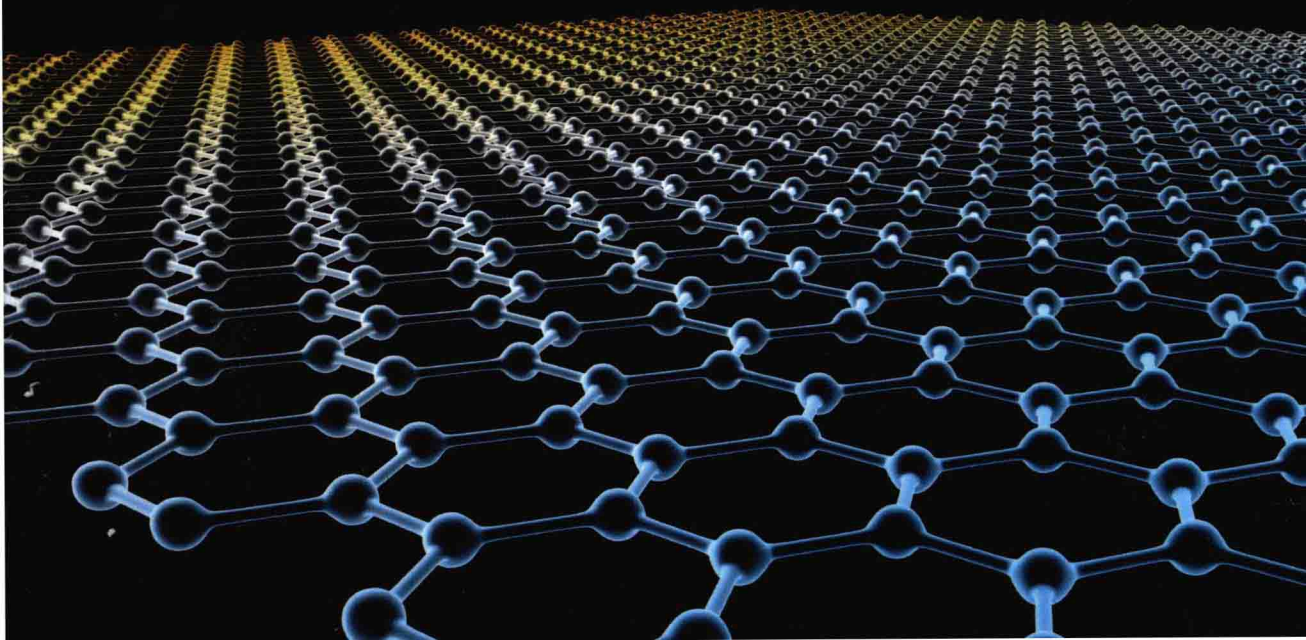


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A NEW PARADIGM IN CONDENSED MATTER
AND DEVICE PHYSICS

E. L. WOLF

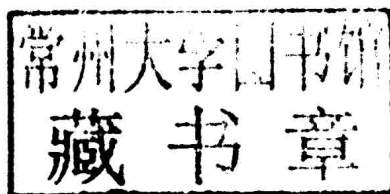


Graphene

*A New Paradigm in Condensed Matter
and Device Physics*

E. L. Wolf

Professor of Physics, Polytechnic Institute of New York University



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Great Clarendon Street, Oxford, OX2 6DP,
United Kingdom

Oxford University Press is a department of the University of Oxford.
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First Edition published in 2014

Impression: 1

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Published in the United States of America by Oxford University Press
198 Madison Avenue, New York, NY 10016, United States of America

British Library Cataloguing in Publication Data

Data available

Library of Congress Control Number: 2013940539

ISBN 978-0-19-964586-2

Printed and bound by
CPI Group (UK) Ltd, Croydon, CR0 4YY

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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 ~ 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	1
1.1	“Crystals” one atom thick: a new paradigm	1
1.2	Roles of symmetry and topology	7
1.2.1	Linear bands, “massless Dirac” particles	7
1.2.2	“Pseudo-spins” from dual sublattices and helicity	11
1.3	Analogies to relativistic physics backed by experiment	14
1.4	Possibility of carbon ring electronics	17
1.5	Nobel Prize in Physics in 2010 to Andre K. Geim and Konstantin S. Novoselov	17
1.6	Perspective, scope and organization	18
2	Physics in two dimensions (2D)	20
2.1	Introduction	20
2.2	2D electrons on liquid helium and in semiconductors	21
2.3	The quantum Hall effect, unique to 2D	24
2.3.1	Hall effect at low magnetic field	25
2.3.2	High field effects	27
2.3.3	von Klitzing’s discovery of the quantized Hall effect	28
2.4	Formal theorems on 2D long-range order	32
2.4.1	Absolute vs. relative thermal motions in 2D	32
2.4.2	The Hohenberg–Landau–Mermin–Peierls–Wagner Theorem	38
2.4.3	2D vs. 2D embedded in 3D	39
2.4.4	Soft membrane, crumpling instability	40
2.5	Predictions against growth of 2D crystals	44
2.6	“Artificial” methods for creating 2D crystals	45
2.7	Elastic behavior of thin plates and ribbons	45
2.7.1	Strain Nomenclature and Energies	47
2.7.2	Curvature and Gaussian curvature	49
2.7.3	Isometric distortions of a soft inextensible membrane	50
2.7.4	Vibrations and waves on elastic sheets and ribbons of graphene	51
2.7.5	An excursion into one dimension	55
3	Carbon in atomic, molecular and crystalline (3D and 2D) forms	57
3.1	Atomic carbon C: $(1s)^2(2s)^2(2p)^2$	57
3.1.1	Wavefunctions for principal quantum numbers $n = 1$ and $n = 2$	58
3.1.2	Linear combinations of $n = 2$ wavefunctions	60

3.1.3	Two-electron states as relevant to covalent bonding	61
3.1.4	Pauli principle and filled states of the carbon atom	61
3.2	Molecular carbon: CH ₄ , C ₆ H ₆ , C ₆₀	63
3.2.1	Covalent bonding in simple molecules	63
3.2.2	Methane CH ₄ : tetrahedral bonding	67
3.2.3	Benzene C ₆ H ₆ : sp ² and π bonding	68
3.2.4	Fullerene C ₆₀	81
3.2.5	Graphane and Fluorographene	82
3.3	Crystals: diamond and graphite	83
3.3.1	Mined graphite	83
3.3.2	Synthetic “Kish” graphite	83
3.3.3	Synthetic HOPG: Highly Oriented Pyrolytic Graphite	84
4	Electron bands of graphene	86
4.1	Semimetal vs. conductor of relativistic electrons	86
4.2	Linear bands of Wallace and the anomalous neutral point	90
4.2.1	Pseudo-spin wavefunction	90
4.3	L. Pauling: graphene lattice with “1/3 double-bond character”	92
4.4	McClure: diamagnetism and zero-energy Landau level	92
4.5	Fermi level manipulation by chemical doping	93
4.6	Bilayer graphene	93
5	Sources and forms of graphene	98
5.1	Graphene single-crystals, flakes and cloths	98
5.1.1	Micro-mechanically cleaved graphite	98
5.1.2	Chemically and liquid-exfoliated graphite flakes	101
5.2	Epitaxially and catalytically grown crystal layers	108
5.2.1	Epitaxial growth on SiC: Si face vs. C face	109
5.2.2	Catalytic growth on Ni or Cu, with transfer	112
5.2.3	Large area roll-to-roll production of graphene	114
5.2.4	Grain structure of CVD graphene films	115
5.2.5	Hybrid boron-carbon-nitrogen BCN films	118
5.2.6	Atomic layer deposition	120
5.3	Graphene nanoribbons	121
5.3.1	Zigzag and armchair terminations	122
5.3.2	Energy gap at small ribbon width, transistor dynamic range	123
5.3.3	Chemical synthesis of perfect armchair nanoribbons	125
6	Experimental probes of graphene	128
6.1	Transport, angle-resolved photoemission spectroscopy	128
6.2	Optical, Raman effect, thermal conductivity	129
6.3	Scanning tunneling spectroscopy and potentiometry	132
6.4	Capacitance spectroscopy	133
6.5	Inverse compressibility with scanning single electron transistor (SSET)	136

7 Mechanical and physical properties of graphene	139
7.1 Experimental aspects of 2D graphene crystals	139
7.1.1 Classical (extrinsic) origin of ripples and wrinkles in monolayer graphene	141
7.1.2 Stability of graphene in supported samples up to 30 inches	146
7.1.3 Phonon dispersion in graphene	150
7.1.4 Experimental evidence of nanoscale roughness	158
7.1.5 Electrical conductivity of graphene in experiment	164
7.2 Theoretical approaches to “intrinsic corrugations”	169
7.3 Impermeable even to helium	176
7.4 Nanoelectromechanical resonators	178
7.5 Metal-insulator Mott–Anderson transition in ultrapure screened graphene	179
7.6 Absence of “intrinsic ripples” and “minimum conductivity” in graphene	183
8 Anomalous properties of graphene	185
8.1 Sublimation of graphite and “melting” of graphene	185
8.2 Electron and hole puddles, electrostatic doping and the “minimum conductivity”	191
8.3 Giant non-locality in transport	193
8.4 Anomalous integer and fractional quantum Hall effects	197
8.5 Absence of backscattering, carrier mobility	199
8.6 Proposed nematic phase transition in bilayer graphene	202
8.7 Klein tunneling, Dirac equation	204
8.8 Superconducting proximity effect, graphene Josephson junction	213
8.9 Quasi-Rydberg impurity states; Zitterbewegung	219
9 Applications of graphene	223
9.1 Transistor-like devices	224
9.1.1 High-frequency FET transistors	225
9.1.2 Vertically configured graphene tunneling FET devices	231
9.1.3 The graphene Barristor, a solid state triode device	237
9.2 Phototransistors, optical detectors and modulators	237
9.3 Wide area conductors, interconnects, solar cells, Li-ion batteries and hydrogen storage	244
9.3.1 Interconnects	248
9.3.2 Hydrogen storage, supercapacitors	249
9.4 Spintronic applications of graphene	251
9.5 Sensors of single molecules, “electronic nose”	254
9.6 Metrology, resistance standard	255
9.7 Memory elements	255
9.8 Prospects for graphene in new digital electronics beyond CMOS	257
9.8.1 Optimizing silicon FET switches	257

9.8.2 Potentially manufacturable graphene FET devices	263
9.8.3 Tunneling FET devices	264
9.8.4 Manufacturable graphene tunneling FET devices	266
10 Summary and assessment	270
References	275
Author Index	296
Subject Index	301

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 $2a = 284 \text{ pm}$,¹ where a is the carbon-carbon spacing (the 1–2 distance) $a = 142 \text{ pm}$. 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 $10 \text{ }\mu\text{m}$ sheet, is thus 35 211 benzene ring diameters (at 284 pm/ring) in linear size, certainly showing long-range order.

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

2 Introduction

(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 \pm multiples of the translation vectors : $1 \rightarrow 3$, $1 \rightarrow 5$ 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 $1 \rightarrow 2$. 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

²Why 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.)

³A slightly different definition of the basis vectors as $1 \rightarrow 3$, $5 \rightarrow 1$ 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

4 Introduction

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 $K = 32Ywt^3/L^3$. 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 $10\ \mu\text{m}$ 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.

⁴The 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.

⁵The 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/m² = 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 $K = d^2E/dx^2$.