited into the cluster by the collision with a He atom, is determined by the nature and multiplicity of the products in reaction (2.14). The temperature of the cluster prior to decay is obtained using a relationship (Fisher 1967), tested successfully in nuclear physics collisions, between the characteristic shape of the fragment mass distribution and the temperature of decaying nuclei (Belkacem et al. 1995).

The results for  $H_3^+$  ( $H_2$ )<sub>N</sub> with N = 6, 8, 9, 11, 12, and 14 (Gobet et al. 2001, 2002) are shown in Figure 2.8. The caloric curves show three parts: after an initial rise, a plateau follows before the curve rises again. The curves show the typical features of a first-order phase transition. According to Gobet et al., the curves show backbending, that is, a negative heat capacity, which has been predicted to be possible for small systems (Gross 1997). This feature becomes more clear by plotting a single curve with the geometric means for all the clusters. There is, however, some controversy on the method of constructing the caloric curves (Chabot and Wohrer 2004).

#### 2.6 Laser Irradiation and Coulomb Explosion

The advances in laser technology permit the study of the interaction between matter and ultrafast lasers with intensities higher than  $10^{14}$  W cm<sup>-2</sup> and pulse duration below 100 fs. Available lasers achieve intensities exceeding the electric field created by an atomic nucleus, and the timescale of femtoseconds is also typical of the electron motion. This field of research allows for the exploration of the nonlinear response of atoms to intense laser pulses, leading to the observation of new processes. The behavior of molecules and clusters under similar

laser conditions offers new challenges due to the existence of additional degrees of freedom, such as the nuclear motion or the presence of intramolecular and intermolecular forces. This gives rise to complex phenomena: above-threshold dissociation, bond softening, and enhanced ionization. Some of these phenomena are followed by a Coulomb explosion. That is, when molecules or clusters are multiply ionized by laser pulses of very short duration, the unbalanced positive charges are sufficiently close together to cause a repulsion-induced explosion of the nuclear skeleton (Poth et al. 2002, Heidenreich et al. 2007).

In a series of interesting experiments, Ditmire and coworkers irradiated a dense molecular beam of large deuterium clusters,  $(D_2)_N$ , with intense femtosecond lasers (Ditmire et al. 1999, Zweiback et al. 2000). The irradiation induces the multiple ionization of the clusters, which then explode due to the repulsive Coulomb forces between the bare nuclei of the ionized atoms of the cluster. Some of those flying nuclei collide with nuclei ejected from other clusters in the plasma, and when the kinetic energies of the colliding nuclei are higher than a few keV, nuclear D-D fusion processes  $D + D \rightarrow {}^{3}He + n$  can occur with high probability. The kinetic energies of the bare deuterium nuclei depend only on the size of the original cluster, and for the cluster sizes in the experiments of Ditmire et al., the resulting kinetic energies are high enough to produce nuclear fusion reactions. Apart from the obvious interest for future thermonuclear devices, this technique has led to the development of tabletop neutron sources (Hartke et al. 2005): the D + D fusion reaction produces a neutron (n) with energy of 2.45 MeV, and those neutrons could potentially be used in neutron radiography and in materials research.

Motivated by those works, two groups (Ma et al. 2001, 2005; Isla and Alonso 2005, 2007) have studied the dynamical response of deuterium clusters irradiated by an intense femto-second laser. This study simulates the first stages in the experiments of Ditmire and coworkers. The time-dependent density functional theory (TDDFT) (Gross et al. 1996) was the method

used for the simulations. The TDDFT gives the response of the system to a time-dependent external perturbation  $V_{\text{ext}}(\mathbf{r}, t)$ , in the present case the laser field, by directly solving the fundamental equations of the formalism, the time-dependent Kohn–Sham equations. This gives directly the time-evolution of the electronic orbitals. One advantage of explicitly propagating the time-dependent Kohn–Sham equations is that it permits to couple the electronic system to the ionic background, which can be, for many purposes, treated classically. It is then possible to perform a combined dynamics of electrons and nuclei. The method allows to study both linear and nonlinear excitations. The simulation of the laser irradiation of  $D_3^+$  ( $D_2$ )<sub>5</sub> and  $D_3^+$  is now described.

The structure of the free  $D_3^+$  ( $D_2$ )<sub>5</sub> cluster is shown in the leftmost panels of Figure 2.9 (the spheres represent the hydrogen atoms, and two mutually perpendicular views of the cluster are presented). The cluster then was perturbed by a laser pulse, whose time-dependent electric field E(t) has a cosinoidal envelope,

$$E(t) = A_0 \cos\left(\frac{\pi}{2} \frac{t - 2\tau_0 - t_0}{\tau_0}\right) sen(\omega t)\hat{e}, \quad |t - t_0| < \tau_0, \quad (2.15)$$

where

ω is the frequency of the field  $\dot{e}$  is the polarization vector  $2τ_0$  is the total duration of the pulse  $A_0$  its amplitude

The frequency of the laser is an important parameter in order to achieve an efficient coupling between the laser radiation and the cluster. The first peak in the calculated photoabsorption spectrum of the cluster occurs at a frequency  $\omega = 0.352$  a.u. ( $\hbar \omega = 9.58$  eV, where  $\hbar$  is the reduced Planck constant). The results of a simulation in which a laser pulse of this resonant frequency is applied to the cluster are shown in Figure 2.9. The duration of the pulse is 9.6 fs and the amplitude of the field is



**FIGURE 2.9** Snapshots of the structure of the cluster  $D_3^+$  ( $D_2$ )<sub>5</sub> at different times after application of a short laser pulse of resonant frequency  $\hbar\omega = 9.58$  eV, intensity of  $1.4 \times 10^{13}$  W cm<sup>-2</sup>, and duration 9.6 fs. A slow fragmentation of the cluster occurs. Two mutually perpendicular views are presented for each snapshot.

0.02 a.u., giving a pulse intensity of  $1.4 \times 10^{13}$  W cm<sup>-2</sup>. A few snapshots showing the evolution of the structure of the cluster in time are shown in that figure. The cluster maintains its original structure during the initial 10 fs of the simulation approximately, due to the inertia of the atoms and the time the cluster needs to absorb the necessary energy to break bonds. The absorbed energy causes the splitting of the inner  $D_3^+$  trimer in two fragments, a D<sub>2</sub> molecule and a D atom, which are emitted in opposite directions. As the emitted molecule moves upward, it passes near two D<sub>2</sub> molecules, and these two molecules are set in motion and move apart. The intramolecular bond lengths of those two molecules oscillate but the bonds remain intact, that is, the molecules do not dissociate. On the other hand, the D atom moving downward collides with a molecule of the solvation shell, and an atom is exchanged in the collision. As the cluster dissociates, the two D<sub>2</sub> molecules originally most distant from the trimer remain little affected. This dissociation mode of the cluster can be characterized as a slow fragmentation. The laser frequency has influence on the results. For pulses of the same intensity as above, but half of the resonance frequency, the atoms oscillate around their equilibrium positions, but the cluster does not dissociate.

The behavior of the irradiated cluster changes drastically for a laser intensity five times larger, that is,  $7 \times 10^{13}$ W cm<sup>-2</sup> (with the same resonant frequency,  $\hbar\omega = 9.58$  eV, and pulse duration, 9.6 fs, as above). The evolution of the cluster structure is shown in Figure 2.10. The laser pulse produces a massive ionization of the deuterium atoms, and this occurs simultaneously in all regions of the cluster. As a consequence, the nuclei repel each other due to the Coulomb interaction and the cluster explodes. Coulomb explosion is a violent dissociation process that generally occurs in molecules and clusters when these are multiply ionized by femtosecond laser pulses. In small clusters, stripping just two electrons may be sufficient to induce Coulomb fragmentation. In fact, cluster size is an important parameter determining whether the cluster will follow this decay channel. This is the mechanism corresponding to the fast dissociation process shown in Figure 2.10. The irradiation of the cluster first produces a localized plasma of electrons and nuclei, and in a short interval, roughly corresponding to the duration of the laser pulse, the plasma loses five electrons which fly away. The loss of the remaining electrons continues afterward, at a slightly slower rate. Besides the size of the cluster, there is another requirement for a pure Coulomb explosion to take place: the cluster must be almost stripped of all their electrons in a timescale of

The kinetic energy of the nuclei resulting from the Coulomb explosion of  $D_3^+$  ( $D_2$ )<sub>5</sub> is about 13 eV. In most nuclear fusion processes, from controlled fusion reactors to solar reactions, the reacting particles have kinetic energies of a few keV, enough to overcome the Coulomb barrier for fusion. This indicates that the Coulomb explosion of  $D_3^+$  ( $D_2$ )<sub>5</sub> delivers kinetic energies that are very small compared to those required to produce nuclear D-D fusion. Of course, this is expected, since the cluster studied in these simulations is very small, whereas the clusters in the experiments of Ditmire and coworkers (Ditmire et al. 1999, Zweiback et al. 2000) are much larger: the average number of atoms is 1000 times larger. The maximum kinetic energy is proportional to  $R^2$ , where R is the radius of the cluster, and a beam of deuterium clusters with radii greater than 50 a.u. is necessary to produce ions with the multi-keV energies required for nuclear fusion. Last and Jortner (2001a,b) have proposed and confirmed by molecular dynamics simulations that very energetic deuterium or tritium nuclei (D<sup>+</sup> or T<sup>+</sup>) can be produced by the Coulomb explosion of D<sub>2</sub>O and T<sub>2</sub>O clusters, similar to water clusters. These clusters will provide substantially higher fusion reaction yields than the homonuclear deuterium or tritium clusters of the same size.

The charged trimer  $D_3^+$  forms the central core of the  $D_3^+(D_2)_N$ clusters. The ground state geometry of D<sub>3</sub><sup>+</sup> is a near equilateral triangle. Its calculated ionization potential, that is, the energy required to form  $D_{3^{2+}}$ , is 35.35 eV, and this high value arises from the unscreened attraction of the electrons by the nuclei. The photoabsorption spectrum of  $D_3^+$  shows two dominant features in the UV range (Isla and Alonso 2007). The first one is a double-peak formed by two near degenerate excitations at 17.5 and 17.8 eV, and its average value is in very good agreement with the lowest excitation energy of  $H_3^+$ , 17.8 eV, found in the experiments of Wolff et al. (1992). The second feature is a peak at 20.1 eV with lower absorption strength. The results of simulations of the cluster excitation with laser pulses of 9.6 fs and different frequencies and intensities are now discussed. First, the laser frequency is tuned to the resonant absorption peak at 17.65 eV (to perform this experiment in practice, this high frequency would require multiphoton absorption). In response to a pulse of intensity 10<sup>12</sup> W cm<sup>-2</sup>, the atoms of the trimer oscillate in the plane of the cluster and the motion resembles a breathing mode. However, when a high-intensity pulse of 10<sup>15</sup> W cm<sup>-2</sup> is applied, the cluster undergoes a Coulomb explosion. This occurs in two steps. First, the system reaches

**FIGURE 2.10** Snapshots of the structure of the cluster  $D_3^+$  ( $D_2$ )<sub>5</sub> at different times after application of a laser pulse of resonant frequency  $\hbar\omega = 9.58 \text{ eV}$ , intensity  $7 \times 10^{13} \text{ W cm}^{-2}$ , and duration 9.6 fs. A Coulomb explosion occurs.

a transient nanoplasma-like state; this state is short lived, and the two electrons quickly escape. The repulsion between the positive nuclear charges then causes the Coulomb explosion of the cluster. When the laser frequency is tuned to match the other absorption peak at 20.1 eV, the dynamical response of the cluster to a pulse of intensity 1012 W cm-2 is again an oscillatory motion of the atoms in the plane of the trimer; however, the amplitude of the oscillations is smaller. For a pulse of 1015 W cm<sup>-2</sup>, a Coulomb explosion occurs but some differences can be noticed compared to the case of frequency  $\hbar\omega = 17.65 \text{ eV}$ . The transient plasma-like state has a longer lifetime and ionization is slower. Consequently, the velocities of the flying nuclei are 25% slower. A last example corresponds to a nonresonant laser frequency of 5 eV. Atomic vibrations occur for low and high pulse intensities; however, the absorption of energy is not large enough to break the bonds.

The electronic response in the linear domain, which is the case for the low-intensity laser field, can be analyzed by following the time evolution of the dipole moment of the cluster, as shown in Figure 2.11. For a laser frequency  $\hbar\omega = 17.65 \text{ eV}$ , the dipole moment is greatly amplified by resonance with the external field, and strong dipole oscillations are observed long after the laser pulse is switched off (the pulse duration is 9.6 fs; see above). The amplification benefits from the fact that both, the electrons and the nuclei, oscillate in the plane of the nuclei. The behavior for a laser frequency  $\hbar \omega = 20.1 \text{ eV}$ is different. A field of this frequency induces oscillations of the electronic cloud perpendicular to the plane of the nuclei. Then, the electrons follow closely the excitation field during the approximately 10 fs that the pulse is acting, although the electronic response is small (this can be noticed by comparing the scales of the left and center panels of Figure 2.11). The amplitude of the dipole oscillations is much less than in the previous case because the absorption strength of this peak is smaller and there is no enhancement due to the nuclear vibrations. The extreme situation is found in the nonresonant case at  $\hbar\omega = 5 \,\text{eV}$  (Figure 2.11c), where the dipole moment first follows closely the laser field, returning practically to its initial value when the field is turned off.

#### 2.7 Endohedrally Confined Hydrogen Clusters

Solid hydrogen at low temperature and normal pressure is a molecular solid. Theoretical calculations have predicted a metallic state at very high pressures; see, for instance, the work by Johnson and Ashcroft (2000). However, the prediction is controversial. Shock-wave, pulsed-laser, and diamond anvilcell experimental techniques have played an important role in studying hydrogen under high pressures (Loubeyre et al. 2002). The metallic state has not yet been achieved for pressures up to about 300 GPa, and recent DFT calculations (Pickard and Needs 2007) have confirmed that hydrogen remains insulating at 400 GPa. Loubeyre et al. (2002) estimated that pressures of at least 450 GPa will be required to achieve the closing of the electronic gap.

DFT calculations have also been performed to explore the effect of pressure on the structure and the properties of hydrogen clusters (Santamaria and Soullard 2005, Soullard et al. 2008). In these studies, the clusters were confined in model containers, rigid fullerene-like cages built of 60 hydrogen atoms, and compression was simulated by reducing the radius of those model containers. The initial radius was chosen large enough so as to exert only a small pressure on the confined hydrogen molecules and to avoid the formation of bonds between the confined molecules and the atoms forming the cage. At any of the simulated pressures, the encapsulated hydrogen molecules assemble into clusters, with equilibrium structures which depend strongly on the number of molecules and the pressure exerted by the cage. Two pressure ranges have been identified. In the first one, with pressures up to 100 GPa, formation of molecular  $(H_2)_N$  clusters occurs. Figure 2.12 shows the preferred packing of the  $(H_2)_N$ clusters with N = 8-13 and 15, at pressures below 100 GPa. The equilibrium geometries can be described as antiprisms and capped antiprisms, with an approximate rotational symmetry axis changing from  $C_4$  (for N = 8, 9, 10, 11) to  $C_5$  (for N = 12, 13) and  $C_6$  (for N = 15). The growth pattern for N = 8 to N = 11 is based on the structure of  $(H_2)_8$ , which is a square antiprism.  $(H_2)_9$  and  $(H_2)_{10}$  are obtained by capping the two opposite basal



**FIGURE 2.11** Evolution of the electric dipole moment of  $D_3^+$  with time after laser irradiation in the linear domain (laser intensity =  $10^{12}$  W cm<sup>-2</sup>) with pulses of 9.6 fs. (a) Laser frequency corresponding to the excitation peak at 17.65 eV in the absorption spectrum. (b) Frequency corresponding to the excitation peak at 20.0 eV. (c) Nonresonant frequency at 5.0 eV. Notice the different scales in the dipole axis. (Reproduced from Isla, M. and Alonso, J.A., *J. Phys. Chem. C*, 111, 17765, 2007. With permission.)



**FIGURE 2.12** Preferred structures of confined  $(H_2)_N$  clusters (N = 8-13, 15) under pressure. The confining cage is not shown. The main rotational symmetry elements (planes and axes) are indicated. (Reproduced from Soullard, J. et al., *J. Chem. Phys.*, 128, 064316, 2008. With permission.)

faces on the antiprism. Placing an extra molecule in the center of the antiprism leads to  $(H_2)_{11}$ . The structure of the antiprism changes from square to pentagonal in  $(H_2)_{12}$ , which can also be considered as an icosahedron with a molecule at the center and a missing molecule on the surface.  $(H_2)_{13}$  is a perfect icosahedron with a molecule at the center. The configuration of  $(H_2)_{15}$  is similar to that of  $(H_2)_{13}$  but with the fivefold molecular rings replaced by sixfold molecular rings. The structures of encapsulated  $(H_2)_{12}$ and  $(H_2)_{13}$  coincide with those calculated for free  $(H_2)_{12}$  and  $(H_2)_{13}$  using DFT (see Section 2.3), but not for other clusters. This indicates that pressure affects the structure of the clusters. Only the magic cluster  $(H_2)_{13}$  and its immediate neighbor  $(H_2)_{12}$ appear to be insensitive to this effect. It is interesting to notice that the structure of  $(H_2)_{15}$  is based on a hexagonal antiprism, while the structure of free  $(H_2)_{15}$  in a similar calculation (see Section 2.3) is a capped icosahedron. This provides a nice visualization of the confinement effect. The capped icosahedron is a prolate (elongated) structure, and transformation to the more spherical structure of the hexagonal antiprism is favorable inside the spherical cage of decreasing diameter (this tendency toward spherical structures is further discussed below).

Application of pressures higher than 100 GPa results in a gradual dissociation of the  $H_2$  molecules, as evidenced by the increasing interatomic distances, and in the formation of mixed clusters of atoms and molecules, with a molecular–atomic ratio dependent on the pressure. As pressure increases, the electronic HOMO–LUMO gap (the difference between the energy of the lowest unoccupied electronic state of the cluster and that of the highest occupied state) decreases. This shows a tendency toward metallization, although for the pressures applied in the simulations, the metallization of the clusters is not yet

achieved. Analysis of the pressure–volume curve for encapsulated  $(H_2)_{13}$  and  $(H_2)_{15}$  leads to a zero-temperature equation of state (Santamaria and Soullard 2005), which was found to be consistent with the experimental data for a macroscopic hydrogen crystal (Hemley et al. 1990).

Motivated by the urgent search for efficient containers of hydrogen for automotive applications, the encapsulation of hydrogen clusters in carbon cages like fullerenes and closed nanotubes has been studied. Komatsu et al. (2005) reported a chemical method to encapsulate hydrogen in the C<sub>60</sub> fullerene by organic synthesis. Using a semiempirical electronic structure method, the MNDO (modified neglect of diatomic overlap), Barajas-Barraza and Guirado-López (2002) have studied the clustering of hydrogen molecules encapsulated in the fullerenes C<sub>60</sub> and C<sub>82</sub>. Although hydrogen encapsulation in fullerene molecules is not directly relevant for gas storage applications, its study may help us to get insight into the structure and properties of small molecules encapsulated in confined environments. On the other hand, porous carbon, a promising hydrogen storage material, contains interconnected pores of nanometric size, some of them with spheroidal shape. The number of encapsulated molecules studied by Barajas-Barraza et al. varied from 1 to 23 for encapsulation in  $C_{60}$ , and from 1 to 35 for  $C_{82}$ . The two upper limits define the maximum storage capacity for those two fullerenes. Beyond that, the cage breaks up. Inside  $C_{60}$ , the structure of  $(H_2)_6$  is an octahedron, and  $(H_2)_{13}$  is an icosahedron with an atom at its center, as shown in Figure 2.13. Encapsulated  $(H_2)_{10}$ forms a spherical structure around a central molecule, different from the elongated (prolate) structure of free  $(H_2)_{19}$ . Actually, the structures of encapsulated  $(H_2)_6$  and  $(H_2)_{13}$  are also rather spherical. To understand this tendency for spherical structures,



**FIGURE 2.13** Calculated lowest energy structures of (a)  $(H_2)_6@C_{60}$ , (b)  $(H_2)_{13}@C_{60}$ , (c)  $(H_2)_{19}@C_{60}$ , (d)  $(H_2)_6@C_{82}$ , (e)  $(H_2)_{13}@C_{82}$ , and (f)  $(H_2)_{19}@C_{82}$  (first and third columns), together with the spatial distribution of the centers of mass of the encapsulated hydrogen molecules (second and fourth columns). (Reproduced from Barajas-Barraza, R.E. and Guirado-López, R.A., *Phys. Rev. B*, 66, 155426, 2002. With permission.)

one can first notice that the equilibrium distance between the two hydrogen molecules in  $(H_2)_2$  obtained in different calculations is 3.4 Å, very close to the radius of the  $C_{60}$  fullerene, 3.5 Å. In addition, the hydrogen molecules maximize their attractive interaction with the carbon cage by occupying positions close to the inner wall of the fullerene. These two features explain the structure of the encapsulated clusters. The axes of hydrogen molecules in encapsulated  $(H_2)_6$  and  $(H_2)_{13}$  show orientational order, which disappears in encapsulated  $(H_2)_{19}$ . Evidently, as the number of molecules increases, the enclosed molecules feel an increasing pressure that would eventually lead to the breaking of the carbon cage.

These ideas are confirmed by the analysis of the structures of the clusters encapsulated in C<sub>82</sub>. The cage of this fullerene shows some distortion from sphericity, and the structures of the encapsulated clusters become deformed, compared to their structures inside C<sub>60</sub>, in order to profit from the interaction with the inner wall of the cage. This is clear in the panels d, e, and f of Figure 2.13. Again, the case of  $(H_2)_{19}$  is interesting. The deformed cage allows  $(H_2)_{19}$  to adopt a structure which is similar, although not identical, to that of free  $(H_2)_{19}$ . The structure of free  $(H_2)_{19}$  is the double icosahedron (see Section 2.3), and it looks like a cylinder formed by three parallel rings (each ring having five molecules) plus one molecule at each end of the cylinder and two molecules inside the cylinder. The encapsulated  $(H_2)_{19}$  is a similar cylinder, but with only a single internal molecule, and the middle ring is formed by six molecules. An additional set of calculations performed for  $(H_2)_6$ ,  $(H_2)_{13}$ , and  $(H_2)_{19}$  encapsulated in a

particular isomer of  $C_{82}$  with spherical symmetry (not shown in the figure) indicate that those hydrogen clusters adopt spherical structures, nearly the same as the ones found inside  $C_{60}$ . In summary, for hydrogen clusters encapsulated inside fullerenes, the interactions of the hydrogen molecules with the carbon walls of the cage dominate over the  $H_2-H_2$  interactions and control the structure of the encapsulated clusters. This supports the expectation that porous carbons can act as efficient containers for hydrogen storage.

The same rules apply to the structures of hydrogen clusters encapsulated in closed nanotubes (Barajas-Barraza and Guriado-López 2002). A (5,5) nanotube closed at both ends can be constructed with 110 carbon atoms. When the number of encapsulated hydrogen molecules is very small, the cluster adopts a linear shape with well-defined orientational ordering of the various molecular axes. Due to the finite length of the nanotube, the structure of the cluster becomes two-dimensional for five H<sub>2</sub> molecules, and three-dimensional for seven molecules. For encapsulation of larger quantities, for example 18 molecules, these form a shell with tubular shape, characterized by a strongly correlated orientation of the molecular axes. The structure changes when the number of encapsulated molecules is about 30: the cylindrical hydrogen shell adsorbed on the nanotube internal wall accommodates a one-dimensional chain of H<sub>2</sub> molecules in its inner channel.

Experimental work to fill fullerenes with hydrogen is in the early stages, although encapsulation of a single molecule has been achieved (Komatsu et al. 2005). But the pressures produced inside by the encapsulated hydrogen and the maximum amount of encapsulated hydrogen before the carbon cage breaks have been studied theoretically. An interesting result obtained by Pupysheva et al. (2008) from DFT calculations is that the energy of formation of the encapsulated cluster

$$\Delta E = E(H_n @C_{60}) - E(C_{60}) - \frac{n}{2}E(H_2)$$
(2.16)

is negative only for one or two molecules, and positive for four molecules and more. That is, all the structures with more than three encapsulated molecules are metastable, although once formed, dissociation of the system may have a substantial activation barrier. This critical number of three molecules may be underestimated, because the DFT calculations of Pupysheva et al. used the generalized gradient approximation (GGA) to electronic exchange and correlation, and there is some evidence that the GGA tends to underestimate the attractive interaction between H<sub>2</sub> and graphite-like carbon surfaces. Actually, Tada et al. (2001) obtained a purely repulsive interaction between  $H_2$  and a graphene layer or a (6,6) nanotube using the GGA approximation. The last metastable structure of the  $H_n @C_{60}$  family in the study of Pupysheva et al. contains 29  $H_2$ molecules. Above that size, the pressure becomes too high, the system becomes unstable, and the carbon cage spontaneously breaks up. For a number of encapsulated atoms n smaller than 20, all the hydrogen inside the fullerene exists only in molecular form. For *n* larger than 20, a part of the hydrogen remains in molecular form, but a few H<sub>2</sub> molecules dissociate, a few triangular H<sub>3</sub> molecules form, and some hydrogen atoms form covalent bonds with the carbon atoms of the cage. The fullerene cage deforms near the covalent C–H bonds in order to favor electronic sp<sup>3</sup> hybridization of those particular C atoms. At the same time, the hydrogenized carbon atoms no longer contribute to the conjugated  $\pi$ -electron system of C<sub>60</sub>, and this breaks the fullerene aromaticity. Consequently, the cage stability is weakened, and breakage occurs for *n* = 58. The estimated hydrogen pressure in H<sub>58</sub>@C<sub>60</sub> is 1.3 Mbar. This pressure is of the order of magnitude of the hydrogen pressure in the giant planets Jupiter and Saturn.

#### 2.8 Supported Clusters

Under normal circumstances, the hydrogen clusters are formed by weakly interacting H<sub>2</sub> molecules, as stressed in the previous sections of this chapter. But, by directly depositing hydrogen atoms on a graphite surface, supported two-dimensional clusters have been obtained in which hydrogen is in the atomic state. Atomic deuterium has been deposited on graphite at 210K in experiments performed under ultra-high-vacuum conditions, and scanning tunneling microscopy (STM) was used to analyze the results (Hornekaer et al. 2006). At very low deuterium coverage (0.03%), STM images show only adsorbed isolated atoms. Those D atoms are in a chemisorbed state, covalently bonded to a C atom of the graphite surface. When the coverage increases to 1%, the STM images show a dominance of deuterium dimers. However, these are not D<sub>2</sub> molecules. The two D atoms of a dimer are chemisorbed on C atoms, and the nearest-neighbor C-C distance is 1.41 Å, much larger than the bondlength, 0.79 Å, of the H<sub>2</sub> molecule. As shown in Figure 2.14, the most stable configuration of the adsorbed dimer is not the ortho configuration in which the two D atoms are adsorbed on first nearest neighbor C atoms, but the para configuration in which the two D atoms are bonded to C atoms on opposite vertices of a hexagon (third nearest neighbors). The para configuration is 0.2 eV more stable than the ortho, and another configuration where the two D atoms are bonded to C atoms in second neighbor sites is 1.2 eV less stable than the para configuration. The formation of dimers and larger clusters was not ascribed to thermal diffusion effects. The barrier for surface diffusion of a D atom, 1.14 eV, is larger than the activation barrier for desorption, 0.9 eV, so an isolated D atom would desorb, rather than diffuse, under heating, and this is corroborated by the experiments, which show that the atoms are immobile at 200K and that heating to room temperature reduces the surface coverage. Instead, the mechanism of formation of dimers and larger deuterium clusters is preferential sticking. As shown by the interaction energy curves of Figure 2.14, constructed from DFT calculations, the chemisorption of the first D atom has a small barrier of 0.15 eV. Then, the barrier for chemisorption of the second D atom in the ortho configuration is only



FIGURE 2.14 (a) Potential energy curves for the chemisorption of a single H atom (solid line), shown in (b), calculated using the density functional formalism, and for the three dimer configurations shown in (c), the ortho-dimer (dash-dotted line), the second neighbor site (dashed line), and the para-dimer (dash-double dotted line). (Reproduced from Hornekaer, L. et al., *Phys. Rev. Lett.*, 97, 186102, 2006. With permission.)

0.10 eV, and there is no barrier for chemisorption in the para configuration. This means that para-dimer configurations should dominate at low coverage because there is no barrier for sticking into this state, and the experiments show that this is the case.

At higher coverages, 3% or more, the majority of the adsorbed D atoms form larger clusters, and the structures are again dominated by preferential sticking. When a dimer is in the para configuration shown in Figure 2.14a, the calculations for the adsorption of a third atom show reduced barriers (of 0.10 eV) when the third atom is in any of the five positions on the right of the inset. One of those positions forms an ortho configuration with one of the atoms of the original dimer, other two positions form para configurations, and the final two are second neighbor positions. For the sticking of a fourth atom, sites with reduced or vanishing barriers for adsorption also exist. In summary, the structures of the two-dimensional hydrogen clusters formed by deposition of atomic hydrogen on graphite are very different from those of the usual molecular clusters. First of all, the basic unit is the chemisorbed H atom, covalently bonded to a surface C atom, and not the H<sub>2</sub> molecule; second, the clusters are not compact and its structure is controlled by preferential sticking.

#### 2.9 Quantum Effects in Hydrogen Clusters

Superfluidity is a fascinating manifestation of quantum behavior at a macroscopic scale. In a superfluid liquid, the viscosity vanishes. Helium becomes superfluid at very low temperature, below its lambda ( $\lambda$ ) point. This lambda point depends on pressure, and for He at a pressure of 0.05 atm, it occurs at 2.17 K. A relevant question is which condensed material, besides helium, can display superfluidity. Molecular para-hydrogen is a candidate because of the bosonic character and the light mass of the para-H<sub>2</sub> molecules. But, unlike helium, bulk para-H2 solidifies at low temperature, because the interaction between two hydrogen molecules is substantially more attractive than the interaction between two He atoms. However, the lowering of the melting point compared to the bulk is a well known and rather general phenomenon in clusters (Alonso 2005), and this has motivated the interest in studying the possible superfluidity in para-H<sub>2</sub> clusters. Using infrared spectroscopy to study the rotational spectrum of a dopant molecule embedded in clusters of <sup>4</sup>He or para-H<sub>2</sub>, the observation of the decoupling of the rotation of the dopant molecule from the surrounding medium gives evidence of the superfluidity of the cluster. Using this technique for a linear carbonyl sulfide (OCS) chromophore molecule surrounded by 14-16 para-H<sub>2</sub> molecules, all inside large He droplets, Grebenev et al. (2000) obtained confirmation of the occurrence of superfluidity in liquid para-H<sub>2</sub>.

Mezzacapo and Boninsegni (2006, 2007) have presented a comprehensive theoretical study of  $(para-H_2)_N$  clusters using path-integral quantum MC simulations and the pair potential of Silvera and Goldman (1978). Tests with other established potentials were also performed and gave similar results. The calculated chemical potential  $\mu(N)$ , or energy to remove one molecule from the cluster  $(H_2)_N$  (see Equation 2.4), has local maxima for N = 13 and N = 26. The first magic number, N = 13, was ascribed to the completion of the first shell around a central atom (which is not inconsistent with liquid behavior; see below), and the peak at N = 26 was ascribed to solid-like behavior. The results for the superfluid character of these clusters are summarized in Figure 2.15, where the superfluid fraction  $\rho_s$  is plotted as a function of the cluster size at a temperature T = 1 K. The superfluid fraction is the fraction of molecules in the superfluid phase, that is, the fraction of the system that decouples from an externally induced rotation. Three regions can be identified in this figure. In the first region, formed by the clusters with less than 22 hydrogen molecules, the clusters are liquid-like and superfluid at low temperature. In these clusters, the superfluid fraction decreases monotonically as T increases. For instance,  $(H_2)_{20}$  is entirely superfluid ( $\rho_s = 1$ ) at temperatures below 1.25 K, and its  $\rho_s$  drops fast with increasing *T*, reaching a value of 0.2 at T = 2.5 K. In the transition region of Figure 2.15, formed by clusters with sizes between N = 22 and N = 30, the evolution from liquid-like character to solid-like character does not occur continuously. The superfluid properties depend sensitively on the



**FIGURE 2.15** Solid symbols are the superfluid fraction of  $(H_2)_N$  clusters as a function on *N*, at T = 1 K, obtained by quantum MC simulations. Other symbols are results of a previous calculation. (Reproduced from Mezzacapo, F. and Boninsegni, M., *Phys. Rev. A*, 75, 033201, 2007. With permission.)

cluster size, and strong differences occur for clusters differing by just one single molecule. This was interpreted as indicating the alternating liquid-like (superfluid) character or solid-like (insulating) character of the clusters. For instance, plots of the atomic structure of the clusters with N = 25 and N = 26 at T = 1 K indicate a clear solid-like structure of  $(H_2)_{26}$ ; that is, the hydrogen molecules show a high degree of spatial localization. Quantum exchanges between molecules are suppressed and the superfluid response is weak. In contrast, the molecules in  $(H_2)_{25}$  are more delocalized and their positions cannot be clearly identified. That delocalization promotes quantum exchanges responsible for the large superfluid response.

A peculiar behavior was observed for some clusters in this region. A good example is  $(H_2)_{23}$ , for which the superfluid fraction shows a local minimum in Figure 2.15. A detailed analysis of the computer simulations reveals the coexistence of two phases in this cluster, a liquid-like superfluid phase and a solid-like phase. This means that in its time evolution at a given temperature, the system visits ordered solid-like configurations and liquid-like superfluid configurations and the value of  $\rho_s$  in Figure 2.15 is the time average. A fascinating feature of this cluster is that, on lowering the temperature, the liquid-like phase becomes dominant as T approaches 0 K, that is, this phase is observed during a higher fraction of the simulation time: the cluster melts at a low temperature. Melting in this case is due to zero-point motion which induces quantum exchanges of the molecules. This behavior, which is driven by Bose statistics, was called quantum melting by Mezzacapo and Boninsegni (2006, 2007). On the other hand, for high T, the quantum exchanges are suppressed and the system solidifies. This behavior becomes reflected in the form of the radial density of particles  $\rho(r)$ , that is, the density of particles taking the cluster center as the origin of coordinates. At T = 2 K,  $\rho(r)$  of  $(H_2)_{23}$  displays a well-defined structure of two shells, a sharp peak at a distance  $r \approx 2$  Å from the center of mass, and a broader peak centered at 5.5 Å; this is consistent with Figure 2.3. Lowering the temperature to T = 0.75 K, the first peak experiences a substantial broadening and a lowering of its height. This indicates that the molecules are less localized and that quantum exchanges between shells as well as within shells increase.  $(H_2)_{23}$ is not the only cluster in the transition region of Figure 2.15 showing quantum melting. Some other clusters in this region show the same features. The behavior just discussed is different from that of a cluster which is liquid but not 100% superfluid. In this case, which corresponds to the region N < 22, the clusters are liquid at all temperatures and the superfluid fraction grows at low T, but there is no coexistence between liquid and solid phases. Finally, Figure 2.15 shows that the superfluid response is significantly depressed above N = 30, consistent with the expectation that a crystalline phase has to appear at large N.

The nucleus of the deuterium atom has total angular momentum J = 1, and molecular ortho-deuterium (ortho-D<sub>2</sub>) occurs in nature as a mixture of S = 0 and S = 2 spin states. The S = 0state is a boson similar to para-H<sub>2</sub> but with a larger mass. The mass difference is responsible of some subtle differences in the properties of para-H<sub>2</sub> and ortho-D<sub>2</sub>. Quantum effects are weakened in ortho-D<sub>2</sub>, or stated in an alternative way, the behavior of these clusters is more classic (Mezzacapo and Boninsegni 2007). The binding energy  $e_b(N)$  and the chemical potential  $\mu(N)$  show peaks at N = 13 and N = 19, and those features are sharper than in para-H<sub>2</sub>. The structure of  $(D_2)_{13}$  and  $(D_2)_{19}$  at T = 0.5 K is solidlike. Actually, the calculated structure of  $(D_2)_{19}$  is quite similar to a classical double icosahedron.

Very recently, the distribution of the superfluid response across the clusters has been discussed with opposite views. Khairallah et al. (2007) have concluded that the superfluid response is largely confined at the surface of small clusters and arises from the exchange cycles involving surface molecules. On the other hand, Mezzacapo and Boninsegni (2008) have presented persuasive arguments that the small clusters are uniformly superfluid, that is, the superfluidity response is not localized at the cluster surface. In summary, the quantum properties of hydrogen clusters are a fascinating subject and intensive and interesting work on these nanoclusters is expected to continue in the near future.

#### 2.10 Conclusions

Hydrogen clusters can be obtained by condensation of hydrogen gas in supersonic expansions. The clusters formed are molecular clusters with formula  $(H_2)_N$ . The experiments show that clusters of some particular sizes N are more abundant that other neighbor sizes, and for this reason those are often called magic clusters. It is difficult to obtain direct experimental information of the structure of the hydrogen clusters, that is, of the geometrical arrangement of the molecules, and theoretical calculations help a lot in this task. The calculations assign the first, and more clear magic number, N = 13, to the completion of a first shell

around a central molecule. Both experiment and theory suggest the existence of other higher magic numbers. If one of the molecules of a hydrogen cluster is ionized, the structure of the cluster suffers a drastic change: Instead of having a charged H<sub>2</sub><sup>+</sup> molecule immersed in the cluster, it is more favorable to eject a neutral H atom and form a charged trimer solvated in the cluster,  $H_3^+$  ( $H_2$ )<sub>u</sub>. Confining the hydrogen clusters in small cages, like fullerenes and nanotubes, affects the structure of the encaged clusters. The cluster roughly adapts its structure in order to maximize the interaction with the inner wall of the cage, and this effect may have consequences for the important technological problem of hydrogen storage. Clusters produced by direct deposition of atomic hydrogen on a substrate form two-dimensional structures where the relevant units are the chemisorbed atoms, not the molecules. Nuclear fusion between colliding deuterium nuclei has been achieved in experiments in which dense molecular beams of large deuterium clusters were irradiated with strong femtosecond lasers. The mechanism generating the flying energetic nuclei is the Coulombic explosion which follows the massive ionization of the deuterium clusters. The atomic part of the process, that is, the interaction between the cluster and the laser leading to ionization and Coulomb explosion is a fascinating area. At very low temperatures, hydrogen clusters display quantum effects, and a beautiful manifestation of these is superfluidity, already detected experimentally in some hydrogen clusters.

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# 3

### Mercury: From Atoms to Solids

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#### 3.1 Introduction

Elemental mercury is the only metal that is liquid at room temperature (melting temperature  $T_{\rm M}$  = -38.83°C); the only other low melting metal is gallium ( $T_{\rm M}$  = 29.76°C) [1]. This has been known since ancient times and is reflected in the Greek name Hydrargyrum meaning "watery silver" and the Latin Argentum vivum meaning "quick silver." It is speculated that its low melting point is due to relativistic effects [2-4], which energetically lowers the 6s band substantially [5], thus making mercury a very hard atom with a static dipole polarizability of only  $\alpha_{\rm D} = 5.025(50)$  Å<sup>3</sup> [6,7]. It is clear that such strong and pronounced relativistic effects for the 6s shell [5], which are close to the relativistic 6s maximum of gold [4,8], makes mercury rather unique in chemical and physical properties among the other Group 12 metals zinc and cadmium. Some of the physical and chemical properties of the Group 12 elements are compared in Table 3.1, and in many of these properties we see anomalies that, most likely, are caused by relativistic effects. For the next Group 12 element (below Hg) with nuclear charge Z = 112 (Copernicium, Cn), even larger relativistic effects are predicted [9-11], and the dipole polarizability of this element is now the lowest of all the Group 12 elements  $(\alpha_{\rm D}(112) = 3.8\,{\rm \AA}^3)$  [12].

Mercury occurs in many natural materials including coal, gas, and oil in small quantities; it is estimated that by burning fossil fuels about 2400 tons per year of mercury are released into the atmosphere [13]. Thus, the contamination of the atmosphere and the bioaccumulation of it, especially in fish, present large-scale problems. Since oxidized mercury is easier removed than mercury in its elemental form, the search for efficient and regenerable oxidation catalysts like noble metals is important [14,15]. For humans, mercury is toxic and leads to damage to the nervous tissue, kidneys, and liver. It is therefore important that mercury be handled with care, which is the main reason why mercury is not the metal of choice in the study and design of new nanomaterials. In fact, most of the nanoscience research here concentrates on the development of sensors for the detection of small amounts of mercury [16].

Mercury is, however, an interesting element to be studied by theoreticians, as mercury clusters range from van der Waals bonded to more covalent systems, before finally reaching the metallic state at larger cluster size [17]. The dissociation energies ( $D_e$ ) therefore vary widely from about 0.05 eV for the dimer [18] to 0.67 eV (cohesive energy  $E_{coh}$ ) for the bulk metal. For an ideal Lennard-Jones system, we have the simple relation  $E_{coh} = 8.61D_e$  [19], which is obeyed for either the face-centered cubic fcc or the hexagonal close-packed hcp solid. Instead,  $E_{coh} = 13.4D_e$ , i.e., mercury does not behave like an ideal Lennard-Jones system. It is therefore a challenge to simulate mercury in the gas, liquid, or the solid phase.

The first appearance of the 6s-6p gap closure to the metallic state at a specific cluster size is still a matter of intense debate [20,21]. Early measurements by Rademann gave an estimated band gap closure for Hg<sub>n</sub> at  $n \approx 70$  [22,23], Singh obtained  $n \approx 80$  [24,25], Pastor et al.  $n \approx 135$  [26–28], and a recent photoelectron study on negatively charged mercury clusters by Busani et al. gave  $n = 400 \pm 30$  [29–31]. In liquid mercury, the single 6s-6p gap opens at a density of  $\rho = 8.8$  g cm<sup>-3</sup> (the density of liquid mercury under standard conditions is 13.59 g cm<sup>-3</sup> [32]). This agrees with experiment where a gradual transition from metallic to semiconducting and insulating properties has been observed at elevated temperatures and pressures [33]. An interesting comparison is to superheavy element 112; due to a very strong relativistic 7s stabilization element 112 never becomes metallic as recent solid-state calculations show [10].

There is also a very large contraction of the Hg–Hg equilibrium bond length  $r_e$  when going from the van der Waals bonded dimer ( $r_e = 3.69$  Å) [18] to the solid state ( $r_e = 3.01$  Å) [1], which is not found in the rare gas elements. Such large differences indicate

**TABLE 3.1**A Comparison of Chemical andPhysical Properties of the Group 12 Elements

Property	Zn	Cd	Hg
<i>I</i> <sub>1</sub> (eV)	9.394	8.994	10.438
$I_2 (eV)$	17.96	16.908	18.757
$I_w$ (eV)	3.63	4.08	4.48
$\alpha_{\rm D}$ (Å <sup>3</sup> )	5.75	7.36	5.02
$T_{\rm M}(^{\circ}{\rm C})$	419.53	321.07	-38.83
$T_{\rm B}(^{\circ}{\rm C})$	907	767	356.62
$T_{\rm c}(^{\circ}{\rm C})$	0.85	0.517	3.95
$\lambda (W \; m^{-1} \; K^{-1})$	116	96.8	8.34
$\rho (10^{-8} \Omega m)$	5.9	7.6	95.78
Μ	0.38	0.38	1.0
B (GPa)	70	42	25
Structure	hcp	hcp	rhomb

Notes:  $I_1$  and  $I_2$  are the first and second ionization potentials of the atom;  $I_w$  is the work function of the bulk;  $\alpha_D$  the static electric dipole polarizability;  $T_M$ and  $T_B$  are the melting and boiling points;  $T_c$  the superconducting transition temperature;  $\lambda$  the thermal conductivity;  $\rho$  the specific resistance; M the electron–phonon coupling constant; B the bulk modulus, and for the bulk structures; hcp refers to hexagonal closed packing; rhomb to rhombohedral. Results are taken from Ref. [1].

the importance of many-body forces beyond the two-body force such as the two-body Lennard-Jones potential [34]. This clearly distinguishes mercury from rare gas interactions, which are reasonably well described by two-body forces only [19]. Further, there is no bonding interaction at the Hartree-Fock level starting from the Hg dimer and up to the solid state, that is the interaction between Hg atoms without taking electron correlation into account is purely repulsive [35,36]. This situation now resembles the bonding behavior in the rare gases. And finally, relativistic effects shorten the bond distance in Hg<sub>2</sub> considerably (by 0.2 Å) [37], and solid Hg changes the crystal structure to hcp when neglecting relativistic effects, the bond distance in the crystal also being somewhat larger (3.06 Å at the nonrelativistic level of theory) than in the rhombohedral relativistic structure (3.00 Å) [38]. The correct description of both relativistic and electron correlation effects is thus very important for the simulation of mercury in clusters, the liquid or the solid state.

Several groups have studied neutral and charged Hg<sub>n</sub> clusters in the gas phase, in particular the transitions in chemical bonding from van der Waals to metallic [17]. For small van der Waals clusters (n < 13) the band gap is large and little 6s-6p hybridization is observed. After a transition region, the bonding becomes covalent (30 < n < 100); 6s-6p hybridization leads to an increase of the binding between the atoms beyond the normal two-body interaction. At much larger cluster size we enter the metallic phase. In this process both the bond distances and the ionization potential decrease toward the bulk value. This transition for a finite system has been described as being somewhat similar to a Mott transition for the bulk [17]. It is clear that mercury is a complex system to be studied by both theoretical and

experimental methods. Here, we want to outline the progress made in the last two decades in simulating Hg clusters, the liquid and the bulk system, and how well the results compare with experiment.

#### 3.2 The Mercury Atom

We briefly mention both, theoretical and experimental work on the Hg atom, mainly to discuss the importance of relativistic effects necessary to understand the physical properties of the Hg clusters. The most accurate calculations for Hg come from Kaldor's group using Fock-space coupled-cluster theory starting from a Dirac-Coulomb Hamiltonian including Breit interactions in the low-frequency limit [39,40]. They reproduce experimental ionization potentials and electronic excitations [1,41] within a few 100 cm<sup>-1</sup>. In fact, such calculations are now so precise that quantum electrodynamic effects have to be taken into account to produce results of experimental accuracy [42]. Figure 3.1 shows ionization potentials and static dipole polarizabilities for all group 12 metals. It is clear that relativistic effects in such properties are large and cannot be neglected anymore. The relativistic increase in the ionization potential and the subsequent decrease in the polarizability has led to the conclusion, that both Hg and element 112 are chemically inert [9]. The (indirect) relativistic expansion of the core 5d orbitals also leads to a larger 5d/6s mixing [5]. Finally, spin-orbit coupling splits both the 5d and 6p levels in Hg. The splitting between the  ${}^{3}P_{0}/{}^{3}P_{2}$  states of neutral Hg is 0.79 eV, while the  ${}^{2}D_{3/2}/{}^{2}D_{5/2}$  splitting in Hg<sup>+</sup> is 1.86 eV [41]. The  $6p_{1/2}$  spin-orbit stabilization will reduce the 6s/6p band gap and therefore shift the onset of metallicity to smaller Hg clusters. Further, in a mercury vapor lamp the UV light produced at 253.7 nm comes from the spin-forbidden  ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ transition, which becomes allowed in the spin-orbit coupled case [45].



**FIGURE 3.1** A comparison between experimental (or relativistic coupled cluster) ionization potentials and static dipole polarizabilities for the group 12 metals with (R) and without (NR) relativistic effects. Experimental values for Zn, Cd, and Hg are taken from Refs. [1,6,43,44], relativistic coupled-cluster calculations come from Refs. [12,39].

#### 3.3 Mercury Clusters

It is obvious that any theoretical method able to accurately describe Hg clusters from small to large sizes has to reproduce experimental values reasonably well for the smallest cluster, the dimer Hg<sub>2</sub>, as well as for the solid metal. For Hg<sub>2</sub>, accurate experimental results are scarce. Table 3.2 shows a comparison between different theoretical results with experiment. As the interaction between two Hg atoms in Hg<sub>2</sub> is of van der Waals (dispersive) type with possibly a rather small dissociation energy of 400 cm<sup>-1</sup> [46], it is currently not easy to obtain accurate values from both theory or experiment. Currently, the most precise calculations come from Peterson [47] using a small-core relativistic pseudopotential for Hg, including spin-orbit corrections and extrapolating to the basis set limit using correlation consistent basis sets at the coupled-cluster level of theory. Relativistic effects are important, as they decrease the bond distance by about 0.2 Å, and slightly lower the dissociation energy [18,37,48]. Table 3.2 clearly shows the huge stabilization effect on removing an electron out of the antibonding orbital in Hg<sub>2</sub>, i.e., the dissociation energy increases by a factor of 29 when going from  $Hg_2$  to  $Hg_2^+$ . This rather large effect will diminish with increasing cluster size toward the solid state. Excited states of Hg<sub>2</sub> and Hg<sub>2</sub><sup>+</sup> were also studied in the past by both experimental [51-53,55,58-60] and theoretical methods [61–64]. Also, some excited states of Hg<sub>2</sub> are found to be more stable due to the excitation of an electron out of the antibonding orbital; the dissociation energy increases up to a factor of 25 and the bond length is strongly reduced to about 3 Å, the distance found in solid Hg (see Ref. [63] and references therein). We note here that the importance of relativistic effects in optical transitions in Hg-containing alloys was already discussed in 1972 by Kisiel and Lee [65].

The study of large mercury clusters to, for example, probe the convergence toward the bulk is a nontrivial task for both theoreticians and experimentalists. As calculations show, for the simple mercury dimer as well as for the solid state, relativistic effects have to be included [24,37,48]. For larger clusters, the computer time becomes prohibitively large for all electron methods at the Hartree–Fock or density functional level of theory, so naturally the relativistic pseudopotential approximation (also called effective core potential method) is used, which has been proven to be very accurate compared to all electron calculations if care is taken for the proper choice of the core and in the adjustment procedure [66]. While the inclusion of scalar relativistic effects is more or less straightforward, spin–orbit effects, electron correlation, and the basis set superposition error present a much larger problem [18,47,67]. Theoretical studies of clusters have therefore been limited to rather small cluster sizes, where the extrapolation to the bulk limit is questionable. Nevertheless, a number of interesting computational studies on mercury clusters have appeared in the past decade.

Dolg and coworkers have studied small neutral and charged mercury clusters [49,68]. An ELF (electron localization function) analysis showed predominantly van der Waals type bonding for Hg<sub>n</sub>  $(n \le 4)$  [68]. They also investigated the size dependence of ionization potentials, electron affinities, and binding energies with increasing cluster size up to Hg15 and found significant covalent bonding character for these clusters. For medium-sized clusters, Dolg and coworkers suggested a hybrid model consisting of a pairwise additive dispersion potential proportional to  $R^{-6}$  together with a two-valence electron relativistic pseudopotential. The latter is a so-called large-core pseudopotential which includes core-polarization effects describing dynamic correlation from the 5d core of Hg, and finally core-core repulsion effects between the Hg atoms [69]. This hybrid model is a good approximation for Hg<sub>2</sub> as comparison with more accurate coupled-cluster calculations using a small-core pseudopotential, which does not include the 5d electrons as core electrons, for Hg show [69]. A simulated annealing procedure confirmed the Lennard-Jones behavior of these structures with icosahedral structures for Hg<sub>13</sub> and Hg<sub>55</sub> [69]. However, in a later paper they used a genetic algorithm procedure when searching for the global minima and found very unusual structures from Hg<sub>7</sub> to Hg<sub>13</sub>, which deviate substantially from the compact Lennard-Jones like shapes [70,71], which for small- to medium-sized closed atom-shell clusters are Mackay icosahedra [72]. As twobody interactions favor compact structures due to maximizing the number of interacting pairs, this result would imply that the many-body expansion of the interaction potential does not converge smoothly. This was indeed found in a recent paper by

**TABLE 3.2** Spectroscopic Properties for the  $Hg_2^{\ 1}\Sigma_g^{\ +}$  and  $Hg_2^{\ +}^{\ 2}\Sigma_g^{\ +}$  Ground States from Experimental and Theoretical Work

Molecule	Method	r <sub>e</sub>	$D_0$	ω <sub>e</sub>	$\omega_e x_e$	I.P.	Refs.
Hg <sub>2</sub>	Theo.	3.687	0.048	19.8	0.23	$8.85^{a}/9.60^{b}$	[47,49]
	Exp.	$3.69\pm0.01$	$0.047\pm0.002$	$19.6\pm0.3$	$0.26\pm0.05$	9.0-9.5	[23,50-55]
$Hg_2^+$	Theo.	2.74	1.40	112	_	_	[49,56]
	Exp.	_	$1.6 \pm 0.2$	_	_	14.5 <sup>a,c</sup>	[57]

*Notes:* The equilibrium bond distance  $r_e$  is given in Å, the dissociation energy  $D_0$  in eV (zero-point vibrational energy correction included), the harmonic vibrational frequency  $\omega_e$  and the anharmonicity correction  $\omega_e x_e$  in cm<sup>-1</sup>, and the ionization potential I.P. in eV.

<sup>a</sup> Adiabatic I.P.

<sup>b</sup> Vertical I.P.

<sup>c</sup> Own unpublished results at the MP2 level of theory. The local minimum of metastable  $Hg_2^{2+}$  was taken as a reference. The vertical I.P. is only slightly different to the adiabatic value.

Moyano et al. [35]. However, more recent accurate coupled-cluster calculations show that, beside the importance of such manybody effects, the mercury clusters do follow the usual growth pattern of compact cluster structures [73], which contradicts the original results [70,71].

Moyano et al. used two-body and effective three-body interactions between the mercury atoms in a simulated annealing approach to obtain global minimum structures for larger mercury clusters up to  $Hg_{40}$  [35]. Again these clusters show rather compact structures similar to the Lennard-Jones structures with magic cluster numbers of 6, 13, 19, 23, 26, and 29 atoms, in agreement with diatomic-in-molecules (DIM) calculations by Kitamura [74]. These values also coincide with the mass distribution of mercury-cesium cluster ions observed by Ito et al. [75]. The calculations of Moyano et al. also reveal a fast convergence of the polarizability toward the bulk limit in contrast to the singlet-triplet gap or the ionization potential. However, the cluster sizes were far too small to accurately predict the onset of metallicity.

It is now evident that it remains a challenge to accurately describe electronic properties for global minimum structures for larger mercury clusters, and, what is required at finite temperatures, to perform molecular dynamic simulations to obtain properties, which can be compared to the experiment. Nevertheless, a number of theoretical studies appeared in the past dealing with neutral or charged mercury clusters in ground and excited electronic states [56,76–78]. Hg<sub>3</sub> is the smallest cluster which can bind an extra electron (electron affinity of 0.13 eV at the coupledcluster, CCSD(T), level of theory) [77]. Gaston et al. studied the photoabsorption spectra of cationic mercury clusters [56]. The experimental photoabsorption spectra of singly charged cationic mercury clusters  $Hg_n^+$  carried out by Haberland and coworkers show a sharp change in behavior at cluster size n = 6 [60,79]. It has been interpreted as the onset of a plasmon-like resonance in the 6s-6p transition. Both, relativistic density functional theory DFT and wavefunction-based methods revealed that the onset of a plasmon-like resonance corresponds to a structural change from linear to three-dimensional cluster isomers, i.e., a change from single electron-hole excitations in small linear clusters to plasmon-like collective transitions for the larger three-dimensional clusters [56].

Medium- to large-sized mercury clusters have been studied extensively in the past by experimental methods [20–23,26–31, 80–84], mainly to answer the question at what cluster size the transition from van der Waals to metallic bonding occurs [26]. An excellent review on cluster size effects and the extrapolation to the bulk for metallic clusters is given by Johnston [21]. Here we mention the most recent work of Busani et al. [29]. They measured photoelectron spectra of the mass-resolved negatively charged mercury clusters up to  $Hg_{250}^{-}$ . Upon photoexcitation, the 6*p* electron can be detached leaving the resulting neutral cluster in its electronic ground state. Alternatively, electrons can be detached from the 6*s* band of the mercury cluster leaving the resulting neutral cluster in an "electron–hole pair" excited state. The difference between both results is a direct measure for the HOMO–LUMO (6s-6p) gap in the photoelectron spectrum of the negatively charged cluster, which approximately provides the excitation band gap for the corresponding neutral cluster. Large changes in the structure of mercury clusters due to the excess electron are not expected at larger cluster size as the charge will be smeared out. Extrapolation to higher cluster sizes indicates a band gap closure at the size range of  $n = 400 \pm 30$ , a considerably larger value than previously reported (see Section 3.1) [29].

Bescós et al. studied time-resolved ultrafast multiphoton ionization and fragmentation dynamics of mercury clusters  $Hg_n (n \le 110)$ with femtosecond pulses [81]. At laser intensities of  $10^{11}$  W cm<sup>-2</sup>, they observed singly, doubly, and triply charged mercury clusters. Ionization potentials and electron excitation energies for mercury clusters up to  $Hg_{109}$  were determined by photoelectron and UV/ vis-photoabsorption spectroscopy by Rademann et al. [22,23,84]. Their estimate for the onset of the metallic phase is at much smaller cluster size compared to Busani et al. [29]. Blanc et al. looked at the stability of triply charged mercury clusters,  $Hg_n^{3+}$  [82]. They found  $Hg_{60}^{3+}$  to be stable with respect to fragmentation into  $Hg_m^{2+}$  and  $Hg_n^{+} (n + m = 60)$ , but not  $Hg_{50}^{3+}$ .

#### 3.4 Liquid Mercury and the Mercury Surface

Along with the lowest melting point  $T_{\rm m} = -38.83^{\circ}\text{C} = 234.32 \text{ K}$ [1] of all metals, assumed but not yet proven to be due to large relativistic effects lowering the 6s band substantially [2-5], mercury also shows the lowest critical temperature of all metals. Accepted experimental values for the liquid-gas critical point are a critical temperature  $T_c = 1751$  K at a critical density  $\rho_c = 5.8 \text{ g cm}^{-3}$  and a critical pressure  $p_c = 1673 \text{ bar } [85,86]$ . Since these values are experimentally accessible, mercury presents an ideal system to investigate liquid properties close to the critical region. Therefore, over the last decades, extensive research on the experimental as well as on the theoretical side of the liquidvapor coexistence curve up to the critical region has been taken place. Most of the studies focus on the interesting region of the metal to nonmetal (M-NM) transition which occurs when fluid mercury is expanded close to the critical values. At ambient conditions, the density of liquid Hg is 13.6g cm<sup>-3</sup>; the M-NM transition takes place at densities around 9g cm<sup>-3</sup> (see, e.g., the review on experimental evidence in Ref. [87] and theoretical calculations in Refs. [32,88]). In recent years, development in experimental techniques, especially the use of x-ray scattering methods based on third-generation synchrotron sources, as well as on the theoretical side (particularly in computational simulations) allowed for an improved understanding of the underlying mechanism of this M-NM transition (see, e.g., Refs. [89-97]) as well as for a better understanding of liquid metal surfaces where the existence of surface-induced atomic layering in liquid mercury was established [98,99]. New developments include the use of liquid Hg as a novel substrate for the deposition of Langmuir monolayers of organic substances [100-103] and the investigation of geometrically confined liquid Hg in nanopores [104-108] or carbon nanotubes [109,110]. Of interest are also the study of the liquid mercury–water interface [111–113] due to its importance in electrochemical cells and the adsorption of Hg on metal surfaces [114] in connection with the search for Hg oxidation catalysts.

Despite the fundamental, unsolved question, why mercury is liquid at ambient conditions, to our knowledge, there has only been one molecular dynamics study by Sumi et al. [115] trying to determine the melting temperature. They found a melting point of 232 K in accidentally good agreement with experiment, regarding the facts that their study relied on an ab initio potential curve of Hg<sub>2</sub> which considerably exceeds the bond length of the Hg dimer by 0.6 Å and that many-body effects were totally neglected. In later work, they used a scaled version of their potential in order to match the bond length better allowing them to reproduce experimental data at the M-NM transition region, but they did not calculate the melting point anew [116]. A promising ansatz to get information about the melting temperature is the cluster approach: Here, the melting temperature of nanoclusters, with several complete shells of atoms around a central atom therefore showing an enhanced stability, are extracted out of MC simulations and are extrapolated to the bulk value. This has recently been shown to be successful for neon and argon [117] where bulk melting points could be determined with high accuracy in a pure ab initio treatment. Of course, for Hg, great care of the treatment of the interparticle potential has to be taken, since the many-body expansion is known to fail (see below).

All computer simulations like molecular dynamics or Monte Carlo methods for liquids need, of course, information about the electron distribution of the system. The electronic distribution can either be modeled by a form of density functional theory (for liquid Hg, see, e.g., Refs. [32,118]) or by modeling or approximating directly the potential energy [119]. In most computational simulations of liquid Hg, the latter ansatz is chosen and the interparticle potential  $V_{\rm int}$  is divided into pairwise  $V^{(2)}$  and higher terms:

$$V_{\text{int}} = \sum_{n} V^{(n)} = \sum_{i < j} V^{(2)}(r_{ij}) + \sum_{i < j < k} V^{(3)}(r_{ij}, r_{ik}, r_{jk}) + \dots$$
(3.1)

The sums run over all particles in the simulation cell or up to a chosen cutoff distance and  $r_{ij}$  is the interparticle distance. Unfortunately, already the three-body terms are becoming quickly too expensive and, for Hg, the expansion is known to be not converging [35,73]. As a result, recent molecular dynamics simulations on liquid metallic mercury using a Lennard-Jones potential cannot reproduce the observed structure factor [120].

Therefore, at the present stage, theoretical studies rely on the construction of effective two-body potentials [121–126] or, most recently, effective three-body potentials [96,97,127–129] based on the accurate *ab initio* Hg<sub>2</sub> potential curve by Schwerdtfeger et al. [18] (see also a recent parameterization of Tang and Toennies [130]). The effective potentials include the many-body effects in an approximate way and are dependent on the temperature. Effective pair potentials have been constructed in a number of different ways and applied with good success to a variety of the structure

and properties of liquid mercury in wide ranges of temperatures and pressures. These works used the link between pair potentials and the pair distribution function, which itself is related by Fourier transform to the experimentally determined static structure factor. Either one starts with guesses for the potential that is refined using experimental data [124,125] or a guessed initial configuration is refined using the experimental structure data like in the reverse Monte Carlo method [121,122,126,131]. The effective two-body potentials are characterized by a steeply rising repulsive branch at short interatomic distances and a relatively weak oscillating branch at larger distances. Effective threebody potentials were constructed by introducing a semiempirical  $C_{o}(T)/r^{9}$  term fitted to experimental data [127,128] or through quantum-chemical calculations of cohesive energies for selected geometries of clusters and bulk crystals yielding effective manybody potentials that depend on the coordination number and the nearest-neighbor distance [96,97].

In Figure 3.2, the gas-liquid coexistence curve close to the critical region is depicted, showing the onset of the M-NM transition in the liquid region at densities around 9g cm<sup>-3</sup> corresponding to a temperature of about 1670K at the gas-liquid coexistence line. First indications for the M-NM transition were found by Franck and Hensel [132]. Different mechanisms for the transition have been proposed, which can be roughly divided into a homogeneous expansion mechanism (dating back to the pseudogap model proposed by Mott [133-135]), where the nearest-neighbor distance is gradually increasing while the coordination number is constant, and a heterogeneous expansion mechanism [88,136] making a decrease in the average coordination of the Hg atoms in the liquid with an (almost) constant next-nearest-neighbor distance responsible for the transition. After extensive experimental and theoretical investigations, the heterogeneous mechanism first proposed by Mattheis and Warren [136] and in the Franz model [88] is now the accepted



**FIGURE 3.2** Gas-liquid coexistence curve and selected isochores at densities of 10, 9, 5, and 1 g cm<sup>-3</sup>. The solid lines are theoretical data from Ref. [98]; the dashed lines refer to experimental data (Refs. [87,138]). The filled diamonds show the experimental and theoretical critical points. The shaded area presents the nonmetallic liquid region.

one and was refined in the last years due to experimental (see work of Hensel [86,87,137] and references therein as well as newer experimental work in Refs. [91,92,138]) and theoretical [32,96,97,121-123,126,129] progress. Exact measurements of the static structure factor and calculations of its Fourier transform, the pair distribution function g(r) (which gives the relative probability of an atom having a neighbor at distance r) proved a clear decrease in the average coordination number while the first peak of g(r) and thus the nearest-neighbor distance remains almost constant. In more detail: Below the M-NM transition, the local structure of liquid Hg is assumed to be similar to the crystal structure of  $\alpha$ -Hg (going back to the early experimental work by Kaplow et al. [139]): There are six hexagonally arranged atoms at 3.5 Å (close to the van der Waals dimer distance) around a central atom and six atoms at 3.0 Å (corresponding to the metallic distance in the solid) in an upper as well as lower plane three by three (see Figure 3.3). Around the M-NM transition, atoms at the shorter distances were shown to be selectively taken away causing the transition to the nonmetallic phase [91,96,97,126,129].

New experiments of the dynamic structure factor that allow the study of dynamical properties of expanded fluid Hg by using inelastic x-ray scattering have shed new light on the M-NM transition [93,94], and suggest that the transition is not a gradual one but a first-order transition at which a new style of fluctuations between metallic and nonmetallic domains appears [94]. Thermodynamically, and thus in all experiments measuring static properties, the discontinuous density jumps in the first-order transition are obscured by strong thermal agitation and structural disorder and feign a gradual transition. Earlier indications for a first-order transition was given in a theoretical investigation of the volume dependence of the free energy by Kitamura [95], who suggested an irregular mixing of high-density metallic domains and low-density nonmetallic domains in the M-NM transition range. Local transformation between the metallic and nonmetallic domains on a slow timescale is caused by thermal fluctuations, supporting experimental evidence of a slow structural relaxation process [89] and an anomalous sound adsorption [90] at the M-NM transition.



**FIGURE 3.3** Rhombohedral lattice of Hg showing the 12 next-nearest neighbors: 6 mercury atoms are arranged in a hexagon around the central atom with a distance of 3.5 Å while the other 6 atoms are located closer to the central atom with a distance of 3.0 Å above and below the plane three by three.

High-resolution inelastic neutron scattering measurements of the dynamic structure factor were also performed at room temperature in order to investigate the microscopic dynamics of liquid mercury [140–142]. It was shown that the so-called cage diffusion plays a dominant role in the collective dynamics of liquid mercury: While moving diffusively, particles find themselves locked up in a cave formed by their nearest neighbors [142]. This behavior was confirmed by recent molecular dynamics simulation by González et al. [143].

Experimental progress also allowed to study the crystal structure and properties of liquid Hg under geometrical confinement by embedding Hg into nanoporous matrices like porous glass, synthetic opals, or zeolites [104-108]. Even a 1D confinement can be realized by filling carbon nanotubes with Hg, which is achieved as a result of electrowetting [109]. Large interest in these nanostructured composites stems from the fact that fundamental questions of condensed matter physics related to finite-size effects can be addressed as well as applications in nanoengineering and nano-fluidics are to be expected. Experiments on Hg in porous glasses and other nanoporous materials have shown that the crystal structure of bulk Hg ( $\alpha$ -Hg) is identical to that of confined Hg [104], whereas the melting/freezing temperatures are shifted toward lower temperatures and the transitions are broadened in comparison to bulk Hg [105,106]. These trends are enhanced with decreasing pore size [107]. These effects caused by the finite size are in analogy to the observed behavior in clusters where one also finds decreasing melting temperatures and line broadening with decreasing cluster size (see, e.g., Ref. [117]). Also the Knight shift and thus the electronic susceptibility was shown to decrease with decreasing pore size [108]. For the carbon nanotubes similar effects are predicted by a molecular dynamics simulations [110]. In this study, an ordering of the Hg atoms near the walls of the nanotubes and density oscillations, which extend several atomic diameters into the bulk, are suggested, even resulting in a closepacked cylindrical shell structure for the smallest nanotubes.

Metallic liquids exhibit a complex surface structure in which the atoms are stratified parallel to the liquid-vapor interface persisting into the bulk for a few atomic diameters and leading to density oscillations along the surface normal. This phenomenon of surface layering has been predicted theoretically [144], but could not be proven unambiguously in experiments [145] until experimental improvement due to access to third-generation x-ray sources finally allowed to resolve these oscillations, first in Hg [98,146] and Ga [147]. In Hg, the layering was found to have a spacing of 2.72 Å and a decay length of less than 5 Å. Surface layering seems to be a more universal property of liquid surfaces in general [148-152] but the reasons behind are not yet clearly identified; possibilities include surface tension, geometrical confinement effects due to the necessarily rapid decay of the density at the liquid-vapor interface [152] and a low ratio of melting and critical temperature  $T_{\rm m}/T_{\rm c}$  [148–151].

Another interface of great interest due to its importance in electrochemical cells is the one between liquid Hg and water. This interface was studied by molecular dynamics simulations with pure water [111] as well as in the presence of alkali cations (see Refs. [112,113] and references therein). In analogy with the just discussed surface layering at the liquid mercury–vapor interface, one finds comparable far-ranging density oscillations in the mercury phase as well as a change in the water density profile up to distances of about 10 Å. The mobility of the adsorbed water is equally restricted parallel and perpendicular to the interface. The bulk densities are, however, almost identical to the pure liquids [111]. When alkali cations are present, it was shown, that the ions are adsorbed within the first layer of mercury losing part of their hydration shell and becoming less mobile. Otherwise, the structure of the hydration shell as well as of the mercury surface are not much changed in its main features [112,113].

Yet another example for the importance of liquid mercury interfaces is the use of liquid Hg as a novel substrate for the deposition of Langmuir monolayers of organic molecules like alkylthiols, fatty acids, and alkanes [100,103]. Langmuir monolayers are studied as models of 2D matter and as a route to nanoengineering and molecular electronics [153]. In contrast to the use of solid metals or of water as substrates, liquid mercury shows no steps or structural defects at the surface and the surface is atomically smooth due to the high surface tension and lack a long-range order of its own, but strong chemical bonds to the functional groups exist. Thus, new structures for the organic monolayers on liquid Hg have been found in synchrotron x-ray scattering experiments, especially until then unknown layers of surface-parallel molecules [101-103]. When the coverage is increased, one finds phase transitions to ordered phases of molecules with surfacenormal orientation [101,103].

As already mentioned in the introduction, huge amounts of Hg are released into the atmosphere by combustion of fossil fuels. The removal of Hg in power plants is therefore an important issue. Since oxidized Hg can be removed quite efficiently, the search for oxidation catalysts is of great interest with the noble metals being regarded as hopeful candidates. Thus, a fundamental understanding of the adsorption of Hg to these metal surfaces is important. It was shown in experimental studies [154,155] as well as in theoretical studies [114,156] that Hg atoms adsorb quite strongly to the metal surfaces. In a recent DFT study [114], Steckel calculated binding energies for adsorption of mercury at Ag, Au, Cu, Ni, Pt, and Pd surfaces (on the 001 and the 111 face) for different amounts of coverage finding binding energies of up to about 1 eV per atom for Pt and Pd. The calculated values should provide a lower estimate to the actual values due to the used (GGA) density functionals, which is also confirmed by comparison with available experimental data (see Refs. [154,155] and references therein). The adsorbed Hg atoms are found in the fourfold or threefold follow positions of the 001 or 111 faces, respectively. This is in contrast to recent findings of Sarpe-Tudoran et al. [156] who found the bridge position as the most stable one.

#### 3.5 Solid Mercury

Mercury freezes at  $T_{\rm m} = -38.83$  °C adopting a rhombohedral crystal structure with lattice constants of a = 3.005 Å and an angle of  $\alpha = 70.53$ ° [1]. The lattice has three equal crystallographic axes

inclined to each other at the angle  $\alpha$  (an angle of  $\alpha = 60^{\circ}$  corresponds to a face-centered cubic [fcc] lattice). Thus, Hg deviates from the hexagonal close-packed (hcp) structure found for the lighter group IIB metals zinc and cadmium. The unusual structure is another anomality of Hg caused by relativistic effects. This was recently shown unambiguously by Gaston et al. [38]. Until recently, not only the lattice constants, but also the cohesive energy  $E_{\rm coh}$  and the bulk modulus could be calculated with increasing accuracy of up to about 1.5% of the experimental data [36,38,73,157,158]. On exerting pressure, one finds a multitude of high-pressure phases for Hg. Besides the rhombohedral  $\alpha$ -Hg, a tetragonal  $\beta$ -phase, an orthorhombic  $\gamma$ -phase, and finally a hcp lattice structure for  $\delta$ -Hg have been discovered [159,160].

Already in the 1960s the general features of the density of states (DOS) and the band structure of Hg were known by experiment giving detailed information on the Fermi surface by measuring the de Haas-van Alphen effect [161] as well as by calculations [162,163]: At the Fermi energy  $E_{\rm F}$ , one finds a broad sp band (width about 10 eV), which mixes at its low-energy part with the narrow d band. This mixing is possible due to indirect relativistic effects. The strong relativistic contraction of the s bands [24,136,162,164] causes the interatomic Hg-Hg spacing in the solid [38], which in turn leads to an energy increase of the *d* bands. Just above  $E_{\rm F}$ , a structure-induced minimum in the DOS separates the sp band from empty states of predominantly p character. The band structure was also calculated by Deng et al., emphasizing the existence of flat and steep bands at the Fermi level, what they used as a possible explanation for the superconductivity of Hg observed below 4K [165]: The pairing of electrons occurs in the flat bands, whose position relative to  $E_{\rm F}$ is periodically changed by lattice distortions (phonons). When the top of the band lies above  $E_{\rm F}$ , the electron pairs are scattered into the steeper bands, whereas when the band maximum lies beyond  $E_{\rm F}$ , the bands are filled up out of the electron reservoir of the steep bands. At the critical temperature, the pairs become stable and a superconducting state results [165].

The rhombohedral lattice structure of  $\alpha$ -Hg in contrast to the hcp structures found for zinc and cadmium was studied intensely over the last decades. It was shown early on that the fcc structure is unstable with respect to a rhombohedral distortion and metastable with respect to a tetragonal distortion of the body-centered cubic (bcc) lattice [163], which was confirmed in later studies by Singh within a DFT framework including the energetically relatively high-lying *d*-electrons explicitly as valence electrons [24,164] and by Kresse and Hafner, who calculated the total energy of Hg as function of a rhombohedral or tetragonal distortion of an fcc or bcc lattice, respectively [32].

Nevertheless, theoretical predictions of the Hg structure that give accurate values for the lattice parameters or the cohesion energy remain a challenge. Whereas a pure mean-field (Hartree–Fock) treatment yields no binding at all [35,36], density functional approaches fail badly when attempting to optimize the lattice structure of Hg or getting sensible values for the cohesive energy. Depending on the underlying functionals, one gets anything from strong overbinding to severe underbinding [35,38,73]. An alternative approach was developed in the last years in the form of a wavefunction-based correlation treatment [36,38,157,158] using the incremental scheme dating back to Stoll [166]. In this approach, the cohesive energy is split into the mean-field (Hartree–Fock) part, calculated for the infinite solid system, and the correlation energy  $E_{\rm corr}$  computed with the following many-body expansion using the wavefunction-based coupled-cluster approach:

$$E_{\rm corr} = \sum_{i} \varepsilon_i + \sum_{i < j} \varepsilon_{ij} + \sum_{i < j < k} \varepsilon_{ijk} + \cdots$$
(3.2)

 $E_{\rm corr}$  is expanded in one-body increments  $\varepsilon_i$ , two-body increments  $\varepsilon_{ii}$ , and so on and the sums extend over groups of localized orbitals. The energy increments are calculated for finite embedded clusters, which mimic the environment found in the solid. Details of this embedding are crucial and have been discussed in detail in Ref. [158]. While Hartree-Fock and the one-body increments of the correlation energy lead to no binding at all, the main contributions to the binding were shown to come from the two-body increments, half of that originating from core-valence correlation of the *d*-shell. Three-body increments are required and account for about 10% of the correlation energy [36,38]. Very high accuracy could be achieved by that treatment yielding lattice constants of a = 2.96 Å and  $\alpha = 69.5^{\circ}$ , a cohesive energy of  $E_{\rm coh} = -0.649 \,\text{eV}$ , and a bulk modulus  $B = 0.360 \,\text{Mbar}$  [38], compared to the experimental values a = 3.005 Å,  $\alpha = 70.53^\circ$ ,  $E_{\rm coh} = -0.67 \, {\rm eV}$  [1], and  $B = 0.382 \, {\rm Mbar}$  [164].

Solid mercury exists in at least four different phases if subjected to pressure. At ambient pressure, Hg is liquid at room temperature, showing a local structure of  $\alpha$ -Hg [139] with six hexagonally arranged atoms at 3.5 Å around a central atom and six atoms at 3.0 Å in an upper as well as lower plane three by three (See Figure 3.3). At  $T_{\rm m}$  = 234 K, Hg solidifies in this rhombohedral  $\alpha$ -Hg structure and may exhibit a tetragonal phase at lower temperatures (below T = 77 K), but only if this phase is formed at high pressures. This transition to the  $\beta$ -phase was already discovered very early by Bridgman [167] and a high potential barrier for the transformation from  $\alpha$  to  $\beta$ -Hg was made responsible for the fact that  $\alpha$ -Hg remains metastable at temperatures below 77 K [168]. Interestingly, also the  $\beta$ -phase becomes a superconductor at slightly lower temperatures, at  $T_c = 3.94$  K compared to 4.15 K for  $\alpha$ -Hg [169]. At room temperature, mercury becomes solid at a pressure of p = 12kbar crystallizing in the  $\alpha$ -form. Further increase of the pressure leads to the body-centered tetragonal  $\beta$ -phase at p = 37 kbar, the orthorhombic  $\gamma$ -phase at p = 120 kbar [170], and finally, at 370 kbar, Hg transforms into a hcp structure named  $\delta$ -Hg [159,160]. In contrast to this observed polymorphism, Zn and Cd stay in the hcp structure over the whole pressure range [159].

#### **3.6 Conclusions**

The electronic configuration of Hg is [Xe]  $4f^{44}5d^{10}6s^2$  with closed 5d and 6s shells. Due to large relativistic 6s contraction, the energy of the 6s orbitals/bands is lowered significantly leading to large

changes in almost all properties observed, from the Hg atom over the clusters to the liquid or solid bulk phase. This sets Hg apart from its lighter homologues zinc and cadmium, with mercury behaving sometimes more like a rare gas. This causes anomalies in almost all atomic properties, like the small electric dipole polarizability or the high ionization potential, in the weak van der Waals binding of the Hg dimer, over to the complicated binding behavior in the clusters, to finally the rhombohedral crystal structure of the solid and low melting and gas-liquid critical temperatures. The unusual high superconducting transition temperature, which led Kamerlingh Onnes to the discovery of this phenomenon, is, most likely, also a manifestation of relativistic effects. The theoretical description of the interaction between Hg atoms is complicated by the necessity of a proper relativistic treatment, and by the need to explicitly consider the 5d electrons as valence electrons, as the corresponding orbitals/bands are energetically elevated by indirect relativistic effects mixing into the 6s orbitals/bands. Furthermore, the many-body decomposition of the interaction potential between Hg atoms is not converging smoothly, i.e., a simple treatment in terms of two-body and perhaps three-body potential terms is not adequate in contrast to the rare gas elements. Nevertheless, progress was made in the last years, giving detailed explanations for the M-NM transition in liquid Hg, and allowing the calculation of lattice parameters and the cohesion energy of solid Hg with high accuracy. Still, a number of fundamental problems remain unsolved, the most prominent are certainly the questions, why Hg is liquid at room temperature, or what causes the high superconducting transition temperature of 4K.

Beside these fundamental questions, experimental as well as theoretical progress has opened up new exciting fields of research with possible application in different areas of nanoscience. Examples are the use of liquid mercury as a novel substrate for Langmuir monolayers of organic molecules and the investigations of liquid/solid Hg embedded in porous nano-matrices or carbon nanotubes. These fields are still at their initial stages and need a detailed understanding of the fundamental properties of Hg from the dimer over the clusters to the bulk.

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## 4

## **Bimetallic Clusters**

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#### 4.1 Introduction

In scientific literature, various terms are used to denote small metal particles. There are no universally accepted definitions, but the various terms usually imply particles with different numbers of atoms N: clusters ( $N \le 100$ ), nanoclusters or nanoparticles (diameter in the 1–100nm range,  $\log_{10} N \approx 2-7$ ), small particles  $(\log_{10} N \approx 7-11)$ . This chapter concerns primarily clusters ( $N \le 100$ ), that is, particles at the lower size limit of nanophysics. A further classification can be made according to the nature of the surface of clusters: free, supported, or passivated clusters. A free bimetallic cluster  $A_m B_n$  contains nothing else than atoms of the two metals. These clusters are inherently unstable because of their high surface energy, which makes them coalesce into larger particles or react with other species. Supported clusters are strongly bound to a solid normally chosen to be a high surface area material like alumina  $(Al_2O_3)$ . In this kind of cluster, some of the metal atoms are bound to the support, usually through strong covalent bonds to oxygen atoms, and the other metal atoms are at the surface. These clusters are marginally stable: The surface metal atoms have a strong tendency to oxidize but can be kept in the metallic (zero oxidation) state by maintaining a high H<sub>2</sub> pressure or high temperature in a flow reactor. Supported metal clusters, whether elemental or bimetallic, are mainly used as heterogeneous catalysts in large-scale industrial reactors, for cracking and ammonia synthesis for instance. Passivated clusters have a central metallic core, which is often icosahedral or crystalline and roughly spherical in shape and entirely covered by ligands. A common small ligand for passivating metal clusters is carbon monoxide; Ni<sub>24</sub>Pt<sub>14</sub>(CO)<sup>4-</sup><sub>44</sub> is one of many examples of CO-passivated bimetallic clusters [1]. Bigger ligands are more often used. Thiols,  $CH_3-(CH_2)_n$ -SH, make good passivating ligands for elemental or bimetallic clusters that have a group 11 metal (Cu, Ag, Au) at the surface because of their high binding affinity to these metals. The "metal end" of the ligand (the S atom for a thiol) strongly binds to surface metal atoms. The "solvent end" is normally designed to assure solubility, e.g., a simple hydrocarbon chain for solubility in nonpolar solvents. But all sorts of designs are possible at the solvent end of a ligand: It can be tailored for purposes like self-assembly, covalent binding to surfaces, molecular recognition of DNA or other biomolecules, or for certain chemical reactions by inclusion of functional groups. As a group, passivated clusters are stable and highly versatile—they make logical building blocks for cluster-assembled materials [2].

Practical applications of clusters depend on their stability, and this increases on going from free to supported and passivated clusters. On the other hand, the number of low-lying excited electronic states, which are responsible for the properties unique to metals (conductivity, magnetism, versatile chemistry and catalytic activity, etc.) decreases in the order free, supported, passivated. Therefore, applications that depend specifically on metallic properties of small clusters (e.g., bimetallic catalysts) present special challenges. In molecular orbital (MO) theory, metallic properties are associated with a zero (or very small) highest occupied MO-lowest unoccupied MO (HOMO-LUMO) gap in orbital energies. In sufficiently large passivated metal clusters, interior atoms do not "see" the passivating ligands, they have bulk-like electronic states with a nearly zero HOMO-LUMO gap, and have metallic properties. But the atoms at the metalligand interface have a local density of electronic states that resembles a semiconductor. In small passivated metal clusters, the HOMO-LUMO gap is large not only for surface atoms, but also interior atoms [3,4]. In that sense, small passivated metal clusters are not metallic.

This chapter gives a brief description of the three kinds of bimetallic clusters and the way they are made (Section 4.2), and their current and potential applications (Section 4.3). Here, the emphasis is on *free* clusters (Section 4.4, and for bimetallics, Sections 4.5 through 4.8) because this is where the metallic character is most pronounced, and because the other types of clusters can be made into cluster-assembled materials, which are discussed in other chapters.

#### 4.2 Types of Bimetallic Clusters and How They Are Made

Free clusters contain no atom other than the two metals. They can be made in the gas phase by laser ablation of the metals (an alloy rod, or two rods, or a powder mixture), or by evaporating the two metals with an intense electrical discharge or otherwise. The vaporized atoms condense into growing clusters as they are carried away from the source by an inert gas. Supersonic expansion rapidly cools the clusters and produces a narrow distribution of cluster velocities. This effectively stops the growth and gives a cluster beam [5]. Free metal clusters are inherently unstable visà-vis coalescence and various chemical reactions: They survive only in the low-pressure environments of molecular beams, or get deposited on surfaces [5–7], or in a matrix [8,9], or in a cryogenic matrix by co-condensation with an inert gas (e.g., Ar) [10]. In ultrahigh-vacuum (UHV) experiments, clusters are often formed with kinetic energies on the order of a few eV/cluster. But mass selection imparts much larger kinetic energies as the cluster ions get accelerated in an electrical field. In order to avoid fragmentation upon cluster deposition on a substrate, two complementary techniques can be used. First, one can apply a retardation potential in the region between mass selection and substrate and bring kinetic energies down to roughly 1 eV/atom. Second, one can condense multiple layers of a rare gas on the substrate prior to deposition. Then, upon deposition, the clusters' kinetic energy is gradually dissipated by heat transfer to desorbing rare gas atoms and to the substrate. This so-called soft-landing method can yield cluster fragmentation rates lower than 15%-20% [11].

Supported clusters are formed or deposited on a surface. One method is to take metal complexes with small and relatively weakly bound ligands, bind them to silica, and heat for a few hours at ~200°C in vacuum. One can get very small (~10-20 atoms) bare metal clusters bound to the silica [12]. Electrochemical synthesis has also been used [13]. The PdPt clusters of Ref. [13] are both supported and passivated, so these two categories are not mutually exclusive. Supported bimetallic catalysts often combine an oxophilic transition metal and a noble metal in a particle that is bound to a high surface area material such as alumina, silica, zeolite, or a carbon powder, in

order to achieve high dispersion (see Section 4.4.1) and maximize activity. The oxophilic metal binds strongly to the oxygen atoms of the support, which helps achieve both high dispersion and stability. If A is oxophilic and the free A<sub>m</sub>B<sub>n</sub> cluster is mixed (alloyed), interaction with the support will promote segregation of A toward the oxygen atoms of the support. The support itself often plays a nontrivial role for the chemistry. The exposed surface of the cluster is normally kept in the metallic state by maintaining a H<sub>2</sub> atmosphere and high temperature, which help reduce any metal oxide that may form. Keeping a cluster catalyst active (keeping the metallic surface intact) is always a concern. The turnover number is defined as the mean number of reaction events catalyzed per unit surface area of catalyst before it gets chemically modified and becomes inactive. Ideally, a catalyst would have an infinite turnover number, but in reality, catalysts become deactivated after some time. Some catalysts are simply discarded and replaced after they are deactivated. Others can be regenerated by chemical means: sometimes deactivation is so rapid that a reactor must alternate between two modes of operation—running the catalytic reaction and regenerating [14]. The methods of preparations of supported bimetallic clusters and their applications in catalysis have been described by Alexeev and Gates [15].

Passivated bimetallic clusters are normally made in solution, often at high temperature, by reduction or decomposition of organometallic precursors in the presence of surfactants. The size and composition of bimetallic clusters made this way can be controlled by adjusting the concentrations and molar ratios of the organometallic precursors. For example, passivated FePt colloids with tunable size in the 3-10 nm range, and with Fe molar fractions of 0.48, 0.52, and 0.72, have been made by simultaneous reduction of  $Pt(acac)_2$  (acac = acetylacetonate) by a diol and thermal decomposition of Fe(CO)<sub>5</sub> in the presence of oleic acid and oleyl amine [16]. Co-reduction of a mixture of metal salts generally gives core-shell clusters A<sub>m</sub>@B<sub>n</sub> where A, the metal with highest redox potential, makes a central core surrounded by a shell of B atoms. But some choices of surfactants can produce the reverse core-shell (B, @A, ) structure [17]. Bimetallic clusters have been made by irradiating aqueous solutions of metal ions with  $\gamma$  rays (radiolysis). The  $\gamma$  rays ionize water molecules producing solvated electrons, which go on to reduce metal ions to neutral metal atoms. Atoms then coalesce and get capped by a polymer like polyvinyl alcohol. Doudna et al. used this method to make AgPt nanoparticles [18]. They got very high aspect ratio wirelike structures with lengths up to 3500 nm and diameters between 3 and 20 nm, but were also able to get spherical clusters with some choices of counterions, mole ratio of the two metals, and capping polymer. Intense ultrasounds also produce solvated electrons that can reduce metal ions in aqueous solutions. This is the basis for sonochemical synthesis, which has been used, for instance, in the preparation of core-shell Au@Pd clusters with an average diameter of 8 nm. Radiolysis and sonochemical synthesis generally produce clusters with different size and morphology [19]. In smaller clusters, the passivating layer, which imparts stability, opens up a gap in the density of electronic states [3,4] and this affects metallic properties. The control afforded by the choice of ligands and possible subsequent chemistry with these ligands is a big advantage for this type of clusters. Passivated clusters can sometimes be assembled into 3-dimensional materials (crystals of nanocrystals) [2,20]. This can be done, for example, by the "tri-layer technique of controlled oversaturation" [21]. In this technique, three immiscible liquids are put on top of each other, in decreasing order of nanoclusters solubility: high solubility (a solution of nanoclusters) at the bottom, slight solubility (buffer layer), and no solubility (nonsolvent) on top. As the nonsolvent and nanoclusters slowly diffuse into the buffer layer, single crystals of nanoclusters nucleate and grow.

#### 4.3 Applications

Bimetallic clusters have current or potential applications in catalysis, biodiagnostics, electronics, and ultra-high-density magnetic recording media [22]. The properties of bulk alloys can be tuned by changing the composition. In bimetallic clusters, more variables can be controlled. As mentioned earlier, it is sometimes possible to control the size, shape, or morphology of the clusters, in addition to their overall composition. Sometimes, one can control the surface composition by making a reverse core-shell cluster  $B_n@A_m$  and doing a partial transformation to the thermodynamically favored form  $(A_m@B_n, \text{ or mixed alloy})$  by a short, controlled annealing. For example, Co<sub>m</sub>@Pt<sub>n</sub> core-shell clusters (m/(m + n) = 0.45, size 6.4 nm) have been synthesized by redox metallation [23]. Upon annealing for 12h at 600°–700°, the diffusion of Co and Pt atoms led to a mixed alloy with very different magnetic properties from the initial Co<sub>n</sub>Pt<sub>m</sub> clusters. Heating by laser irradiation offers better controlled annealing [24]. Pairs of elements that are not miscible in the bulk often mix and form alloy-like structures in very small clusters like RuCu.

Small bimetallic clusters are qualitatively different from mixtures of the clusters of the two pure metals. This opens up possibilities, especially for catalysis. A catalytic reaction normally involves a sequence of events at the molecular scale, or, steps. Different metal catalysts have different effects on the rate of the individual steps. So, one can in principle speed up two or more rate-limiting steps and achieve superior catalytic activity by using a catalyst having two (or more) metals in close proximity of each other [25]. Combining two metals can have a more profound effect: the electronic structure of each metal is altered by the presence of the other. For instance, Pt, a good catalyst in itself, can be modified and have its catalytic activity toward some reaction optimized by adding the right amount of a chosen metal partner [26]. In the case of highly structured bimetallic particles (e.g., alloyed or core-shell), completely different electronic or geometric structures could emerge. Supported bimetallic cluster catalysts have been studied by Sinfelt and coworkers since the 1960s. It has been observed that the activity of a catalytically active metal can be drastically reduced by the presence of a group 11 metal for some reactions, but not others, which then makes these bimetallic catalysts highly selective [27]. The MPt (M = Re, Sn, Ir) catalysts are very important and have replaced pure Pt catalysts for large-scale naphtha reforming [27]. Bimetallics like RhPt are used for conversion of automobile exhaust [15]. Very small (~10–20 atoms) supported RuX bimetallic clusters (X = Cu, Pd, Ag, Sn, Pt) exhibit high activity and high selectivity for hydrogenation reactions [12]. Supported bimetallic clusters are comparatively costly, but the possibility of varying composition, size, and support makes them interesting for applications where high selectivity is needed, for example, in the pharmaceutical industry or for fine chemicals. Several PtX clusters (X = Cr, Mn, Fe, Co, Ni, Mo, Ru, Sn) in the 1–10 nm size range supported on high surface area carbon powders have been used as catalysts in fuel cells [28].

Some bimetallic clusters have potential applications associated with their unusual magnetic properties. Vapor-deposited granular films of ferromagnetic-noble metal combinations, like Fe<sub>n</sub>Ag<sub>m</sub>, display giant magnetoresistance effects, i.e., large changes in resistance upon application of a magnetic field [29]. It has been seen, in a variety of systems, that the orbital magnetic moment and magnetic anisotropy energy (MAE) increase for atoms with a low coordination [30], and such atoms make up a significant fraction of nanostructures. On the other hand, the addition of Pt to Co nanoparticles was shown to increase the volume contribution to the MAE [30]. Three-dimensional lattices of FePt clusters (3-10 nm) also display large MAE and other interesting properties [16]. It has been estimated that magnetic nanoclusters as small as 4nm could maintain their magnetic moment orientation at room temperature, so they could form the basis for ultra-high-density recording with densities on the order of terabits per square inch [31]. For this reason, there are ongoing efforts to improve synthetic control over the size and structure of CoPt and FePt nanoparticles [32].

Passivated bimetallic clusters can be used as probes in biomedical applications. The ligands on the outer shell of the clusters can be tailored to optimize their binding affinities to specific biomolecular targets. In one example, it was shown that oligonucleotide-modified 13 nm gold clusters interact with a specific DNA sequence and aggregate under its influence. Upon aggregation of the clusters, the color of the solution changed from red to blue, giving a simple colorimetric detection test for this specific DNA [33]. But the small number and small size of the Au nanocluster colorimetric probes gives this method a low sensitivity. The sensitivity can be increased by several orders of magnitude by catalytic reduction of Ag onto the Au nanoclusters that are attached to the target DNA because the Au@Ag clusters are much easier to detect [34]. In principle, one can detect and analyze several different DNA strands simultaneously by a variation of this method: use bimetallic clusters of various size, shape, and composition, each having its own optical properties (its own "signature"), and each being attached to one specific type of oligonucleotide. The ability to make in a controlled way many different clusters, each with its own intense and unique signal (optical, mass spectrometric, ...), is the key in these kinds of applications.
# 4.4 Free Metal Clusters

# 4.4.1 Dispersion, Surface Energy

We now turn our attention to free clusters. We will first look at ideas that apply to elemental as well as bimetallic clusters. The *dispersion* D of a particle is the fraction of its atoms that are at the surface. In metal clusters, as in metallic solids, atoms have a tendency to arrange in a compact way. If a metal particle is quasi-spherical with diameter d = 2R, the interatomic nearest-neighbor distance is  $R_{NN} = 2r$ , and the packing is compact and similar to fcc, then the number of atoms N and dispersion D can be estimated as follows:

$$N \approx f(R/r)^3; \quad D \approx 1 - (R_2/R_1)^3$$
 (4.1)

where 
$$R_1 = [(N/f)^{1/3} - \sqrt{2}/2]r$$
 and  $R_2 = R_1 - \sqrt{2}r$  (4.2)

and  $f \approx 0.7$  is an effective packing fraction. These formulas assume a spacing between concentric layers of atoms close to that in close-packed crystals ( $\approx \sqrt{2}r$ ). Taking a nearest-neighbor distance of 2r = 2.7 Å (a typical value for metals) gives diameters of roughly 0–1.4 nm for clusters ( $N \le 100$ ), 1.4–70 nm for nanoparticles, and 70–1400 nm for small particles ( $N \ge 10^7$ ). A rough calculation of surface energy shows a strong thermodynamic force to destroy free clusters via coalescence, oxidation, or passivation with ligands. Empirically, the surface energy per metal atom is roughly 0.16 times the cohesive energy [14]. We will assume a surface dominated by a square lattice (e.g., fcc(100) facets) and typical transition metal values for the nearest-neighbor distance ( $R_{\rm NN} \approx 2.7$  Å) and cohesive energy ( $E_c \approx 4.5 \text{ eV}$ ). Then, the surface contribution to the total energy of a quasi-spherical N-atom metal particle is roughly (0.16 $E_cDN$ ). Using Equations 4.1 and 4.2, one can calculate particle diameters  $d = 2R_1$  in nm, the dispersion D, and the surface energy on a per atom basis in eV/atom, (0.16 $E_cD$ ). This is shown below

$\log_{10} N$	1	2	3	4	5	6	7	8	9
d (nm)	0.7	1.4	3.0	6.5	14	30	65	140	300
D	0.99	0.68	0.35	0.17	0.08	0.037	0.017	0.008	0.004
$(0.16E_{c}D)$	0.72	0.49	0.25	0.12	0.058	0.027	0.013	0.006	0.003

Typical surface energies are  $1-3 \text{ J/m}^2$  for metals but only 0.02– 0.08 J/m<sup>2</sup> for organic liquids, with 0.03 J/m<sup>2</sup> being a typical value for long alkanes [35]. This is because organic molecules interact through van der Waals interactions and these are much weaker than metal-metal bonds. It is clear that passivating a cluster brings about a large drop in surface energy in absolute terms (in eV). But the relative energy change (in eV/atom) is rather small (compared to  $k_{\rm B}T$ ) for  $\log_{10} N > 7$ . The energy decrease associated with coalescence of two *N*-atom clusters into one 2*N*-atom cluster is also very large in absolute term, but it gets smaller, on a per atom basis, as *N* increases. This energy is roughly  $(2 - 2^{2/3}) = 0.41$  times the surface energy  $(0.16E_cD)$ in the above table. Other contributions to cluster energies scale in different ways. In particular, the energy associated with spin pairing, electronic shell closings, and details in geometry (e.g., small displacement of one or few atoms) are on the order of 1 eV and do not scale up with N. There are no clear demarcations, but roughly speaking, the energy terms that do not scale up with N (those caused by the molecular aspects of geometric and electronic structure) become negligible compared to the surface energy at around  $N \approx 100$ , and the surface energy itself becomes small (relative to  $k_{\rm B}T$ ) at around  $N \approx 10^7$ . These general considerations explain why at small N every atom counts, why small metal clusters can survive only under special conditions or stabilized by a support or ligands, and why only larger particles can be in the form of a pure metal (and without special care even these usually develop an oxide skin).

#### 4.4.2 Size Evolution of Properties

The atomization energy (AE) of a cluster  $X_n$  is the energy of the reaction  $X_n \rightarrow nX$ , with the cluster  $X_n$  and atoms X in their ground states. Consider the AE in a family of metal clusters. The size dependence of AEs can be fitted rather well by the formula

$$AE(N) \approx AE_{fit}(N) = E_i N + E_s N^{2/3} + E_e N^{1/3}$$
 (4.3)

In this formula, the coefficients  $E_i$ ,  $E_s$ , and  $E_e$  represent energy contributions from interior (or "bulk") atoms, surface atoms, and edge atoms respectively. It is difficult to determine  $E_e$  accurately by fitting the AEs of very small clusters ( $N \leq 30$ ), but the  $(E_{\rm e}N^{\rm 1/3})$  term is surely a lot smaller than the other two. Setting  $E_e = 0$ , one finds that the ratio of the coefficients  $E_i/E_s$  varies between -0.8 and -1.1 among 11 series of elemental metal clusters (Li, Be, Mg, Al, V, Fe, Co, Ni, Nb, Ag, Au) with data that includes a mix of experimental [36] and theoretical results from various sources. So, in a typical case,  $E_i/E_s \approx -1$  and the cohesive energy of a small N-atom metal cluster is roughly  $E_c(N) \approx (1 - 1)^{-1}$  $N^{-1/3}$ ) $E_{\rm c.bulk}$ . The difference between the actual and fitted AEs, or residual  $E_{\rm res}$ , is of interest because it shows the effect on energy of many nontrivial things such as the precise geometrical structure of clusters, electron spin pairing, and the symmetry and filling of orbitals (electronic shell closings). For the 11 elemental clusters above, the range over which  $E_{\rm res}$  varies is roughly 0.5 eV (i.e., ±0.25 eV) for Li clusters, 1 eV for Al, Ag, and Au, and 1.5 eV for transition metals and group 2 metals. Figure 4.1 shows  $E_c$  and  $E_{res}$  (calculated relative to a fit using Equation 4.3 with  $E_e = 0$ ) as a function of N for two very different metals, Ni and Mg. The data used for Ni is from collision-induced dissociation experiments [37], and data for Mg comes from density functional theory (B3PW91 method) calculations [38].

It is apparent from these and other examples that the shape of the  $E_{res}(N)$  curve depends a lot on the position of the element in the periodic table. For example, the  $E_{res}(N)$  curve of Co resembles Ni; Ag and Au are similar and have much bigger even-odd



FIGURE 4.1 Cohesive energies (eV/atom) and difference between AE data and its fit (eV) for Ni and Mg clusters as a function of number of atoms N.

oscillations than other elements; alkali metals have local minima in  $E_{\rm res}(N)$  at N = 8, 20, instead of N = 4, 10, 20 for Mg and Be; etc. But in any case, the magnitude of  $E_{\rm res}$  is rarely larger than 1 eV. So, as a fraction of the total,  $E_{\rm res}$  is appreciable only for clusters with  $N \leq 100$ .

Variations on the order of 1 eV are common for ionization energies (IE) and lowest excitation energies  $(E_{\alpha})$  among isomers, and among clusters that differ only by one or two atoms. Those kinds of energy differences can have dramatic consequences for a number of other properties, most notably for chemical reactivity [39]. For this reason, it is often said that in small clusters every atom counts. Properties other than the AE can also be fitted with a formula like Equation 4.3, and one observes that different properties converge toward the bulk value in different ways. Calculations on clusters with up to 225 atoms confirmed the  $N^{-1/3}$  scaling of cohesive energies but also showed a very different scaling for the mean nearest-neighbor interatomic distance,  $R_{\rm NN}$ , as a function of N:  $R_{NN}$  varies linearly with the mean coordination number [40]. Assuming a coordination of roughly 6 or 7 for surface atoms and 12 for interior atoms, and using the formula given earlier for dispersion D, one can estimate the mean coordination number c as a function of N. For N < 1000, c increases by roughly 0.55 every time N doubles, so it is roughly 6.5 for N = 10, 7.4 for N = 40, 8.7 for N = 160, and 9.8 for N = 640. For any property P, there is a certain value of N beyond which P changes monotonically with N. This is called the scalable regime for that cluster and property. It has been shown that the key features of the density of electronic states reaches the scalable regime near N = 80 [40]; adsorption energies on Pd clusters also get in the scalable regime at around N = 80 [41]. All of the above also holds for bimetallic clusters A<sub>m</sub>B<sub>n</sub>, but in addition, qualitative changes in geometric structure can occur at relatively large values of (m + n). For example, holding (m/n) constant, there could be a transition from alloy structures to core-shell A<sub>m</sub>@B<sub>n</sub> segregated structures at some critical value of N = (m + n). In such a case, one would normally require two separate curves and fit parameters to describe the size variations for each structure type.

#### 4.4.3 Magic Clusters

In elemental clusters, some cluster sizes show special stability as evidenced by a higher abundance in mass spectra [42] or by cohesive energies that lie above polynomial fits, as shown in the previous section. These have been called "magic clusters." Much effort has gone into identifying and explaining magic numbers in elemental clusters. Two simple models that have been used a lot are *electronic shells* [42,43] and *atomic shells* [44,45]. These models have limited reliability and scope but remain useful conceptually because no simpler model can explain so much about metal clusters.

The *electronic shells* model is based on the idea that some metal clusters are liquid-like, their geometric configuration is not essential, and the number of valence electrons  $N_e$  is the critical variable. Electronic shells are usually predicted using the *ellipsoidal jellium model* (EJM) [43,46]. In the EJM, clusters consist of a hypothetical uniform positive charge background bounded by an ellipsoid (instead of point charge nuclei) and  $N_e$  electrons. Calculations show that electrons fill cluster orbitals of *ns*, *np*, *nd*, *nf*, ... type where  $n \ge 1$  irrespective of angular momentum. The usual order of filling these orbitals is 1s 1p 1d 2s 1f 2p 1g 2d 1h 3s ...It is reproduced, except for inversions of (3s, 1h) and (4s, 1i), by drawing oblique lines from upper right to lower left across the orbital types arranged in this manner:

1s	1p	1d	1f	1g	1h	li
	2s	2p	2d	2f	2g	
		3s	3p	3d	3f	
			4s	4p	4d	

This produces electronic shell closings at  $N_e = 2,8,(18),20,(34)$ , 40,58,(68),(90),92, where minor shell closings are indicated by parentheses. Electronic shells and the EJM have been successful in accounting for unusually high atomization and ionization energies in clusters of group 1, group 2, and group 11, and a few

tallic clusters, the electronic shell closings generally follow the same pattern if the two elements have similar valence electron densities, for example, the combinations (K, Na), (Na, Ba), or (Na, Li) [48]. But when A and B have very different electron densities, such as K and Mg, the basic assumption of the jellium model (uniform potential and density) breaks down and other electron counts must be used. If A and B separately satisfy the EJM assumptions of a free metal, one still has EJM orbitals but the order of their filling is different: 1s 1p 2s 1d ...giving the sequence of magic numbers (8), 10, 20, ... Also, in  $A_{N-1}B$  clusters where A is well described in the jellium model (e.g., a group 1 or 11 metal) and B is a transition metal, the electron count corresponding to shell closing is not trivial. If B is rather well described by the jellium model (e.g., Pt) it can be seen as bringing a single s electron to the system and normal rules apply. But most transition metals can also be described as a +Z ion with Z valence electrons (e.g., Z = 4 for Zr). In that case, B often has a higher cohesive energy than A and takes a central location in the cluster. Then, the effective potential felt by the electrons is a lot deeper in the center of the cluster than elsewhere and, overall, the potential is intermediate between those of a jellium and of a hydrogenoid atom. Evidence for this effect comes from the observed stability of the 18-electron species Au<sub>16</sub>Y<sup>+</sup> and Au<sub>16</sub>In<sup>+</sup> [49], and ScCu<sub>16</sub><sup>+</sup> [50], and theoretical predictions [51]. We confirmed this effect with calculations on a series of icosahedra doped with multivalent central atoms: They show small HOMO-LUMO gaps for 20-electron species like Fe@Ag<sub>12</sub> ( $N_e = 20$ ), and large HOMO-LUMO gap for 18-electron species like Mo@Ag<sub>12</sub>  $(N_e = 18)$ . Another complicating factor is that only delocalized electrons should be counted. For instance, a Nb atom is probably best seen as a Nb<sup>+</sup> ion plus one loosely bound s-type electron that can easily delocalize, not a 5+ ion with 5 electrons. Magic numbers in mass abundance spectra of Au<sub>n</sub>X<sup>+</sup> clusters (X = Sc to Ni) suggest the following rules [52]: (1) Prominent shell closings occur at  $N_e = 18$ , 34, but not 20; (2) To calculate  $N_e$ , one considers that Sc and Ti contribute 3 and 4 electrons to the delocalized system of electrons, respectively; (3) heavier TM elements contribute either one or twos-type electrons, whichever produces an even total number of electrons; (4) as a result of (3) the magnitude of even-odd oscillations in cluster stabilities correlate with the magnitude of the dopant's s - d excitation energy, e.g., large for Mn and small for Ni.

The *atomic shells* model supposes that, as clusters grow in size, the atoms pack according to a specific pattern that minimizes, or nearly minimizes, the exposed surface area. From that point of view, the optimal packing is triangle, tetrahedron, trigonal bipyramid (TBP), a face-capped TBP, and so on, producing polytetrahedral clusters. This packing can continue at n = 7 (pentagonal bipyramid, PBP) only by admitting small distortions in the tetrahedra, and it can only continue at n = 13 (the icosahedron, ICO) and beyond by having some strain, i.e., with interatomic distances that differ between intralayer and interlayer bonds. This growth sequence is illustrated in Figure 4.2 for N = 4-8, 12, 13, and 55. Note that the lowest energy structure at N = 6for pair potentials is normally the octahedron, not the structure in Figure 4.2c. In the ICO, the interlayer distance is 5% smaller than the intralayer distance. The number of atoms of ICO or fcc-packed clusters with K layers is

$$N_{\rm K} = \frac{10}{3}K^3 - 5K^2 + \frac{11}{3}K - 1,$$

so the first few magic numbers in that model are 1, 13, 55, 147, 309, 561, 923, 1415, ..., and  $K \approx 0.7 N_{\rm K}^{1/3}$  when  $N_{\rm K}$  is large. The mass



**FIGURE 4.2** Polytetrahedral (icosahedral) growth sequence leading to atomic shells in clusters with N atoms, N = 4, 5, 6, 7, 8, 12, 13, and 55 (a-h).

spectra of van der Waals clusters, in particular, rare gas atoms do show several of these magic numbers [53].

Optimization of bimetallic clusters structures with respect to a semiempirical potential energy suggests that polyicosahedral structures are still favored [54]. However, the pattern in atomic shells and magic numbers generally depends on composition and that complicates matters. In particular, a large size mismatch between atoms of A and B favors segregation of the larger atoms to the surface. Extra stability may ensue when A has a higher cohesive energy, and a somewhat smaller size than B. In such a case, a perfect  $A_m@B_n$  core-shell arrangement should correspond to enhanced stability as this structure removes the strain inherent in pure polyicosahedral clusters. For example, results of a computational study suggest that  $Cu_{13}@Ag_{27}$  minimizes the excess energy (see Equation 4.10 below) of 40-atom mixed Ag–Cu clusters [55].

# 4.5 Geometric Structure of Bimetallic Clusters

In the bulk, two metals A and B will mix to form a homogeneous solid  $A_x B_{1-x}$ , or will not mix, depending on A, B, the mole fraction x, temperature T, and pressure P. When they do mix, different phases are possible, depending on A, B, x, T, P. Some phases have definite crystal structures while others are mixed in a somewhat random way. Alloy phase diagrams summarize this kind of information and have been compiled for many AB binary solids. But clusters are quite different from the bulk. Metals that do not mix in the bulk can form mixed clusters; it is often thermodynamically favorable for  $A_{2m}$  and  $B_{2m}$  clusters to mix and give two A<sub>m</sub>B<sub>m</sub> clusters for elements A and B that do not mix in the bulk [56]. Some combinations of elements have a strong tendency to form just one kind of mixed or segregated structure. This is driven by thermodynamics and mostly tied to the relative cohesive energy, surface energy, and electronegativity of the two elements (see Section 4.7). But chemical ordering also depends on the method of preparation. For instance, three kinds of AgAu bimetallic clusters (mixed, Ag,@Au,, Au,@Ag,) have been made by simply changing the sequence of Ag and Au deposition on an alumina substrate [57]. In fact, all free clusters are unstable (or metastable) and must be made with some kind of kinetic control. So the composition and structure of possible  $A_m B_n$  clusters is limited primarily by the degree of control that can be achieved.

Theoretically, the number of possible isomers of a  $A_m B_n$  cluster is much greater than for an elemental cluster X<sub>p</sub>. Take an arbitrary configuration of the p atoms of  $X_p$ . By substituting m of the atoms of X by atoms of A, and the rest by B, one gets one  $A_m B_n$  homotop (also called *permutational isomer*) of the parent structure. If there is no symmetry, there are p!/(m!n!) ways to make these substitutions, i.e., p!/(m!n!) distinct homotops [58]. Classification of  $A_m B_n$  cluster structures is broken in these two parts: (1) parent structure (sometimes called "isomer" in the literature) and (2) homotop. There is already a rich diversity of structures among elemental metal clusters (parent structures) [59], but we will discuss only the mixing aspect (homotops). A lot of experimental and theoretical work pertains to fairly large quasi-spherical clusters. Homotops that have been observed or computed usually resemble one of these ideal forms [22]: maximally mixed (MM), left-right segregated (LRS), core-shell (CS), and "onion layers structures" (OLS) [60,61]. The MM, LRS, and CS types are illustrated in Figure 4.3 using the 55-atom Mackay icosahedron as the parent structure.

Different variables have been used to quantify mixing in  $A_m B_n$ , such as the number of A–B bonds *M*, the weighted mean distance between pairs of unlike atoms  $\delta^n$ , the distance between centers of mass *D*, and difference in mean distances of A and B atoms to the center of mass, *S*:

$$M = \sum_{i \in A} \sum_{j \in B} f(d_{ij}/d_0)$$
 (4.4)

where  $d_0 = r_A + r_B$  and f(x) = 1 if x < 1.2, f(x) = 0 otherwise

$$\delta^{n} = \frac{\sum_{i \in A} \sum_{j \in B} (d_{ij})^{1-n}}{\sum_{i \in A} \sum_{j \in B} (d_{ij})^{-n}}$$
(4.5)

$$D = \left| (1/m) \sum_{i \in A} \vec{R}_i - (1/n) \sum_{j \in B} \vec{R}_j \right|$$
(4.6)



FIGURE 4.3 Maximally mixed (MM), left-right segregated (LRS), and core-shell segregated (CS) types of homotop for a 55-atom Mackay icosahedron.

$$S = (1/m) \sum_{i \in A} |\vec{R}_i - \vec{R}_{\rm cm}| - (1/n) \sum_{j \in B} |\vec{R}_j - \vec{R}_{\rm cm}| \qquad (4.7)$$

where

 $d_{ij}$  is the distance between atoms *i* and *j* 

 $i \in A$  means the sum is over atoms of element A

 $\vec{R}_{cm}$  is the cluster center of mass obtained after assigning a fictitious unit mass to every atom

A convenient way to characterize a cluster structure is to first calculate M,  $\delta^n$ , D, and S for that structure *and for all of its homotops*, and then normalize the variable in one of two possible ways. We illustrate this for M:

$$\overline{M} = \frac{M - M_{\text{avg}}}{\sigma(M)} \text{ or } \overline{M} = \frac{M - M_{\min}}{M_{\max} - M_{\min}}$$
 (4.8)

where  $M_{\text{avg}}$ ,  $M_{\text{min}}$ ,  $M_{\text{max}}$ , and  $\sigma(M)$  are, respectively, the average, minimum, maximum, and standard deviation, of M evaluated over the set of all homotops of M.

# 4.6 Properties of Bimetallic Clusters

Properties of  $A_m B_n$  vary in complex ways with A, B, *m*, *n* and structure. Few generalizations can be made. Some of the unique properties of bimetallic clusters were mentioned in Section 4.3. Here, we will make a few more comments about how properties of  $A_m B_n$  may or may not relate to properties of the elemental clusters, and also about optical properties.

A central question in studies of elemental clusters  $X_p$  is this: How do properties evolve with size p? This is also relevant to bimetallic clusters, but two other questions come up. The first is How do the properties of  $A_m B_n$  (m + n = p) compare to those of  $A_p$ and  $B_p$ ? The second, slightly different, question is For a given p =n + m, how do the properties of  $A_m B_n$  vary as a function of (m/p)? Answers vary a lot according to property and cluster, but there are standard ways to approach these questions. In particular, one is often interested in the excess property associated with a property P, which can be defined in at least two ways.

$$P_{\text{excess}}(\mathbf{A}_{m}\mathbf{B}_{n}) = \frac{P(\mathbf{A}_{m}\mathbf{B}_{n}) - (m/p)P(\mathbf{A}_{p}) - (n/p)P(\mathbf{B}_{p})}{(m/p)P(\mathbf{A}_{p}) + (n/p)P(\mathbf{B}_{p})} \times 100\%$$
(4.9)

$$\Delta(A_m B_n) = \frac{P(A_m B_n) - (m/p)P(A_{\text{bulk}}) - (n/p)P(B_{\text{bulk}})}{p^{2/3}}$$
(4.10)

A comparison of clusters with same size but different compositions can be made with  $P_{\text{excess}}$ , whereas  $\Delta$  is useful for comparing clusters that differ in both size and composition [56]. Some properties depend much more on surface atoms than interior atoms, e.g., surface energy, chemical reactivity, collective resonance in photoabsorbtion spectra [62], and in many clusters one of the elements, say "A," segregates to the surface. In such a case,  $P(A_mB_n)$  should be closer to  $P(A_p)$  than to  $P(B_p)$ . This can be accounted for by modifying the above equations so that only surface atoms are counted in all of the species involved (clusters and bulk solid). In most cases  $P_{\text{excess}}$  is at most a few percent.

It seems natural to classify bimetallic cluster properties into three categories: (1) those where  $P_{\text{excess}}$  calculated with all atoms is a few percent or less; (2) those where  $P_{\text{excess}}$  calculated using only the surface atoms is a few percent or less; (3) others having properties that deviate a lot from the weighted average of the two pure metals, no matter what kind of atoms (surface, interior, both) are counted. It is dangerous to generalize, but it appears that energy, surface energy, bond lengths (or density), and polarizability normally fall in categories (1) or (2). Some other properties, for instance, chemical reactivity and magnetization, are more complex, more sensitive to composition, and often fall in category (3).

In theory, the energy can sometimes be decomposed into a sum of atomic contributions, in which case it is convenient to consider the *mixing energy*  $E_{mix}$  and mixing coefficient  $M_E$  for a  $A_m B_n$  cluster with nuclear configuration **X** defined like this [58]:

$$E_{\min}(\mathbf{A}_m \mathbf{B}_n; \mathbf{X}) = E(\mathbf{A}_m \mathbf{B}_n; \mathbf{X}) - E(\mathbf{A}_m \text{ in } \mathbf{A}_m \mathbf{A}_n; \mathbf{X})$$
$$- E(\mathbf{B}_n \text{ in } \mathbf{B}_m \mathbf{B}_n; \mathbf{X})$$
(4.11)

$$M_{\rm E} = E_{\rm mix} / E(A_m B_n) \tag{4.12}$$

The optical spectra of small clusters have several peaks, like molecules. But larger clusters are characterized by a single intense peak, called plasmon [63]. The plasmon can be understood as a collective excitation of the electrons: To a first approximation, the change in electric dipole is due to a rigid displacement of the electronic cloud (valence electrons) relative to the positions of the ions. The shape and frequency of the plasmon resonance depend strongly on the size and shape of the particle [63]. Studies of Ag, Au, have shown that the plasmon resonance also varies a lot with composition and morphology [64]. Laser irradiation or annealing of core-shell Au,@Ag,, clusters leads to mixing of the two metals, which gives a way to tune optical properties [24]. The UV-visible absorption of small clusters can be modeled in detail by theory. A fairly standard technique for this is timedependent density functional theory (TDDFT). A recent application of TDDFT showed that there are many absorption peaks in the spectra of  $Ag_n Ni_{p-n}$  ( $p \le 8$ ) clusters, and many nontrivial differences between those spectra as a function of composition and structure [65].

# 4.7 Structure–Energy Principles for Bimetallic Clusters

It has been shown that for a cluster  $X_{13}$  where atoms interact via a Lennard-Jones (LJ) potential,  $E = \sum_{j>i} 4\epsilon \left[ (\sigma/d_{ij})^{12} - (\sigma/d_{ij})^6 \right]$ , there are more than 1500 distinct geometric isomers (energy minima) [66]. If a pair potential can model a system adequately,

then the number of minima depends on the range of the pair interactions, with a shorter range giving more minima [67]. There are probably more isomers for clusters described by accurate energy methods (ab initio, DFT), compared to a LJ potential, considering the different possible atomic hybridizations and cluster spin states. Neglecting symmetry, the number of homotops for a small clusters like  $A_7B_6$  is (7!6!/13!) = 1716. This gives an estimated total number of distinct minima on the order of 106. Obviously, it is very difficult to find, without making a priori assumptions, the experimental or computed lowest energy structures of even moderate-size bimetallic clusters. Therefore, it is desirable to have structure-energy principles that would allow quick educated guesses of cluster structures. It must be said at the outset that no simple set of rules allows reliable detailed predictions of cluster structure. The structure-energy principles that we are about to show summarize empirical observations, or correlations, drawn from a variety of experimental and computational sources and they are good only for qualitative predictions.

One can relate some aspects of cluster structure to certain properties of the constituent atoms. On the atom side of the problem, we have the ionization energy (IE) and electron affinity (EA), or, electronegativity  $\chi$  and hardness  $\eta$ :

$$\frac{\chi = (IE + EA)}{2}; \quad \eta = \frac{(IE - EA)}{2}$$
 (4.13)

The atomic radius  $R_A$  and cohesive energy  $E_{c,A}$  of an element A are also critical, and so is the ratio  $(E_{c,A}/R_A^2)$  (it correlates with the surface energy of that element). Another important thing is whether the atom's d orbitals are partially filled (sometimes the precise d electronic configuration matters). On the cluster side, it is useful to consider geometry descriptors such as the number of nearest-neighbor pairs or the surface area (these two things are strongly correlated); the cluster shape (roughly spherical, or oblate, or prolate), which may be quantified using the three moments of inertia; the distribution function g(d) of interatomic distances; and the distribution function  $h(\theta)$  of *ijk* angles, where atom *j* is a neighbor to both atoms *i* and *k*. Note that the first two peaks in g(d), at  $d_1$  and  $d_2$ , quickly characterizes familiar structures: the ratio  $(d_2/d_1)$  is 1.414 for fcc, 1.155 for bcc, and 1.050 for an ideal 13-atom icosahedron. The width of the first peak  $w_1$  (and to a lesser extent, widths of other peaks) is also informative: a small  $w_1$  indicates little or no strain, or, high "crystallinity." Relative peak intensities in  $h(\theta)$  (especially at 60°, 90°, and 108°) also show very clear differences between the different structure types like fcc, bcc, ICO, etc. Finally, note that in a pair-potential model, the range of interaction is correlated to the IE of the atom because the long-range form of an atom's electronic density depends essentially on IE [68]) (a small IE correlates with a long-range and "soft" pair potential).

There are some rules that seem to govern *parent structures* of elemental [59] (and also bimetallic) clusters. (1) There is a general tendency to minimize the exposed surface area, or, maximize the number of bonds. (2) Structures where the first peak in g(d) is narrow (i.e., the strain is small) are favored, especially for

elements with a large IE. (3) Elements with a large atomic hardness  $\eta$ , or a large IE, tend to favor structures where all atoms have nearly the same number of neighbors: in extreme cases, this gives cage structures, as in several gold clusters, for example. (4) Atoms that have a ground state electronic configuration with a number of valence *d* electrons that differs from 0, 5, or 10 often exhibit 90° bond angles. (5) Clusters of elements of groups 1, 2, and 11, and other elements that are well described in the jellium model (e.g., Al) tend to adopt shapes that conform to the EJM [42,43]. (6) There is sometimes a competition between high-spin, high-symmetry structures, and low-spin, EJM-distorted structures, Li<sub>13</sub> being one example of that.

There are some rules about *homotops*. Elements A and B have a tendency to (1) mix if they have very different electronegativities  $\chi$ ; (2) segregate if they have very different cohesive energies  $E_c$ , or very different ratio  $(E_{c,X}/R_X^2)$ , with the element with smallest  $E_c$  (or smallest  $(E_{c,X}/R_X^2)$ ) going to the surface; (3) segregate into a core-shell structure with B outside if  $R_B$  is much larger than  $R_A$  [54] since that decreases the strain; (4) segregate if one element (A or B) has a stronger interaction to the environment (support, ligand, or ambient gas); (5) when the surface is composed of A and B atoms, the atom with the lowest  $E_c$  tends to occupy the sites with lowest coordination; and (6) when the difference  $(E_{c,A} - E_{c,B})$  is large and positive, the structure of  $A_m B_n$  has a compact  $A_m$  core with a structure that maximizes the number of A–A bonds, whereas the total number of bonds is much less important.

# 4.8 Special Bimetallic Clusters

Some clusters should be relatively stable in theory because they satisfy two or more stability criteria simultaneously. We refer to them as doubly magic clusters (DMC) even if they satisfy more than two criteria. The interest in free DMCs is largely theoretical because, for metals, even the most stable-free DMCs of size  $N \leq 100$  are probably not stable enough to be used for materials. But there is also a practical side to DMCs. The metal core part of stable passivated clusters are probably DMC cations in many cases. For example, the stable thiolate-protected cluster  $Au_{25}(RS)_{18}$  has a metallic icosahedral core  $Au_{13}^{5+}$  with closed atomic and electronic shells [4] (the 12 other Au atoms have nonzero oxidation numbers). Conversely, passivation of neutral DMCs or of their charged isovalent analogs could yield truly stable clusters. Also, the polyanions of known stable Zintl phases, like  $\operatorname{Ge}_{9}^{4-}(N_{e} = 40)$ , may be viewed as magic clusters. This suggests the possibility of stable core-shell bimetallic clusters  $A_m @B_n$  where A and B have a large difference of electronegativity, though maybe not as large as in the true Zintl phases [69,70]. What follows is a short and partial list of free clusters having unusual stability. Each of these has many isovalent (neutral or charged) bimetallic analogs, which may also be stable.

The unusual stability of  $MAl_4^-$  clusters (M = Li, Na, Cu) was explained by proposing the concept of *metal aromaticity* that would apply to the square planar  $Al_4^{2-}$  unit [71]. The Na<sub>6</sub>Pb cluster is an octahedron with the Pb atom at the center and with the  $N_e = 10$  shell closing characteristic of inverted EJM orbital order  $(1s^22p^62s^2)$  [72,73]. The Al<sub>13</sub><sup>-</sup> icosahedral cluster satisfies the EJM closing at  $N_e = 40$ , whereas neutral Al<sub>13</sub> can be seen as a kind of "halogen superatom" [74]. Relatively stable bimetallic species can be derived by reaching  $N_e = 40$  in different ways, e.g., Al<sub>13</sub>Ag [75], Sn@Al<sub>12</sub>, etc. Generally, many doped (bimetallic) icosahedra A@B<sub>12</sub> have been predicted to have large HOMO-LUMO gaps on the order of 2–3 eV: Al@Pb $_{12}^+$  [76], WAu $_{12}$  [77], MoCu<sub>12</sub> [78], etc. The Au<sub>20</sub> cluster is a pyramidal fragment of the fcc crystal with a large HOMO-LUMO gap (1.8 eV) that was identified by the combined use of photoelectron spectroscopy and computations [79]. Many tetrahedral clusters with  $N_e = 18$ or 20 and special stability can be derived from it. Removal of the four apex atoms gives Au<sub>16</sub> which is interesting in its own right because, in the anion, the four symmetry equivalent atoms move outward giving a cage structure [80]. Substitution of these four atoms by a divalent metal gives a series  $A_4B_{12}$  of clusters. In particular, Mg<sub>4</sub>Ag<sub>12</sub> has the tetrahedral structure as its global minimum and a HOMO-LUMO gap of approximately 2.5 eV [81]. In addition to its compact strain-free geometric structure and closed-shell electron count, the electrons and nuclei in Mg<sub>4</sub>Ag<sub>12</sub> make coincident electrically neutral shells (CENS): the Mg<sup>2+</sup> and Ag<sup>+</sup> ions' spatial distribution has high symmetry  $(T_d)$  and yields cumulative ionic charges that match two successive EJM shell closings (8 and 12 + 8 = 20), which gives extra stability to the T<sub>d</sub> homotop. The CENS property might be useful as an additional shell closing criterion. The basic  $T_d M_{16}$  structure can be either fcc-like (compact) or cage-like and, in the latter case, it can easily accommodate a central atom impurity. If the impurity brings the electron count to 18 (not 20), special stability ensues as in, for example,  $Sc@Cu_{16}^+$  [50].

# 4.9 Summary and Conclusion

The properties of clusters are often very different from the bulk, which leads to various applications, particularly in catalysis, bioanalysis (as probes), and for magnetic materials. Compared to elemental clusters, bimetallic clusters obviously offer more possibilities for design and applications. Small clusters are characterized by a high surface area. Generally speaking, this makes them unstable. However, there exist several methods for synthesizing small bimetallic clusters either in the gas phase (sometimes followed by deposition in or on a substrate), or in solution, or by using precursor metal complexes on a support, or by solid-state chemistry. Synthetic methods, and the tools and instruments for characterization of clusters, are improving rapidly and give increasingly better control and understanding of the shape and composition of bimetallic clusters. It is possible, in some cases, to make core-shell structures  $A_m @B_n$  or  $B_m @A_n$ , or mixed A<sub>m</sub>B<sub>n</sub> structures, for a given A-B combination by using different synthetic approaches. Some principles help rationalize the geometric structure and relative stability of bimetallic clusters, in particular: special stability is associated with electronic shell closings (e.g., electron counts of 8, 20, 40, ... in the jellium model); clusters tend to minimize surface energy, therefore the element with smaller surface tension tends to segregate to the surface; clusters tend to minimize strain, so bigger atoms tend to segregate to the surface; A and B tend to mix if they have very different electronegativities; and there is extra stability associated with the simultaneous closing of electronic and atomic shells. Improvements to synthetic methods, characterization tools, theory and modeling, and multidisciplinary approaches to design and prototyping for specific applications have been, and will continue to be, essential for progress in the field of bimetallic clusters.

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# 5 Endohedrally Doped Silicon Clusters

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The ongoing trend toward miniaturization in microelectronics has triggered interest in small particles made of silicon, the most used element in the semiconductor industry. An important discovery of the unique nanoscale properties of silicon has been the observation of bright luminescence from porous silicon nanostructures (Canham 1990), whereas bulk silicon is a bad emitter of light due to its indirect band gap. This phenomenon has attracted much attention toward its quantum mechanical origin. By downsizing bulk silicon to the nanoscale, there is hope to induce a more efficient luminescence and to shift the emission wavelength from 1.1 eV into the visible region (Canham 1990, Iyer and Xie 1993, Ledoux et al. 2000). Possible visible-light emitters made out of silicon are of great relevance because of their potential for new functional silicon-based optoelectronic devices. Moreover, the tunability of the emission wavelength by changing only their particle size is still one of the open demands associated with a large variety of applications.

Elemental silicon clusters, however, are unsuitable as building blocks for future nanomaterials, since their dangling bonds make them chemically reactive (Röthlisberger et al. 1994). Contrary to carbon, the formation of silicon fullerenes and nanotubes is disfavored due to the tendency of silicon to prefer  $sp^3$ -rather than  $sp^2$ -like hybridization. A possible approach to stabilize a silicon cage is to locate a guest atom in the center of the cluster.

In 1987, Beck succeeded in preparing mixed metal-silicon cluster ions by laser vaporization and found strikingly high abundances of  $Si_{15}M^+$  and  $Si_{16}M^+$  for three different transition-metal dopants M, namely chromium, molybdenum, and tungsten, and low abundances for other sizes (Beck 1987, 1989). However, despite a valuable attempt based on a topological model (King 1991), the magic behavior of these structures remained unexplained for a long time, presumably due to the fact that understanding the structures and properties of bare silicon clusters was itself evolving as an active field of research and that the investigation of clusters doped with transition-metal atoms was a difficult and challenging experimental task.

Another 5 years later, Hiura and coworkers showed experimentally that many types of transition-metal ions can be introduced into silicon cages and that the smallest possible cage size crucially depends on the dopant atom. In addition to the experiments, ab initio calculations were performed to identify the precise structure of Si<sub>12</sub>W, which resulted in a regular hexagonal Si<sub>12</sub> cage with a tungsten atom in the center (Hiura et al. 2001). The finding of this dopant-encapsulating cluster in combination with the progress made in understanding the structures and properties of bare silicon clusters attracted renewed interest in the very stable  $Si_{15}M^+$  and  $Si_{16}M^+$  (M = Cr, Mo, W) species, detected by Beck 15 years earlier. Kumar and Kawazoe (2002) computationally attributed the strong stability of these species to highly symmetric cages with exceptionally pronounced highest occupied-lowest unoccupied molecular orbital (HOMO-LUMO) gaps and large embedding energies of the dopant atom.

Today, the interest in doped silicon clusters is so high that theoretical studies have investigated  $Si_nM$  structures for dopants from almost every group of the periodic table. Recent investigations on metal-encapsulated silicon cages have proposed novel functional silicon devices (Hiura et al. 2001, Khanna et al. 2002, Kumar and Kawazoe 2003b, Kumar 2006). As compared to elemental silicon clusters, doped clusters are predicted to bear higher stabilities and more symmetric structures, making them attractive for cluster-assembled materials. The novel interest by theoreticians has been quickly followed by experimentalists' efforts. Today, a variety of methods, which go beyond simple mass spectrometry, are applied to study doped silicon clusters.

The focus of this chapter lies on the developments of the experimental approaches. Section 5.2 provides a brief summary of the different models that explain the enhanced stabilities of certain cluster sizes and stoichiometries, stressing that it is generally the interplay between geometric and electronic factors that results in "magic" clusters. Section 5.3 reviews the history of the investigation of doped silicon clusters by different means. In Section 5.3.1, mass spectrometric studies are covered starting with the pioneering work of Beck and arriving at more recent contributions that found some general trends for especially stable species. Several reactivity probes have been developed, especially for investigating the transition from exo- to endohedrally doped silicon clusters. These approaches are presented in Section 5.3.2. Due to these experiments, doped silicon clusters came into the focus of quantum mechanical studies, which are reviewed in Section 5.3.3. Exemplifying the successful interplay between theory and experiment, nowadays innovative instrumental techniques are used to probe the theoretical predictions. Section 5.3.4 shows how the electronic structure of doped silicon clusters

can be analyzed in detail by means of photoelectron spectroscopy (PES). For the investigation of the geometric structure, infrared (IR) spectroscopy is a powerful method. Section 5.3.5 demonstrates how the vibrational fingerprint of doped silicon clusters is obtained upon infrared multiple photon dissociation (IR-MPD) spectroscopy of their complexes with rare-gas atoms.

# 5.2 Stabilization of Clusters

In the mass spectrometric detection of clusters, their size distribution is not necessarily smooth. Often certain clusters are much more pronounced in intensity than their adjacent sizes. Such modulations often reflect the thermodynamic stability of the clusters under investigation. The origin of an enhanced stability can either be due to geometric or to electronic reasons. Both are briefly discussed in the following section.

### 5.2.1 Geometric Stabilization

When in 1981 Echt and coworkers recorded the mass spectrum of an effusive beam of xenon clusters, they observed enhanced intensities for clusters containing 13, 55, 147, etc., atoms (Echt et al. 1981). These "magic" sizes reflect the tendency of the cluster's atoms to maximize their number of nearest neighbors and their average coordination, while minimizing their surface area. The numbers can be rationalized by geometric shell closings of icosahedral clusters, known as Mackay icosahedra. Icosahedra are not closed-packed structures and, e.g., in a 13-atom icosahedron, the surface bonds are approximately 6% longer than the radial bonds from the center to the surface atoms. This frustration increases for larger clusters and eventually favors closed-packed geometries. A way to stabilize an icosahedron is the substitution of the central atom by a smaller dopant. One example is the magic AlPb<sub>12</sub><sup>+</sup> cage (Neukermans et al. 2004). It is remarkably pronounced in the mass spectrum of cationic aluminum-doped lead clusters (see Figure 5.1), and its closed-packed  $I_h$  geometry is calculated to be the most stable isomer by not less than 1.96 eV to the next stable isomer.

Another example of a particularly stable high symmetric geometry is neutral  $Au_{20}$  (Li et al. 2003, Gruene et al. 2008a). Here the cluster is a pyramid of perfect tetrahedral symmetry and represents a fragment of the bulk fcc structure with four 111 surfaces.

Clusters not necessarily need to be closed-packed in order to gain from a geometric stabilization. The Buckminster fullerene is a hollow cage but is drastically stabilized because it is the smallest cluster size in which all five-membered carbon rings are separated from each other by six-membered rings (Kroto et al. 1985).

#### 5.2.2 Electronic Stabilization

Similar to the mass spectrum of xenon clusters, the spectrum of sodium clusters is highly structured with pronounced peaks for clusters containing 8, 20, 40, 58, and 92 atoms (Knight et al. 1984). These findings were immediately rationalized by assuming a one-electron shell model. In this phenomenological shell



**FIGURE 5.1** Mass abundance spectrum of mixed  $AlPb_n^+$  clusters, showing the extremely enhanced stability and magic character of  $AlPb_{10}^+$  and  $AlPb_{12}^+$  (see Neukermans et al. 2004).

model, which bears a lot of resemblance with the shell model as it is well known in nuclear physics, the 3s electrons of the sodium atoms are independently delocalized and move in a spherical potential. Obviously this model can describe only clusters with a spherical geometry, while for species with lower symmetries, the model must be modified accordingly (Clemenger 1985, de Heer 1993). Meanwhile, various implementations of shell models for electrons exist, including the so-called jellium model where the electron problem is solved quantum mechanically, assuming a smeared-out homogeneous positively charged ion distribution.

For binary clusters, a two-step spherical jellium model has been developed (Baladron and Alonso 1988, Janssens et al. 2004) to explain the occurrence of the magic electron number 10 in case of electronegative dopants and 18 for electropositive dopants. For an electronegative dopant in the center of the cluster, the effective potential is more attractive in the vicinity of the dopant. This stabilizes the orbitals that have a high electron density in the center of the cluster, like *s* and *p* orbitals, while *d* and f orbitals are destabilized. Accordingly, the 2s orbital is more favorable than the 1d orbital in case of electronegative dopants, resulting in a shell closing at 10 valence electrons. The opposite is true for electropositive dopants, giving rise to the magic number 18 (Figure 5.2). This model works nicely for spherical main group elements. A good example is the CuAu<sub>16</sub><sup>-</sup> anion with a compact structure and a very high adiabatic detachment energy of 4.12 eV (Wang et al. 2007).

For transition-metal dopants, it is not always clear how many d electrons are donated to the quasi-free electron gas. While radially extended d-orbitals bear a high propensity to hybridize strongly with s and d electrons from the host, this behavior decreases along a row. Transition-metal-doped clusters are often better described by concepts originating from organometallic chemistry. The 18-electron rule takes into account that a total of 18 electrons is needed to fill the s, p, and d orbitals of the valence



**FIGURE 5.2** Schematic representation of the single-particle energy levels in the standard jellium model (b) and in the two-step jellium model with a depression (a) and an increase (c) in the central part of the background potential. Note the magic numbers 10 and 26, caused by the lowering of the 2*s* and the 2*p* levels in (b), and the enhanced magic number 18 by lifting the 2*s* level in (c) (see Baladron and Alonso 1988; Janssens et al. 2004).

shell of a transition-metal atom.  $WAu_{12}$  obeys the 18-electron rule and was calculated to be a very stable cluster (Pyykkö and Runeberg 2002). Shortly afterward, the anion  $WAu_{12}^{-}$  was synthesized in the gas phase and studied by means of PES (Li et al. 2002). The large HOMO-LUMO gap of 1.68 eV measured with PES support the electronic stability of this species. Other examples are 16-atom gold cluster cations endrohedrally doped with a trivalent metal, that all exhibit extraordinary stability with respect to neighboring sizes, as demonstrated with photofragmentation mass spectrometry (Bouwen et al. 1999, Neukermans et al. 2003, Veldeman et al. 2008).

More recently, the concept of aromaticity has been introduced for explaining the stability of metal clusters (Li et al. 2001, Boldyrev and Wang 2005). Also for doped clusters, aromaticity has been used to account for certain especially stable stoichiometries, with  $Au_5Zn^+$  being a prominent example (Tanaka et al. 2003). This planar cluster has 6 valence electrons (4n + 2 with n = 1, according to a Hückel-aromatic molecule) and a strong magnetic shielding inside and above the structure caused by a diamagnetic ring-current, an effect ascribed to its aromaticity. Aromaticity is not limited to planar species but can also account for enhanced stabilities of spherical clusters (Chen and King 2005).

# 5.2.3 Combined Effects

It has been realized early on that enhanced stability is achieved best when both geometric and electronic stabilization conditions are fulfilled (Khanna and Jena 1992, Chen et al. 2006). For example,  $Al_{13}^{-}$  is a compact icosahedral structure and its 40 valence electrons result in an electronic shell closing within the jellium model (Bergeron et al. 2004). Similarly, the stability of  $Au_{20}$  lies in its tetrahedral geometry, as well as 20 valence electrons satisfying the shell model. The WAu<sub>12</sub> cluster is stabilized by three factors: the above-mentioned 18-electron rule, a relativistic contraction with strengthening of the W–Au and Au–Au bond, and aurophilic interactions in the gold shell.  $AlPb_{12}^+$  is stable due to its compact geometric structure but also due to the spherical aromaticity of the  $Pb_{12}^{2-}$  cage, which surrounds the formal  $Al^{3+}$  dopant.

# 5.3 Investigation of Doped Silicon Cages

In this section, it is shown how the concepts from Section 5.2 have been used to explain the enhanced intensity of certain doped silicon clusters in mass spectra (Section 5.3.1). The first simple mass spectrometric investigations have been followed by reactivity studies and a wealth of quantum mechanical calculations (Sections 5.3.2 and 5.3.3). In the last years, innovative experimental methods have been applied to doped silicon clusters in order to probe those theoretical predictions (Sections 5.3.4 and 5.3.5).

#### 5.3.1 Mass Spectrometry

Contrary to carbon fullerenes and nanotubes, the formation of a silicon hollow cage or tube is very unlikely. Since the dangling bonds in  $sp^3$ -hybridized silicon clusters make them chemically reactive and thus unstable, it is very important to quench these bonds for allowing the formation of cluster-assembled materials. One of the strategies for doing so is the doping of a suitable metal atom into a pure Si cluster, as was first experimentally revealed in 1987 (Beck 1987).

Beck first reported mass spectra for cationic transition-metaldoped silicon clusters  $Si_{\mu}M^{+}$  (M = Cr, Mo, W). Silicon clusters were formed by laser ablation from a silicon wafer. When the carrier gas was seeded with the corresponding transition-metal carbonyl, doped clusters were formed with identical stoichiometries, irrespective of the dopant element. This is shown in Figure 5.3, where high-fluence (1 mJ/cm<sup>2</sup>) 193 nm ionization mass spectra of bare and doped silicon clusters are compared. Spectrum 3a was obtained using pure helium as carrier gas and shows bare silicon clusters. The spectrum is dominated by clusters containing 6-11 atoms. These cluster cations are particularly stable and result from fragmentation of larger silicon clusters upon absorption of multiple UV photons. Figure 5.3b through d presents the spectra obtained when the helium carrier gas was seeded with metal carbonyls. These latter spectra exhibit additional peaks, darkened in the figure, which were assigned to clusters containing one transition-metal atom and varying amounts of silicon atoms. It is striking how the most prominent new peaks are always due to  $Si_{15}M^+$  and  $Si_{16}M^+$  clusters (M = Cr, Mo, and W) and that the observed abundances of other sizes of metal-doped silicon clusters are very low. The spectra clearly reveal that incorporating a single metal atom in the Si<sub>15</sub> and Si<sub>16</sub> clusters stabilizes these sizes with respect to photofragmentation. In order to



**FIGURE 5.3** 193 nm (6.4 eV) ArF laser photoionization time-of-flight mass spectra showing: (a) bare silicon clusters formed by laser vaporization of a silicon wafer followed by supersonic expansion, (b) reaction products formed in a supersonic nozzle between chromium atoms and silicon to form Si<sub>n</sub>Cr clusters, (c) Si<sub>n</sub>Mo, and (d) Si<sub>n</sub>W clusters. The metal-atom-silicon cluster peaks in each spectrum are darkened for emphasis. Undarkened peaks represent bare silicon clusters. ArF laser fluence in each case was about 1 mJ/cm<sup>2</sup>. At this fluence, very little intensity is seen for elemental silicon clusters with more than 11 atoms. (Reproduced from Beck, S.M., *J. Chem. Phys.*, 90, 6306, 1989. With permission.)

understand this behavior, Beck postulated a possible scenario where the metal atom acts as a seed and silicon atoms form a shell structure with a specific number of atoms around the metal dopants (Beck 1989). While the observed mass spectra for the three group 6 metals Cr, Mo, and W with silicon are very similar, doping with copper provided different results (Beck 1989). First, no copper-silicon reaction products containing less than six silicon atoms were observed. Further, the most intense product peak in the spectrum was due to Si<sub>10</sub>Cu<sup>+</sup>.

Since Beck described the remarkable formation of  $Si_{15}M^+$ and  $Si_{16}M^+$ , more mass spectrometric investigations have been presented. The enhanced stability of  $Si_{15,16}Cr^+$  and  $Si_{10}Cu^+$  was confirmed by Neukermans and coworkers who presented a mass spectrometric stability investigation of Cr, Mn, Cu, and Zn-doped  $Si_n$ ,  $Ge_n$ ,  $Sn_n$ , and  $Pb_n$  clusters (Neukermans et al. 2006). Moreover, significantly enhanced abundances for  $Si_{15}Mn^+$ and  $Si_{16}Mn^+$  were found.

Ohara and coworkers studied mass spectrometrically anionic silicon clusters doped with the group 4 transition metals titanium and hafnium and the group 6 transition metals molybdenum and tungsten (Ohara et al. 2003). Typical time-of-flight mass spectra were dominated by pure silicon cluster anions with n = 4-11. In addition to the pure Si<sub>n</sub> clusters, Si<sub>n</sub> anions doped with a single transition-metal atom were observed in the mass spectra again with a predominant formation of clusters containing 15 and 16 silicon atoms. They thus revealed that the striking stability of certain

#### Endohedrally Doped Silicon Clusters

cationic silicon clusters doped with group 6 metals, as observed by Beck (1987), also persists in the case of anionic clusters and in the case of dopants of other groups. This behavior rather pointed to a geometric stabilization and a special role of the  $Si_{16}$  cage, as the number of electrons seemed to be of minor importance.

However, in 2005 Koyasu and coworkers presented an experimental investigation of scandium-, titanium-, and vanadium-doped silicon clusters (Koyasu et al. 2005). This study revealed very clearly that the electronic structure also plays an important role. Neutral  $Si_{16}$ Ti species could selectively be produced by fine-tuning the cluster source, as shown in Figure 5.4b. The mass spectra of neutral scandium- and vanadium-doped silicon clusters, however, hardly showed any preference for the size containing 16 silicon atoms. Only when isoelectronic species were formed, magic clusters could be detected; thus, a change of the charge state was required. The three magic sizes  $ScSi_{16}^-$ ,  $TiSi_{16}$ , and  $VSi_{16}^+$  (see Figure 5.4a through c) point toward a closed electron configuration. Koyasu and coworkers proposed that the transition-metal dopants each contribute their 4 valence

electrons in order to yield, together with the 16  $3p_z$  electrons of the  $sp^2$  hybridized Si atoms, a closed electronic shell of 20 electrons according to the jellium model.

Koyasu and coworkers continued their investigations by systematically changing the dopant atoms among the group 3, 4, and 5 elements (Koyasu et al. 2007). Figure 5.4 shows the typical mass spectra of the transition-metal atom-doped clusters Si<sub>"</sub>M<sup>-/0/+</sup> (M = Sc, Y, Lu, Ti, Zr, Hf, V, Nb, and Ta). The neutral clusters of Si, Ti, Si, Zr, and Si, Hf were photoionized by a pulsed F<sub>2</sub> laser (7.90 eV) for mass spectrometric detection, while the charged metal-silicon clusters were directly accelerated in a pulsed electric field. In all of the mass spectra of Si, M<sup>-/0/+</sup>, bimodal size distributions were observed. The two distributions are indicated in Figure 5.4 by solid squares (distribution I, n = 6-11) and open circles (distribution II, n = 12-20), respectively. As confirmed by a chemical-probe method (described in detail in Section 5.3.2), the bimodal distributions correspond to the structural transition from exohedral to endohedral geometries, i.e., a transition from structures where the dopant is located on the cluster's surface to



**FIGURE 5.4** Mass spectra of metal-atom-doped silicon clusters  $(Si_nM)$ : (a)  $Si_nSc^-$ , (b)  $Si_nTi$ , (c)  $Si_nV^+$ , (d)  $Si_nY^-$ , (e)  $Si_nZr$ , (f)  $Si_nNb^+$ , (g)  $Si_nLu^-$ , (h)  $Si_nHf$ , and (i)  $Si_nTa^+$ . Left three columns are anionic  $Si_nM^-$  (M = Sc, Y, and Lu), middle three columns are neutral  $Si_nM$  (M = Ti, Zr, and Hf), and right three columns are cationic  $Si_nM^+$  (M = V, Nb, and Ta). Bimodal distributions were typically observed. The solid squares and open circles represent the two distributions (I and II). Distribution I was similar to that of pure  $Si_n$  in their charge state, while distribution II had a prominent peak at  $Si_{16}M$ , indicating that these species are particularly stable. Arrows indicate the mass peaks of the  $Si_{16}M^{-10/+}$  clusters. (Reproduced from Koyasu, K. et al., *J. Phys. Chem. A*, 111, 42, 2007. With permission.)

structures in which the dopant is fully surrounded by the silicon atoms (Koyasu et al. 2007). Indeed, the abundance of smaller Si<sub>n</sub> clusters (n = 6-11) is relatively rich, while larger-sized Si<sub>n</sub> clusters ( $n \ge 12$ ) are formed to a much smaller extent; a finding very similar to the one in Beck's early work. The similarity of the size distribution for small (n = 6-11) bare and doped silicon clusters was presumed to be due to the stability of the bare Si clusters and indicated that clusters of distribution I exhibit an exohedral dopant. Distribution II, on the other hand, was completely different from that of pure Si clusters. It exhibited a prominent peak at Si<sub>16</sub>M<sup>-/0/+</sup>, whereas Si<sub>16</sub> was hardly formed at all. In particular, doping with the transition-metal atoms Sc, Ti, V, Zr, Nb, Hf, and Ta resulted in the magic behavior of Si<sub>16</sub>M, while the intensities of Si<sub>16</sub>Y<sup>-</sup> and Si<sub>16</sub>Lu<sup>-</sup> were hardly more intense than their neighboring sizes with n = 15 and 17.

#### 5.3.2 Reactivity and Chemical-Probe Studies

The work of Hiura and coworkers constitutes another landmark in the investigation of doped silicon clusters (Hiura et al. 2001). They introduced metal ions into an ion trap by resistive heating of a metal wire and subsequent ionization by electron irradiation. As a silicon source,  $SiH_4$  gas was introduced into the trap. The transition-metal cation reacted subsequently with silane, resulting in the formation of  $Si_n MH_x^+$  species. It was observed that the sequential growth of  $Si_n MH_x^+$  species almost stopped when n approached a specific number m. Moreover, a clear dependence of *m* on the metal element M was noted, e.g., m = 14for Hf, 13 for Ta, 12 for W, 11 for Re, and 9 for Ir. Furthermore, for elements of the same group in the periodic table, the same termination number *m* was found. When n = m, the clusters tended to lose all of their H atoms, and dehydrogenated clusters,  $Si_m M^+$ , were highly abundant in the mass spectrum. This finding suggested that the clusters were not chainlike but that the metal atom was highly coordinated and saturated all dangling bonds of the silicon atoms. Strikingly, the sum of *m* and the atomic number of the transition-metal element was often found to keep a constant value of 86, which corresponds to the atomic number of the rare gas Rn. Thus, the maximum amount of silane molecules that would be added is to a large extent determined by the 18-electron rule (see Section 5.2.1). In  $Si_{12}W$ , each Si atom in the cluster donates a single electron to the central tungsten atom, which then possesses 18 electrons in total (12 electrons from the

 $Si_{12}$  cage and 6 valence electrons by the tungsten atom itself), resulting in a closed electronic shell. Three valence electrons on each silicon atom are left and thus allow for the formation of a silicon polyhedron without appreciable dangling bonds. The same argument accounted for the termination numbers for M = Hf, Ta, Re, and Ir as well (Hiura et al. 2001). Hiura and coworkers based their discussion of the termination numbers mainly on electronic arguments. They mentioned that probably geometric factors also add to the enhanced stabilities; however, they did not make any claims whether the experimental findings corresponded to the smallest cage possible. Since most probably the transition-metal atom constitutes the reactive site toward silane, the reduced reactivity from a certain size onward could also mark the onset of endohedrally doped silicon cages.

This question was explicitly tackled by another method by Nakajima and coworkers (Ohara et al. 2002). This group produced doped silicon clusters by ablation from two target rods by means of two independent lasers. In the work from 2002, anionic terbium-doped silicon clusters were produced and allowed to react with H<sub>2</sub>O vapor downstream of the source in a flow reactor. Upon exposure to H<sub>2</sub>O, doped clusters that contained less than 10 silicon atoms were found to react away, while larger clusters remained unreactive. Presuming that an exohedral terbium atom was the reactive site for the adsorption reaction with water, the low reactivity of TbSi<sub>n</sub><sup>-</sup> for  $n \ge 10$  indicated cage clusters, in which silicon completely surrounds the terbium dopant. Correspondingly, at least 10 silicon atoms were therefore needed to fully cover a terbium atom (problems with impurities were noted later, which, however, should not have affected the size range of the basket-to-cage transition [Ohara et al. 2007]). For Si<sub>n</sub>Ti<sup>+</sup> clusters, the decrease upon reaction toward H<sub>2</sub>O was observed at n = 7-11, whereas clusters with n = 13-17 remained practically unaffected (Ohara et al. 2003).

After improvements in their source design that allowed for a better mixing of the two plasmas in the cluster formation process, the Nakajima group extended their reactivity studies to all stable group 3, 4, and 5 transition-metal doped silicon clusters in their cationic, neutral, and anionic form (Koyasu et al. 2007). The results are summarized in Table 5.1. An element and charge-state dependence can be noted. Obviously, within the same row of the periodic system and the same charge state, the threshold sizes for dopant encapsulation decreases with increasing atomic number. This can be understood in terms of atomic radii, which

TABLE 5.1 Smallest Doped Silicon Cages MSi, for Cationic, Neutral, and Anionic Species for Various Transition-Metal Dopants

	Cation	Neutral	Anion	Cation	Neutral	Anion	Cation	Neutral	Anion	Cation	Cation	Cation
М		Sc			Ti			V		Cr	Со	Cu
Ν	17 <sup>a</sup>	15ª	15 <sup>a</sup>	13 <sup>a,b</sup>	13ª	$11^a$	12 <sup>a,b</sup>	10 <sup>a</sup>	9ª	$11^{b}$	8 <sup>b</sup>	12 <sup>b</sup>
М		Y			Zr			Nb				
Ν	21ª	20 <sup>a</sup>	20 <sup>a</sup>	15 <sup>a</sup>	14 <sup>a</sup>	12 <sup>a</sup>	13ª	12 <sup>a</sup>	$11^{a}$			
М		Lu			Hf			Та				
Ν	21ª	16 <sup>a</sup>	18 <sup>a</sup>	14 <sup>a</sup>	14 <sup>a</sup>	12 <sup>a</sup>	13 <sup>a</sup>	10 <sup>a</sup>	$11^{a}$			

Sources: Koyasu, K. et al., J. Phys. Chem. A, 111, 42, 2007; Janssens, E. et al., Phys. Rev. Lett., 99, 063401/1, 2007.

Note: The threshold sizes have been determined experimentally upon their reactivity with water vapor (a) or argon (b).

generally decrease with increasing atomic number in one row. A larger dopant obviously requires more silicon atoms to be fully surrounded than a smaller one. As for the charge-state dependence, the threshold sizes decrease going from cations to neutrals to anions, although the charge-state dependence of anionic Si<sub>n</sub>Lu<sup>-</sup> and Si<sub>n</sub>Ta<sup>-</sup> is exceptional. The threshold size dependence on the charge state was rationalized by metal encapsulation as well. According to mobility experiments on pure silicon clusters, the anions have systematically longer drift times, and hence smaller mobilities, than the cations (Hudgins et al. 1999). Consequently, the anions are effectively larger than the cations. This systematic shift was assigned not to a structural change, but to the extra charge causing the surface electron density of the anions to spill out further than for the cations. Here, however, it seems that the anionic silicon cages are actually larger as compared to the cationic ones and afford for transition-metal encapsulation already at smaller cluster sizes. The species that were richly abundant in the mass spectra (e.g., Si<sub>16</sub>Sc<sup>-</sup>, Si<sub>16</sub>Ti<sub>16</sub> Si<sub>16</sub>V<sup>+</sup>, Si<sub>16</sub>Zr, Si<sub>16</sub>Nb<sup>+</sup>, Si<sub>16</sub>Hf, and Si<sub>16</sub>Ta<sup>+</sup>, as shown in Figure 5.4) all exhibit no adsorption reactivity, pointing toward especially stable cages.

To investigate the structure of doped Si clusters, not only molecules such as SiH<sub>4</sub> and H<sub>2</sub>O can be used in chemical-probe techniques. This was recently shown by Janssens and coworkers who reported that the physisorption of argon atoms acts as a structural probe for transition-metal-doped silicon clusters (Janssens et al. 2007). Ar is an ideal probe as it has a negligible influence on the cluster and merely serves as a spectator atom. Further, it has no internal degrees of freedom and represents a good compromise in terms of polarizability. It can be attached to the cluster ion without much perturbation of the electronic structure. The study focused on cationic silicon clusters doped with 3d transition metals. Doped clusters were formed in a dualtarget source (Bouwen et al. 2000) using a mixture of 1% of Ar in He as a carrier gas. All clusters passed through a thermalization channel that was cooled by a flow of liquid nitrogen to 80 K. In the mass spectra of mixed  $Si_n M_m^+$  (M = Ti, V, Cr, Co, Cu) clusters, the highest ion signals were recorded for bare Si<sup>"</sup> and singly doped Si<sub>n</sub>M<sup>+</sup> clusters, but also a fraction of Si<sub>n</sub>M<sub>2</sub><sup>+</sup> clusters was formed. For both singly and doubly doped clusters,  $Si_n M_{1,2}^+ Ar_{1,2}$  complexes were formed, whereas for bare  $Si_n^+$  no argon complexes were observed at all. Moreover, the abundance of the  $Si_n M_{1,2}^+$  Ar<sub>1,2</sub> complexes was strongly size dependent and collapsed after a certain critical number of Si atoms in the cluster. These effects are represented best by plotting the total fraction of Ar complexes as a function of n, as is shown in Figure 5.5. Both for singly and doubly doped silicon clusters, critical sizes for argon attachment, which depend on the dopant element, are observed. Figure 5.5 shows how, in agreement with the observations of Koyasu et al., for singly doped silicon clusters the threshold size (defined as the smallest size that does not form complexes) changes along the 3d row, i.e., Si<sub>13</sub>Ti<sup>+</sup>, Si<sub>12</sub>V<sup>+</sup>, Si<sub>11</sub>Cr<sup>+</sup>, and Si<sub>8</sub>Co<sup>+</sup>. The threshold number for copper doping increases for Si<sub>12</sub>Cu<sup>+</sup> in agreement with the increasing covalent radius, when going from cobalt to copper (Cordero et al. 2008). With the knowledge that  $Si_n^+$  clusters do not form stable complexes with Ar at 80K, it was assumed that Ar must bind to the dopant. As for SiH<sub>4</sub> and H<sub>2</sub>O, binding to the transition-metal atom was only feasible if the dopant was located on the surface of the host cluster. If the dopant resided in the interior of a Si, cage, the Ar atom could only interact with Si surface atoms; thus, no Ar complexes were formed. The disappearance of the Ar complexes marked the formation of endohedral clusters. Additionally, for doubly doped silicon clusters, the threshold size also decreases along the 3d row:  $Si_{20}Ti_2^+$ ,  $Si_{18}V_2^+$ ,  $Si_{17}Cr_2^+$ , and  $Si_{14}Co_2^+$ , as seen in Figure 5.5. The gradual transition of the Ar sticking probability for  $Si_nV_2^+$  and  $Si_nCo_2^+$  was attributed to the possible coexistence of endohedral and exohedral isomers.

#### 5.3.3 Quantum Chemical Calculations

In 1996, Jackson and Nellermoe published their observation of a remarkably strongly bound endohedral zirconium atom inside a  $Si_{20}$  cage. Based on local-density approximation calculations, they found a binding energy of 11.2 eV with respect to an isolated Zr atom and the most stable  $Si_{20}$  isomer known at the time (Jackson and Nellermoe 1996). Interestingly, they were obviously unaware of the experimental study by Beck almost 10 years earlier, since they encourage experimentalists to start studying doped silicon clusters without citing Beck's work. For 5 years, the call for



**FIGURE 5.5** Fraction of argon complexes formed for  $Si_nM^+$  (M = Ti, V, Cr, Co, Cu) as a function of cluster size. A critical size for which argon complexes no longer are formed is found for both singly and doubly doped species. The corresponding sizes are the smallest clusters, exhibiting endohedrally doped silicon cage structures (see Janssens et al. 2007).



**FIGURE 5.6** Shrinkage of the Si cage. (a) Dodecahedral Zr-encapsulated  $Zr@Si_{20}$ , as found by Jackson and Nellermoe (1996), (b)–(e) optimized structures of  $Zr@Si_{20}$ ,  $Zr@Si_{20}$ ,  $Zr@Si_{19}$ ,  $Zr@Si_{17}$ , and  $Zr@Si_{16}$ , respectively. The arrows indicate the atoms that were removed. (f) The Frank-Kasper polyhedral structure of  $M@Si_{16}$  (M = Ti and Hf). (Reproduced from Kumar, V. and Kawazoe, Y., *Phys. Rev. Lett.*, 87, 045503/1, 2001. With permission.)

experimental verification remained unheard until Hiura et al. triggered again the interest in doped silicon clusters. A few months later, Kumar and Kawazoe used the Jackson and Nellermoe work as a basis for the reinvestigation of Zr-doped silicon clusters (Kumar and Kawazoe 2001). They found that the cage proposed by Jackson is not stable but that the cage shrinks with one silicon atom sticking out (Figure 5.6a and b). The removal of this atom and reoptimization lead to a ZrSi<sub>19</sub> cage with two silicon atoms sticking out (Figure 5.6c). The further removal of these two atoms and reoptimization lead to ZrSi172 a cage from which again one atom sticks out (Figure 5.6d). Finally, the removal of this atom yielded a compact, fullerene-like ZrSi<sub>16</sub> cage (Figure 5.6e). The embedding energy of the Zr atom was calculated to be almost 14 eV. For titanium as the dopant element, a Frank-Kasper (FK) polyhedron (Figure 5.6f) was found to be the most stable isomer with an exceptionally large HOMO-LUMO gap of 2.36 eV (Kumar and Kawazoe 2001, 2003a).

Since the Hiura and Kumar work, many theoretical studies have addressed the structures of  $Si_nM$  clusters with dopants from almost every group of the periodic table. Additional quantum chemical investigations have focused on periodic trends when doping silicon clusters. A review of all theoretical work on doped silicon clusters would go far beyond the scope of this chapter. Instead, only some selected studies are chosen, which deal with systems that have been presented in the Sections 5.3.1 and 5.3.2.

While it seems that alkaline-doped clusters containing up to 20 silicon atoms are always more stable when the dopant

is situated on the surface of the cluster (Sporea and Rabilloud 2007), transition-metal doped silicon clusters form cage-like geometries from a certain size onward (Guo et al. 2008).

Beck had already assigned the enhanced stability of the group-6-doped cluster cations MSi<sub>15</sub><sup>+</sup> and MSi<sub>16</sub><sup>+</sup> to a highly coordinated central transition-metal atom. Their structures remained unknown until Kumar and Kawazoe confirmed that metal-encapsulated Si, cage structures account for their unusual stability, performing ab initio calculations on Si"M clusters (M = Cr, Mo, and W; n = 14-17) (Kumar and Kawazoe 2002). For CrSi15, different isomers have been proposed as ground-state structures over the years by the same group. While initially a structure was proposed that was constructed by placing one silicon atom on the face of a body-centered cubic structure (Kumar and Kawazoe 2002), in a later study three very similar structures based on a decahedral isomer were found to be almost degenerate in energy (Kawamura et al. 2004). In a more recent work, a FK-type polyhedron has been proposed to be the ground-state geometry (Kumar 2006). The calculated global minimum of CrSi<sub>16</sub> was constructed by capping a higher-energy fullerene-like isomer of CrSi<sub>15</sub>. Kumar found competing growth models that gave rise to rather different structures of group-6-encapsulated 15- and 16-atom silicon clusters and account for their simultaneous strong abundances (Kumar and Kawazoe 2002).

Also, the findings of Koyasu and coworkers can be understood better with the help of theory. As mentioned above, TiSi<sub>16</sub> has been found to adopt an FK polyhedral geometry with a remarkable HOMO-LUMO gap of 2.36 eV (Kumar and Kawazoe 2001, 2003a). This isomer was found to lie 0.18 eV lower in energy than the fullerene-like isomer (Figure 5.6e), while the zirconium-doped fullerene-like isomer has been calculated to be more than 1 eV more stable than the FK isomer (Kumar et al. 2003). Reveles and Khanna (2006) found that the compact FK isomer was also the ground-state structure for ScSi<sub>16</sub><sup>-</sup> and VSi<sub>16</sub><sup>+</sup>. Whenever the number of valence electrons was different from 20, the structures distorted. However, the stability cannot be explained only by adding together the number of valence electrons of the dopant and the number of silicon atoms, since, e.g., ScSi<sub>17</sub> or TiSi<sub>17</sub> were not found to be more pronounced in the mass spectra. It was proposed that it was necessary to identify the silicon sites, which contribute an electron to the free-electron gas of the cluster. Such sites were identified upon the bond critical points in the charge density. Only in the compact structures, all silicon atoms were directly coordinated to the metal atom and could therefore contribute an electron. Thus, both the geometry and the electron counting needed to be considered to correctly predict stable clusters (Reveles and Khanna 2006). Recently, it was found that the perfectly symmetric FK polyhedron might not be the global minimum for the 16-atom cage but that slightly distorted geometries lie a bit lower in energy (Torres et al. 2007).

Reactivity studies, as described in Section 5.3.2, mainly addressed the question at what size the transition from exo- to endohedrally doped silicon clusters occurs. Hiura et al. (2001) explained their findings for the 5d transition-metal dopants mainly on the basis of an 18-electron rule. However, the reduced reactivity from a certain size onward could also be explained by endohedral cages, since the sizes for which the reactivity dropped are the same as the threshold sizes identified for cationic Hf and W-doped silicon clusters by their reactivity with water vapor by Koyasu and coworkers (Table 5.1) (Koyasu et al. 2007). In the case of Hf-doped clusters, theory does not reproduce the experimental transition size precisely but calculates basket-like structures up to HfSi12 and cage-like structures for larger species (Kawamura et al. 2005). Studies by Guo and coworkers found the smallest cages for cationic and neutral tantalum-doped silicon clusters at TaSi<sub>12</sub> (Guo et al. 2004, 2006), and therefore did not reproduce the experimental findings neither for the cations nor for the neutrals (see Table 5.1). The reduced reactivity of  $WSi_{12}^+$  is in agreement with a highly symmetric  $D_{6h}$  cage structure, as calculated for neutral WSi<sub>12</sub> (Miyazaki et al. 2002, Lu and Nagase 2003).

Some better agreement has been achieved between theory and the experimental studies for 3*d* transition-metal dopants (Janssens et al. 2007, Koyasu et al. 2007). The proposed basketshaped structures for  $Si_nTi$  (n = 8-12) and endohedral systems for larger sizes (Kawamura et al. 2005) agree nicely with the experiment, though Guo and coworkers predicted an endohedral structure already for  $Si_{12}Ti$  (Guo et al. 2007). Also for  $Si_{12}V$ , Guo found a cage, which is in agreement with the critical size obtained for the cationic cluster but not with the threshold size

measured for neutral vanadium-doped silicon clusters (Table 5.1) (Guo et al. 2008). It was predicted by Khanna and coworkers that Cr is small enough to occupy the center of Si<sub>n</sub> (n = 11-14) cages (Khanna et al. 2002). Other groups, however, found caged structures for Si<sub>n</sub>Cr from  $n \ge 12$  and open basket-like structures for n < 12 (Kawamura et al. 2004, Guo et al. 2008). The argonphysisorption experiments identified Si<sub>11</sub>Cr<sup>+</sup> as the smallest endohedral Si<sub>n</sub>Cr<sup>+</sup> cluster (see Figure 5.5) (Janssens et al. 2007). In the case of similar structures for cations and neutral clusters, these findings would favor the findings of Khanna et al. The exohedral structure of neutral Si<sub>9</sub>Co found by different groups (Lu and Nagase 2003, Guo et al. 2008) is different from the disappearance of the Ar complexes from Si<sub>s</sub>Co<sup>+</sup> onward. Ma and coworkers are one of the very few groups that have applied a global-minimum search based on a genetic algorithm (Ma et al. 2005). The genetic algorithm used a tight-binding model and resulted mainly in structures in which the cobalt atom prefers to sit in the center of the silicon cluster. The identified low-lying isomers were further optimized with density functional theory (DFT) within the generalized gradient approximation. They identified Si<sub>9</sub>Co as the smallest cage, while Si<sub>8</sub>Co was a cluster in which cobalt is almost fully surrounded by silicon atoms (Ma et al. 2005). In that regard, the results are in quite good agreement with the critical size found for argon physisorption (Figure 5.5).

Hagelberg and coworkers have been interested in copperdoped silicon clusters since the late 1990s. They have shown that  $Si_{12}Cu$  is most stable in a cage geometry, while in  $Si_{10}Cu$  the Cu atom occupies a surface site (Xiao et al. 2002). Again, the argonphysisorption experiments support the computations.

In general, quantum chemical calculations have helped a lot in the understanding of the physical and chemical properties of doped silicon clusters. The enhanced stabilities of certain cluster sizes have been reproduced or, e.g., in the case of TiSi<sub>16</sub>, even predicted. Stabilization has been shown to be mainly due to geometric shell closings and especially compact structures, like the FK polyhedron and the 20 electron system of TiSi<sub>16</sub>. Also, the onset of cage formation is often predicted correctly. However, cages are only formed for rather large particles, and the potential energy surface of such species is characterized by an enormous number of local minima. The binary composition of doped silicon clusters enhances the complexity of the problem even further. In general, an effective sampling of the potential energy surface of binary clusters for identifying its global minimum requires global-optimization techniques (Johnston 2003, Ferrando et al. 2008). Probably due to the high computational costs, only very few studies on doped silicon clusters have employed global-minimum search schemes (Ona et al. 2004, Ma et al. 2005, Wu and Hagelberg 2006). Still, these studies have been limited by the computational method that has been used for the global optimization or they have been restricted to a rather small size range.

Even if a putative global minimum can be identified, the error associated with the theoretical method still makes definite assignments difficult. The situation is somewhat different once detailed experimental data that characterize the species produced under laboratory conditions are available. In such cases, the search can be stopped once an isomer is found whose calculated characteristics fit the experiment. Mass spectrometry and reactivity studies have added a great deal to the knowledge of doped silicon clusters. However, they are somewhat limited regarding the content of detailed information on the electronic and geometric structure of the particle. For such insights, two methods have been proven to be of major importance, namely photoelectron and vibrational spectroscopy.

#### 5.3.4 Photoelectron Spectroscopy

The credit for the first photoelectron spectrum of an anionic transition-metal-doped silicon cluster goes again to Nakajima and coworkers. They published spectra for mixed terbium-silicon clusters containing between 6 and 16 silicon atoms (Ohara et al. 2002). It was found that the electron affinities changed remarkably from ~2.2 eV for TbSi<sub>9</sub> to 3.6 eV for TbSi<sub>10</sub>. In agreement with their reactivity studies (see Section 5.3.2), they interpreted this result as support for the onset of cage formation. A drastic drop in the electron affinities for clusters of masses corresponding to species containing 12 and more silicon atoms could not be explained and was later shown to be due to Tb<sub>3</sub>OSi<sub>n</sub> clusters. With better mass resolution and cleaner spectra, the electron affinities of clusters TbSi<sub>n</sub> with  $n \ge 12$  were determined to be around 3 eV (Ohara et al. 2007).

Ohara and coworkers extended their photoelectron studies to silicon cluster anions doped with Ti, Hf, Mo, and W (Ohara et al.

2003). Differences between the spectra of bare silicon clusters and the doped species immediately pointed to structural rearrangements upon doping. Local minima in the electron affinities for doped clusters containing 16 silicon atoms were noted. However, the authors did not comment on the already visible large HOMO-LUMO gap of these cluster sizes but supposed a geometric stabilization upon cage formation (Ohara et al. 2003).

A large HOMO-LUMO gap of 1.9 eV was reported explicitly by the Nakajima group in 2005 to account for the enhanced intensity of  $\text{TiSi}_{16}$  in the mass spectrum (Koyasu et al. 2005). The electron affinity of  $\text{TiSi}_{16}$  was found to be only 2.03 eV (Figure 5.7). The large gap confirmed the stability of a closed 20 electron shell. The experimental findings were in reasonable agreement with theoretical predictions of an electron affinity of 1.91 eV and a HOMO-LUMO gap of 2.35 eV (Kumar and Kawazoe 2001, Kumar et al. 2003). For the anions  $\text{ScSi}_{16}^-$ ,  $\text{VSi}_{16}^-$ , and  $\text{TiSi}_{16}\text{F}^$ instead, the HOMO-LUMO gap was too small to be detected, further confirming the unique stability of  $\text{TiSi}_{16}$  (Figure 5.7) (Koyasu et al. 2005).

Remarkably large HOMO-LUMO gaps were measured also for  $ZrSi_{16}$  and  $HfSi_{16}$  with 1.36 and 1.37 eV, respectively. Compared to the 1.9 eV in the case of titanium doping, the trend of these values reproduces the order of the atomic radii, which are 1.45 Å for titanium, 1.59 Å for zirconium, and 1.56 Å for hafnium (Koyasu et al. 2007). Extending the studied size range, local maxima in the electron affinity were found for group-3-doped silicon cluster anions containing 10 silicon atoms. This effect was rationalized by an especially stable electronic configuration of the assumed  $Si_{10}^{4-}$  frame (Koyasu et al. 2008).



**FIGURE 5.7** Photoelectron spectra of  $SCSi_{16}^-$  (a and b),  $TiSi_{16}^-$  (c and d), and  $VSi_{16}^-$  (f and g) at two different photon energies, at 266 nm (4.66 eV; top three spectra) and at 213 nm (5.82 eV; bottom four spectra). The HOMO-LUMO gap can be assigned by comparing the photoelectron spectra of  $TiSi_{16}^-$  with that of  $TiSi_{16}F^-$  (e). Photoelectrons were analyzed with a magnetic bottle-type photoelectron spectrometer calibrated using a known spectrum of Au<sup>-</sup>. (Reproduced from Koyasu, K. et al., *J. Am. Chem. Soc.*, 127, 4998, 2005. With permission.)

A second group that has studied doped silicon clusters by means of PES is the one of Bowen and coworkers. They produced Cr-doped silicon cluster anions upon laser ablation from a chromium-coated silicon rod (Zheng et al. 2005). Their photoelectron spectrum of  $\text{CrSi}_{12}^-$  started with a smooth onset and then exhibited a very sharp narrow peak. This peak has been argued to represent the transition from the ground state of the anion to the ground state of the neutral and confirmed that the geometry of the anions and the neutral species are similar. Also, their measured vertical detachment energy of 3.18 eV nicely reproduced the predicted value of 3.11 eV (Zheng et al. 2005). Unfortunately, they were not able to confirm the predicted HOMO-LUMO gap of ~1 eV.

Using a two-laser vaporization source, Bowen and coworkers recently managed to produce sufficient amounts of europiumdoped silicon cluster anions to record their photoelectron spectra (Grubisic et al. 2008). They noted a large increase in the electron affinity from 1.9 to 2.8 eV, when going from  $EuSi_{11}$  to  $EuSi_{12}$ . This finding was similar to the one by Ohara and coworkers for terbium-doped silicon clusters and has been consequently attributed to a structural rearrangement from exo- to endohedrally doped silicon clusters (Grubisic et al. 2008).

#### 5.3.5 Infrared Spectroscopy on Doped Silicon Clusters

PES yields valuable information on the electronic structures of gas-phase clusters. However, it is not always clear in how far structural rearrangements are responsible for measured changes in the electronic structures. Vice versa, the similar photoelectron spectra of different clusters do not necessarily mean that the geometric structure is similar.

IR spectroscopy is very sensitive to the cluster's internal structure as molecular vibrations directly reflect the arrangements of atoms in the cluster and the forces acting between them. Unfortunately, achievable cluster densities in the gas phase are usually too low for the detection of direct absorption in the IR. One way to circumvent this problem is to deposit and accumulate clusters inside a cryogenic matrix. This technique has been used to assign the structures of small bare silicon clusters (Honea et al. 1993) but has not been applied to doped silicon clusters yet.

If one wants to study true gas-phase clusters, coupling spectroscopic techniques with mass spectrometry allows, in principle, for detection efficiency close to unity. The use of mass spectrometric detection requires a reaction of the cluster in response to the absorption of IR light, which can, e.g., be fragmentation. A similar approach has been used by Duncan and coworkers in the visible range, using a 532 and 355 nm laser to dissociate cationic silicon clusters doped with copper, silver, and chromium atoms (Jaeger et al. 2006). The clusters that contained seven silicon atoms tended to lose primarily the dopant atom, indicating exohedral structures. The same was true for  $AgSi_{10}^+$  and  $CuSi_{10}^+$ . For  $CrSi_{15}^+$  and  $CrSi_{16}^+$ , however, dissociation occurred mainly through the loss of silicon atoms, confirming endohedral cages, as predicted earlier (Jaeger et al. 2006). Tunable table-top laser systems do not provide sufficient fluence in the IR to excite strongly-bound clusters to a point where fragmentation can occur. Only with the access to powerful freeelectron lasers like the Free Electron Laser for Infrared eXperiments (FELIX, see [Oepts et al. 1995]), a variety of innovative means of gas-phase spectroscopy became possible (Asmis et al. 2007).

In IR-MPD spectroscopy, either the depletion of parent ions or the formation of the photofragments is monitored to probe the absorption process. Probing the fragments relies on an initial mass selection and gives rise to almost background-free spectra (Asmis and Sauer 2007). The measurement of depletion has the advantage that all complexes in the molecular beam are probed, and since the detection method is mass-selective, the simultaneous measurement of IR spectra for different cluster sizes is possible (Lyon et al. 2009). Further, also neutral molecules can be probed with FELIX radiation (Fielicke et al. 2005, Gruene et al. 2008a). A disadvantage of measuring the depletion is that the spectra are not background-free and can suffer from a limited signal-to-noise ratio.

The vibrational transitions of doped silicon clusters lie in the far-infrared (FIR), typically between 150 and  $600 \,\mathrm{cm^{-1}}$ , which corresponds to an energy per photon of only ~20–75 meV. On the other hand, the clusters are rather strongly bound with bond dissociation energies of around 4eV for bare silicon clusters (Jarrold 1995). Even with the high laser power that is provided by FELIX, IR-MPD of such species has not been observed. This problem can be overcome by using the so-called messenger method, in which a loosely bound ligand that is supposed to have a minor to negligible influence on the structure and vibrational properties, is attached to the species that is to be analyzed (Fielicke et al. 2004).

As has been shown in Section 5.3.2, argon binds to exohedrally doped silicon clusters at 80 K. Therefore, the vibrational spectra of small exohedral vanadium- and copper-doped silicon cluster cations have been obtained upon IR-MPD of their complexes with one argon atom (Gruene et al. 2008b). Figure 5.8 shows the experimental and theoretical vibrational spectra of  $Si_nCu^+$  and  $Si_nV^+$  (n = 6-8). Only the theoretical spectrum of the particular isomer that reproduced the experimental spectrum the best is shown here. In general, the peak positions are in good agreement while the peak intensities deviate between theory and experiment. In particular, the low-energy absorptions around 300 cm<sup>-1</sup> are less pronounced in the experiment, which could be due to the larger number of photons needed for photodissociation. Furthermore, it has to be kept in mind that the IR-MPD spectra do not correspond directly to linear absorption spectra (Oomens et al. 2006). In almost all cases, the experimental spectrum was reproduced best by the calculated lowest-energy structure. For Si<sub>6</sub>V<sup>+</sup>, theory found a Si-capped octahedron as the lowest-energy structure, while the experiment was reproduced much better by the spectrum of a triplet-state pentagonal bipyramid with vanadium in an equatorial position, which was calculated to be 0.03 eV higher in energy. Interestingly, the experiment did not show any features that would point to the coexistence