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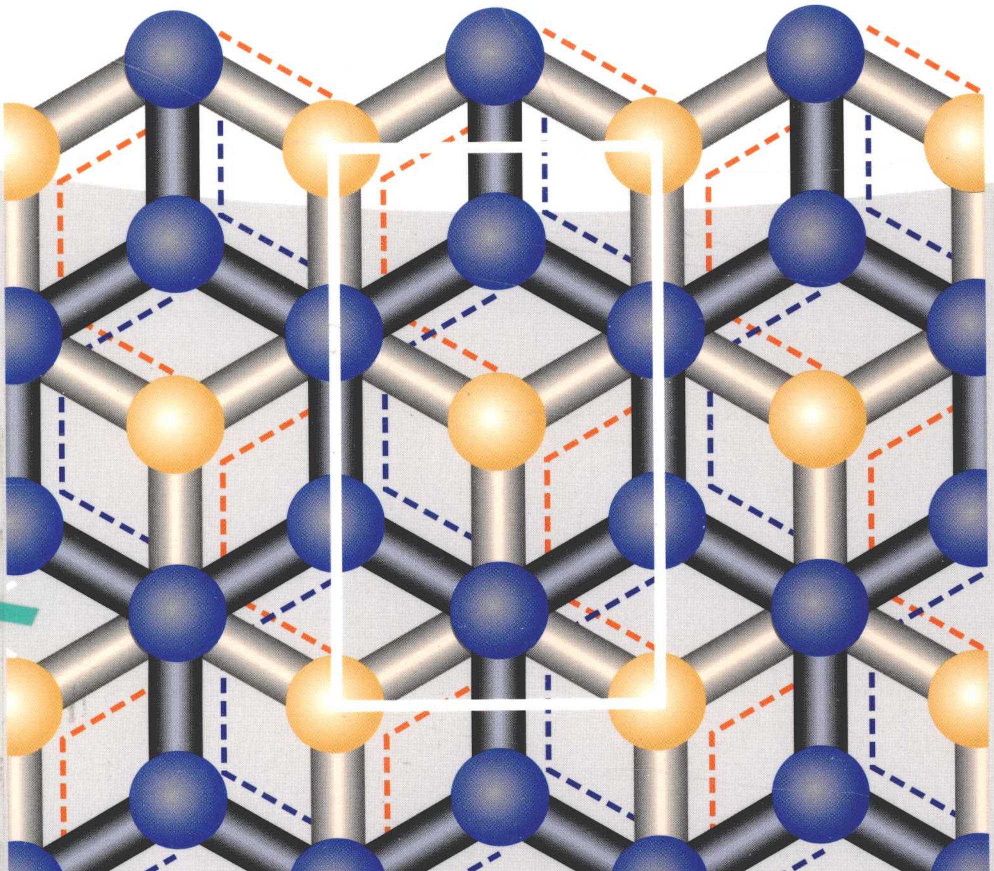

PHYSICS TEXTBOOK

Shigeji Fujita and Akira Suzuki

Electrical Conduction in Graphene and Nanotubes

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Preface

Brilliant diamond and carbon black (graphite) are both made of carbon (C). Diamond is an insulator while graphite is a good conductor. This difference arises from the lattice structure. Graphite is a layered material made up of sheets, each forming a two-dimensional (2D) honeycomb lattice, called *graphene*. The electrical conduction mainly occurs through graphene sheets. Carbon nanotubes were discovered by Iijima[1] in 1991. The nanotubes ranged from 4 to 30 nm in diameter and were microns (μm) in length, had scroll-type structures, and were called *Multi-walled Nanotubes* (MWNTs) in the literature. *Single-Wall Nanotubes* (SWNTs) have a size of about 1 nm in diameter and microns in length. This is a simple two-dimensional material. It is theorists' favorite system. The electrical transport properties along the tube present, however, many puzzles, as is explained below. Carbon nanotubes are very strong and light. In fact, carbon fibers are used to make tennis rackets. Today's semiconductor technology is based on silicon (Si) devices. It is said that carbon chips, which are stronger and lighter, may take the place of silicon chips in the future. It is, then, very important to understand the electrical transport properties of carbon nanotubes. The present book has as its principal topics electrical transport in graphene and carbon nanotubes.

The conductivity σ in individual carbon nanotubes varies, depending on the tube radius and the pitch of the sample. In many cases the resistance decreases with increasing temperature while the resistance increases in the normal metal. Electrical conduction in SWNTs is either semiconducting or metallic, depending on whether each pitch of the helical line connecting the nearest-neighbor C-hexagon centers contains an integral number of hexagons or not. The second alternative occurs more often since the pitch is not controlled in the fabrication process. The room-temperature conductivity in metallic SWNTs is higher by two or more orders of magnitude than in semiconducting SWNTs. Currents in metallic SWNTs do not obey Ohm's law linearity between current and voltage. Scanned probe microscopy shows that the voltage does not drop along the tube length, implying a superconducting state. The prevailing theory states that electrons run through the one-dimensional (1D) tube ballistically. But this interpretation is not the complete story. The reason why the ballistic electrons are not scattered by impurities and

1) Iijima, S. (1991) *Nature (London)*, **354**, 56.

phonons is unexplained. We present a new interpretation in terms of the model in which superconducting Bose-condensed Cooper pairs (bosons) run as a supercurrent. In our text we start with the honeycomb lattice, construct the Fermi surface, and develop Bloch electron dynamics based on the rectangular unit cell model. We then use kinetic theory to treat the normal electrical transport with the assumption of "electrons," "holes," and Cooper pairs as carriers.

To treat the superconducting state, we assume that the phonon-exchange attraction generates Cooper pairs (pairons). We start with a Bardeen–Cooper–Schrieffer (BCS)-like Hamiltonian, derive a linear dispersion relation for the moving pairons, and obtain a formula for the Bose–Einstein Condensation (BEC) temperature

$$k_B T_c = 1.24 \hbar v_F n^{1/2} , \quad (2D)$$

where n is the pairon density and v_F the Fermi speed. The superconducting temperature T_c given here, is distinct from the famous BCS formula for the critical temperature: $3.53 k_B T_c = 2\Delta_0$, where Δ_0 is the zero-temperature electron energy gap in the weak coupling limit. The critical temperature T_c for metallic SWNTs is higher than 150 K while the T_c is much lower for semiconducting SWNTs.

MWNTs have open-ended circumferences and the outermost walls with greatest radii, contribute most to the conduction. The conduction is metallic (with no activation energy factor) and shows no pitch dependence.

In 2007 Novoselov *et al.* [2] discovered the room-temperature *Quantum Hall Effect* (QHE) in graphene. This was a historic event. The QHE in the GaAs/AlGaAs heterojunction is observed around 1 K and below. The original authors interpreted the phenomenon in terms of a Dirac fermion moving with a linear dispersion relation. But the reason why Dirac fermions are not scattered by phonons, which must exist at 300 K, is unexplained. We present an alternative explanation in terms of the *composite bosons* traditionally used in QHE theory. The most important advantage of our bosonic theory over the Dirac fermion theory is that our theory can explain why the plateau in the Hall conductivity (σ_{xy}) is generated where the zero resistivity ($\rho_{xx} = 0$) is observed.

This book has been written for first-year graduate students in physics, chemistry, electrical engineering, and material sciences. Dynamics, quantum mechanics, electromagnetism, and solid state physics at the senior undergraduate level are prerequisites. Second quantization may or may not be covered in the first-year quantum course. But second quantization is indispensable in dealing with phonon-exchange, superconductivity, and QHE. It is fully reviewed in Appendix A.1. The book is written in a self-contained manner. Thus, nonphysics majors who want to learn the microscopic theory step-by-step with no particular hurry may find it useful as a self-study reference.

Many fresh, and some provocative, views are presented. Experimental and theoretical researchers in the field are also invited to examine the text. The book is based on the materials taught by Fujita for several courses in quantum theory of solids and quantum statistical mechanics at the University at Buffalo. Some of the

2) Novoselov, K.S. *et al.* (2007) *Science*, **315**, 1379.

book's topics have also been taught by Suzuki in the advanced course in condensed matter physics at the Tokyo University of Science. The book covers only electrical transport properties. For other physical properties the reader is referred to the excellent book *Physical Properties of Carbon Nanotubes*, by R. Saito, G. Dresselhaus and M.S. Dresselhaus (Imperial College Press, London 1998).

The authors thank the following individuals for valuable criticisms, discussions and readings: Professor M. de Llano, Universidad Nacional Autonoma de México; Professor Sambandamurthy Ganapathy, University at Buffalo, Mr. Masashi Tanabe, Tokyo University of Science and Mr. Yoichi Takato, University at Buffalo. We thank Sachiko, Keiko, Michio, Isao, Yoshiko, Eriko, George Redden and Kurt Borchardt for their encouragement, reading and editing of the text.

Buffalo, New York, USA | *Shigeji Fujita*
Tokyo, Japan | *Akira Suzuki*
December, 2012

Physical Constants, Units, Mathematical Signs and Symbols

Useful Physical Constants

Quantity	Symbol	Value
Absolute zero temperature		$0\,\mathrm{K} = -273.16\,^\circ\mathrm{C}$
Avogadro's number	N_A	$6.02 \times 10^{23}\,\mathrm{mol}^{-1}$
Bohr magneton	$\mu_B = e\hbar/(2m_e)$	$9.27 \times 10^{-24}\,\mathrm{J\,T}^{-1}$
Bohr radius	$a_B = 4\pi\varepsilon_0\hbar^2/(m_e e^2)$	$5.29 \times 10^{-11}\,\mathrm{m}$
Boltzmann's constant	$k_B = R/N_A$	$1.38 \times 10^{-23}\,\mathrm{J\,K}^{-1}$
Coulomb's constant	$k_0 = 1/(4\pi\varepsilon_0)$	$8.988 \times 10^{9}\,\mathrm{N\,m\,C}^{-2}$
Dirac's constant (Planck's constant/(2π))	$\hbar = h/(2\pi)$	$1.05 \times 10^{-34}\,\mathrm{J\,s}$
Electron charge (magnitude)	e	$1.60 \times 10^{-19}\,\mathrm{C}$
Electron rest mass	m_e	$9.11 \times 10^{-31}\,\mathrm{kg}$
Gas constant	$R = N_A k_B Z$	$8.314\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1}$
Gravitational constant	G	$6.674 \times 10^{-11}\,\mathrm{N\,m}^2\,\mathrm{kg}^{-2}$
Gravitational acceleration	g	$9.807\,\mathrm{m\,s}^{-2}$
Magnetic flux quantum	$\Phi_0 = h/(2e)$	$2.068 \times 10^{-15}\,\mathrm{Wb}$
Mechanical equivalent of heat		$4.184\,\mathrm{J\,cal}^{-1}$
Molar volume (gas at STP)		$2.24 \times 10^{4}\,\mathrm{cm}^3 = 22.4\,\mathrm{L}$
Permeability of vacuum	μ_0	$4\pi \times 10^{-7}\,\mathrm{H\,m}^{-1}$
Permittivity of vacuum	ε_0	$8.85 \times 10^{-12}\,\mathrm{F\,m}^{-1}$
Planck's constant	h	$6.63 \times 10^{-34}\,\mathrm{J\,s}$
Proton mass	m_p	$1.67 \times 10^{-27}\,\mathrm{kg}$
Quantum Hall conductance	e^2/h	$3.874 \times 10^{-6}\,\mathrm{S}$
Quantum Hall resistance	$R_H = h/e^2$	$25\,812.81\,\Omega$
Speed of light	c	$3.00 \times 10^{8}\,\mathrm{m\,s}^{-1}$

Subsidiary Units

newton	$1\,\mathrm{N} = 1\,\mathrm{kg\,m\,s}^{-2}$
joule	$1\,\mathrm{J} = 1\,\mathrm{N\,m}$

coulomb	$1\,\mathrm{C} = 1\,\mathrm{A\,s}$
hertz	$1\,\mathrm{Hz} = 1\,\mathrm{s}^{-1}$
pascal	$1\,\mathrm{Pa} = 1\,\mathrm{N\,m}^{-2}$
bar	$1\,\mathrm{bar} = 10^5\,\mathrm{Pa}$

Prefixes Denoting Multiples and Submultiples

10^3	kilo (k)
10^6	mega (M)
10^9	giga (G)
10^{12}	tera (T)
10^{15}	peta (P)
10^{-3}	milli (m)
10^{-6}	micro (μ)
10^{-9}	nano (n)
10^{-12}	pico (p)
10^{-15}	femto (f)

Mathematical Signs

$\mathbb{N}$	set of natural numbers
$\mathbb{Z}$	set of integers
$\mathbb{Q}$	set of rational numbers
$\mathbb{R}$	set of real numbers
$\mathbb{C}$	set of complex numbers
$\forall x$	for all x
$\exists x$	existence of x
$\mapsto$	maps to
$\therefore$	therefore
$\because$	because
$=$	equals
$\simeq$	approximately equals
$\neq$	not equal to
$\equiv$	identical to, defined as
$>$	greater than
$\gg$	much greater than
$<$	smaller (or less) than
$\ll$	much smaller than
$\geq$	greater than or equal to
$\leq$	smaller (or less) than or equal to
$\propto$	proportional to
$\sim$	represented by, of the order
$\mathcal{O}(x)$	order of x

$\langle x\rangle$, $\overline{x}$	the average value of x
ln	logarithm of base e (natural logarithm)
Δx	increment in x
$\mathrm{d}x$	infinitesimal increment in x
$z^* = x - \mathrm{i}y$	complex conjugate of complex number; $z = x+\mathrm{i}y$ ($x, y \in \mathbb{R}$, i = imaginary unit $= \sqrt{-1}$)
$\alpha^\dagger$	Hermitian conjugate of operator α
$\boldsymbol{\alpha}^\dagger$	Hermitian conjugate of matrix $\boldsymbol{\alpha}$
P^{-1}	inverse of P
$\delta(x)$	Dirac's delta function
$\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$	Kronecker's delta
$\Theta(x) = \begin{cases} 1 & \text{if } x \geq 0 \\ 0 & \text{if } x < 0 \end{cases}$	Heaviside's step function
$\mathrm{sgn}x = \begin{cases} 1 & \text{if } x > 0 \\ -1 & \text{if } x < 0 \end{cases}$	sign of x
$\dot{x} = \mathrm{d}x/\mathrm{d}t$	time derivative
$\mathrm{grad}\phi \equiv \nabla\phi$	gradient of ϕ
$\mathrm{div}\boldsymbol{A} \equiv \nabla \cdot \boldsymbol{A}$	divergence of $\boldsymbol{A}$
$\mathrm{curl}\boldsymbol{A} \equiv \mathrm{rot}\boldsymbol{A} \equiv \nabla \times \boldsymbol{A}$	curl (or rotation) of $\boldsymbol{A}$
∇	Nabla (or del) operator
$\Delta \equiv \nabla^2$	Laplacian operator

List of Symbols

The following list is not intended to be exhaustive. It includes symbols of frequent occurrence or special importance in this book.

Å	ångstrom ($= 10^{-8}$ cm $= 10^{-10}$ m)
$\boldsymbol{A}$	vector potential
a_0	lattice constant
$\boldsymbol{a}_1$, $\boldsymbol{a}_2$	nonorthogonal base vectors
$\boldsymbol{B}$	magnetic field (magnetic flux density)
C_V	specific heat at constant volume
c	heat capacity per particle
$c_{\mathbb{V}}$	heat capacity per unit volume
c	speed of light
$\mathcal{D}(\varepsilon)$	density of states in energy space
$\mathcal{D}(\omega)$	density of states in angular frequency
$\mathcal{D}(p)$, $\mathcal{D}(k)$	density of states in momentum space
E	total energy

E	internal energy
E_F	Fermi energy
$\boldsymbol{E}$	electric field vector
$\boldsymbol{E}_H$	electric field vector due to the Hall voltage
e	electronic charge (absolute value)
$\hat{\boldsymbol{e}}_x, \hat{\boldsymbol{e}}_y, \hat{\boldsymbol{e}}_z$	orthogonal unit vectors
F	Helmholtz free energy
f	one-body distribution function
f_B	Bose distribution function
f_F	Fermi distribution function
f_0	Planck distribution function
G	Gibbs free energy
g	g-factor
$\mathcal{H}$	Hamiltonian
$\boldsymbol{H}_a$	applied magnetic field vector
H_c	critical magnetic field (magnitude)
h	Planck's constant
h	single-particle Hamiltonian
$\hbar$	Planck's constant divided by 2π
I	magnetization
$\mathrm{i} \equiv \sqrt{-1}$	imaginary unit
$\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$	Cartesian unit vectors
$\boldsymbol{J}$	total current
$\boldsymbol{j}$	single-particle current
$\boldsymbol{j}$	current density
K	thermal conductivity
$\boldsymbol{k}$	wave vector (k-vector)
k_0	Coulomb's constant
k_B	Boltzmann constant
$\mathcal{L}$	Lagrangian function
L	normalization length
ℓ	mean free path
$\boldsymbol{l}$	angular momentum
M	molecular mass
M^*	magnetotransport mass
M	(symmetric) mass tensor
m	electron mass
m^*	cyclotron mass
m^*	effective mass
N	number of particles
$\mathcal{N}$	number operator
N_L	Landau level
n	particle number density
n_c	number density of the dressed electrons
n_p	number density of pairons

P	pressure
$\boldsymbol{P}$	total momentum
$\boldsymbol{p}$	momentum vector
p	momentum (magnitude)
Q	quantity of heat
$\boldsymbol{q}$	heat (energy) current
q	charge
R	resistance
$\boldsymbol{R}$	Bravais lattice vector
$\boldsymbol{R}$	position vector of the center of mass
R_{H}	Hall coefficient
r	radial coordinate
$\boldsymbol{r}$	position vector
S	entropy
S	Seebeck coefficient
T	absolute temperature
T_0	transition temperature
T_{c}	critical temperature
T_{F}	Fermi temperature
$\mathcal{T}$	kinetic energy
TR	grand ensemble trace
Tr	many-particle trace
tr	one-particle trace
$V, \mathbb{V}$	volume
V_{H}	Hall voltage
$\mathcal{V}$	potential energy
v	speed (magnitude of $\boldsymbol{v}$)
$\boldsymbol{v}$	velocity
$\boldsymbol{v}_{\mathrm{thermal}}$	thermal velocity
$\boldsymbol{v}_{\mathrm{d}}$	drift velocity
$v_{\mathrm{d}}(= \lvert\boldsymbol{v}_{\mathrm{d}}\rvert)$	drift speed
$\boldsymbol{v}_{\mathrm{F}}$	Fermi velocity
$v_{\mathrm{F}}(= \lvert\boldsymbol{v}_{\mathrm{F}}\rvert)$	Fermi speed
W	work
$\boldsymbol{w}$	wrapping vector
Z	partition function
$\alpha = -e/(2m)$	magnetogyric (magnetomechanical) ratio
$\mathrm{e}^{\alpha} \equiv z$	fugacity
$\beta \equiv 1/(k_{\mathrm{B}}T)$	reciprocal temperature
χ	magnetic susceptibility
ε	single-particle energy
ε_{F}	Fermi energy
ε_{g}	energy gap
ε_{p}	pairon energy
$\Theta(x)$	step function

θ	polar angle
λ	wavelength
λ	penetration depth
$\lambda(\equiv e^{\beta\mu})$	fugacity
κ	curvature
κ	quantum state
μ	chemical potential
$\boldsymbol{\mu}$	magnetic moment
μ_{B}	Bohr magneton
ν	frequency
ν	Landau level occupation ratio (filling factor)
Ξ	grand partition function
ξ	dynamical variable
ξ	coherence length
ρ	mass density
ρ	density operator
ρ	many-particle distribution function
ρ	resistivity
$\rho(B)$	magnetoresistivity
ρ_{H}	Hall resistivity
σ	total cross section
σ	electrical conductivity
σ_{H}	Hall conductivity
$\sigma_x, \sigma_y, \sigma_z$	Pauli spin matrices
τ	relaxation time
τ_{c}	collision time, average time between collision
τ_{d}	duration of collision
φ	distribution function
ϕ	azimuthal angle
ϕ	scalar potential
Φ	magnetic flux
Φ_0	flux quantum
Ψ	quasiwavefunction for many condensed bosons
ψ	wavefunction for a quantum particle
$d\Omega = \sin\theta\, d\theta\, d\phi$	element of solid angle
$\omega \equiv 2\pi\nu$	angular frequency
ω_{c}	cyclotron frequency
ω_{c}	rate of collision (collision frequency)
ω_{D}	Debye frequency
$\langle\vert$	bra vector
$\vert\rangle$	ket vector
(hkl), $[hkl]$, $\langle hkl\rangle$	crystallographic notation
$[\ ,\ ]$	commutator brackets
$\{\ ,\ \}$	anticommutator brackets
$\{\ ,\ \}$	Poisson brackets

Units

In much of the literature quoted, the unit of magnetic field $\boldsymbol{B}$ is the gauss. Electric fields are frequently expressed in $\mathrm{V\,cm^{-1}}$ and resistivity in Ω cm.

$$1\ \text{tesla (T)} = 10^4\ \text{gauss (G, (Gs))} \quad 1\ \Omega\ \text{m} = 10^2\ \Omega\ \text{cm}$$

The Planck constant h over 2π, $\hbar \equiv h/(2\pi)$, is used in dealing with an electron. The original Planck constant h is used in dealing with a photon.

Crystallographic Notation

This is mainly used to denote a direction, or the orientation of a plane, in a cubic metal. A plane (hkl) intersects the orthogonal Cartesian axes, coinciding with the cube edges, at a/h, a/k, and a/l from the origin, a being a constant, usually the length of a side of the unit cell. The direction of a line is denoted by $[hkl]$, the direction cosines with respect to the Cartesian axes being h/N, k/N, and l/N, where $N^2 = h^2 + k^2 + l^2$. The indices may be separated by commas to avoid ambiguity. Only occasionally will the notation be used precisely; thus, [100] or [001] usually means any cube axis and [111], any diagonal.

B and *H*

When an electron is described in quantum mechanics, its interaction with a magnetic field is determined by $\boldsymbol{B}$ rather than $\boldsymbol{H}$; that is, if the permeability μ is not unity, the electron motion is determined by $\mu \boldsymbol{H}$. It is preferable to forget $\boldsymbol{H}$ altogether and use $\boldsymbol{B}$ to define all field strengths. The $\boldsymbol{B}$ is connected with a vector potential $\boldsymbol{A}$ such that $\boldsymbol{B} = \nabla \times \boldsymbol{A}$. The magnetic field $\boldsymbol{B}$ is effectively the same inside and outside the metal sample.

List of Abbreviations

1D	one dimensional
2D	two dimensional
3D	three dimensional
ARPES	angle-resolved photoemission spectroscopy
bcc	body-centered cubic
BCS	Bardeen–Cooper–Schrieffer
BEC	Bose–Einstein condensation
c-	composite-
c.c.	complex conjugate
C-	carbon-
CM	center of mass

CNT	carbon nanotube
cub, cub	cubic
dHvA	de Haas–van Alphen
dia	diamond
DOS	density of states
DP	Dirac picture
"electron"	see p. 7
EOB	Ehrenfest–Oppenheimer–Bethe
f (c-)	fundamental (composite-)
fcc	face-centered cubic
h.c.	Hermitian conjugate
hcp	hexagonal closed packed
"hole"	see p. 7
hex	hexagonal
HP	Heisenberg picture
HRC	high-resistance contacts
HTSC	high-temperature superconductivity
KP	Kronig–Penney
lhs	left-hand side
LL	Landau level
LRC	low-resistance contacts
mcl, mcl	monoclinic
MIT	metal-insulator transition
MR	magnetoresistance
MWNT	multiwalled (carbon) nanotube
NFEM	nearly free electron model
NT	nanotube
orc	orthorhombic
QH	quantum Hall
QHE	quantum Hall effect
rhs	right-hand side
rhl	rhombohedral
sc	simple cubic
SdH	Shubnikov–de Haas
SP	Schrödinger picture
sq	square
SQUID	superconducting quantum interference device
SWNT	single-wall (carbon) nanotube
tcl	triclinic
tet	tetragonal
vrh	variable range hopping
WS	Wigner–Seitz
ZBA	zero-bias anomaly

Contents