1
Introduction

1.1
Carbon Nanotubes

Graphite and diamond are both made of carbons. They have different lattice structures and different properties. Diamond is brilliant and it is an insulator while graphite is black and it is a good conductor.

In 1991 Iijima [1] discovered carbon nanotubes (CNTs) in the soot created in an electric discharge between two carbon electrodes. These nanotubes ranging from 4 to 30 nm in diameter were found to have helical multiwalled structures as shown in Figures 1.1 and 1.2 after electron diffraction analysis. The tube length is about 1 μm.

The scroll-type tube shown in Figure 1.2 is called a *multiwalled carbon nanotube* (MWNT). A *single-wall nanotube* (SWNT) was fabricated by Iijima and Ichihashi [2] and by Bethune *et al.* [3] in 1993. Their structures are shown in Figure 1.3.

The tube is about 1 nm in diameter and a few micrometers in length. The tube ends are closed as shown. Because of their small radius and length-to-diameter ratio $> 10^4$, they provide an important system for studying two-dimensional (2D)

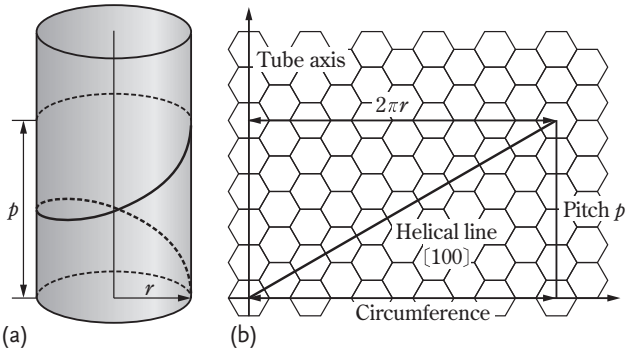

Figure 1.1 Schematic diagram showing (a) a helical arrangement of graphitic carbons and (b) its unrolled plane. The helical line is indicated by the heavy line passing through the centers of the hexagons.

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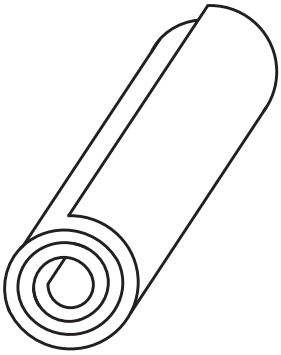

Figure 1.2 A multiwalled nanotube. The tube diameter ranges from 4 to 30 nm and its length is about 1 μm. (Original figure, Iijima [1])

physics, both theoretically and experimentally. Unrolled carbon sheets are called *graphene*.[1)] They have a honeycomb lattice structure as shown in Figure 1.1b.

A SWNT can be constructed from a slice of graphene (that is a single planar layer of the honeycomb lattice of graphite) rolled into a circular cylinder.

Carbon nanotubes are light since they are entirely made of the light element carbon (C). They are strong and have excellent elasticity and flexibility. In fact, carbon fibers are used to make tennis rackets, for example. Their main advantages in this regard are their high chemical stability as well as their strong mechanical properties.

Today's semiconductor technology is based mainly on silicon (Si). It is said that carbon-based devices are expected to be as important or even more important in the future. To achieve this purpose we must know the electrical transport properties of CNTs, which are very puzzling, as is explained below. The principal topics in this book are the remarkable electrical transport properties in CNTs and graphene on which we will mainly focus in the text.

The conductivity σ in individual CNTs varies, depending on the tube radius and the pitch of the sample. In many cases the resistance decreases with increasing temperature. In contrast the resistance increases in the normal metal such as copper (Cu). The electrical conduction properties in SWNTs separates samples into two classes: *semiconducting* or *metallic*. The room-temperature conductivities are higher for the latter class by two or more orders of magnitude. Saito *et al.* [6] proposed a model based on the different arrangements of C-hexagons around the circumference, called the *chiralities*. Figure 1.3a–c show an *armchair*, *zigzag*, and a general *chiral* CNT, respectively. After statistical analysis, they concluded that semiconducting SWNTs should be generated three times more often than metallic SWNTs. Moriyama *et al.* [7] fabricated 12 SWNT devices from one chip, and observed that

1) Graphene is the basic structural element of some carbon allotropes including graphite, CNTs, and fullerenes. The name comes from graphite + -ene; graphite itself is composed of many graphene sheets stacked together. Graphene as a name indicates a single, two-dimensional layer of three-dimensional graphite which contains many layers of carbon hexagons. Two-dimensional graphene can exist in nature as the spacing between layers (3.35 Å) is longer than the distance to neighboring atoms $a_{C\text{–}C}$ (1.42 Å) within the same plane. It has been challenging to isolate one layer from bulk graphite.

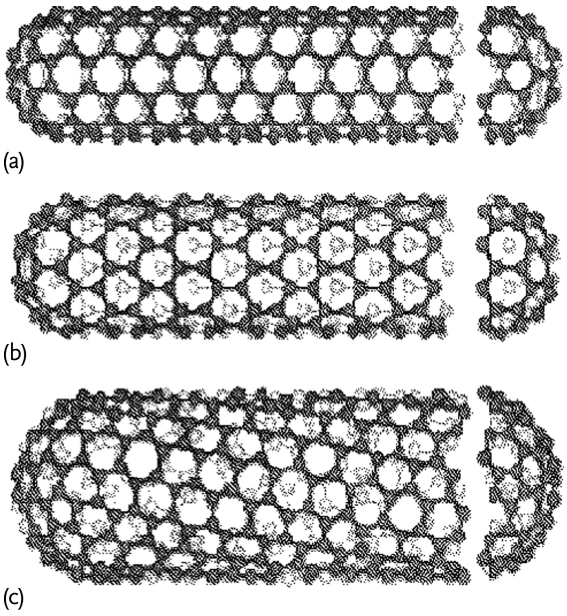

Figure 1.3 SWNTs with different chiralities and possible caps at each end: (a) shows a so-called *armchair* carbon nanotube (CNT), (b) a *zigzag* CNT, and (c) a general *chiral* CNT. One can see from the figure that the orientation of the C-hexagon in the honeycomb lattice relative to the tube axis can be taken arbitrarily. The terms "armchair" and "zigzag" refer to the arrangement of C-hexagons around the circumference. (From [4, 5]).

two of the SWNT samples were semiconducting and the other ten were metallic, a clear discrepancy between theory and experiment. We propose a new classification. The electrical conduction in SWNTs is either *semiconducting* or *metallic* depending on whether each pitch of the helical line connecting the nearest-neighbor C-hexagon contains an integral number of hexagons or not. The second alternative (metallic SWNT) occurs more often since the helical angle between the helical line and the tube axis is not controlled in the fabrication process. In the former case the system (semiconducting SWNT) is periodic along the tube length and the "holes" (and not "electrons") can travel along the wall. Here and in the text "electrons" ("holes"), by definition, are *quasi*electrons which are excited above (below) the Fermi energy *and* which circulate clockwise (counterclockwise) when viewed from the tip of the external magnetic field vector. "Electrons" ("holes") are generated in the negative (positive) side of the Fermi surface which contains the negative (positive) normal vector, with the convention that the positive normal points in the energy-increasing direction. In the Wigner–Seitz (WS) cell model [7] the primitive cell for the honeycomb lattice is a rhombus. This model is suited to the study of the ground state of graphene. For the development of the electron dynamics it is necessary to choose a *rectangular unit cell* which allows one to define the effective masses associated with the motion of "electrons" and "holes" in the lattice.

Silicon (Si) (germanium (Ge)) forms a diamond lattice which is obtained from the zinc sulfide (ZnS) lattice by disregarding the species. The electron dynamics of Si are usually discussed in terms of cubic lattice languages. Graphene and graphite have hexagonal lattice structures. Silicon and carbon are both quadrivalent materials but because of their lattice structures, they have quite different physical properties.

1.2 Theoretical Background

1.2.1 Metals and Conduction Electrons

A metal is a conducting crystal in which electrical current can flow with little resistance. This electrical current is generated by moving electrons. The electron has mass m and charge $-e$, which is negative by convention. Their numerical values are $m = 9.1 \times 10^{-28}$ g and $e = 4.8 \times 10^{-10}$ esu $= 1.6 \times 10^{-19}$ C. The electron mass is about 1837 times smaller than the least-massive (hydrogen) atom. This makes the electron extremely mobile. It also makes the electron's quantum nature more pronounced. The electrons participating in the transport of charge are called *conduction electrons*. The conduction electrons would have orbited in the outermost shells surrounding the atomic nuclei if the nuclei were separated from each other. Core electrons which are more tightly bound with the nuclei form part of the metallic ions. In a pure crystalline metal, these metallic ions form a relatively immobile array of regular spacing, called a *lattice*. Thus, a metal can be pictured as a system of two components: mobil electrons and relatively immobile lattice ions.

1.2.2 Quantum Mechanics

Electrons move following the quantum laws of motion. A thorough understanding of quantum theory is essential. Dirac's formulation of quantum theory in his book, *Principles of Quantum Mechanics* [9], is unsurpassed. Dirac's rules that the quantum states are represented by *bra* or *ket* vectors and physical observables by Hermitian operators are used in the text. There are two distinct quantum effects, the first of which concerns a single particle and the second a system of identical particles.

1.2.3 Heisenberg Uncertainty Principle

Let us consider a simple harmonic oscillator characterized by the Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + \frac{kx^2}{2}\,, \tag{1.1}$$

where m is the mass, k the force constant, p the momentum, and x the position. The corresponding energy eigenvalues are

$$\varepsilon_n = \hbar\omega_0\left(n + \frac{1}{2}\right), \quad \omega_0 \equiv \left(\frac{k}{m}\right)^{1/2}, \quad n = 0, 1, 2, \ldots \tag{1.2}$$

The energies are quantized in (1.2). In contrast the classical energy can be any positive value. The lowest quantum energy $\varepsilon_0 = \hbar\omega_0/2$, called the *energy of zero-point motion*, is not zero. The most stable state of any quantum system is not a state of *static equilibrium* in the configuration of lowest potential energy, it is rather a *dynamic equilibrium* for the zero-point motion [10, 11]. Dynamic equilibrium may be characterized by the minimum total (potential + kinetic) energy under the condition that each coordinate q has a range Δq and the corresponding momentum p has a range Δp, so that the product $\Delta q \Delta p$ satisfies the *Heisenberg uncertainty relation*:

$$\Delta q \Delta p > h\,. \tag{1.3}$$

The most remarkable example of a macroscopic body in dynamic equilibrium is liquid helium (He). This liquid with a boiling point at 4.2 K is known to remain liquid down to 0 K. The zero-point motion of He atoms precludes solidification.

1.2.4
Bosons and Fermions

Electrons are fermions. That is, they are indistinguishable quantum particles subject to the *Pauli exclusion principle*. Indistinguishability of the particles is defined by using the permutation symmetry. According to Pauli's principle no two electrons can occupy the same state. Indistinguishable quantum particles not subject to the Pauli exclusion principle are called bosons. Bosons can occupy the same state with no restriction. Every elementary particle is either a *boson* or a *fermion*. This is known as the *quantum statistical postulate*. Whether an elementary particle is a boson or a fermion is related to the magnitude of its spin angular momentum in units of $\hbar$. Particles with integer spins are bosons, while those with half-integer spins are fermions [12]. This is known as Pauli's *spin-statistics theorem*. According to this theorem and in agreement with all experimental evidence, electrons, protons, neutrons, and μ-mesons, all of which have spin of magnitude $\hbar/2$, are fermions, while photons (quanta of electromagnetic radiation) with spin of magnitude $\hbar$, are bosons.

1.2.5
Fermi and Bose Distribution Functions

The average occupation number at state $\boldsymbol{k}$, denoted by $\langle n_k \rangle$, for a system of free fermions in equilibrium at temperature T and chemical potential μ is given by the

Fermi distribution function:

$$\langle n_k \rangle = f_{\mathrm{F}}(\varepsilon_k) \equiv \frac{1}{\exp((\varepsilon_k - \mu)/(k_{\mathrm{B}}T)) + 1} \quad \text{for fermions,} \tag{1.4}$$

where ε_k is the single-particle energy associated with the state $\boldsymbol{k}$. The average occupation number at state $\boldsymbol{k}$ for a system of free bosons in equilibrium is given by the *Bose distribution function*:

$$\langle n_k \rangle = f_{\mathrm{B}}(\varepsilon_k) \equiv \frac{1}{\exp((\varepsilon_k - \mu)/(k_{\mathrm{B}}T)) - 1} \quad \text{for bosons.} \tag{1.5}$$

1.2.6 Composite Particles

Atomic nuclei are composed of *nucleons* (protons, neutrons), while atoms are composed of nuclei and electrons. It has been experimentally demonstrated that these composite particles are indistinguishable quantum particles. According to *Ehrenfest–Oppenheimer–Bethe's rule* [12, 13], the center of mass (CM) of a composite moves as a fermion (boson) if it contains an odd (even) number of elementary fermions. Thus, He^4 atoms (four nucleons, two electrons) move as bosons while He^3 atoms (three nucleons, two electrons) move as fermions. Cooper pairs (two electrons) move as bosons.

1.2.7 Quasifree Electron Model

In a metal at the lowest temperatures conduction electrons move in a nearly stationary periodic lattice. Because of the Coulomb interaction among the electrons, the motion of the electrons is correlated. However, each electron in a crystal moves in an extremely weak self-consistent periodic field. Combining this result with the Pauli exclusion principle, which applies to electrons with no regard to the interaction, we obtain the *quasifree electron model*. The quasifree electron moves with the effective mass m^* which is different from the gravitational mass m_{e}. In this model the quantum states for the electron in a crystal are characterized by wave vector (k vector: $\boldsymbol{k}$) and energy

$$\varepsilon = E(k)\,. \tag{1.6}$$

At 0 K, all of the lowest energy states are filled with electrons, and there exists a sharp Fermi surface represented by

$$E(k) = \varepsilon_{\mathrm{F}}\,, \tag{1.7}$$

where ε_{F} is the *Fermi energy*. Experimentally, the electrons in alkali metals, which form body-centered cubic (bcc) lattices, including lithium (Li), sodium (Na), and potassium (K), behave like quasifree electrons.

1.2.8
"Electrons" and "Holes"

"Electrons" ("holes") in the text are defined as *quasiparticles* possessing charge e (magnitude) that circulate counterclockwise (clockwise) when viewed from the tip of the applied magnetic field vector $\boldsymbol{B}$. This definition is used routinely in semiconductor physics. We use the quotation-marked "electron" to distinguish it from the generic electron having the gravitational mass m_e. A "hole" can be regarded as a particle having positive charge, positive mass, and positive energy. The "hole" does not, however, have the same effective mass m^* (magnitude) as the "electron," so that "holes" are not true antiparticles like positrons. We will see that "electrons" and "holes" are thermally excited particles and they are closely related to the curvature of the Fermi surface (see Chapter 3).

1.2.9
The Gate Field Effect

Graphene and nanotubes are often subjected to the so-called *gate voltage* in experiments. We will show here that the gate voltage polarizes the conductor and hence the surface charges ("electrons," "holes") are induced. The actual conductor may have a shape and a particular Fermi surface. But in all cases surface charges are induced by electric fields. If a bias voltage is applied, then some charges can move and generate currents.

A.
Let us take a rectangular metallic plate and place it under an external electric field $\boldsymbol{E}$, see Figure 1.4.

When the upper and lower sides are parallel to the field $\boldsymbol{E}$, then the remaining two side surfaces are polarized so as to reduce the total electric field energy. If the plate is rotated, then all side surfaces are polarized.

B.
Let us now look at the electric field effect in k-space. Assume a quasifree electron system which has a spherical Fermi surface at zero field. Upon the application of a static field $\boldsymbol{E}$, the Fermi surface will be shifted towards the right by $qE\tau/m^*$, where τ is the mean free time and m^* the effective mass, as shown in Figure 1.5. There is a steady current since the sphere is off from the center O. We may assume

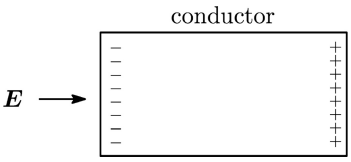

Figure 1.4 The surface charges are induced in the conductor under an external electric field $\boldsymbol{E}$.

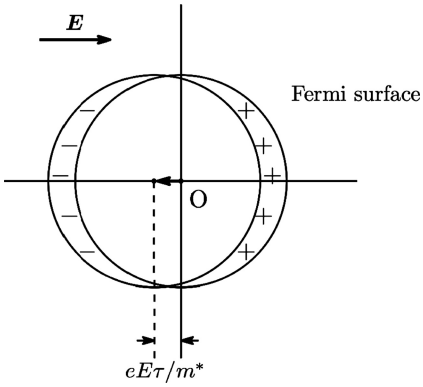

Figure 1.5 The Fermi surface is shifted by $eE\tau/m^*$ due to the electric field $\boldsymbol{E}$.

that the ionic lattice is stationary. Then, there is an unbalanced charge distribution as shown, where we assumed $q = -e < 0$. This effect will appear only on the surface of the metal. We used the fermionic nature of electrons in $\boldsymbol{B}$.

1.3 Book Layout

In Chapters 2 and 3 kinetic theory and Bloch electron dynamics are developed, respectively. Phonon and electron–phonon interaction are discussed in Chapter 4. These chapters are preliminaries for the theory of the conductivity of carbon nanotubes, which is discussed in Chapters 5 and 6. Semiconducting SWNTs are discussed in Chapter 6. A quantum statistical theory of superconductivity is summarized in Chapter 7. Chapter 8 deals with the supercurrents in metallic SWNTs, starting with the BCS-like Hamiltonian and deriving expressions for a linear dispersion relation, and a critical (superconducting) temperature. Metallic SWNTs exhibit non-Ohmic behavior, and charged particles appear to run through the tube length with no scattering. We interpret this in terms of the condensed Cooper pairs (pairons).

An applied static magnetic field induces a profound change in the electron states. Pauli's paramagnetic and Landau's diamagnetism are described in Chapter 9. Landau states generate an oscillatory density of states that induces de Haas–van Alphen oscillation which is discussed in Chapter 10. The Quantum Hall Effect (QHE) in GaAs/AlGaAs is summarized in Chapter 11. The QHE in graphene observed at room temperature is discussed in Chapter 12. The QHE occurs where the "hole" ("electron") density becomes high near the neck Fermi surface, which develops by charging the graphene through the gate voltage. The different temperatures generate different carrier densities and the resulting carrier diffusion generates a thermal electromotive force. A new formula for the Seebeck coefficient is obtained and is applied to multiwalled carbon nanotubes in Chapter 13. In Chapter 14, we discuss miscellaneous topics.

1.4
Suggestions for Readers

Graphene and CNTs are composed entirely of carbons but their lattice structures are distinct from each other. The simple free electron model does not work. To describe the electrical conduction of graphene and CNTs it is necessary to understand a number of advanced topics including superconductivity and Fermi surfaces.

1.4.1
Second Quantization

Reading Chapter 7 Superconductivity requires a knowledge of second quantization. The authors suggest that the readers learn the second quantization in two steps.

1. Dirac solved the energy-eigenvalue problem for a simple harmonic oscillator in the Heisenberg picture, using creation and annihilation operators $(a^\dagger, a)$, see Chapter 4, Section 4.3. We follow Dirac [9] and obtain the eigenvalues, $(n' + 1/2)\hbar\omega$, where n' is the eigenvalues of $n = a^\dagger a$, $n' = 0, 1, 2, \ldots$
2. Read Appendix A.1, where a general theory for a quantum many-boson and fermion system is presented.

1.4.2
Semiclassical Theory of Electron Dynamics

Electrons and phonons are regarded as *waves packets* in solids. Dirac showed that the wave packets move, following classical equations of motion [9]. The conduction electron ("electron," "hole") size is equal to the orthogonal unit cell size. The phonon size is about two orders of magnitude greater at room temperature. The "electron" and "hole" move with effective masses m^* which are distinct from the gravitational effective mass m_e. Bloch electron dynamics are described in Chapter 3.

1.4.3
Fermi Surface

The time-honored WS cell model can be used for cubic lattice systems including a diamond lattice. For hexagonal systems including graphene and graphite an orthogonal unit cell model must be used to establish the k-space. Read Sections 5.2 and 5.4. The same orthogonal unit cell model must be used for the discussion of phonons.

In our quantum statistical theory we do not jump to conclusions. We make arguments backed up by step-by-step calculations. This is the surest way of doing and learning physics for ordinary men and women.

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