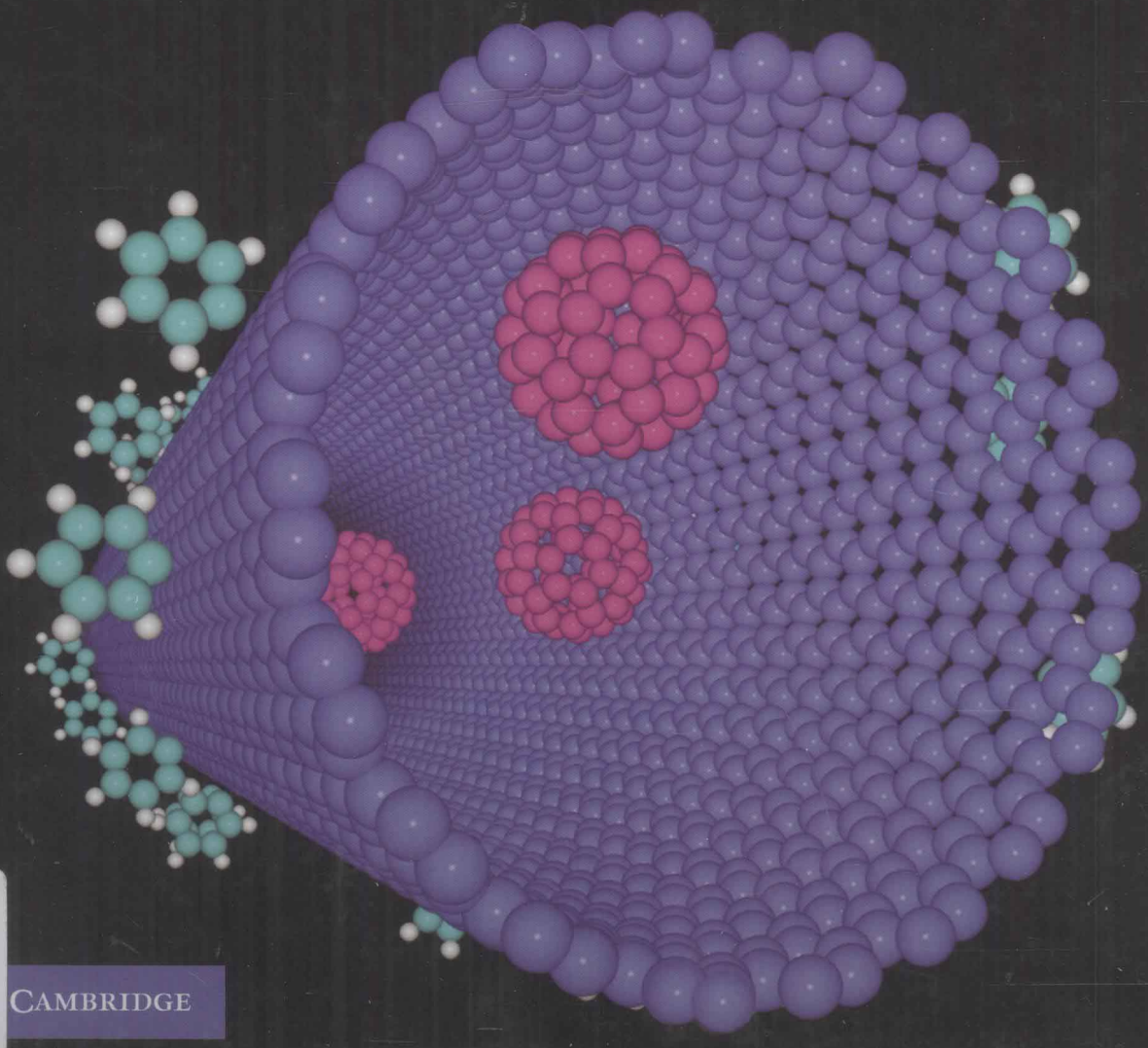
Computational Physics of Carbon Nanotubes

H. Rafii-Tabar



CAMBRIDGE

COMPUTATIONAL PHYSICS OF CARBON NANOTUBES

H. RAFII-TABAR
Shahid Beheshti University of Medical Sciences and the Institute for Research in Fundamental Sciences, Iran

CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE UNIVERSITY PRESS
Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo

Cambridge University Press
The Edinburgh Building, Cambridge CB2 8RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9780521853002

First published 2008

Printed in the United Kingdom at the University Press, Cambridge

A catalogue record for this publication is available from the British Library

ISBN 978-0-521-85300-2 hardback

COMPUTATIONAL PHYSICS OF CARBON NANOTUBES

Carbon nanotubes are the fabric of nanotechnology. Investigation into their properties has become one of the most active fields of modern research. This book presents the key computational modeling and numerical simulation tools to investigate carbon nanotube characteristics. In particular, methods applied to geometry and bonding, mechanical, thermal, transport and storage properties are addressed. The first half describes classic statistical and quantum mechanical simulation techniques, (including molecular dynamics, monte carlo simulations and *ab initio* molecular dynamics), atomistic theory and continuum based methods. The second half discusses the application of these numerical simulation tools to emerging fields such as nanofluidics and nanomechanics. With selected experimental results to help clarify theoretical concepts, this is a self-contained book that will be of interest to researchers in a broad range of disciplines, including nanotechnology, engineering, materials science and physics.

HASHEM RAFII-TABAR is Professor of Computational Nano-Science and Head of the Medical Physics and Biomedical Engineering Department, Shahid Beheshti University of Medical Sciences in Iran. He is also Professor of Computational Condensed Matter Physics and Head of the Nano-Science Department at the Institute for Research in Fundamental Sciences in Iran. He was the founding member and the Head of the Nano-Technology Committee of the Ministry of Science, Research and Technology in Iran, and was elected the number one researcher of the year in 2006. He shared the Elegant Work Prize of the Institute of Materials London in 1994 for his investigations on nano-scale systems.

To Fariba, Ardalan, and Elizabeth

Preface

The appearance of powerful high-performance computational facilities has led to the emergence of a new approach to fundamental research, namely computational modelling and computer-based numerical simulations, with applications in practically all areas of basic and applied sciences, from physical sciences to biological sciences, from medical sciences to economic and social sciences. The applications of computational simulations over the past two decades have been so phenomenal that a new academic discipline, called computational science, with its own research centres, laboratories and academia, has appeared on the educational and industrial scenes in almost all the developed, and many developing, countries. Computational science complements the two traditional strands of research, namely analytical theory-building, and laboratory-based experimentation, and is referred to as the *third* approach to research. Numerical simulations present the scientists with many unforeseen scenarios, providing a backdrop to test the physical theories employed to model the energetics and dynamics of a system, the approximations and the initial conditions. Furthermore, they offer clues to the experimentalists as to what type of phenomena to expect and to look for. It is no exaggeration to suggest that we are now experiencing a monumental *numerical revolution* in physical, biological and social sciences, and their associated fields and technologies.

One of the most active and very productive applications of computational modelling is in the field of computational nanoscience and its associated field of computational molecular nanotechnology. Nanoscience and nanotechnology together with molecular biology, molecular genetics, information technology and cognitive science, form the pillars of the current industrial–scientific revolution. The overlap of these scientific disciplines will lead to the emergence of what has come to be referred to as the *convergent technology* which will provide the real possibility to artificially design and produce biomimetic-based functional devices, and complex smart systems and materials that embody the basic characteristics

and performance of biological, and intelligent, systems, such as their ability to self-repair, self-assemble and self-organise. This convergence will take place at the nanoscopic level, the most fundamental level at which the basic building blocks of the physical, the biological and the cognising matter, namely the physical and biological nanostructures, are formed and the laws governing their dynamics are established.

This book is concerned with the application of computational modelling to the physics of one of the most fundamental and truly amazing man-made nanostructures discovered so far, namely the carbon nanotubes. These structures have unique, and in many ways extraordinary, mechanical, electronic, thermal, storage and transport properties, having, for example, a very high Young's modulus that makes them the material with the highest tensile strength known by far, capable of sustaining high strains without fracture. Nanotubes are proposed as the functional units for the construction of the future molecular-scale machines and nanorobots, providing the simplest forms of molecular bearings, shafts and gears in highly complex nanoelectromechanical systems (NEMS). As highly robust mechanical structures, they are also increasingly being used as probes in scanning tunnelling microscopy (STM) and atomic force microscopy (AFM), the tip-based devices that have provided revolutionary tools for a nanoscopic inspection of the morphology and the electronic structure map of material surfaces, and the manipulation of matter on atomic and molecular levels.

This book is largely written for practising research scientists but, by providing enough details, I hope it is also useful for postgraduate and Ph.D. students involved in both computational and experimental work in such areas as condensed matter physics, computational materials science, computational biophysics, computational and experimental nanoscience, computational nanoengineering and the conceptual design of ultra-small, nanotechnology-related components, such as nanoscale sensors. Although there exist several books and many review papers on the physics of carbon nanotubes, this is the first book that systematically addresses the *computational* physics of the nanotubes and provides the underlying computational methods, and physical theories, and considers the applications of these methods and theories to the investigation of the mechanical, thermal and transport properties of nanotubes. I have not covered the topic of electronic conductance properties of nanotubes, as this is a huge topic that requires a separate treatise of its own, a task that I am presently involved in.

I owe special thanks to all my colleagues and students at both the Institute for Research in Fundamental Sciences (Pajoheshgah Daneshhaye Bonyadi, formerly the IPM), and the Department of Medical Physics and Biomedical Engineering at Shahid Beheshti University of Medical Sciences, who provided me with the

facilities and a near-perfect opportunity to be able to concentrate my efforts in completing this book. I have also benefited greatly from the discussions that I have had with them while writing this book. My thanks and deep gratitude also go to my wife Fariba for all her encouragement, support and understanding, without which I would not have dared to undertake the task of writing this book.

Contents

Preface *page* ix

1 Introduction 1

Part I **13**

2 Formation of carbon allotropes 15
- 2.1 Diamond 18
- 2.2 Graphite 19
- 2.3 Fullerenes 22
- 2.4 Carbon nanotubes and nanohorns 23

3 Nanoscale numerical simulation techniques 43
- 3.1 Essential concepts from classical statistical mechanics 44
- 3.2 Key concepts underlying the classical molecular dynamics (MD) simulation method 61
- 3.3 Key concepts underlying the classical Monte Carlo (MC) simulation method 71
- 3.4 *Ab initio* molecular dynamics simulation methods 80

4 Interatomic potentials and force-fields in the computational physics of carbon nanotubes 91
- 4.1 Interatomic potential energy function (PEF) 91
- 4.2 Force-field (molecular mechanics) method 94
- 4.3 Energetics of carbon nanotubes 95
- 4.4 Energetics of SWCNT–C_{60} and C_{60}–C_{60} interactions 106
- 4.5 Energetics of fluid flow through carbon nanotubes 109
- 4.6 Energetics of gas adsorption inside carbon nanotubes and nanohorns 119

5 Continuum elasticity theories for modelling the mechanical properties of nanotubes 135
- 5.1 Basic concepts from continuum elasticity theory 135

5.2 Nonlinear thin-shell theories 152
5.3 Theories of curved plates 159
5.4 Theories of vibration, bending and buckling of beams 166
6 Atomistic theories of mechanical properties 186
6.1 Atomic-level stress tensor 186
6.2 Elastic constants from atomistic dynamics 190
6.3 Bulk and Young's moduli 192
7 Theories for modelling thermal transport in nanotubes 195
7.1 Thermal conductivity 195
7.2 Specific heat 202
Part II **209**
8 Modelling fluid flow in nanotubes 211
8.1 Modelling the influence of a nanotube's dynamics and length on the fluid flow 212
8.2 Modelling the flow of CH_4 through SWCNTs 215
8.3 Modelling self- and collective diffusivities of fluids in SWCNTs 217
8.4 Modelling the capillary flow in an SWCNT 219
8.5 Modelling the confinement and flow of liquid water inside SWCNTs 221
8.6 Modelling the dynamics of C_{60}@nanotubes 223
9 Modelling gas adsorption in carbon nanotubes 225
9.1 Atomic and molecular hydrogen in nanotubes 225
9.2 Adsorption of rare gases in SWCNTs 251
9.3 Adsorption of gases in the assemblies of SWCNHs 264
10 Modelling the mechanical properties of carbon nanotubes 277
10.1 Modelling compression, bending, buckling, vibration, torsion and fracture of nanotubes 279
10.2 Modelling the elastic properties of SWCNTs and MWCNTs 383
10.3 Stress–strain properties of nanotubes 416
10.4 Validity of application of continuum-based theories to model the mechanical properties of nanotubes 439
11 Modelling the thermal properties of carbon nanotubes 450
11.1 Computation of thermal conductivity 451
11.2 Specific heat of nanotubes 468
References 477
Index 487

1

Introduction

Carbon is a unique and, in many ways, a fundamental element. It can form several different structures, or allotropes. Up to the end of the 1970s, diamond, graphite and graphite-based fibres were the only known forms of carbon assemblies. The discovery in 1985, and subsequent synthesis, of the class of cage-like fullerene molecules, starting with the discovery of the spherically shaped C_{60} buckyball molecule composed of 20 hexagonal and 12 pentagonal carbon rings, led to the emergence of the third form of condensed carbon. By the beginning of the 1990s, elongated forms of the fullerene molecule, consisting of several layers of graphene sheets, i.e. graphite basal planes, rolled into multi-walled cylindrical structures and closed at both ends with caps containing pentagonal carbon rings, were discovered [1]. Soon afterwards, another form of these cylindrical structures, made from only a single graphene sheet, was also discovered. These two structures have come to be known as carbon *nanotubes*, and they form the fourth allotrope of carbon.

Three experimental techniques have so far become available for the growth of carbon nanotubes. These are the arc-discharge technique [1], the laser ablation technique [2] and, recently, the chemical vapour deposition technique [3]. The use of these techniques has led to the worldwide availability of this material, and this has ushered in new, very active and truly revolutionary areas of fundamental and applied research within many diverse and already established fields of science and technology, and also within the new sciences and technologies associated with the new century. The diverse fields, wherein carbon nanotubes are intensely studied and considered to have a huge potential application in all sorts of nanoscale devices, nanostructured materials or instrumentations containing nanoscale components, include computational and experimental nanoscience, theoretical and applied nanotechnology and molecular engineering, theoretical, computational and experimental condensed matter physics and chemistry, theoretical and experimental materials science and engineering, biological physics and physical biology, medical sciences, medical technologies and instrumentations, molecular genetics,

biotechnology, environmental science and technology, information-technology devices, optics, electro-mechanical systems and electronics.

The original carbon nanotubes produced in 1991 were in fact *multi-walled* carbon nanotubes (MWCNT) having outer diameters in the range of 4–30 nm, and lengths of up to 1 μm [4]. These are seamless cylindrical objects composed of several concentric shells, with each shell made of a rolled-up two-dimensional graphene sheet, separated from each other by an inter-shell spacing of 3.4 Å. In 1993, the fundamental form of the nanotubes, i.e. the *single-walled* carbon nanotube (SWCNT), was also grown in an arc-discharge soot obtained from graphite [5, 6]. These latter nanotubes have typical diameters on the order of 1.4 nm, similar to the diameter of a C_{60} molecule, and lengths usually on microscopic orders [4]. It was also revealed that SWCNTs can aggregate to form *ropes*, or *bundles*, normally arranged in hexagonal formations that constitute the nanocrystals of carbon nanotubes. The structure of these bundles closely mimics that of porous materials, and membranes, with nanometre spaces available both inside the tubes and also in the interstitial spaces between them. These spaces are available for the *storage* of adsorbed gases, particularly atomic and molecular hydrogen, and *flow* of fluids, so that these bundles can act as low-dimensional filtering channels and molecular sieves.

A further variation of the SWCNT, known as the single-walled carbon *nanohorn* (SWCNH), has also been synthesised [7]. This is a closed-up structure that has the shape of a horn, with a cylindrical part that is supplemented by a horn tip. Being a closed structure, its internal space is not directly available as a storage medium, but heat treatment of this object in an oxygen environment can lead to the appearance of windows on the walls, and these allow for the flow of gas, and liquid, particles into the interior of the horns.

Recently, carbon nanotubes incorporating fullerenes, such as C_{60} molecules, have also been observed [8]. Such structures are popularly referred to as *peapods*, wherein all of the SWCNT space is filled with fullerenes, arranged in a regular pattern [4]. These peapods provide interesting objects to study in the physics and chemistry of nanoscale structures. For example, when they are heated to 1000–1200°C, the encapsulated molecules coalesce and generate double-walled nanotubes [4]. They can also be used as a model for constructing targetted drug delivery systems.

The importance of carbon nanotubes to the future development of nanoscience and nanotechnology has been such that they are routinely referred to as the *fabric* of nanotechnology, molecular-scale engineering and quantum technology, with widespread use in nanoelectronic, nanomechanical and nanoelectro-mechanical device technologies. Carbon nanotubes exhibit exceptional properties. For example, their electronic conductance properties depend on their geometry, which can

transform them into metallic or semiconducting nanowires, depending on the way the graphene sheet is rolled up. Furthermore, these electronic properties are very sensitive to local distortions in the geometry that can originate from mechanically induced deformations, such as deformations brought about by the van der Waals interaction during contact with a supporting substrate, or another nanotube. Several varieties of nanotube-based electronic devices have been proposed and fabricated, including a current-rectifying diode made from a semiconducting nanotube doped with local impurity, a nanotube–nanotube junction wherein the top nanotube creates a tunable tunnel barrier for transport along the bottom nanotube, and a nanotube interconnect, bridging two electrodes separated by less than 30 nm, acting as a quantum wire [9]. Recently, the electronic properties of nanotubes have been exploited in the emerging field of spin-electronics, or *spintronics*, wherein the spin degree of freedom of the electron is utilised for transfer and storage of information and communication. Nanotubes, as one-dimensional ballistic conductors, provide ideal objects for spin transport over long distances.

The investigation into the properties of carbon nanotubes, either as single isolated nanostructures, or as components in nanoscale machines, such as molecular motors, or as reinforcement fibres in new composites, has emerged as one of the most active fields of research in condensed matter physics, materials physics and chemistry, nanoscience and nanotechnology over the past decade. The basic and applied research on carbon nanotubes has been very versatile, and has followed several directions. These include the development of new methods for their synthesis and growth, their electronic conductance properties as nanointerconnects, their field emission properties for use in panel displays and as tips in probe-based microscopes, their fracture and buckling properties, due to external stresses, in free-standing condition, and when they are embedded in a polymeric matrix, their thermal conductivity and specific heat as individual nanotubes, and when they form mats, ropes and bundles, their properties as porous materials and nanopipes for conveying fluids, their properties as media for the adsorption and storage of gases, their properties as reinforcement agents in composites, and, very recently, in such fields as oncological medicine, their properties as functionalised nanoscale sensors, and markers, for the early detection and destruction of *individual* cancer cells.

A significant contribution to our understanding of the properties and structural behaviour of carbon nanotubes in all these diverse lines of research has been made by the application of computational modelling, and computer-based numerical simulations, which also form indispensable research methods in many other areas associated with both the soft (biological) and the hard (solid-state) nanoscience and nanotechnology. These two fields of scientific and technological activity are primarily concerned with the *purposeful* manipulation of the structure and

properties of condensed phases, starting at their most fundamental levels. They provide the practical means to exercise complete control, at atomic and molecular levels, over the design, structure, functioning and properties of physical and biological nanoscale systems, i.e. systems whose sizes are between 1 nm and 100 nm. This control implies that we are now able, for the first time in human history, to interrogate physical and biological matter, atom by atom and molecule by molecule, and design new types of devices, and materials, that embody specified and pre-arranged properties, by a precise positioning of their individual atoms. This ability to manipulate individual atoms has created a perspective for molecular nanotechnology, as Richard Feynman saw first in 1959, to design and manufacture programmable nanoscale machines that can carry enough information to replicate themselves, assemble similar machines and perform pre-assigned tasks, such as delivering drug parcels to specified locations in the body. Computational modelling has, therefore, created real possibilities for understanding the structure and behaviour of nanostructures, such as carbon nanotubes, that exist and operate at highly reduced length, time and energy scales that may, as yet, not be amenable to experimental manipulations.

Computational modelling of properties of nanostructures in general, and carbon nanotubes in particular, is based either on the use of methods rooted in the many-body theories of quantum mechanics, such as the density functional theory (DFT) of atoms and molecules, or on the use of methods rooted in advanced classical statistical mechanics, such as the molecular dynamics (MD) simulation method. The quantum-mechanical approach allows for an *ab initio*, or first principles, study of nanoscale systems composed of several tens to, at most, several hundreds of atoms, with current computational platforms. The classical approach, on the other hand, can be used to study the time evolution of nanostructures and nanoscale processes involving several thousand to several billion atoms. This approach employs phenomenological interatomic potential energy functions, and classical force-field functions, to model the energetics and dynamics of the nanoscale systems in order to obtain the forces experienced by their atoms. These potentials, therefore, play an all-important and very crucial role in classical simulation studies. The more physically realistic and accurate these potentials are, the more confident we are that the simulation results are close to the experimental data and reflect the actual properties of the real systems. It is, therefore, no surprise that such an intense effort has been spent to develop highly accurate interatomic potentials, and force fields, for the description of various classes of materials, and in particular the covalently bonding materials. Some of these potentials, such as the Tersoff potential and the Brenner potentials, which have been employed to model the energetics of carbon nanotubes, are quite complex *many-body* interatomic potentials. We shall see in this book that, in many of the atomistic-based simulations, the dynamics

of carbon nanotubes have been modelled on the basis of these two particular potentials, to the extent that it is now generally agreed that they represent the *state-of-the-art* potentials for the description of carbon allotropes, and hydrocarbon systems.

The investigation into the physical properties of individual carbon nanotubes, and nanoscale systems made from them, has entailed the active participation of thousands of research physicists, chemists and materials scientists, engaged in extensive research programmes, both experimental and theoretical/computational, worldwide. Their efforts have led to the publication of several thousand research papers over the last decade. Several very informative reviews, dealing with the experimental side of the subject, have appeared [10, 11, 12, 13, 14, 15]. However, the number of reviews that deal with the application of computational modelling to this field has been very scant indeed. In view of the fact that simulation of the physics of carbon nanotubes has reached a very developed and mature stage, and a so-called critical mass of research results has been obtained via this approach, we need to take stock of the present state of our knowledge in this field, and provide the necessary background for the future directions of research. This is the object of the present book.

This is a rather comprehensive, and self-contained, book that utilises the research material produced as far as the year 2005. In addition to drawing on the results obtained via computational studies, I have also included the discussions and summaries of many experimental results where I have deemed it useful that the inclusion of such results can help clarify the particular aspects of the physics of nanotubes. In order for the book to be self-contained, I have presented all the relevant theories, computational methods and physical models that I believe are essential for grasping the existing research materials and for engaging in future research. This has meant that I had to include, for completeness, those theories that may not have been directly employed so far, but which I consider to be relevant, as background material for a better understanding of the current research papers and for the future research in this field.

As we shall see, a significant portion of the field of modelling that deals with the mechanical properties of nanotubes has been based on the use of models and theories from the fascinating field of continuum solid mechanics. The aim here has been to describe the energetics of the nanotubes in terms of the energetics of such structures as curved plates, shallow shells, vibrating rods and bending beams. These topics are not generally covered in standard undergraduate, or even postgraduate, courses in physics. They are rather mathematically involved, and only the readers with a background in mechanical and structural engineering may be familiar with them. I have given a fairly easy-to-follow description of these topics, together with the required background concepts from the theories of continuum elasticity.

The atomistic-level description of the energetics of nanotubes, both isolated and when they are in contact with foreign atoms and molecules, such as fluid and gas particles, requires either the use of quantum-mechanical methods that explicitly take into account the dynamics of the electrons when deriving the interatomic forces, or the use of classical statistical mechanics-based techniques that begin with the atoms themselves and employ interaction potentials, and force fields, to derive these forces. The majority of the research studies dealing with the mechanical, thermal and transport properties of nanotubes employ the latter techniques, as the numbers of atoms involved is far too large for the application of the first principles methods. A chapter of the book is, therefore, completely devoted to the description of the pertinent interatomic potential energy functions that have been in use to model the energetics of the nanotubes themselves, the energetics of fluid flow through nanotubes, and the energetics of gas adsorption in nanotubes and nanohorns.

The description of the computational tools, either those based on the many-body quantum theory or those employing the classical statistical mechanics that are necessary for the simulation of the structure and properties of nanotubes, is available in several text books and in many review articles. I have selected a set of these tools, such as the density functional theory, the molecular dynamics (MD) simulation method and the Monte Carlo (MC) simulation method and have given enough details about their essential concepts that the reader will have gained an adequate background to consult more specialised sources if the need arises. The same applies to the introduction of the fundamental concepts from classical statistical mechanics, such as the theories of various ensembles, that are required for computing the dynamic and entropic properties of nanoscale systems in a simulation.

The organisation of this book is as follows. The book is divided into two parts, Part I (Chapters 1–7) and Part II (Chapters 8–11). In Chapter 2 we shall consider the physics of covalent bonding in carbon allotropes, and then give a thorough description of the geometry of carbon nanotubes and nanohorns, starting from an analysis of the geometrical and lattice properties of the graphene sheet, the fundamental two-dimensional graphitic surface from which all forms of carbon nanotubes are constructed.

Chapter 3 gives a broad overview of the essential ingredients of both the classical and the quantum-mechanical simulation techniques, i.e. the molecular dynamics and Monte Carlo methods on the classical side, and the *ab initio* molecular dynamics methods on the quantum-mechanical side. These techniques are now well established in the computational condensed matter physics community, and constitute the main tools for conducting computational research in most areas of physics at nanoscale. Key concepts from classical statistical mechanics are also described, as they form the foundations upon which the classical methods of

simulation rely to obtain the material properties in numerical simulations. As I have described these concepts with a view to their use in numerical simulations, it is recommended that all readers, even those familiar with the basic tenets of statistical mechanics, go over the sections of this chapter.

In Chapter 4 we consider the specific interatomic potential energy functions that model the energetics in studies involving carbon nanotubes. To my knowledge, this is the first time that these potentials have been compiled, and detailed descriptions of their properties are given. These potential energy functions cover all areas of carbon nanotube research, from mechanical properties to flow of fluids and adsorption of gases in them.

In Chapter 5, starting from the basic concepts from the continuum elasticity theory, I have provided detailed accounts of all the continuum-based theories that have been employed so far to model the mechanical behaviour, and the mechanical properties, of carbon nanotubes, such as their stability, buckling, vibration and elastic constants.

Chapter 6 gives the atomistic theories describing the distribution of the stress field in a crystal, and the elastic constants. These theories are needed in such areas of nanotube research as crack propagation and the computation of various mechanical constants.

Theories dealing with thermal transport in nanotubes are covered in Chapter 7. Here the theories relevant to the computation of thermal conductivity, and the specific heat, of nanotubes are presented.

Part II of the book is concerned with the application of the numerical simulation tools and models described in Part I to the study of the flow of fluids, the adsorption of gases and the mechanical and thermal properties of nanotubes.

In Chapter 8, the simulation of flow of atomic and molecular fluids through nanotubes is considered. Here we see that, on the basis of the present evidence, the flow properties of fluids in a nanoscale structure, such as a nanotube, are radically different from the corresponding properties in a large-scale structure. This is because the dynamic of the conveying medium, i.e. the nanotube, has a significant impact on the flow dynamic. This area of research is very useful to the new field of *nanofluidics*, wherein the aim is to design devices that can be used for molecular separation and detection. Such devices can also be used as filters, and as bypasses in biomedical applications. We will see in Chapter 8 that in order to properly describe the flow of a fluid through nanoscale channels, the motion of the nanotube walls, and the mutual interaction between the fluid and the walls, must be taken into account. Furthermore, at these levels of description, the motion of the walls shows a strong size dependence. The use of such classical concepts as viscosity and pressure remains ambiguous, as these concepts are not well-defined at these length scales.