

Electrons in Solids: Electrical and Thermal Properties

W7.1 Boltzmann Equation

In Section 7.2 of the textbook,[†] formulas were derived on the basis of Newtonian mechanics and the assumption that all of the conduction electrons contribute to the electrical current. In the Sommerfeld theory this is not correct. Electrons with energies less than $\approx E_F - k_B T$ have difficulty being accelerated by the electric field since the states above them are already filled. Only those electrons in the immediate vicinity of the Fermi surface are excitable. The question is how to rederive the conductivity formula taking into account the Pauli exclusion principle. Here a semiclassical approach is adopted.

One introduces a distribution function $f(\mathbf{r}, \mathbf{p}, t)$ to describe the system of electrons in phase space. The quantity $2f(\mathbf{r}, \mathbf{p}, t) d\mathbf{r} d\mathbf{p}/h^3$ gives the number of electrons within volume element $d\mathbf{r}$ and within a momentum bin of size $d\mathbf{p}$ at time t (the factor of 2 is for spins). The distribution function evolves in time due to collisions. The Boltzmann equation relates the total time derivative of f to the difference between f and the equilibrium distribution function $f_0 = F(E, T)$, where E is the energy,

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{d\mathbf{r}}{dt} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{d\mathbf{p}}{dt} \cdot \frac{\partial f}{\partial \mathbf{p}} = \frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{p}} = -\frac{f - f_0}{\tau(\mathbf{p})}, \quad (\text{W7.1})$$

where \mathbf{v} is the velocity and $\mathbf{F} = -e\mathbf{E}_0$ is the force on the electron. This equation has been written in what is called the *relaxation-time approximation*: it is assumed that the relaxation of f to f_0 occurs in a time $\tau(\mathbf{p})$ as a result of collisions. Interest here is in the steady-state behavior, so $\partial f/\partial t = 0$ and $f = f(\mathbf{r}, \mathbf{p})$. Attention will also be restricted to the case of an infinite medium where a spatially homogeneous solution is sought, so $f = f(\mathbf{p})$. It will also be assumed that τ depends only on E .

An approximate expression for f is developed by substituting f_0 for f in the left-hand side of Eq. (W7.1):

$$f = f_0 - \tau \left(\mathbf{v} \cdot \nabla f_0 - e\mathbf{E}_0 \cdot \frac{\partial f_0}{\partial \mathbf{p}} \right) + \cdots \quad (\text{W7.2})$$

[†] The material on this home page is supplemental to *The Physics and Chemistry of Materials* by Joel I. Gersten and Frederick W. Smith. Cross-references to material herein are prefixed by a “W”; cross-references to material in the textbook appear without the “W.”

Since $f_0 = F(E, T)$, the derivatives may be reexpressed in terms of energy derivatives:

$$f = f_0 - \tau \frac{\partial f_0}{\partial E} \mathbf{v} \cdot \left[\frac{1}{\beta} \nabla(\beta(E - \mu)) - e\mathbf{E}_0 \right]. \quad (\text{W7.3})$$

The electrical-current density is

$$\mathbf{J}(\mathbf{r}, t) = -2e \int \mathbf{v} f(\mathbf{r}, \mathbf{p}, t) \frac{d\mathbf{p}}{h^3}, \quad (\text{W7.4})$$

and the heat-current density is

$$\mathbf{J}_Q(\mathbf{r}, t) = 2 \int (E - \mu) \mathbf{v} f(\mathbf{r}, \mathbf{p}, t) \frac{d\mathbf{p}}{h^3}. \quad (\text{W7.5})$$

Note that the thermal energy transported is positive when E exceeds μ and negative when E is less than μ . Upon inserting Eq. (W7.3) into Eqs. (W7.4) and (W7.5), the need to angular-average a product of two velocities over momentum space is encountered. One uses $\langle \mathbf{v} \mathbf{v} \cdot \mathbf{A} \rangle = v^2 \mathbf{A} / 3 = 2 < E \mathbf{A} > / 3m$, where \mathbf{A} is a constant vector, and obtains

$$\mathbf{J} = -\frac{16\pi e \sqrt{2m}}{3h^3} \int E^{3/2} \tau(E) \frac{\partial f_0}{\partial E} \left(\frac{E - \mu}{T} \nabla T + \nabla \mu + e\mathbf{E}_0 \right) dE, \quad (\text{W7.6})$$

$$\mathbf{J}_Q = \frac{16\pi \sqrt{2m}}{3h^3} \int E^{3/2} (E - \mu) \tau(E) \frac{\partial f_0}{\partial E} \left(\frac{E - \mu}{T} \nabla T + \nabla \mu + e\mathbf{E}_0 \right) dE. \quad (\text{W7.7})$$

An expression for μ is given in Eq. (7.24). Evaluation of the integrals leads to the formulas

$$\mathbf{J} = \sigma \mathbf{E}_0 - \sigma S \nabla T, \quad (\text{W7.8})$$

$$\mathbf{J}_Q = \sigma S T \mathbf{E}_0 - \kappa \nabla T, \quad (\text{W7.9})$$

which are called the *Onsager relations*.

W7.2 Random Tight-Binding Approximation

In this section we study the behavior of $\rho(E)$ for a random one-dimensional solid. Two models for randomness are studied: the first with “bond” randomness and the second with “site” randomness. In the bond case the tunneling integral, t , varies randomly from bond to bond, but the site energy, ϵ , remains constant. As an example, let t assume two values, t_1 and t_2 , with probabilities p_1 and p_2 , respectively. Numerical results are displayed in Fig. W7.1, where results are shown for $\rho(E)$ for the case where $N = 125$ sites, $t_1 = 1$, $t_2 = 2$, and $p_1 = p_2 = \frac{1}{2}$. A suitable average over many independent configurations has been made. A comparison is made with the uniform case involving an average tunneling integral $\langle t \rangle = p_1 t_1 + p_2 t_2$. It is apparent that near the band center the densities of states are the same, while near the band edges the

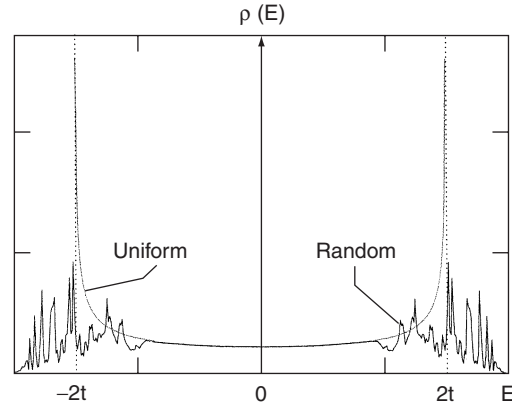


Figure W7.1. Comparison of electron densities of states for the random-bond and uniform one-dimensional solids.

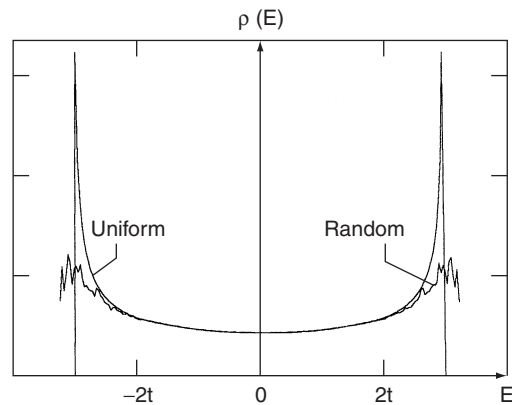


Figure W7.2. Comparison of electron densities of states for the random-site and uniform one-dimensional solids.

random solid exhibits an irregular behavior in contrast to the smooth but divergent behavior of the uniform solid.

In Fig. W7.2 the result for the random-site model is presented. In this model the site energy is allowed to have one of two values, ϵ_1 or ϵ_2 , with probabilities p_1 and p_2 , respectively. The tunneling integral is held fixed at $t = 1.5$. As before, there is some rough but reproducible behavior near the band edges. Note that in both the random-site and random-bond cases there is a tailing off of the density of states beyond the band edges.

W7.3 Kronig-Penney Model

An analytic solution to Bloch's difference equation can be found when all Fourier coefficients are equal (i.e., $V_G = U$) and the problem is one-dimensional. Then Eq. (7.54)

becomes

$$\left[\frac{\hbar^2}{2m}(\mathbf{k} + \mathbf{G})^2 - E \right] u_{\mathbf{G}}(\mathbf{k}) + U \sum_{\mathbf{G}'} u_{\mathbf{G}-\mathbf{G}'}(\mathbf{k}) = 0. \quad (\text{W7.10})$$

Let $S = \sum u_{\mathbf{G}}$. If $S = 0$, then $u_{\mathbf{G}} = 0$ and there is no nonzero solution. If $S \neq 0$, dividing by the first factor and summing over all \mathbf{G} yields

$$S + U \sum_{\mathbf{G}} \frac{1}{(\hbar^2/2m)(\mathbf{k} + \mathbf{G})^2 - E} S = 0. \quad (\text{W7.11})$$

This will have a non-trivial solution when

$$1 + U \sum_{\mathbf{G}} \frac{1}{(\hbar^2/2m)(\mathbf{k} + \mathbf{G})^2 - E} = 0. \quad (\text{W7.12})$$

In one dimension $G_n = 2\pi n/a$, where n is an integer, and the sum converges. The dispersion relations are given by the roots $E(k)$ of the equation

$$1 + \sum_{n=-\infty}^{\infty} \frac{U}{(\hbar^2/2m)(k + 2\pi n/a)^2 - E} = 0. \quad (\text{W7.13})$$

Note some simple properties of the left-hand side of this equation: (1) it is periodic under the replacement $k \rightarrow k \pm 2\pi/a$; (2) it is an analytic function of k except for simple poles at $k = -2\pi n/a \pm \sqrt{2mE/\hbar^2}$; and (3) as $k \rightarrow \pm i\infty$ in the complex plane, the left-hand side approaches 1. From the theory of complex variables (Carlson's theorem) it follows that these properties are uniquely shared by the function on the left-hand side of the following equation:

$$1 + \frac{Ua}{2\hbar} \sqrt{\frac{m}{2E}} \left\{ \cot \left[\frac{a}{2} \left(k - \sqrt{\frac{2mE}{\hbar^2}} \right) \right] - \cot \left[\frac{a}{2} \left(k + \sqrt{\frac{2mE}{\hbar^2}} \right) \right] \right\} = 0. \quad (\text{W7.14})$$

Letting $y = a\sqrt{2mE/\hbar^2}$, one has, after some trigonometric manipulation,

$$\cos ka = \cos y + \frac{ma^2 U}{4\hbar^2} \frac{\sin y}{y}. \quad (\text{W7.15})$$

It is important to note that the left-hand side of this equation is bounded by ± 1 . For arbitrary y , the right-hand side can exceed these bounds. No real solution is possible for such values. Thus there are certain y values, and consequently certain energies, for which no solution exists. These are called *forbidden bands* or *gaps*. Correspondingly, the regions of energy for which solutions exist are called *allowed bands*.

An example of the energy spectrum for the Kronig–Penney model is given in Fig. W7.3. As before, the energy gaps open at the boundaries of the first Brillouin zone. The Kronig–Penney model considered here corresponds to the case where the

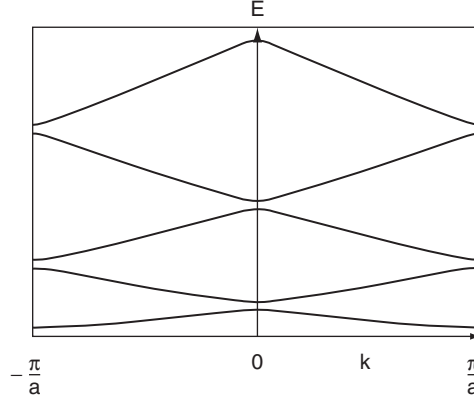


Figure W7.3. Energy spectrum for the one-dimensional Kronig-Penney model. Here $ma^2U/(4\hbar^2) = -10$.

potential consists of a periodic array of delta-function potentials for which

$$V(x) = U \sum_{n=-[N/2]}^{[N/2]} e^{i(2\pi n/a)x} = UN \sum_{n=-[N/2]}^{[N/2]} \delta_{x,na}, \quad (\text{W7.16})$$

where N has been assumed to be odd and $[N/2]$ stands for the integer part of $N/2$. It is also possible to formulate the Kronig–Penney model for the case of a periodic square-well potential.

W7.4 Hall Effect in Band Theory

A discussion of the Hall effect from the perspective of band theory predicts a more complicated behavior than that of classical Drude theory. The Boltzmann equation for the distribution function, f_n , in a given band n is

$$\mathbf{v}_n \cdot \nabla f_n + \mathbf{F}_n \cdot \frac{\partial f_n}{\partial \mathbf{p}} = -\frac{f_n - f_{n0}}{\tau_n(\mathbf{p})}, \quad (\text{W7.17})$$

with $\mathbf{F}_n = -e(\mathbf{E} + \mathbf{v}_n \times \mathbf{B})$ and $\mathbf{v}_n = \partial \varepsilon_n / \partial \mathbf{p}$ [see Eq. (W7.1)]. Henceforth the band index n will be suppressed. Equation (W7.17) is rewritten as

$$f = f_0 - \tau \mathbf{v} \cdot \nabla f + e\tau \mathbf{E} \cdot \frac{\partial f}{\partial \mathbf{p}} + e\tau \mathbf{v} \times \mathbf{B} \cdot \frac{\partial f}{\partial \mathbf{p}} \quad (\text{W7.18})$$

and is iterated to produce an expansion in increasing powers of the fields:

$$f = f_0 + e\tau \mathbf{E} \cdot \mathbf{v} \frac{\partial f_0}{\partial \varepsilon} + e^2 \tau \mathbf{v} \times \mathbf{B} \cdot \frac{\partial}{\partial \mathbf{p}} \left(\tau \mathbf{E} \cdot \mathbf{v} \frac{\partial f_0}{\partial \varepsilon} \right) + \dots \quad (\text{W7.19})$$

It is seen from this expression that filled bands do not contribute to the currents, since $\partial f_0 / \partial \varepsilon = 0$, and no current is supported by the equilibrium distribution. The current

density from Eq. (W7.4) is

$$\begin{aligned}\mathbf{J} &= -2e \int \frac{d\mathbf{p}}{h^3} f \mathbf{v} \\ &= \sigma \mathbf{E} - \frac{2e^3}{h^3} \int d\mathbf{p} \frac{\partial f_0}{\partial \varepsilon} \tau \mathbf{v} \mathbf{v} \times \mathbf{B} \cdot \frac{\partial}{\partial \mathbf{p}} (\tau \mathbf{E} \cdot \mathbf{v}).\end{aligned}\quad (\text{W7.20})$$

Attention here is restricted to the case of an isotropic metal. Assume $\tau = \tau(\varepsilon)$ and write $\mathbf{p} = m(\varepsilon)\mathbf{v}$, so

$$\mathbf{J} = \sigma \mathbf{E} + \lambda \mathbf{E} \times \mathbf{B}, \quad (\text{W7.21})$$

where

$$\lambda = \frac{2e^3}{3h^3} \int d\mathbf{p} \frac{\partial f_0}{\partial \varepsilon} \frac{(\tau v)^2}{m(\varepsilon)}. \quad (\text{W7.22})$$

In a multiband case one would sum this expression over all partially occupied bands. For a perpendicular geometry ($\mathbf{E} \perp \mathbf{B}$), the Hall coefficient may be expressed as

$$R_H = \frac{\lambda}{\sigma^2}. \quad (\text{W7.23})$$

The expression for λ shows that its magnitude and sign depends on the effective mass at the Fermi level. This mass may be either positive or negative, depending on the curvature of the energy band. For example, in the case of aluminum, the Fermi surface lies outside the first Brillouin zone and has contributions from the second, third, and fourth Brillouin zones. The net contributions from these bands produces a net positive value for the Hall coefficient, opposite to that predicted by the classical Drude theory. The Hall effect in semiconductors is discussed in Section 11.8.

W7.5 Localization

A measure of the ease with which a carrier can move through a crystal is the mobility $\mu = \langle v \rangle / E$, where $\langle v \rangle$ is the drift velocity and E is the electric field strength. In a metal the mobility is determined by the collision time through the formula $\mu = e\tau/m$. The connection between the mobility and the conductivity differs in two and three dimensions. In $d = 3$ the relation is $\sigma = ne\mu$, whereas in $d = 2$ it is $\sigma = Ne\mu$, where n and N are the number of electrons per unit volume and per unit area, respectively. Obviously, the units for are different in the two cases, being $\Omega^{-1} \text{ m}^{-1}$ and Ω^{-1} , respectively. For a thin film of thickness t , $n = N/t$.

In this section, disordered solids, in which the electron mean free path is determined by the amount of disorder, are studied. The mean free path is related to the collision time by $\lambda = v_F \tau$, v_F being the Fermi velocity. There is a minimum value that λ can have for the solid still to have finite conductivity. Ioffe and Regel[†] (1960) argued that for conductivity, the electron waves would have to be able to propagate throughout the metal. The presence of a mean free path introduces an uncertainty in the wave vector, $\Delta k \approx 1/\lambda$, as may be inferred from Heisenberg's uncertainty principle. However, for the wave vector to have a meaning, $\Delta k < k \approx k_F$. Using $mv_F = \hbar k_F$, this gives $\mu_{\min} = e/\hbar k_F^2$ as

[†] A. F. Ioffe and A. R. Regel, Prog. Semicond., **4**, 237 (1960).

the minimum metallic mobility. The Ioffe–Regel criterion for localization is $k_F\lambda < 1$. The Fermi wave vector is given by $k_F = (2\pi N)^{1/2}$ and $k_F = (3\pi n)^{1/3}$ for $d = 2$ and 3 , respectively. This implies the existence of a minimum metallic conductivity given by

$$\sigma > \sigma_{\min} \equiv \begin{cases} \frac{e^2}{2\pi\hbar} = \frac{1}{25,813 \, \Omega} & \text{if } d = 2, \\ \frac{e^2 k_F}{3\pi^2\hbar} & \text{if } d = 3. \end{cases} \quad (\text{W7.24a})$$

$$(\text{W7.24b})$$

Note that in $d = 2$, σ_{\min} is independent of the properties of the metal. In $d = 3$, $\sigma_{\min} = 1.12 \times 10^5 \, \Omega^{-1}\text{m}^{-1}$ for Cu, compared with $\sigma = 5.88 \times 10^7 \, \Omega^{-1}\text{m}^{-1}$ at $T = 295 \, \text{K}$.

Quantum-mechanical effects modify the classical Drude expression for the conductivity. For weak disorder the rate for elastic backscattering is enhanced due to constructive interference of direct and time-reversed scattering events. Thus, suppose that there is a sequence of scattering events for the electron from ion sites labeled A, B, C, ..., X that lead to the electron being backscattered. The time-reversed scattering sequence, X, ..., C, B, A, also leads to backscattering of the electron. In quantum mechanics one must add together all amplitudes for a given process to determine the total amplitude. Adding the above-mentioned amplitudes before squaring leads to constructive interference and an enhanced backscattering. If the backscattering is increased, probability conservation implies that it comes at the expense of forward scattering, and hence the conductivity. This effect is called *weak localization*. One may show that the conductivity change is approximately

$$\frac{\Delta\sigma}{\sigma} \approx -\frac{3}{\pi(k_F\lambda)^2}. \quad (\text{W7.25})$$

Suppose that one looks at impurities in a solid with a distribution of electron site energies $\{E_i\}$ whose width is W . The sites are coupled by tunneling matrix elements, which decay exponentially with distance. In the familiar tight-binding model, all the site energies are degenerate and the bandwidth, B , is determined by the NN tunneling matrix element. All the states are extended Bloch waves and the conductivity is infinite.

In the disordered solid, things are not as simple. For conduction to occur, an electron must tunnel from one site to another, and this requires a mixing of the local site wavefunctions. From perturbation theory, two conditions must be satisfied for this to occur: There must be a sizable tunneling matrix element connecting the sites, and the energy difference between the site levels must be very small. These conditions are not likely to occur simultaneously for any given pair of states. The problem is to explore this competition as the size of the system becomes large. This is usually best done by computer experiment. The results depend on the dimensionality of the system.

As disorder is introduced, some of the states separate from the allowed band and reside in what was previously the forbidden region (e.g., the bandgap). This phenomenon was seen in the discussion of the one-dimensional tight-binding solid when randomness was present and there was an irregular component to the density of states (see Section W7.2). These states are localized in space, meaning that their wavefunctions die off rapidly with distance away from a given point in the crystal. As more disorder is introduced, some of the previously occupied band states are converted to localized states. The line of demarcation between the localized and extended states is called the *mobility edge*. With increasing disorder, W is increased, and a critical value

of W/B is ultimately reached for which all states become localized. This is called the *Anderson localization transition*. The solid then becomes an insulator.

An estimate of the critical value of W/B can be made as follows. For electrons to hop from site to site, one needs degeneracy. What determines whether two states are degenerate or not is the size of the tunneling matrix element t compared with their energy separation ΔE . If t is larger than ΔE , the states will mix and one may consider them to be effectively degenerate. Since W represents the full spread of site energies, the probability that two states will be “degenerate” is given by $p = 2t/W$. Delocalization may be interpreted as a percolation phenomenon and it is possible for the electron to propagate a large distance by following a percolation cluster. In the discussion of percolation in Section 7.16 it was found that the percolation transition occurs when $p = d/Z(d-1)$ [see Eq. (7.130)]. It was also found in the discussion of the tight-binding approximation in Section 7.9 that the bandwidth is $B = 2Zt$ [see Eq. (7.94)]. Thus the transition occurs when

$$\frac{W}{B} = \frac{d-1}{d}. \quad (\text{W7.26})$$

For $d = 3$ this gives $B/W = 1.5$, in rough agreement with computer experiments. For $B/W < 1.5$ the states are localized, while for $B/W > 1.5$ they are extended. For $d = 1$ the critical value of B/W is infinite, meaning that unless $W = 0$, all states will be localized.

It is also useful to compare this formula to the Ioffe–Regel criterion. A measure of the size of the bandwidth B is the Fermi energy. For example, a metal with a half-filled band would have $B \approx 2E_F$, where the Fermi energy is measured with respect to the bottom of the band. If the mean free path is λ , one may think of the electron as effectively bound in a spherical box of mean size λ . The confinement energy would then be a measure of the spread of energies brought about by the inhomogeneities, so $W \approx \hbar^2/2m\lambda^2$ since $k \approx 1/\lambda$. Combining these formulas with Eq. (W7.26) and using $E_F = \hbar^2 k_F^2/2m$ gives the condition when localization occurs as

$$k_F \lambda < \sqrt{\frac{d}{2(d-1)}}. \quad (\text{W7.27})$$

Note that in $d = 3$, $k_F \lambda < \sqrt{3/4} \approx 1$. For a metal such as Cu, $k_F \approx 5/a$, where a is the lattice constant, and so $\lambda < a/5$ for localization of electrons to occur.

It must be cautioned, however, that the current theoretical picture is not completely understood. There are theoretical arguments based on single-electron scattering from random potentials which say that in two dimensions there is only localization. There are also some experiments that seem to point to the existence of conductivity in two dimensions. There are also recent experiments suggesting that the M–I transition may be associated with the formation of a Wigner crystal (i.e., a two-dimensional crystallization of the electrons). Just what possible role many-body effects play in conductivity has yet to be clarified.

There are two factors involved in localization. One is, as has been seen, percolation. The other is phase interference of electrons traveling along different paths but connecting the same pair of points. In a random medium the phase differences

can be quite large, resulting in destructive interference. The effects of phase interference in lower dimensions are more extreme and may contribute to suppression of the conductivity.

W7.6 Properties of Carbon Nanotubes

Termination of Nanotubes. The nanotube must be capped at both ends for it not to have dangling bonds. An understanding for how this capping comes about can be had from examining Euler's theorem. Consider a polyhedron with N_v vertices, N_f faces, and N_e edges. Then for a simply connected body, $N_e - N_f - N_v = -2$. It will be assumed that each vertex connects to three adjoining polygons and each edge to two adjoining polygons. Let N_i denote the number of i -sided polygons in the structure. Then

$$N_e = \frac{1}{2} \sum_{i=3}^{\infty} i N_i, \quad (\text{W7.28a})$$

$$N_v = \frac{1}{3} \sum_{i=3}^{\infty} i N_i, \quad (\text{W7.28b})$$

$$N_f = \sum_{i=3}^{\infty} N_i. \quad (\text{W7.28c})$$

Combining these equations with Euler's theorem gives

$$\sum_{i=3}^{\infty} (i - 6) N_i = -12. \quad (\text{W7.29})$$

For example, using only pentagons with $i = 5$ to terminate the ends of the nanotube, then $N_5 = 12$ and $N_i = 0$ for $i \neq 5$. Thus six pentagons are needed at each end since only half of the 12-sided polyhedron is needed. The fullerene molecule C_{60} has $N_5 = 12$ and $N_6 = 20$, so $(N_e, N_v, N_f) = (90, 60, 32)$.

Conductivity of Carbon Nanotubes. Adding a single electron to the nanotube costs electrostatic charging energy $E_c = e^2/8\pi\epsilon_0 C$, where C is the capacitance (relative to infinity) of the nanotube ($\approx 3 \times 10^{-17}$ F). Unless the potential bias across the tubule satisfies the condition $-eV + E_c < 0$, no current will flow. One refers to this as a *Coulomb blockade*. Similar phenomena occur in granular metals. However, if a quantum state of the wire overlaps the occupied states of one electrode and an empty state of the second electrode, conduction can occur via resonant tunneling through the quantum state. In this case there is zero-bias conductance. The conductance will be temperature dependent, being proportional to

$$\begin{aligned} G &\propto \int dE \int dE' \rho(E) \rho(E' + V) f(E) [1 - f(E' + V)] \delta(E - \Delta E) \delta(E' - \Delta E + V) \\ &\propto \text{sech}^2 \left[\frac{\beta}{2} (\Delta E - \mu) \right], \end{aligned} \quad (\text{W7.30})$$

where the value of the quantum energy level relative to the chemical potential can be changed by a gate voltage $\Delta E - \mu = e\Delta V_{\text{gate}}/\alpha$, α being a constant determined by capacitance ratios. Thus there is a rapid variation of conductance with gate voltage.

Appendix W7A: Evaluation of Fermi Integrals

The Fermi integral to be evaluated is

$$I_j(\beta, \beta\mu) = \int_0^\infty \frac{E^{j+1/2}}{e^{\beta(E-\mu)} + 1} dE. \quad (\text{W7A.1})$$

Let $x = \beta(E - \mu)$, so

$$I_j(\beta, \beta\mu) = \int_{-\beta\mu}^\infty \frac{dx}{\beta} \frac{(u + x/\beta)^{j+1/2}}{e^x + 1}. \quad (\text{W7A.2})$$

Integrate this by parts to obtain

$$I_j(\beta, \beta\mu) = \frac{1}{(j + \frac{3}{2})\beta^{j+3/2}} \int_{-\beta\mu}^\infty (\beta\mu + x)^{j+3/2} \frac{e^x}{(e^x + 1)^2} dx. \quad (\text{W7A.3})$$

Make a power series development in x and extend the lower limit of the integral to $-\infty$, to obtain

$$I_j(\beta, \beta\mu) = \frac{1}{(j + \frac{3}{2})\beta^{j+3/2}} \int_{-\infty}^\infty \left((\beta\mu)^{j+3/2} + \frac{1}{2} \left(j + \frac{3}{2} \right) \left(j + \frac{1}{2} \right) \right. \\ \left. \times (\beta\mu)^{j-1/2} x^2 + \dots \right) \frac{e^x}{(e^x + 1)^2} dx, \quad (\text{W7A.4})$$

where the term linear in x integrates to zero. The integrals required are

$$\int_{-\infty}^\infty \frac{e^x}{(e^x + 1)^2} dx = 1, \quad (\text{W7A.5})$$

$$\int_{-\infty}^\infty \frac{x^2 e^x}{(e^x + 1)^2} dx = 2 \int_0^\infty \frac{x^2 e^{-x}}{(1 + e^{-x})^2} dx = 2 \int_0^\infty dx x^2 \sum_{n=1}^\infty (-)^{n+1} n e^{-nx} \\ = 4 \sum_{n=1}^\infty \frac{(-)^{n+1}}{n^2} = \frac{\pi^2}{3}. \quad (\text{W7A.6})$$

The final result is

$$I_j(\beta, \beta\mu) = \frac{1}{(j + \frac{3}{2})\beta^{j+3/2}} \left[(\beta\mu)^{j+3/2} + \frac{\pi^2}{6} \left(j + \frac{1}{2} \right) \left(j + \frac{3}{2} \right) (\beta\mu)^{j-1/2} + \dots \right]. \quad (\text{W7A.7})$$

Using Eq. (W7A.7), two useful formulas may be derived. If $\psi(E)$ is a function of the form $\psi(E) = \sum p_j E^{j+1/2}$ with $j \geq 0$, then

$$\int_0^\infty \psi(E) f(E, T) dE = \int_0^\mu \psi(E) dE + \frac{\pi^2}{6} k_B^2 T^2 \left. \frac{\partial \psi}{\partial E} \right|_{E=\mu} + \cdots, \quad (\text{W7A.8})$$

where $f(E, T)$ is the Fermi–Dirac distribution. Also, letting $\psi(E) = \partial \phi(E)/\partial E$ and integrating by parts, one obtains

$$\int_0^\infty \phi(E) \frac{\partial f(E, T)}{\partial E} dE = -\phi(\mu) - \frac{\pi^2}{6} k_B^2 T^2 \left. \frac{\partial^2 \phi}{\partial E^2} \right|_{E=\mu} + \cdots. \quad (\text{W7A.9})$$