Introduction to Graphene-Based Nanomaterials

Beginning with an introduction to carbon-based nanomaterials, their electronic properties, and general concepts in quantum transport, this detailed primer describes the most effective theoretical and computational methods and tools for simulating the electronic structure and transport properties of graphene-based systems.

Transport concepts are clearly presented through simple models, enabling comparison with analytical treatments, and multiscale quantum transport methodologies are introduced and developed in a straightforward way, demonstrating a range of methods for tackling the modeling of defects and impurities in more complex graphene-based materials. The authors also discuss the practical applications of this revolutionary nanomaterial, contemporary challenges in theory and simulation, and long-term perspectives.

Containing numerous problems for solution, real-life examples of current research, and accompanied online by further exercises, solutions, and computational codes, this is the perfect introductory resource for graduate students and researchers in nanoscience and nanotechnology, condensed matter physics, materials science, and nanoelectronics.

Luis E. F. Foa Torres is a Researcher at the Argentine National Council for Science and Technology (CONICET) and an Adjunct Professor at the National University of Córdoba, Argentina, specializing in quantum transport with emphasis on inelastic effects and driven systems.

Stephan Roche is an ICREA Research Professor at the Catalan Institute of Nanoscience and Nanotechnology (ICN2), where he is Head of the Theoretical and Computational Nanoscience Group, focusing on quantum transport phenomena in materials such as graphene.

Jean-Christophe Charlier is a Professor of Physics at the University of Louvain, Belgium, whose interests include condensed matter physics and nanosciences. His main scientific expertise focuses on first-principles computer modeling for investigating carbon-based nanomaterials.
Torres, Roche, and Charlier have written a very attractive book on graphene-based materials that takes a reader or student with no prior exposure to this topic to a level where he or she can carry out research at a high level and work in this area professionally, assuming a standard background of a condensed matter physics graduate student. The material is nicely organized into chapters which can be subdivided into daily learning segments and with problem sets that could be helpful for either formal course presentation or self study. Four appendices with more detailed presentations allow readers to develop the skills needed for using and extending present knowledge to advancing the science of few-layered materials or for developing applications based on these materials. All in all I would expect this to become a popular text for present and future researchers who will be active in the present decade, advancing science and launching technological innovation.

Mildred Dresselhaus, Massachusetts Institute of Technology

This book covers the fundamental aspects of graphene, starting from the very beginning. By reading this book, most basic subjects on graphene and some special theoretical methods can be understood at a high level. Starting with the current status of graphene science, the authors proceed to a self-contained description of the electronic structure of graphene, then an especially detailed description of the transport properties of graphene, such as back scattering, Klein tunnelling, quantum dots, Landau levels etc., based on the authors’ work. Methods introduced to investigate these subjects range from the tight binding method to ab initio calculations, so that the readers can select their preferred method, and the appendices contain useful mathematical explanations for these methods. Thus, without reading the other textbooks, the reader can understand the text. The book should be useful not only for theoretical researchers but also for graduate students and experimental researchers, who will quickly understand the theorists’ perspective. This book will be an important basic textbook on the physics of graphene.

R. Saito, Tohoku University
Introduction to Graphene-Based Nanomaterials
From Electronic Structure to Quantum Transport

Luis E. F. Foa Torres
Argentine National Council for Science and Technology (CONICET) and National University of Córdoba, Argentina

Stephan Roche
ICREA and Catalan Institute of Nanoscience and Nanotechnology

Jean-Christophe Charlier
University of Louvain, Belgium
Contents

Preface xi

1 Introduction to carbon-based nanostructures 1
  1.1 Carbon structures and hybridizations 1
  1.2 Carbon nanostructures 4
  1.3 Guide to the book 8
  1.4 Further reading 10

2 Electronic properties of carbon-based nanostructures 11
  2.1 Introduction 11
  2.2 Electronic properties of graphene 12
    2.2.1 Tight-binding description of graphene 12
    2.2.2 Effective description close to the Dirac point and massless Dirac fermions 17
    2.2.3 Electronic properties of graphene beyond the linear approximation 22
  2.3 Electronic properties of few-layer graphene 26
  2.4 Electronic properties of graphene nanoribbons 31
    2.4.1 Electronic properties of armchair nanoribbons (aGNRs) 34
    2.4.2 Electronic properties of zigzag nanoribbons (zGNRs) 38
  2.5 Electronic properties of carbon nanotubes 41
    2.5.1 Structural parameters of CNTs 41
    2.5.2 Electronic structure of CNTs within the zone-folding approximation 43
    2.5.3 Curvature effects: beyond the zone-folding model 48
    2.5.4 Small-diameter nanotubes: beyond the tight-binding approach 50
    2.5.5 Nanotubes in bundles 51
    2.5.6 Multiwall nanotubes 53
  2.6 Spin–orbit coupling in graphene 55
  2.7 Magnetic field effects in low-dimensional graphene-related materials 57
    2.7.1 Short historical perspective 57
    2.7.2 Peierls substitution 58
Contents

2.7.3 Parallel field, Aharonov–Bohm gap opening and orbital degeneracy splitting 58
2.7.4 Perpendicular field and Landau levels 62
2.7.5 Landau levels in graphene 65
2.8 Defects and disorder in graphene-based nanostructures 67
2.8.1 Structural point defects in graphene 68
2.8.2 Grain boundaries and extended defects in graphene 71
2.8.3 Structural defects at graphene edges 76
2.8.4 Defects in carbon nanotubes 82
2.9 Further reading and problems 85

3 Quantum transport: general concepts 91
3.1 Introduction 91
3.1.1 Relevant time and length scales 91
3.1.2 Coherent versus sequential transport 92
3.2 Landauer–Büttiker theory 94
3.2.1 Heuristic derivation of Landauer’s formula 97
3.3 Boltzmann semiclassical transport 98
3.3.1 The relaxation time approximation and the Boltzmann conductivity 99
3.4 Kubo formula for the electronic conductivity 101
3.4.1 Illustrations for ballistic and diffusive regimes 105
3.4.2 Kubo versus Landauer 107
3.4.3 Validity limit of Ohm’s law in the quantum regime 108
3.4.4 The Kubo formalism in real space 108
3.4.5 Scaling theory of localization 111
3.5 Quantum transport beyond the fully coherent or decoherent limits 115
3.6 Further reading and problems 116

4 Klein tunneling and ballistic transport in graphene and related materials 118
4.1 The Klein tunneling mechanism 118
4.1.1 Klein tunneling through monolayer graphene with a single (impurity) potential barrier 119
4.1.2 Klein tunneling through bilayer graphene with a single (impurity) potential barrier 124
4.2 Ballistic transport in carbon nanotubes and graphene 126
4.2.1 Ballistic motion and conductance quantization 127
4.2.2 Mode decomposition in real space 128
4.2.3 Fabry-Pérot conductance oscillations 132
4.2.4 Contact effects: SWNT-based heterojunctions and the role of contacts between metals and carbon-based devices 135
### Contents

4.3 Ballistic motion through a graphene constriction: the 2D limit and the minimum conductivity 140
4.4 Further reading and problems 141

5 Quantum transport in disordered graphene-based materials 143

5.1 Elastic mean free path 143
  5.1.1 Temperature dependence of the mean free path 146
  5.1.2 Inelastic mean free path in the high-bias regime 148
  5.1.3 Quantum interference effects and localization phenomena in disordered graphene-based materials 150
  5.1.4 Edge disorder and transport gaps in graphene nanoribbons 152
5.2 Transport properties in disordered two-dimensional graphene 154
  5.2.1 Two-dimensional disordered graphene: experimental and theoretical overview 154
  5.2.2 Metallic versus insulating state and minimum conductivity 158
  5.2.3 Boltzmann transport in two-dimensional graphene 158
  5.2.4 Kubo transport: graphene with Anderson disorder 166
  5.2.5 Kubo transport: graphene with Gaussian impurities 169
  5.2.6 Weak localization phenomena in disordered graphene 173
  5.2.7 Strong localization in disordered graphene 181
5.3 Quantum Hall effect in graphene 182
  5.3.1 Hall quantization in graphene 183
  5.3.2 The mystery of the zero-energy Landau level splitting 184
  5.3.3 Universal longitudinal conductivity at the Dirac point 185
5.4 Graphene with monovacancies 187
  5.4.1 Electronic structure of graphene with monovacancies 190
  5.4.2 Transport features of graphene with monovacancies 191
5.5 Polycrystalline graphene 195
  5.5.1 Motivation and structural models 195
  5.5.2 Electronic properties of polycrystalline graphene 199
  5.5.3 Mean free path, conductivity and charge mobility 201
5.6 Amorphous graphene 202
  5.6.1 Structural models 202
  5.6.2 Electronic properties of amorphous graphene 203
  5.6.3 Mean free path, conductivity and localization 204
5.7 Phonon transport in graphene-related materials 206
  5.7.1 Computational phonon propagation methodology 206
  5.7.2 Disordered carbon nanotubes with isotope impurities 208
  5.7.3 Disordered graphene nanoribbons with edge disorder 209
5.8 Graphene quantum dots 211
  5.8.1 Generalities on Coulomb blockade 212
  5.8.2 Confining charges in graphene devices 214
5.9 Further reading and problems 217
6 Quantum transport beyond DC

6.1 Introduction: why AC fields? 219
6.2 Adiabatic approximation 220
6.3 Floquet theory 221
   6.3.1 Average current and density of states 222
   6.3.2 Homogeneous driving and the Tien–Gordon model 224
   6.3.3 Time-evolution operator 224
6.4 Overview of AC transport in carbon-based devices 225
6.5 AC transport and laser-induced effects on the electronic properties of graphene 227
6.6 Further reading and problems 230

7 Ab initio and multiscale quantum transport in graphene-based materials

7.1 Introduction 232
7.2 Chemically doped nanotubes 233
   7.2.1 Tight-binding Hamiltonian of the pristine carbon nanotube 233
   7.2.2 Boron-doped metallic carbon nanotubes 233
   7.2.3 Nitrogen-doped metallic carbon nanotubes 236
7.3 Two-dimensional disordered graphene with adatoms defects 242
   7.3.1 Monatomic oxygen defects 242
   7.3.2 Atomic hydrogen defects 246
   7.3.3 Scattering times 248
7.4 Structural point defects embedded in graphene 249
7.5 Ab initio quantum transport in 1D carbon nanostructures 251
   7.5.1 Introduction 251
   7.5.2 Carbon nanotubes 253
   7.5.3 Defective carbon nanotubes 255
   7.5.4 Doped carbon nanotubes 259
   7.5.5 Functionalized carbon nanotubes 261
   7.5.6 Carbon nanotubes decorated with metal clusters 269
   7.5.7 Graphene nanoribbons 278
   7.5.8 Graphene nanoribbons with point defects 280
   7.5.9 Graphene nanoribbons with edge reconstruction 281
   7.5.10 Graphene nanoribbons with edge disorder 282
   7.5.11 Doped graphene nanoribbons 288
   7.5.12 GNR-based networks 293
7.6 Conclusion 298

8 Applications

8.1 Introduction 300
8.2 Flexible electronics 301
8.3 High-frequency electronics 302
### Contents

8.4 Optoelectronics–photonics–plasmonics 304  
8.4.1 Opacity of graphene and fine structure constant 304  
8.4.2 Harnessing graphene with light: a new dimension of possibilities 305  
8.5 Digital logic gates 306  
8.6 Digital nonvolatile graphene memories 307  
8.7 Graphene nanoresonators 308  
8.8 Spintronics 309  
8.9 Further reading 313  

**Appendix A**  
Electronic structure calculations: the density functional theory (DFT) 314  

A.1 Introduction 314  
A.2 Overview of the approximations 314  
A.2.1 The Schrödinger equation 314  
A.2.2 The Born–Oppenheimer approximation 315  
A.2.3 The Hartree approximation 316  
A.2.4 The Hartree–Fock approximation 317  
A.3 Density functional theory 318  
A.3.1 The Thomas–Fermi model 318  
A.3.2 The Hohenberg–Kohn theorem 319  
A.3.3 The Kohn–Sham equations 320  
A.3.4 The exchange–correlation functionals 322  
A.4 Practical calculations 324  
A.4.1 Crystal lattice and reciprocal space 324  
A.4.2 The plane wave representation 325  
A.4.3 k-point grids and band structures 326  
A.4.4 The pseudopotential approximation 326  
A.4.5 Available DFT codes 330  

**Appendix B**  
Electronic structure calculations: the many-body perturbation theory (MBPT) 332  

B.1 Introduction 332  
B.2 Many-body perturbation theory (MBPT) 333  
B.2.1 Hedin’s equations 333  
B.2.2 $GW$ approximation 334  
B.3 Practical implementation of $G_0W_0$ 335  
B.3.1 Perturbative approach 335  
B.3.2 Plasmon pole 336  

**Appendix C**  
Green’s functions and *ab initio* quantum transport in the Landauer–Büttiker formalism 338  

C.1 Phase-coherent quantum transport and the Green’s function formalism 338  
C.2 Self-energy corrections and recursive Green’s functions techniques 344
## Contents

C.3 Dyson’s equation and an application to treatment of disordered systems 347  
C.4 Computing transport properties within *ab initio* simulations 351

### Appendix D  Recursion methods for computing the DOS and wavepacket dynamics 358

D.1 Lanczos method for the density of states 358

D.1.1 Termination of the continued fraction 361

D.2 Wavepacket propagation method 363

D.3 Lanczos method for computing off-diagonal Green’s functions 367

---

*References* 370  
*Index* 405
Once deemed impossible to exist in nature, graphene, the first truly two-dimensional nanomaterial ever discovered, has rocketed to stardom since being first isolated in 2004 by Nobel Laureates Konstantin Novoselov and Andre K. Geim of the University of Manchester. Graphene is a single layer of carbon atoms arranged in a flat honeycomb lattice. Researchers in high energy physics, condensed matter physics, chemistry, biology, and engineering, together with funding agencies, and companies from diverse industrial sectors, have all been captivated by graphene and related carbon-based materials such as carbon nanotubes and graphene nanoribbons, owing to their fascinating physical properties, potential applications and market perspectives.

But what makes graphene so interesting? Basically, graphene has redefined the limits of what a material can do: it boasts record thermal conductivity and the highest current density at room temperature ever measured (a million times that of copper!); it is the strongest material known (a hundred times stronger than steel!) yet is highly mechanically flexible; it is the least permeable material known (not even helium atoms can pass through it!); the best transparent conductive film; the thinnest material known; and the list goes on ...

A sheet of graphene can be quickly obtained by exfoliating graphite (the material that the tip of your pencil is made of) using sticky tape. Graphene can readily be observed and characterized using standard laboratory methods, and can be mass-produced either by chemical vapor deposition (CVD) or by epitaxy on silicon carbide substrates. Driven by these intriguing properties, graphene research is blossoming at an unprecedented pace and marks the point of convergence of many fields. However, given this rapid development, there is a scarcity of tutorial material to explain the basics of graphene while describing the state-of-the-art in the field. Such materials are needed to consolidate the graphene research community and foster further progress.

The dearth of up-to-date textbooks on the electronic and transport properties of graphene is especially dramatic: the last major work of reference in this area, written by Riichiro Saito, Gene Dresselhaus, and Mildred Dresselhaus, was published in 1998. Seeking to answer the prayers of many colleagues, who have had to struggle in a nascent field characterized by a huge body of research papers but very little introductory material, we decided to write this book. It is the fruit of our collective research experience, dating from the early days of research on graphene and related materials, up through the past decade, when each of us developed different computational tools and
theoretical approaches to understand the complex electronic and transport properties in realistic models of these materials.

We have written *Introduction to Graphene-Based Nanomaterials: From Electronic Structure to Quantum Transport* for everyone doing (or wishing to do) research on the electronic structure and transport properties of graphene-related systems. Assuming basic knowledge of solid state physics, this book offers a detailed introduction to some of the most useful methods for simulating these properties. Furthermore, we have made additional resources (computational codes, a forum, etc.) available to our readers at cambridge.org/foatorres, and at the book website (introductiontographene.org), where additional exercises as well as corrections to the book text (which will surely appear) will be posted.

Graphene and related materials pertain to a larger family that encompasses all kinds of two-dimensional materials, from boron nitride lattices, to transition-metal dichalogenides (MoS$_2$, WS$_2$), to the silicon analogue of graphene, silicene, a recently discovered zero-gap semiconductor. Researchers are beginning to explore the third dimension by shuffling two-dimensional materials and by fabricating three-dimensional heterostructures (BN/graphene, BN/MoS$_2$/graphene, etc.) with unprecedented properties.

Interestingly, low-energy excitations in two-dimensional graphene (and in one-dimensional metallic carbon nanotubes), known as massless Dirac fermions, also develop at the surface of topological insulators (such as BiSe$_2$, Bi$_2$Te$_3$, etc.), which are bulk insulators. Topological insulators thus share commonalities with graphene, such as Berry’s phase-driven quantum phenomena (Klein tunneling, weak antilocalization, ...), and exhibit other features such as spin-momentum locking that offer different and ground-breaking perspectives for spintronics. Therefore, we believe that our presentation of the fundamentals of electronic and transport properties in graphene and related materials should prove useful to a growing community of scientists, as they touch on advanced concepts in condensed matter physics, materials science, and nanoscience and nanotechnology.

The book starts with an introduction to the electronic structures and basic concepts in transport in low-dimensional materials, and then proceeds to describe the specific transport phenomena unique to graphene-related materials. Transport concepts are then presented through simple disorder models, which in some cases enable comparison with analytical treatments. Additionally, the development of multiscale quantum transport methodologies (either within the Landauer–Büttiker or Kubo–Greenwood formalisms) is introduced in a straightforward way, showing the various options for tackling defects and impurities in graphene materials with more structural and chemical complexity: from combined *ab initio* with tight-binding models, to transport calculations fully based on first principles. To facilitate reading, the essential technical aspects concerning the formalism of Green functions, as well as transport implementation and order-N transport schemes are described in dedicated appendices.

This book encompasses years of scientific research that has enabled us to establish certain foundations in the field, a work made possible by the efforts of collaborators, including many postdoctoral and doctoral students. We are particularly indebted to Hakim Amara, Rémi Avriller, Blanca Biel, Andrés Botello-Méndez, Victoria Bracamonte, Hernán Calvo,
We would also like to express our sincere gratitude to the following inspiring individuals with whom we have worked over the past decade: Pulickel Ajayan, Tsuneya Ando, Marcelo Apel, Adrian Bachtold, Carlos Balseiro, Florian Banhart, Robert Baptist, Christophe Bichara, Xavier Blase, Roberto Car, Antonio Castro-Neto, Mairbek Chshiev, Gianaurelio Cuniberti, Silvano De Franceschi, Hongjie Dai, Alessandro De Vita, Millie and Gene Dresselhaus, Francois Ducastelle, Reinhold Egger, Peter Eklund, Morinobu Endo, Walter Escoffier, Chris Ewels, Andrea Ferrari, Albert Fert, Takeo Fujiwara, Xavier Gonze, Andrea Latgé, Caio Lewenkopf, Annick Loiseau, Jose-Maria Gomez Rodriguez, Nicole Grobert, Paco Guinea, Luc Henrard, Eduardo Hernandez, Jean-Paul Issi, Ado Jorio, Philip Kim, Jani Kotakoski, Vladimir Kravtsov, Philippe Lambin, Sergio Makler, Ernesto Medina, Vincent Meunier, Natalio Mingo, Costas Mouloupolos, Joel Moser, Yann-Michel Niquet, Kentaro Nomura, Kostya Novoselov, Pablo Ordejon, Pedro Orellana, Monica Pacheco, Horacio Pastawski, Marcos Pimenta, Bertrand Raquet, Gian-Marco Rignanese, Angel Rubio, Riichiro Saito, Bobby Sumpter, Mauricio and Humberto Terrones, Gonzalo Usaj, and Sergio Valenzuela.

We thank our home institutions for supporting our research, as well as the Alexander von Humboldt Foundation (SR and LEFFT) and the Abdus Salam International Centre for Theoretical Physics (LEFFT). Finally, we are indebted to our respective wives (Sandra Rieger, Encarni Carrasco Perea and Mireille Toth-Budai) and our children (Hector and Gabriel Roche, and Ilona, Elise, and Mathilde Charlier) for their warm enthusiasm and continuous support during all these years of time-consuming work.

We hope that you find this book to be a useful companion for starting in this field and perhaps even for your day-to-day research. We recommend that you start by reading Chapter 1 and then follow the advice in the Guide to the book (Section 1.3). And we wish you an exciting journey in Flatland!...