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A NEW PARADIGM IN CONDENSED MATTER AND DEVICE PHYSICS

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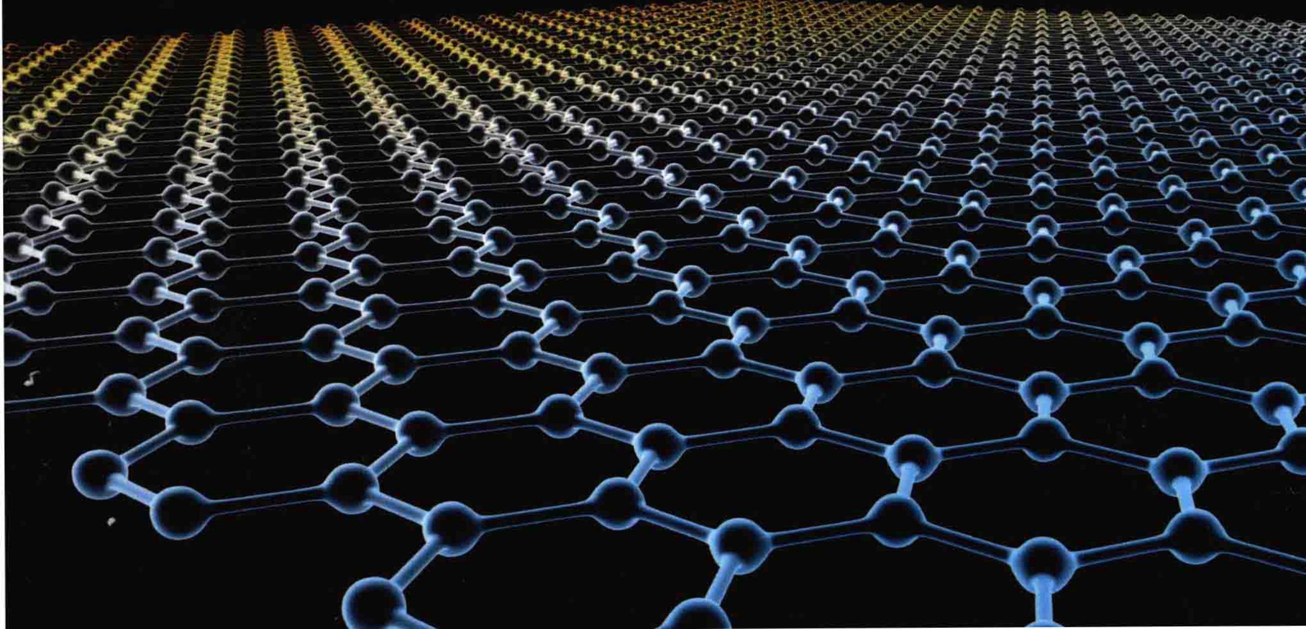

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A New Paradigm in Condensed Matter and Device Physics

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Graphene

Dedicated To
P. R. Wallace
G. W. Semenoff
A. K. Geim
K. S. Novoselov

Preface

Graphene, discovered in 2004 as a new phase of crystalline matter one atom thick, exhibits electronic conduction distinct from and superior to conventional metals and semiconductors and thus opens new opportunities for device design and fabrication. The single plane of graphite is now known to represent a new class of two-dimensional materials, one to several atoms in thickness that are conventionally crystalline in lateral dimensions micrometers to centimeters. The electrons in graphene move rapidly in a way that resembles massless photons and nearly massless neutrinos. They indeed exhibit Klein tunneling, a quantum phenomenon of unit probability specular tunneling through a high potential barrier that was originally conceived as a property of electrons and positrons in vacuum. These remarkable properties, endowed by the hexagonal "honeycomb" carbon-atom array onto ordinary electrons, fortunately are well explained by the methods of condensed matter physics, but that "explaining" has several initially puzzling aspects that we address.

This book is intended as such an explication: to introduce and simply explain what is so remarkably different about graphene. It describes the unusual physics of the material, that it offers linear rather than parabolic energy bands. The Dirac-like electron energy bands lead to high constant carrier speed, similar to light photons. The lattice symmetry further implies a two-component wave-function, which has a practical effect of cancelling direct backscattering of carriers. The resulting high carrier mobility allows observation of the quantum Hall effect at room temperature, unique to graphene. The material is two-dimensional, and in sizes micrometers to nearly meters displays great tensile strength but vanishing resistance to bending. We are intent as well to summarize the progress toward better samples and the prospects for important applications, mostly in electronic devices. The book is aimed at researchers and advanced undergraduate and beginning graduate students as well as interested professionals. This book is intended not as a text but a comprehensive summary and resource on a scientific and technological area of rapid advance and promise. The hope is to span the range between the painstaking small-science extraction from graphite of high quality graphene layers (that are, of course, part of every pencil lead) and high flying physics topics, including an anomalous integer quantum Hall effect at room temperature, bipolar transmission of Cooper pairs in a superconducting proximity effect, light-like charged particles only explainable by the Dirac equation, evidence for a unit-probability tunneling behavior (Klein tunneling) heretofore predicted, but never before observed. This book is also intended to suggest possibilities for new families of electron devices in a post-Moore's Law version of nanoelectronics. Benzene rings, whose "radii" are about 0.190 nm, are excellent conductors (it is estimated that a screening current of $\sim$3.9 nanoamperes/Tesla is estimated to flow around a benzene ring at room temperature) and might be viewed as basic units in graphene electronics.

Silicon and metal crystals lose their conductivity in small scale structures but the basic unit of graphene, essentially a benzene ring, still conducts well. A form of "chemistry" appears in the arrangement of broken bonds at the edges of graphene ribbons (e.g., terminations in zig-zag vs. armchair edges). A premium now is placed on experimental methods for epitaxial growths, from which a new "semiconductor technology" might arise. Device technologies that will necessarily depend on fabrication and patterning schemes for graphene layers are in a rapid state of development.

This book is dedicated to four physicists, two of them theorists and two experimentalists. P. R. Wallace first understood the unusual linear bandstructure in graphene (conceived as an approximation to graphite). G. W. Semenoff first understood the unusual two-sublattice origin of the chiral carriers, avoiding conventional backscattering and improving the mobility. A. K. Geim and K. S. Novoselov, two brilliant, resourceful and persistent experimentalists, showed how to isolate the individual planes and convincingly demonstrated their unique properties, indeed as representative of a new class of two-dimensional crystals.

The author is grateful to Sönke Adlung and Jessica White at Oxford University Press for invaluable help in conceiving and completing this project. It is a pleasure to acknowledge assistance from the Department of Applied Physics at NYU Poly, particularly from Prof Lorcan Folan and Ms. DeShane Lyew. Ankita Shah, Harsh Bhosale, Vijit Jain, Kiran Koduru and Manasa Medikonda, who have assisted with aspects of preparing the manuscript and clearing the way to publication. My wife Carol has helped in many ways and has been a constant source of support and encouragement.

E. L. Wolf, Brooklyn, New York, September, 2013

Contents

1 Introduction

"Graphene" is the name given to a single-layer hexagonal lattice of carbon atoms, an extended two-dimensional lattice of benzene rings, devoid of hydrogen atoms. This one-atom-thick material has recently been found to be robust, if not completely planar, in samples tens of micrometers up to 30 inches in extent, on a supporting substrate. Graphene is a contender in the new information technology (and other) applications, beyond being a scientific breakthrough and curiosity. As we will see, electrons in graphene display properties similar to photons and neutrinos, never before observed in a condensed-matter environment. The new electron properties arise in a straightforward way from the symmetry of the atomic positions and the resulting cone-shaped, rather than parabolic, regions in the electron energy surfaces. It is reassuring to see that all the new effects are well described by the Schrödinger-equation-based methods of condensed matter physics that have served well in understanding solids from semiconductors to superconductors. Dirac-equation-like electron behavior in graphene is obtained directly from appropriate simplification of the Schrödinger theory of atoms, molecules and solids. Beyond this, graphene is the first example of a new class of two-dimensional crystals, a new phase of matter. This is a surprise in many ways that offers new opportunities, especially, in electronics.

The discovery of graphene extends, beyond some theoretical predictions, what useful forms matter can take. It is truly a new paradigm.

1.1 "Crystals" one atom thick: a new paradigm

A crystal is an ordered array of identical repeating units. We can think of the unit, in graphene, as the hexagonal benzene ring, whose diameter (between opposite carbon atoms, say those numbered 1 and 4) is $2a = 284$ pm,[1] where a is the carbon-carbon spacing (the 1–2 distance) $a = 142$ pm. Benzene, C_6H_6, has one electron per atom binding a hydrogen atom at each ring location 1, 2, . . . to 6. In graphene, H is absent and that one electron per atom is delocalized over the whole crystal. The resulting perfectly ordered honeycomb lattice, for a 10 μm sheet, is thus 35 211 benzene ring diameters (at 284 pm/ring) in linear size, certainly showing long-range order.

[1]One picometer (pm) $= 10^{-12}$ m. Common units on the atomic scale include Ångströms (10^{-10} m) and nanometers 1nm $= 10^{-9}$ m. The Bohr radius of the hydrogen atom, also taken as the base unit of length on the atomic scale, is $a_0 = 0.0529$ nm.

(Actually the lattice repeat distance, the "cell constant," is the 1–3 distance in the ring, namely 246 pm.) And for the 30-inch sample the number of benzene ring diameters is 2.68 billion! (The corresponding two-dimensional honeycomb crystalline array will then certainly have defects, grain boundaries and dislocations, as are well known in conventional crystals.)

The honeycomb array in graphene is dictated by the facile three-fold planar bonding, via Schrödinger's equation, of the quantum states of the carbon atom called 2s and 2p (discussed in Chapter 3). (One possibly might ask how honeybees chose the honeycomb lattice, composed of hexagons? Perhaps in the evolution of honeybees, the 3-fold lattice (that would put centers in all the hexagons) did not leave enough room for honey, and the cubic 4-fold lattice might collapse flat, like a cardboard box without the ends, squeezing the honey out.)[2]

In fact, the most economical description of the honeycomb lattice is that generated by fundamental translations of the *basis atoms* 1 and 2 (called A and B by physicists). This two-atom unit, when translated by ± multiples of the translation vectors : **1→3**, **1→5** gives the honeycomb lattice.[3]

The angle between these vectors is 60°, and we see that atoms 1, 3, 5 and 2, 4, 6 form triangles (they lie on the A and B sublattices, respectively), and that the two sublattices are separated by the interatomic vector **1→2**. So the honeycomb lattice is fundamentally two interpenetrating triangular lattices, known as A and B. Thus *nearest-neighbor* atoms lie on *opposite* sublattices, with profound consequences in the unusual electronic bandstructure, as first recognized by the American physicist Wallace in 1947.

But the achieved 30-inch, one-atom-thick graphene sample certainly will be so floppy that it will have to be supported on some surface. This is the real question as to whether it is a crystal. If we imagine the honeycomb sheet as unsupported, we realize it is very susceptible to being bent out of its flat planar condition. The chemical bonds ("pi-bonds" = "π-bonds" between two $2p_z$ electrons) will tend to return it to a flat planar condition, but this restoration force is weak. The large graphene sheet is very strong in tension, but weak against flexing motion. It is like a bedsheet, in being flexible but inextensible, but, unlike a bedsheet, it retains a weak restoring force toward a perfectly planar condition. We may italicize the word "crystal," because inherent in two dimensions (2D) (embedded in three dimensional space) are long-wavelength flexural phonons that allow large root-mean-square (rms) fluctuational displacements, much larger than a lattice constant. How floppy the sheet will be depends on its size, as we will see shortly. It may be a matter of semantics whether a slightly bent crystal is still crystalline. From a familiar example: on a diving board, the deflections imposed by the diver's weight exceed the cell dimension, but obviously do not suggest

[2]Why the honeybee evolution avoided 5-fold rings or tilings, all having unequal angles that do not permit an infinite crystal (but of course a honeycomb is finite), may have to do with eyes and brains better able to generate 120° angles, than the several angles in any 5-fold tiling.)

[3]A slightly different definition of the basis vectors as **1→3**, **5→1** is given in Fig. 1.2b. In that choice, the angle between the basis vectors is 120°. Figure 4.1 shows the same choice of basis vectors as our present text.

collapse of the material supporting the diver. By formal definition, long-range order does not occur, but in practice the local distortions can be small, so that it is still useful to consider the sample as a crystal, if slightly distorted. For graphene in practice, the out-of-plane deflections are the main concern as to whether the system is crystalline.

But there is more, fortunately not of much practical importance, to the story of crystallinity in two dimensions. In addition, there are more subtle points, really only of academic interest that lead theorists to say that any 2D array, *even if arbitrarily kept absolutely planar*, cannot have long-range (infinite) order except at $T = 0$. (The planarity would have to be imposed without transverse pinning; the closest system of this type may be electron crystals on the surface of liquid helium.) We will discuss these points in Chapter 2, including a proof that an infinitely large 2D array would exhibit, at any finite temperature, large absolute in-plane motions (but without sensibly affecting local inter-atom distances). This might have a real effect, for example, in smearing the electron- or x-ray- diffraction spots on a sufficiently large sample, unless that sample was in effect pinned to be stationary at the measurement site. But since the phonon wavelengths (now in 2D) involved are large, local regions move *intact* so that local order is not disrupted. For example, the cohesive energy of the system is not reduced and this has nothing to do with the melting point of the system (that we connect with local order). In the words of Das Sarma (2011) "There is nothing mysterious or remarkable about having finite 2D crystals with quasi-long-range positional order at finite temperatures, which is what we have in 2D graphene flakes." We return to this subject in Chapter 2, but simply comment here that the academic points in the literature do not in any way detract from the important potential uses of graphene in electronics and nano-electromechanical systems, as examples.

While there had been earlier suggestions that the single planes of graphite might be extracted for individual study (contrary to a theoretical literature that suggested that crystals in two dimensions should not be stable), Novoselov *et al.* (2004, 2005) were the first to demonstrate that such samples were viable, and indeed represented a new class of 2D materials with useful properties and potential applications. (Hints toward isolating single layers had earlier been given by Boehm *et al.* (1962), Van Bommel *et al.* (1975), Forbeaux *et al.* (1998) and Oshima *et al.* (2000), among others. And, as we will see in Section 5.1.2, chemists, since 1859, with notable work in 1898, have developed bulk processes to "exfoliate" graphite, as extracted from the ground, into "expanded," typically oxidized, forms exposing, to a greater or lesser degree, the individual planes now called graphene.)

On small size scales, perhaps 10 nm to 10 μm, the graphene array of carbon atoms is "crystalline," and has sufficient local order to provide electronic behavior as predicted by calculations based on an infinite 2D array. Micrometer-size samples of graphene show some of the best electron mobility values ever measured. In microscopy, on scales 10 nm to 1 μm, it sometimes may appear that the atoms are not entirely planar, but undulate slightly out of the plane. While it has been suggested that such "waves" are intrinsic (Morozov *et al.*, 2006), it is quite likely, on the contrary that they actually originate as the classical response of the thin membrane to inevitable stress from its mounting, or as a result of adsorbed molecules, since in graphene every carbon atom is exposed. Monolayer graphene is strong and continuous, but, because of its small thickness,[4] $t \sim 0.34$ nm, all but the shortest samples are extremely "soft" in the sense of easily bending with a small transverse force. This can be understood from the classical "spring constant K"[5] for deflection x of a cantilever of width w, thickness t and length L (with Young's modulus Y) under a transverse force F: $F = -Kx$. Since $K \sim Ywt^3/L^3$ (discussed in Section 7.4), with t near a single atom size, one sees that graphene, in spite of a large value of Young's modulus, $Y \sim 1$ TPa, is the softest possible material against transverse deflection.

As we will see in Chapter 7, graphene rectangles, length L, width w and thickness t, quantitatively bend and vibrate as predicted by classical engineering formulas. For example, the spring constant K defined for deflection and applied force at the center of a rectangle clamped on two sides depends strongly on the dimensions as $K = 32Yw\, t^3/L^3$. A square of graphene, of size $L = w = 10$ nm, from the above formula, gives $K = 12.6$ N/m, while a square of size 10 μm has $K = 12.6 \times 10^{-6}$ N/m. If the sample is short, approaching atomic dimensions, the spring constant is large and the object appears to be rigid. For example, the spring constant of a graphene square ten benzene molecules on a side against bending can be estimated as ~156 N/m, using the formula, while the spring constant of a carbon monoxide (CO) molecule (in extension), deduced from its measured vibration at 64.3 THz, is known to be 1860 N/m. A further quantity in the graphene literature is Yt, a 2D rigidity that has a value of about 330 N/m. But for graphene longer than a few micrometers, with the spring constant K of a square falling off as $1/L^2$, the material is exceedingly soft.

Accordingly, graphene, on micrometer-size scales, conforms to any surface under the influence of attractive van der Waals forces. In an electron micrograph, graphene on a substrate appears adherent, more like a wet dishrag or "membrane" than a playing card, quite unlike a 10-inch diameter wafer of silicon. These 2D "crystals" cannot, at present, be grown from a melt, as is silicon and as were graphite and diamond in the depths of the earth at high temperature. Graphene crystals can only be obtained (see Chapter 5) by extraction from an existing crystal of graphite, or by being grown epitaxially on a suitable surface such as SiC or catalytically on Cu or Ni from a carbon-bearing gas such as methane.

[4]The space per layer in graphite is 0.34 nm that is widely quoted as the nominal thickness of the graphene layer. An equivalent elastic thickness of graphene, closer to the actual atomic thickness, is about 0.1 nm, see Section 2.7.

[5]The spring constant K is a macroscopic dimension-related engineering quantity quoted in SI units as N/m. It is related to the "bending rigidity" or "rigidity" $\kappa = Yt^3$, a microscopic property usually quoted in eV that is about 1 eV for graphene. (The Young's modulus Y, an engineering quantity, is defined as pressure/(relative strain) = $P/(\delta x/x)$ and is about 10^{12} N/m^2 = 1 TPa for graphene, but see Section 2.7.1) The rigidity κ has units of energy, as force times distance. One sees that the rigidity κ of graphene, by virtue of the minimal atomic value of thickness t, is the lowest of any possible material. In connection with extension of a chemical bond, the spring constant K relates to the bond energy E as $K = \mathrm{d}^2E/\mathrm{d}x^2$.