Preface

Nanochemistry, a branch of nanoscience, is focused on building nanoscale systems (1–100 nm) mainly using atom or molecule as building block. Nanochemistry brings together multiple disciplines using physical methods and chemical theories and experiments to investigate properties of materials at the nanoscale. Of the latter, the nanoclusters continue to attract much interest due not only to their intriguing physicochemical features but also to a manifold of potential industrial applications.

What are atomic clusters? A cluster is first defined as a finite group of atoms that are held together mainly, or at least to a significant extent, by chemical interactions directly between the atoms. The concept of cluster can also be used for characterizing molecular complexes as they are formed in plasmas by clusterification processes.

Clusters M_N are thus aggregates of a finite number N of atoms or molecules M, thus, bridging the gap between the isolated atom/molecule and the macroscopic solid state of matter. Depending on the methodology and experimental techniques, clusters and their aggregation can either be formed in gas or liquid phase or be deposited on solid surfaces. The continuous variations in properties of clusters in going from a small number of atoms to a larger scale is a consequence of the quantum size regime in which each additional atom makes a unique difference in the properties. In addition, the cluster growth mechanism allows the transition from atoms to clusters and to bulk materials to be understood (bottom-up approach) in a systematic way.

Cluster science has deep roots in both physics and chemistry, but also has unique features making it relevant to many fields including materials science, environment, biology, medicine, etc. Cluster science is thus regarded as a bridge across many scientific disciplines. The stabilities and properties of clusters depend on both the nature of constituent elements and their interactions and sizes. The well-known carbon buckyball C_{60} is a cluster having high symmetry and thermodynamic stability whereas that of the element next to the carbon, the boron buckyball B_{80}, is not stable in the high symmetry form. In addition, combination of various types of elements results in a large number of mixed clusters. Binary clusters composed of two elements are of particular interest due to the high propensity for control, tuning

properties and a wide range of potential applications. Depending on the atoms ratio in a binary cluster the elements can be classified as host (having larger percentage) or dopant (having smaller percentage). Certain clusters that are referred to as superatoms, have a *magic number*, both in terms of electronic structure and atomic number, exhibit high thermodynamic stability and can be used as potential building blocks for cluster-assembled materials. The latter are currently of great interest as they take advantage of novel properties of clusters and make them accessible in bulk materials. Cluster-based nanostructures are promising to become pivotal for a new generation of catalysts for chemical reactions, semiconducting materials and electronic devices with tailored properties.

In recent years, a large number of papers have been published on elemental clusters. Stability, structural and electronic characteristics of clusters generated from different experimental techniques have been interpreted with the help of theoretical models, or by quantum chemical computations. Bottlenecks still remain in the prediction of their geometric and electronic structures, especially for clusters with a large number of atoms. While concepts and rules for rationalizing and predicting structural motifs, properties and reactivities of different classes of organic and inorganic compounds have long reached maturity, relatively less has been formulated for atomic clusters. In this context, much effort has been devoted to the establishment of a set of general rules for nanoclusters using quantum chemical computations and theoretical models.

Although a number of excellent reviews and books on elemental clusters are available in the literature, it appears to us that there is a need for an account on recent developments in the field. This is the purpose of the present volume with ten chapters that have been written by experts and active researchers in the field.

This collection begins with Chapter "Global Optimisation Strategies for Nanoalloys" by Heard and Johnston describing the efforts involved in finding the global minima for nanoalloys. Identifying the most stable configuration state of a given system is vital for understanding its properties. The authors discuss the advantages and shortcomings of various methods of global optimizations. In addition, the authors draw our attention to more complex environments such as surface deposition and ligand passivation on which little attention has been paid.

The following two chapters are devoted to the characterization of atomic clusters using spectroscopic techniques. Li, Fielicke, Lievens and Janssens report in Chapter "Structural Identification of Doped Silicon Clusters" a critical review of the current state-of-the-art mass, infrared, photoelectron and X-ray and magnetic circular dichroism spectrometric methods in experimental characterizations of pure and doped silicon clusters. In Chapter "Structural Evolution, Vibrational Signatures and Energetics of Niobium Clusters from Nb_2 to Nb_{20}", Nhat, Majumdar, Leszcynski and Nguyen analyze the determination of structures using experimental vibrational spectra with the help of density functional theory computations for a series of small pure niobium clusters. The results point out how a combined experimental and theoretical investigation can allow the structural motifs of clusters to be determined with confidence.

Falvo analyzes in Chapter "Submersion Kinetics of Ionized Impurities into Helium Droplets by Ring-Polymer Molecular Dynamics Simulations" the characteristics of the clusters of the lightest rare gas, the helium droplets that provide a unique medium sensitive to the weakest interactions. The kinetics of the submersion of ionized alkali dopants into helium droplets are investigated using ring polymer molecular dynamics simulations. The interplay between experiment and theory on this challenging class of compounds is also discussed.

Next in Chapter "Structure, Stability and Electron Counting Rules in Transition Metal Encapsulated Silicon and Germanium Clusters", Sen discusses in depth the structures and stability of transition metal encapsulated silicon and germanium clusters. Arguably silicon is still the most important element in the semiconductor industry. It has been known for some time that pure silicon or germanium clusters are unstable and not suitable for rational design of materials and applications. However, TM-doped Si/Ge clusters showed enhanced stability over a certain size range. In this chapter a comprehensive review of this field is provided in order to answer some fundamental questions on the clusters' stability and the use of electron counting rules. This issue is pursued further in Chapter "Transition Metal Doped Boron Clusters: Structure and Bonding of B_nM_2 Cycles and Tubes" in which Pham and Nguyen attempt to rationalize the structural motifs and growth patterns of transition metal doped boron clusters. Orbital interactions and partitions of the total electron density into basins are extensively used to probe the chemical bonding phenomena. Establishment of simple electron count rules to understand and predict shapes of clusters remains a challenging subject for future research.

In Chapter "Silicate Nanoclusters: Understanding Their Cosmic Relevance from Bottom-Up Modelling", Bromley discusses in detail how the bottom-up computational modelling provides fundamental insights into one of the most abundant materials on earth and in cosmos as well. Despite the importance and long history of silicates, several important questions remain unanswered. How the silicon suboxide clusters transform to basic units seen in bulk, and what is the significance of the incorporation of metals such as Mg and Fe in silicate nucleation process and subsequently in the formation of silicate minerals, to name a few. This chapter highlights the importance of atomic-scale computational modelling in the understanding of the transition from sub-nano to nano to bulk.

In Chapter "Magnetic Anisotropy Energy of Transition Metal Alloy Clusters", Hoque, Baruah, Reveles and Zope examine the magnetic properties of transition metal alloy clusters such as the $As@Ni_{12}@As_{20}$ cluster. Transition metal clusters often show high spin moments but generally are also reactive with the environment. The doping effect leads to a passivation of the surface atoms stabilizing the doped clusters. In particular, the anisotropy energy is computed using density functional theory. As the growth patterns from atoms to bulk state remain a subject of current and intensive debate, the formation of baby-crystals from clusters is of great interest, and this issue is treated in Chapter "Growth Pattern and Size-Dependent Properties of Lead Chalcogenide Nanoclusters" by Gill, Sawyer, Salavitabar, Kiran and Kandalam. The structural evolution of lead chalcogenide $(PbX)_n$ (X= S, Se, and Te; n = 1 – 32) nanoclusters and how various properties of these clusters vary with

increasing cluster size are investigated using different experimental techniques and computational (DFT-based) studies are also discussed in detail. The importance of the synergy between computation and experiment is again demonstrated.

Finally, one of the most promising applications of elemental clusters is the field of catalysis of chemical reactions. Lang and Bernhardt provide in Chapter "Chemical Reactivity and Catalytic Properties of Binary Gold Clusters: Atom by Atom Tuning in a Gas Phase Approach" insights into the reaction mechanisms, energetics, and kinetics of the catalytic processes of free clusters. Free clusters in the gas phase represent simplified but suitable model systems which allow insight into catalytic processes to be obtained on a rigorously molecular level. Experimental and theoretical studies are described on the reactivity and catalytic activity of free gold clusters and the change of their chemical properties induced by doping these clusters with transition metal atoms. Three catalytic reactions selected include the oxidation of carbon monoxide, the conversion of methane, and the coupling of methane and ammonia.

We hope that this monograph will prove to be a useful source of information for researchers on the current experimental techniques and theoretical methods and also results on different specific classes of elemental clusters.

We are grateful to the authors for their contributions and their patience. We sincerely thank the editorial staff of Springer, in particular Dr. Karin De Bie and Dr. Sathya Karuppaiya, for their efficient assistance. Finally, we would express our gratitude toward our spouses, Mai Phuong Le and Nallini Persaud, for their constant support.

Leuven, Belgium — Minh Tho Nguyen
Lake Charles, LA, USA — Boggavarapu Kiran

http://www.springer.com/978-3-319-48916-2

Clusters
Structure, Bonding and Reactivity
Nguyen, M.T.; Kiran, B. (Eds.)
2017, XII, 363 p. 161 illus., Hardcover
ISBN: 978-3-319-48916-2