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Electric Conductivity of Solid Metals

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Electric Conductivity of Solid Metals

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Abstract. This paper was written to graduate and postgraduate students of Physics and Engineering to show the fundamental aspects of the electric conductivity in solid metals. The classical Drude's model and the Bloch quantum theory of bands are briefly analyzed. We see that the measured resistivity $\rho(T)$ can be satisfactorily explained only using quantum mechanics and taking into account the electron - phonon interaction. The resistivity $\rho(T)$ is calculated using the Schrödinger equation and the Second Quantization approach.

Key words: *electrical resistivity in metals; phonons; electron-phonon interaction.*

(I) Introduction.

This paper was written to graduate and postgraduate students of Physics and Engineering analyzing and clarifying fundamental aspects of the electric conductivity in metallic solids. Basic ideas are found in many textbooks of physics.^[1-4] We study here the phenomenon in simple metallic conductors^[5,6] like copper, silver, gold, sodium, magnesium, zinc, nickel, aluminum, tin and lead, at ambient temperatures and at low temperatures, respectively. In Section 1 is briefly show how the resistivity is calculated in basic courses using a classical model and that there is satisfactory agreement between theory and experiment. In next Sections we show that it is necessary to use Quantum Mechanics to explain satisfactorily the electrical conductivity at ambient and at low temperatures. In Section 2 we see that due to the interactions with the atoms the electrons energies are distributed in **energy bands (valence and conduction bands)**; electrons that occupy the **conduction bands** (named “*nearly free*” electrons) are responsible for the electrical conductivity. In Section 3 is presented the illuminating Bloch quantum approach that is also unable to describe the resistivity process. Since the electronic motion is a non-equilibrium process in Section 4 are given the main features of the theoretical approach known as “Boltzmann Transport Equation” (BTE). In Section 5 are remembered the main features of the elastic vibrations in solids or “phonons”. In Section 6 using the BTE and taking into account the electron-phonon interaction we verify that it is possible explain satisfactorily the resistivity phenomena. The resistivity estimations have been performed using the Schrödinger equation in Section 6 and the Second Quantization approach in Appendix C.

(1) Classical Model for the Electric Conductivity in Metals.

According to the classical model or Drude's model for the electric conduction seen in basic physics courses^[1-4] the "conductor" is a metallic solid where are present "free electrons" named "conduction electrons". This theory is incorrect in many respects, despite the fact that it gives several rather convincing results.^[5,6] This solid with volume V can be amorphous or composed by a regular lattice of N stationary atoms. The free electrons are as numerous as the number N of atoms of the solid and are considered as an "ideal gas" ("ideal electron gas") obeying the Maxwell-Boltzmann distribution at a temperature T . These electrons confined in a volume V are chaotically colliding with the atoms of the solid. If there is no external electric field \mathbf{E} the average velocity $\langle \mathbf{v} \rangle$ of the electrons is equal to zero and there is no net electric current in the conductor. However, when an electric field \mathbf{E} is applied besides the thermal chaotic motion the electrons suffer a slow drift in the opposite direction of \mathbf{E} with a "drift velocity" \mathbf{v}_d given by $\mathbf{v}_d = (e\mathbf{E}/m)\tau$, where e and m are charge and mass of the electron, respectively, and τ is mean free time between two successive collisions. In these conditions the density of current \mathbf{J} is given by $\mathbf{J} = ne\mathbf{v}_d = (ne^2\tau/m)\mathbf{E}$, where $n = N/V$ is the electronic density. According to Ohm's law $\mathbf{J} = \sigma \mathbf{E}$ we verify that the electrical conductivity σ is given by $\sigma = ne^2\tau/m$ and that the electrical resistivity ρ is equal to $\rho = 1/\sigma = m/ne^2\tau$. Since^[1-4] $\tau = \lambda/v$, where λ is the mean free path between two collisions and $v = (8k_B T/\pi m)^{1/2}$ is the average velocity and k_B the Boltzmann constant, the *classical* resistivity would be given by $\rho(T) = (m/ne^2)(v/\lambda)$. As $\lambda = 1/n_a\pi d^2$, where n_a is the density of atoms and d is atomic radius, we verify that the classical resistivity $\rho(T)$ would be given by, assuming that $n_a = n = (N/V)$,

$$\rho(T) = (m/ne^2)(v/\lambda) = (mv/ne^2)n_a\pi d^2 = (mv/e^2)\pi d^2 = \sqrt{8\pi m k_B} (d/e)^2 \sqrt{T} \quad (1.1).$$

High temperature experiments^[7,8] show that $\rho(T)$ is proportional to T , for low temperatures it is proportional to T^5 and that for very low temperatures, that is, for T approaching the absolute zero it tends to a finite non-zero value. This non-zero residual resistivity is due essentially to collisions between electrons and impurities or imperfections of the metal (see Section 4). Conductors that obey the condition $\rho(T) \rightarrow 0$ when $T \rightarrow 0$ K are called *superconductors*.^[7,8]

Drude's model is consistent with Ohm's law, explains qualitatively the phenomenon of electrical resistivity and gives good values for the conductivity.^[1-8] However, it has severe limitations like, for instance, to explain the observed $\rho(T)$ temperature dependence. In next Sections we show that to get a satisfactory description of the $\rho(T)$ temperature dependence resistivity it is necessary to adopt a quantum mechanical approach.

(2) Quantum Mechanical Approach.

As pointed out above, despite the successes of Drude's model there are many features of the electrical conductivity of solids that cannot be explained by this model.^[5-8] To satisfactorily explain the experimental results the electrical conductivity phenomenon must be analyzed within the framework of the quantum mechanics. In this Section is shown that the energies of the electrons in a solid conductor, due to the interaction between the N atoms of the solid, are confined in **energy bands**. In particular, we show that the "free electrons" of Section 1 taken as responsible for the electrical conductivity are localized in particular bands named **conduction bands**.

Electronic Energy Bands

The **electronic energy bands** are created by the many body interaction among the N atoms in a solid metal. As is known,^[1-8] electrons of a single isolated atom occupy a discrete set of energy levels. Measuring the energies of electrons in an isolated atom, we do not find a continuous distribution of energies, but a set of quantized energies. This discrete energy levels model can also be applied to simple compound molecules as can easily be verified by analyzing the emission and absorption spectra of gases. These levels are indicated by $1s$, $2p$, $3s$,... Figure 1^[6] shows the energy levels $1s$, $2s$ and $3s$ of one electron bounded in an isolated atom. Note that the electrons are localized about the single atom.

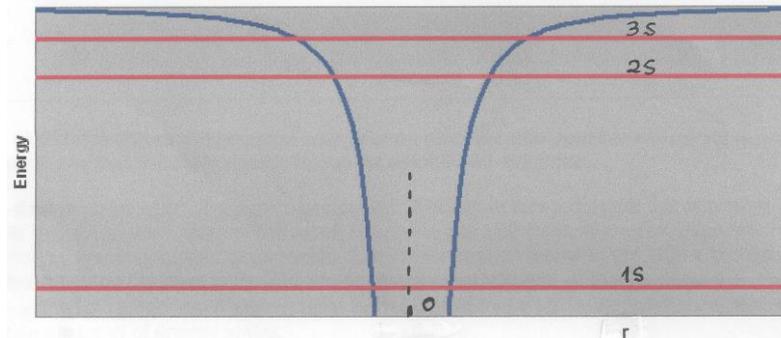


Figure 1. The curved blue lines represent the attractive interaction potential well and the horizontal red lines represent the energy levels $1s$, $2s$ and $3p$ of a bounded electron.

When 2 atoms, initially isolated, are brought close their energy levels become degenerate creating 2 separate energy levels. The division of the original energy level increases when the number atoms put together increases. When this procedure is repeated N times (that is, $N \sim 10^{23}$) each energy level will split into N levels, effectively forming a **continuous band of allowed energy states**. In Figure 2 is shown what occurs, for example, with the level $3s$.^[3] Note that when the distance between the atoms decreases the energy of the new levels increases.

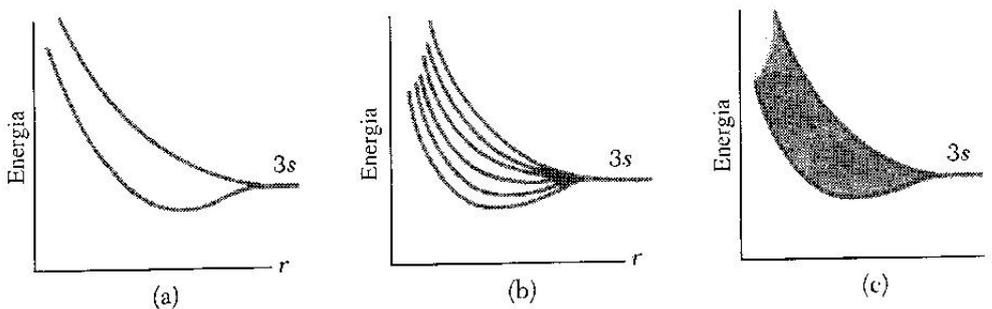


Figure 2. Division of the level $3s$ when N atoms are put together as a function of the distance r between them: (a) $N = 2$, (b) $N = 6$ and (c) $N \gg 1$.

The energy of the more tightly bound electrons changes very little and these electrons remain localized about a single atom. The bands of localized electrons are called **valence bands**. The less tightly bound electrons do not remain localized forming **delocalized bands** with allowed values of energy usually higher than the initial isolated

atomic states $n\ell$. In Figure 3^[6] is illustrated a simple case with 3 bands, one **valence band** (bellow) and two **delocalized bands** (above).

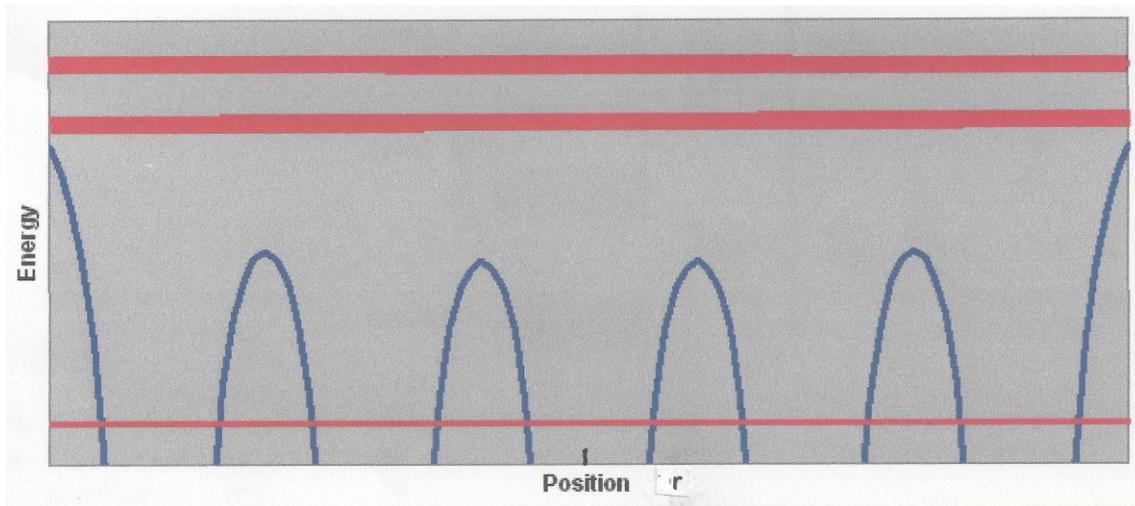


Figure 3. Energy bands: 1 **valence band** (bellow) and 2 **delocalized bands** (above).

There may be an infinite number of **bands** in the band structure of a given material. The **bands** are separated by **gaps**. Electrons cannot have energies that would fall into the **gaps**. **Gaps** are also called **forbidden bands**. Note that in a **band** $n\ell$ there are at most $2(\ell+1)$ electrons. The electrons of a **valence band** are localized close to the atoms and the electrons of the **delocalized bands** are uniformly distributed in the volume V . The **valence bands** are completely filled with electrons and the **delocalized bands** can be completely or partially filled with electrons or completely empty. To illustrate our analysis let us consider the solid sodium usually taken as an example of metallic conductor. Figure 4 shows some **bands** of the solid sodium with N atoms. Let us remember^[1-4] that the electronic configuration of the Na atom is $1s^2 2s^2 2p^6 3s^1$.

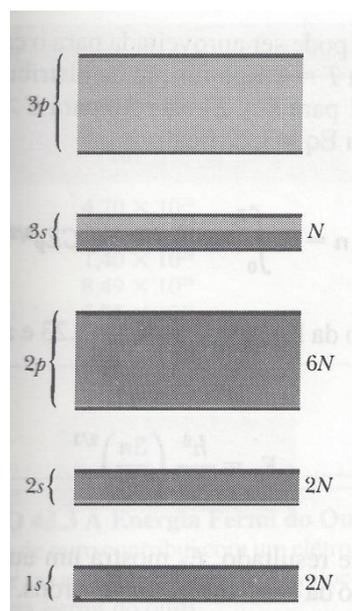


Figure 4. Some **energy bands** of the solid sodium with N atoms.^[3] Between two **bands** are seen the **gaps**.

The bands 1s, 2s and 2p are completely filled, respectively, with 2N, 2N and 6N electrons, according to the capacity relation $2(\ell+1)N$. Since the sodium has *only one 3s valence electron* the 3s **band** is only partially filled with only N electrons instead of 2N. The 3p, 4p, ... **bands** are completely empty. The partially filled and completely empty bands are named **conduction bands**. The electrons of a partially filled band form an **ideal Fermi-Dirac gas**. The energies of these electrons at $T = 0$ K go from 0 up to the maximum value given by the Fermi energy ^[1-4] $E_F = (\hbar^2/2m)(3n/8\pi)^{2/3}$, where m is the electron mass and $n = N/V$.^(*) All energy levels below the E_F are occupied and the energy levels above are empty. When an electrical field **E** is applied the electrons close to the Fermi energy only need a very small additional quantity of energy to attain the neighbor energy states and empties creating an electric flux $\mathbf{J} = \sigma\mathbf{E}$. If all states in a band are occupied, no net movement of electrons can occur and the band cannot contribute to the conduction current. For $T > 0$ K some electrons that due to the thermal excitation also occupy the empty levels contribute to increase **J**.

(*)The determination of the Fermi energy for Au, for instance, is more difficult because the states arising up to 5p levels of the atom will be completely filled. Only 5d and 6s levels of the atom are expected to form the conduction band. Hence while finding the Fermi energy we take into account only the ten d electrons and one s electron per atom. ^[19]

(3) Bloch Quantum Approach.

The first person to tackle the problem of the **energy bands** was F. Bloch in 1925 studying the motion of electrons in solids with periodic perfect lattices. He developed a quantum model known as **Bloch's model**^[7-9] to explain the **energy bands**. To explain the **valence bands** he combined electronic atomic orbitals, each localized on a particular atom, to represent a state running throughout the crystal. Indicating by $\phi_a(\mathbf{r} - \boldsymbol{\ell})$ the atomic orbital for a free atom with center at $\boldsymbol{\ell}$ he assumed that electron submitted to a periodic crystal $\mathbf{V}(\mathbf{r}) = \mathbf{V}(\mathbf{r}+\mathbf{a})$, where **a** is the lattice periodicity, is represented by a wavefunction

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_{\boldsymbol{\ell}} \exp[i\mathbf{k}\cdot\boldsymbol{\ell}] \phi_a(\mathbf{r} - \boldsymbol{\ell}). \quad (3.1).$$

This function looks like a series of strongly localized atomic orbitals multiplied by wave phase factors $\exp[i\mathbf{k}\cdot\boldsymbol{\ell}]$. Within each atom the local orbital predominates and outside the atom the wave behavior predominates. With this good ansatz and using the Schrödinger equation with the periodic potential $\mathbf{V}(\mathbf{r})$ one can evaluate the **valence bands**.^[7,8] This approach known as **tight-binding model** will not be analyzed here. We will study only the **conduction bands** using the **nearly-free electron** approach.

In Section (2) we learned that the conductivity is due to a flux of “free electrons” in the **conduction band** due the application of an electrical field on the conductor. It is assumed that the number of free electrons in the conduction band is small so that the electric interactions and exchange effect ^[9-11] between them can be neglected. These electrons, however, are not “free” because they move inside a solid. To study the motion of these electrons in a perfect lattice crystal Bloch developed the **nearly-free electron** approach. In this approach the electrons with energy $E = \hbar\mathbf{k}^2/2m$ move in the crystal submitted to a weak attractive periodic potential $\mathbf{V}(\mathbf{r})$ created by static ions. We analyze here only the simplest case of a **one-dimensional** lattice. In Figure 5 is illustrated a one-dimensional periodic potential $V(x)$ with rectangular sections with height V_0 and period length a .

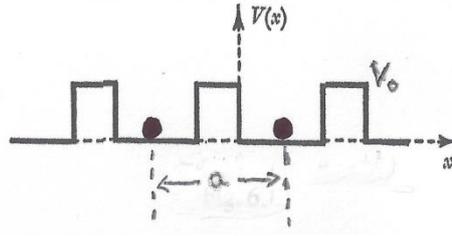


Figure 5. One-dimensional potential $V(x)$ with rectangular sections with period length a .

In this case the electron $\psi_k(x)$ obeys the Schrödinger equation

$$d^2\psi_k(x)/dx^2 + (2m/\hbar^2)[\epsilon(k) - V(x)]\psi_k = 0 \quad (3.1),$$

where $\epsilon(k) = \hbar^2 k^2 / 2m > V_0$ and $V(x) = V(x + a)$. If $V(x) = 0$ the electron is represented by plane waves $\psi_k(x) = \exp(ikx)/\sqrt{L}$, where $L = Na$ is the 1-dimensional crystal length.

If $V(x)$ is weak, using the perturbation theory,^[9-11] the new wavefunctions $\Psi_k(x)$ and energies $E(k)$ are given, respectively, by

$$\Psi_k = \psi_k + \sum_{k'(\neq k)} V_{k'k} \psi_{k'} / [\epsilon(k) - \epsilon(k')] \quad \text{and} \quad (3.2a)$$

$$E(k) = \epsilon(k) + V_{kk} + \sum_{k'(\neq k)} |V_{k'k}|^2 / [\epsilon(k) - \epsilon(k')] \quad (3.2b),$$

where $V_{k'k} = \langle k' | V(x) | k \rangle$ and $V_{kk} = 0$ using a convenient normalization of the potential. Due to the $V(x)$ periodicity the matrix elements $V_{k'k}$ vanish always except when

$$k - k' = g = (2\pi/a)m, \quad m = \pm 1, \pm 2, \dots \quad (3.3).$$

Thus, in order to simultaneously satisfy (3.2a) and (3.3) we must have $\epsilon(k) = \epsilon(k' = k - g)$. That is, the energy spectrum is 2-fold degenerate. So, to solve the problem^[9-11] we write in the zeroth order approximation $\Psi_k^{(0)}$ as a linear combinations of the degenerate states

$$\Psi_k^{(0)} = A \psi_k + B \psi_{k-g} \quad (3.4).$$

Using the 2-fold degenerate approach^[9-11] it can be shown that the two normalized resulting zero-order wavefunctions are given by the **standing waves**^[7,8]

$$\begin{aligned} \Psi_k^-(x) &= \sqrt{2} \cos(gx/2) = \sqrt{2} \cos(\pi mx/a) \\ \text{and} \\ \Psi_k^+(x) &= \sqrt{2i} \sin(gx/2) = \sqrt{2i} \sin(\pi mx/a) \end{aligned} \quad (3.5),$$

with energies $E_{\pm}(k)$ given by

$$E_{\pm}(k) = \epsilon(k) \pm \sqrt{|V_g|^2} \quad (3.6).$$

where

$$V_g = \langle k | V(x) | k - g \rangle = \int_{-\infty}^{+\infty} V(x) \exp(igx) dx$$

The functions $|\Psi_k^+(x)|^2$, $|\Psi_k^-(x)|^2$ and the periodic potential $V(x)$ are shown in Fig.6.^[8]

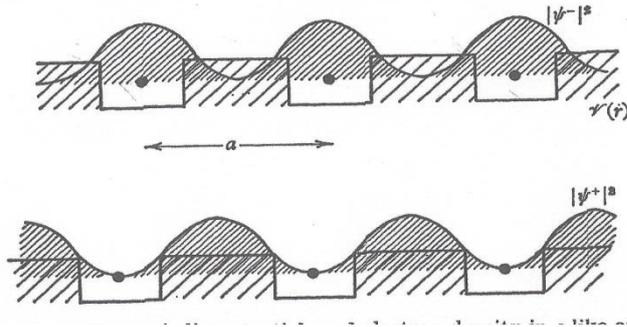


Figure 6. The periodic potential $V(x)$ and the functions $|\Psi^+(x)|^2$ and $|\Psi^-(x)|^2$. In the state $\Psi^-(x)$ the electron is more concentrated on the atoms than in the states $\Psi^+(x)$.

Note that $V_g \neq 0$ only for $g = (2\pi/a)m$ ($m = \pm 1, \pm 2, \dots$). For these particular values there are energy **gaps** Δ given by

$$\Delta = E_I - E_{II} = 2 |V_g|.$$

The energies $E(k)$ as a function of $k = \pi m/a$ in Figure 7 shown how the parabolic free electron energies $\varepsilon(k) = \hbar^2 k^2 / 2m$ are modified by the periodic lattice. At the points $k = \pi m/a$ ($m = \pm 1, \pm 2, \dots$) are located the **energy gaps** Δ in the conduction band.

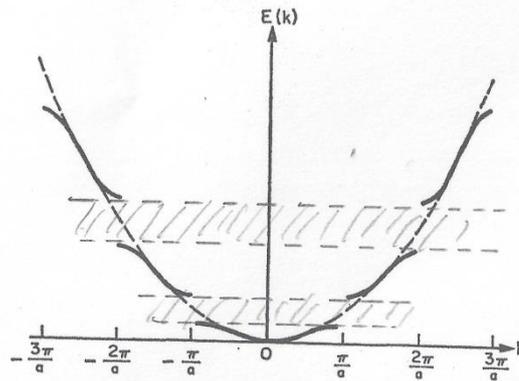


Figure 7. Electron energies $E(k)$ in one-dimensional lattice showing the **allowed energy bands** and the **forbidden energy bands** or, simply, **gaps** (dashed regions).^[9]

So, we verify that in a perfect crystal lattice electron move, without being deflected at all, with energies $\varepsilon(k) = \hbar^2 k^2 / 2m$ that are only inside the **allowed energy bands**. They cannot move with energies outside the allowed bands, that is, energies that are inside the **forbidden bands** or **gaps**. Since the resistivity is due only to the scattering of electrons by the atoms (ions) perfect lattices offer no resistance to an electrical current. In this way it is necessary to find a new alternative model. Probably the flaw in our reasoning is that it was assumed that the crystal is perfect. Imperfections in the crystal will cause the electrons deflections so the mean free path in an imperfect crystal is not infinite and, consequently, the material has a non-zero resistance. Essentially three different types of imperfections can produce electron scattering:^[5-9]

(a) Ions are not stationary but in a state of **continual thermal vibration** about their equilibrium positions. At any instant of time they are not occupying the positions of a perfect lattice, electrons are scattered due to these vibrations giving rise to a resistance.

(b) Scattering produced by the presence **impurities**. This is particularly significant if the impurity is much larger or smaller than the host ions or if it has a different valence. For

example, in brass, which is a copper-zinc alloy, the zinc ions are about 9% larger in diameter than the copper ions and have a charge of +2e compared with +1e on the copper ions.

(c) Scattering caused by **imperfections** in the crystal structure that disrupt the lattice.

(3.a) Conclusions.

Bloch's model of **nearly-free electron** does not explain the electric resistance in metals. Thus, it would be necessary to take into account the scattering of electrons by processes like (a), (b) and (c), pointed above. In Section 4 are proposed mechanisms where electron scattering is produced by impurities or due to the vibrations of atoms occupying the positions of a perfect lattice.

(4) Electrical Resistivity: a Non-Equilibrium Phenomenon.

Let us assume that the electronic motion in a conductor is only produced by an applied electric field **E**. Since the motion of conducting electrons is a non-equilibrium phenomenon the Boltzmann Transport Equation (BTE) theory will be adopted to estimate the electrical resistivity. So, it can be shown^[1-7,8,12] that the resistivity ρ is given by

$$\rho = (m^*/ne^2) (1/\tau) = (m^*/ne^2) (v_F/\Lambda) = (m^*v_F/ne^2)(1/\Lambda) \quad (4.1),$$

where n the density of electrons at the conduction band, m^* the effective electron mass (see Appendix A), τ is *mean free time* between two successive collisions, v_F is the velocity of the electrons at Fermi level and $\Lambda = v_F\tau$ is the electron *mean free path* between two collisions.

According to the BTE approach $1/\tau$ is proportional to the total electronic scattering transition probability per unit of time^[7,8,12] $P_{\mathbf{k}\mathbf{k}'} = P(\mathbf{k} \rightarrow \mathbf{k}') = P(\mathbf{k}' \rightarrow \mathbf{k})$. For instance, for very thin metallic films when the bulk resistivity is negligible ρ is due only to the scattering produced by the surface roughness of the films.^[12] In this paper will be assumed that the bulk resistivity is dominant. So, ρ is generated by (a) *impurities* or (b) *atoms and phonons*. In these cases $1/\Lambda$ can be written as^[12]

$$1/\Lambda = (2\pi N^*/J) \int_0^{2\pi} (d\Pi_{\mathbf{k}\mathbf{k}'}(\varepsilon, \theta)/d\Omega) (1 - \cos\theta) \sin\theta d\theta \quad (4.2),$$

where N^* is the density of scattering centers, $|J|=J$ the flux of incident electrons, $d\Pi_{\mathbf{k}\mathbf{k}'}(\varepsilon, \theta)/d\Omega$ is the scattering probability per unit of time due to: (a) only *atoms (ions)*; (b) *atoms and phonons*, $\varepsilon = (\hbar\mathbf{k})^2/2m^*$ is the energy of the incident electron ($\varepsilon = \varepsilon_F$), θ is the scattering angle between \mathbf{k} and \mathbf{k}' and $d\Omega$ is the element of solid angle.

(4.1) Resistivity due to Impurities.

If N_i is the density of atomic (or ionic) impurities in the crystalline array the transition probabilities $\mathbf{k} \rightarrow \mathbf{k}'$ per unit of time ($d\Pi_{\mathbf{k}\mathbf{k}'}/d\Omega$) is given by (see Appendix B):

$$(d\Pi_{\mathbf{k}\mathbf{k}'}/d\Omega) = (dP_{\mathbf{k}\mathbf{k}'}/d\Omega) = v (d\sigma(\varepsilon, \theta)/d\Omega) \quad (4.3),$$

where $v = \hbar\mathbf{k}/m^*(=v_F)$, $\varepsilon = (\hbar\mathbf{k})^2/2m^*(= \varepsilon_F)$, $d\sigma(\varepsilon, \theta)/d\Omega$ is the scattering cross section due to an impurity and $d\Omega = \sin\theta d\theta d\phi$ is the element of solid angle. In what follows, to simplify the notation, we put $d\sigma(\varepsilon, \theta)/d\Omega \equiv \sigma(\theta)$. Taking into account (4.2) and Appendix B the mean free Λ_i is given by^[12]

$$1/\Lambda_i = 2\pi N_i \int_0^{2\pi} \sigma(\theta) (1 - \cos\theta) \sin\theta d\theta \quad (4.4).$$

Supposing that the potential of a charged impurity in a metal is screened^[7-11] its interaction with the conducting electron is given by

$$U(r) = (Ze^2/r) \exp(-\lambda r) \quad (4.5),$$

where Z is the charge of the impurity and λ is range of the interaction potential.^[7-11] Taking into account $U(r)$ defined by (4.5) one can show that the (elastic) differential collision cross section $\sigma(\theta)$ is given by^[8-11]

$$\sigma(\theta) = (2m^*Ze^2/\hbar^2)^2 / (K^2 + \lambda^2)^2 \quad (4.6),$$

where $K = 2k_F \sin(\theta/2)$ is momentum change in the collision and $k_F = m^*v_F/\hbar$. From (4.3), (4.4) and (4.6) the resistivity ρ_i due to *impurities* is given by

$$\rho_i = (m^*v_F/n e^2) 2\pi N_i \int_0^{2\pi} \sigma(\theta) (1 - \cos\theta) \sin\theta d\theta \quad (4.7).$$

Eq. (4.7) will be estimated taking $1/\lambda \sim a$ where a is the “radius” of the ion (radius of the electron cloud that screens the ion) and assuming that $k_F/\lambda \sim k_F a \gg 1$. In this case we get^[8]

$$\rho_i \approx (m^*v_F/n e^2) N_i \{4\pi m^* Z^2 e^2 a^2 / \hbar^4 k_F^2\} \quad (4.8).$$

Taking, according to the Thomas-Fermi statistical atomic theory^[8], $a \sim \hbar^2/m e^2 Z^{1/3}$ we obtain

$$\rho_i \approx (m^*v_F/n e^2) N_i 4\pi Z^{4/3}/k_F^2 \quad (4.9).$$

Using Drude’s model (see Eq.(1.1)) we see that the charged impurity behaves like a geometrical obstacle of radius $R \sim (2Z^{2/3}/k_F)$. A more precise estimation of this radius could be obtained assuming that the screening parameter is given by^[13] $\lambda^2 = 4\pi e^2 N(E_F)$, where $N(E_F)$ is the density of states for the electrons at the Fermi level. However, the main point to notice is that, in both cases, the predicted *impurity resistivity* is independent of the temperature and that it increases linearly with the impurity density N_i in agreement with experimental results. The experiments show that resistivity of metals obey the relation^[5-8]

$$\rho = \rho_o [1 + \beta x] \quad (4.10),$$

where ρ_o is the *ideal resistivity* of a perfect lattice material with 0% of impurities and with no imperfections (see Sections 5 and 6), β is a constant and x is the % of impurities.^[5-8] The ideal resistivity ρ_o due to electronic interactions with *phonons* and lattice atoms will be estimated in Section 6.

(5) Lattice Vibrations.

In what follows it is assumed that there is only one atom in the unit cell. In this way only acoustic vibrational modes will be considered. As is seen in basic textbooks there are normal modes of elastic vibrations^[7,8,16,17] in crystal lattices. The lowest frequencies are in the sonic region, corresponding to wavelengths a half or a third or a tenth of the crystal dimensions. Taking into account that the total number of coordinates (degrees of freedom) of the N atoms is $3N-6 \approx 3N$ there are only $\sim 3N$ different standing waves. Some of them are compressional waves and some are shear waves. The highest frequencies are in the infrared

and correspond to wavelengths of the size of the interatomic distances. The lowest frequencies are sonic with wavelengths of the size of the crystal dimensions. To simplify the calculations let us suppose that the crystal is a very large cube with side L and that the unit cells are also cubic with side with only one atom. In this way the periodic atomic potential is equal to $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{a})$. To obtain the standing waves satisfying periodic conditions (Bloch conditions^[7,8]) we define a wavevector $\mathbf{q} \equiv (q_x, q_y, q_z)$ given by $q_x(n) = 2\pi/\lambda_n$, $q_y(m) = 2\pi/\lambda_m$ and $q_z(k) = 2\pi/\lambda_k$, where $\lambda_p = L/p$ ($p = n, m, k = 1, 2, \dots$) are the discrete wavelengths along the axis x , y and z , respectively. The atom in the unit cell moves along 3 axis (x, y, z) and can vibrate assuming all possible $3N$ standing waves.

In a quantum approach these standing waves are called *phonons* that, like photons, obey the Bose-Einstein (BE) statistics^[15,16] with a chemical potential $\mu = 0$ (since the number of photons or phonons is not constant). Indicating by $\epsilon_{\mathbf{q}} = \hbar\omega_{\mathbf{q}}$ the phonon energy the average number $\langle n_{\mathbf{q}} \rangle$ of phonons in the \mathbf{q} th mode at the temperature T is given by

$$\langle n_{\mathbf{q}} \rangle = 1/[\exp(\hbar\omega_{\mathbf{q}}/k_B T) - 1] \quad (5.1),$$

that contribute with an energy

$$\langle \epsilon_{\mathbf{q}} \rangle = (\langle n_{\mathbf{q}} \rangle + 1/2) \hbar\omega_{\mathbf{q}} \quad (5.2).$$

Thus the total average energy of the system is given by

$$\langle E \rangle = \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}}/[\exp(\hbar\omega_{\mathbf{q}}/k_B T) - 1] \quad (5.3),$$

where the summation is over all modes of the crystal (i.e. over all polarizations, as well different wavevectors). To obtain a crude estimate^[8] of (5.1)-(5.3) let us consider only acoustic modes, that all them have the same constant sound velocity c and that^[8,14,15]

$$\omega_{\mathbf{q}} = c q \quad (5.4),$$

where $q = 2\pi/\lambda_{\mathbf{q}}$ is the wavenumber of the \mathbf{q} th mode. Eq.(5.4) connects the energy $\hbar\omega_{\mathbf{q}}$ of the \mathbf{q} th mode with the wavelength of the \mathbf{q} th standing mode. For photons with wavenumber k there is a similar relation $\omega = ck$, where c is the light velocity.

Note that the \mathbf{q} summation in (5.3) is over discrete numbers associated with the discrete wavelengths of the standing modes. Assuming that the volume V is sufficiently large we can pass in the usual way from a discrete to a continuous distribution of frequencies.^[7,8,17] In this way the total number $dN_{\mathbf{q}}$ of \mathbf{q} th mode phonons in the interval $dq_x dq_y dq_z$ is given by $dN_{\mathbf{q}} = [V/(2\pi)^3] q^2 dq d\Omega = [V/(2\pi)^3] d^3 \mathbf{q}$. Consequently (5.3) can be written as

$$\langle E \rangle = [V/(2\pi)^3] \iiint d^3 \mathbf{q} \hbar\omega_{\mathbf{q}}/[\exp(\hbar\omega_{\mathbf{q}}/k_B T) - 1] \quad (5.5).$$

Taking into account that $q = \omega_{\mathbf{q}}/c$, that there are $3N$ \mathbf{q} modes and that there is only one atom per unit cell (5.5) becomes

$$\langle E \rangle = 3N(V\hbar/\pi^2 c^3) \int \omega^3 d\omega/[\exp(\hbar\omega/k_B T) - 1] \quad (5.6).$$

Considering that there is a minimum wavelength $\lambda_{\min} = 2a$ for the lattice waves the maximum value for ω_m is given by $\omega_m \sim c q_{\min} \sim \pi c/a$. This maximum value ω_m can also be estimated as follows remembering that the maximum number of quantum modes is $3N$:

$$3N = \int_0^{\omega_m} dN_{\mathbf{q}} = V \omega_m^3/2\pi^2 c^3 \quad (5.7),$$

putting $dN_q = 4\pi[V/(2\pi)^3]q^2 dq = (V/2\pi^2c^3)\omega^2 d\omega$. From (5.7) we see that ω_m , called *Debye frequency* ω_D , is given by

$$\omega_m = \omega_D = (6\pi^2 N c^3 / V)^{1/3} \quad (5.8).$$

The *Debye temperature* Θ and *Debye wavenumber* q_D are defined, respectively, by

$$\Theta = \hbar\omega_D/k_B \quad \text{and} \quad q_D = k_B\Theta/\hbar v \quad (5.9).$$

(6) Electron Scattering by Lattice Vibrations and Atoms.

Now using the Schrödinger quantum mechanics ρ is obtained calculating the electronic scattering generated simultaneously by the lattice atoms and by the thermal vibrations (phonons). The scattering will be estimated with the perturbation theory in a first order Born approximation.

So, let us assume that the interaction potential $V(\mathbf{r})$ between the free electron and atoms is not necessarily periodic and that it is the result of the superposition of individual atomic potentials $V_a(\mathbf{r})$:

$$V(\mathbf{r}) = \sum_{\ell} V_a(\mathbf{r} - \mathbf{R}_{\ell}) \quad (6.1),$$

where \mathbf{R}_{ℓ} is the position of the atom (or ion) at the lattice site ℓ . Assuming that the incident and scattered electron is represented, respectively by the plane waves $|\Psi_{\mathbf{k}}\rangle = \exp(i\mathbf{k}\cdot\mathbf{r})$ and $|\Psi_{\mathbf{k}'}\rangle = \exp(i\mathbf{k}'\cdot\mathbf{r})$ where \mathbf{k} and \mathbf{k}' are, respectively, the electron wavenumbers before and after the collision, the matrix element $M_{\mathbf{k}\mathbf{k}'}$ for transition $\mathbf{k} \rightarrow \mathbf{k}'$ is given by

$$\begin{aligned} M_{\mathbf{k}\mathbf{k}'} &= \int \exp(-i\mathbf{k}'\cdot\mathbf{r}) \left\{ \sum_{\ell} V_a(\mathbf{r} - \mathbf{R}_{\ell}) \right\} \exp(i\mathbf{k}\cdot\mathbf{r}) d^3\mathbf{r} \\ &= \sum_{\ell} \exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}] V_a(\mathbf{r} - \mathbf{R}_{\ell}) d^3\mathbf{r} \\ &= \sum_{\ell} \exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{\ell}] \int \exp[i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{r}-\mathbf{R}_{\ell})] V_a(\mathbf{r} - \mathbf{R}_{\ell}) d^3\mathbf{r} \end{aligned} \quad (6.2).$$

Defining the scattering vector as $\mathbf{K} = \mathbf{k}' - \mathbf{k}$ (6.2) becomes written as

$$M_{\mathbf{k}\mathbf{k}'} = V_a(\mathbf{K}) F(\mathbf{K}) \quad (6.3),$$

where $V_a(\mathbf{K})$ is an *atomic factor* given by the Fourier transform of the atomic potential $V_a(\mathbf{r})$

$$V_a(\mathbf{K}) = \int V_a(\mathbf{r}) \exp(-i\mathbf{K}\cdot\mathbf{r}) d^3\mathbf{r} \quad (6.4),$$

and $S(\mathbf{K})$ is a *structure factor* given by

$$F(\mathbf{K}) = (1/N) \sum_{\ell} \exp[-i\mathbf{K}\cdot\mathbf{R}_{\ell}] \quad (6.5)$$

Suppose now that the lattice modes of our crystal are excited and that each atom is displaced from its ideal lattice site \mathbf{R}_{ℓ} by a very small dislocation $\mathbf{u}_{\ell}(t)$ becoming,^[8]

$$\mathbf{R}_{\ell}(t) = \boldsymbol{\ell} + \mathbf{u}_{\ell}(t) = \boldsymbol{\ell} + \sum_{\mathbf{q}} [U_{\mathbf{q}}(t)\exp(i\mathbf{q}\cdot\boldsymbol{\ell}) + U_{\mathbf{q}}^*(t)\exp(-i\mathbf{q}\cdot\boldsymbol{\ell})] \quad (6.5),$$

where $\mathbf{U}_q(t) = \mathbf{U}_q \exp(i\omega_q t)$ is the vector amplitude of the mode of wavenumber \mathbf{q} (or *phonon wavenumber* – see Appendix C). The summation is only over positive \mathbf{q} to make the displacements \mathbf{u}_t real since $\mathbf{U}_{\mathbf{q}^*} = \mathbf{U}_{-\mathbf{q}}$. As $\mathbf{u}_t(t)$ are very small it can be shown that^[8] the transition probability $|M_{\mathbf{k}\mathbf{k}'}|^2$ can be written as

$$|M_{\mathbf{k}\mathbf{k}'}|^2 = |V_a(\mathbf{K})|^2 |F(\mathbf{K})|^2 = |V_a(\mathbf{K})|^2 S(\mathbf{K}) \quad (6.6),$$

where $|V_a(\mathbf{K})|^2$ takes into account the atomic scattering and that $S(\mathbf{K})$ defined by

$$S(\mathbf{K}) \approx N \left\{ \sum_{\mathbf{q}} |\mathbf{K} \cdot \mathbf{U}_{\mathbf{q}}|^2 \right\} \quad (6.7)$$

gives essentially the phonons contribution to the scattering. From (6.7) we note that the transition probability $\mathbf{k} \rightarrow \mathbf{k}'$ is given by the product of two factors, $|V_a(\mathbf{K})|^2$ and $S(\mathbf{K})$. To obtain the total transition probability per unit of time (see Appendix B) it is necessary to multiply $|V_a(\mathbf{K})|^2$ by $(2\pi/\hbar)$, by the density of final states of the electrons $\rho(E_f) = dN_f/d\varepsilon_f = [1/(2\pi\hbar)^3] m p_f d\Omega = [1/(2\pi\hbar)^3] m^2 v_f d\Omega$, remembering that $p_f = \hbar k'$, $\varepsilon_f = (\hbar k')^2/2m^*$, multiply by $S(\mathbf{K})$ which takes into account the sum over *all possible final states* of the phonons and, finally, perform the integration over Ω . In this way, according to (4.2), the mean free path Λ_o becomes given by

$$\begin{aligned} 1/\Lambda_o &= 2\pi N_a \int_0^{2\pi} |M_{\mathbf{k}\mathbf{k}'}|^2 (1 - \cos\theta) \sin\theta \, d\theta \\ &= 2\pi N_a \int_0^{2\pi} |V_a(\mathbf{K})|^2 S(\mathbf{K}) (1 - \cos\theta) \sin\theta \, d\theta \\ &\approx 2\pi N_a \int_0^{2\pi} \sigma_a(\theta) S(\mathbf{K}) (1 - \cos\theta) \sin\theta \, d\theta \quad (6.8), \end{aligned}$$

where $N_a = N/V$ and $\sigma_a(\theta)$ is the differential scattering cross-section of a “free-atom” given, according to (B.5), by

$$\sigma_a(\theta) = d\sigma/d\Omega = |V_a(\mathbf{K})|^2 [m/(2\pi\hbar^2)]^2 (k'/k).$$

This last approximation may be justified by an appeal to the “adiabatic principle”.^[8] Physically this means that the electrons interact with single atoms and simultaneously with collective vibrations (*phonons*). In what follows we assume that the electron-atom and electron-phonon collision are elastic, that is, $k = k' = k_F$ and $|\mathbf{K}| = K = 2k_F \sin(\theta/2)$ where θ is the scattering angle. In truth the lattice is in constant motion and, consequently, the electronic diffraction is **inelastic**. That is, there is an exchange of momentum between the electron and lattice given by $\hbar\mathbf{k}' = \hbar\mathbf{k} + \hbar\mathbf{q}$. In Fig.8 are represented using Feynman’s diagrams the scattering processes when one phonon is absorbed or emitted (see Appendix C) exchanging energy $\hbar\omega_q$ with the crystal. This is the argument that justifies the name *phonon*, as a quantized acoustic excitation with “particle-like” properties, by analogy with *photon*. Note that in the scattering process the electron can gain, or lose, an extra momentum $\hbar\mathbf{g}$ in addition to the momentum of the phonon $\hbar\mathbf{q}$. We call such process *Umklapp process* or *U-process*.^[8] The momentum $\hbar\mathbf{g}$ is transferred to the crystal as a whole. When $\hbar\mathbf{g} = 0$ the scattering is named *Normal process* or *N-process*.^[8]

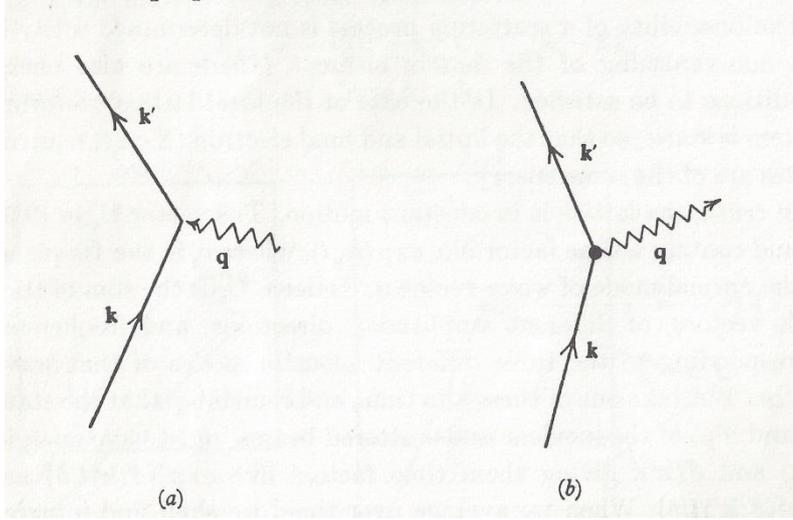


Figure 8. Electron scattering process: (a) phonon absorption; (b) phonon emission^[8]

(6.a) High Temperatures.

To evaluate (6.7) we need to obtain the amplitude U_q of the q th lattice mode which is a function of the temperature. For high temperatures this can be done using a semi-classical approach. Classically, we know that the average energy of each simple-harmonic oscillator mode is the sum of its kinetic and potential energies and that they are equal. Thus, the total average energy $\langle E \rangle$ of a system with N particles with mass M

$$\langle E \rangle = \sum_t M |\dot{\mathbf{u}}_t(t)|^2 = \sum_q NM |\dot{U}_q(t)|^2 = N \sum_q M \omega_q^2 |U_q|^2 = N \sum_q \langle \epsilon_q \rangle \quad (6.8),$$

which implies putting $\langle \epsilon_q \rangle = (\langle n_q \rangle + 1/2) \hbar \omega_q$ that:

$$|U_q|^2 = \langle \epsilon_q \rangle / NM \omega_q^2 = (\langle n_q \rangle + 1/2) \hbar / NM \omega_q \quad (6.9).$$

For any polarization we have on the average $\langle |\mathbf{K} \cdot \mathbf{U}_q|^2 \rangle = (1/3) \mathbf{K}^2 |U_q|^2$ however assuming that there are three different polarizations we have $\langle |\mathbf{K} \cdot \mathbf{U}_q|^2 \rangle = \mathbf{K}^2 |U_q|^2$.

Thus, using (6.5), (6.7) and taking $\omega_q = cq$ for acoustic modes we have,

$$S(\mathbf{K}) \approx N \left\{ \sum_q |\mathbf{K} \cdot \mathbf{U}_q|^2 \right\} \approx N \mathbf{K}^2 \left\{ \sum_q |U_q|^2 \right\} \quad (6.10),$$

that is,

$$\begin{aligned} S(\mathbf{K}) &= (1/16\pi^3) (\hbar^2 \mathbf{K}^2 / M) \iiint (\langle n_q \rangle + 1/2) d^3q / \omega_q \\ &= (3\hbar^2 \mathbf{K}^2 T^2 / 2M k_B \Theta^3) \int_0^{\Theta/T} \{z / [\exp(z) - 1] + 1/2\} dz \end{aligned} \quad (6.11)$$

with $z = \hbar\omega/k_B T$. For high temperatures the upper limit of the integral (6.12) is small, that is, $\Theta/T \ll 1$. In these conditions the integrand can be expanded in powers of z , that is, we can write $z / [\exp(z) - 1] \approx 1 - z/2 + z^2/12 - z^4/720 + \dots$. Thus, we verify that

$$S(\mathbf{K}) \approx (3/2) (\hbar^2 \mathbf{K}^2 T / M k_B \Theta^2) \quad (6.12).$$

From (6.8) the mean free path Λ_o due to electron-phonon interaction, using (6.10) and (6.13), is given by

$$\begin{aligned}
1/\Lambda_o &= 2\pi N_a \int_0^{2\pi} \sigma_a(\theta) S(\mathbf{K})(1 - \cos\theta) \sin\theta d\theta \\
&\approx 2\pi N_a (3/2)(\hbar^2 \mathbf{K}^2 T / M k_B \Theta^2) \int_0^{2\pi} \sigma_a(\theta) (1 - \cos\theta) \sin\theta d\theta \\
&\approx N_a \langle \sigma_a \rangle (3\pi \hbar^2 \mathbf{K}^2 T / M k_B \Theta^2) \approx N_a \langle \sigma_a \rangle \hbar^2 q_D^2 k_B T / M k_B^2 \Theta^2 \quad (6.14)
\end{aligned}$$

assuming that \mathbf{K} is independent of θ and that

$$\langle \sigma_a \rangle = 2\pi \int_0^{2\pi} \sigma_a(\theta) (1 - \cos\theta) \sin\theta d\theta \quad (6.15)$$

is the total scattering cross-section of an isolated atom. Using (4.1) we see that the ideal resistivity $\rho_o = m^* v_F / (\Lambda_o n e^2)$ for *high temperatures* is given by

$$\rho_o = N_a \langle \sigma_a \rangle (m^* v_F / n e^2) (\hbar^2 q_D^2 k_B / M k_B^2 \Theta^2) T \quad (6.16),$$

that is, ρ_o *increases linearly* with T in good agreement with experimental results.^[7]

(6.b) Low and High Temperatures.

For any temperature, low and high, $S(\mathbf{K})$ cannot be calculated assuming the classical statistics as done in (6.a). So, $|\mathbf{U}_q|^2$ given by (6.9) is now taken as, putting $\omega_q = cq$ and $\mathbf{K} \approx k$:

$$|\mathbf{U}_q|^2 = \langle \epsilon_q \rangle / NM \omega_q^2 = \langle n_q \rangle \hbar \omega_q / NM \omega_q^2 \approx (1/NM v^2 k^2) \{ \hbar \omega_q / [\exp(\hbar \omega_q / k_B T) - 1] \} \quad (6.17).$$

From (6.8), (6.10) and (6.17) we can calculate more or less exactly Λ_o if we suppose that $\sigma(\theta)$ is not strongly dependent varying function of θ . In this way we obtain:

$$1/\Lambda_o = N_a \langle \sigma_a \rangle (\hbar^2 q_D^2 k_B T / M k_B^2 \Theta^2) (T/\Theta)^4 \int_0^{\Theta/T} 4z^4 dz / [\exp(z) - 1] \quad (6.18),$$

where $z = (\hbar \omega_q / k_B T) = (q/q_D)(\Theta/T)$. It is important to note that at *high temperatures*, when $\Theta/T \ll 1$ the above integral tends to $(\Theta/T)^4$. So, (6.18) gives

$$1/\Lambda_o \approx N_a \langle \sigma_a \rangle (\hbar^2 q_D^2 k_B T / M k_B^2 \Theta^2) \quad (6.19),$$

and we are back at (6.14). On the other side, at *low temperatures* since $\Theta/T \gg 1$ the (6.18) integral tends to a constant value (~ 100) showing a resistivity proportional to T^5 :

$$\rho_o \approx N_a \langle \sigma_a \rangle (m^* v_F / n e^2) (\hbar^2 q_D^2 k_B / M k_B^2 \Theta) (T/\Theta)^5 \quad (6.20).$$

This strong T^5 dependence of the ideal resistivity ρ_o at low temperatures is a characteristic quantum effect,^[8] comparable with the Debye T^3 -specific heat law.

In the high temperature region the calculated resistivity is proportional to T , and in the low temperature region it is proportional to T^5 . The agreement of the calculated temperature dependence with experiment is quite good, as is shown in Fig.9, although T^5 is seldom actually obtained.^[7,8] In Fig.9 is shown the temperature variation calculated with the semi-empirical Grüneisen formula^[8, 18] and the experimental values for various metals.

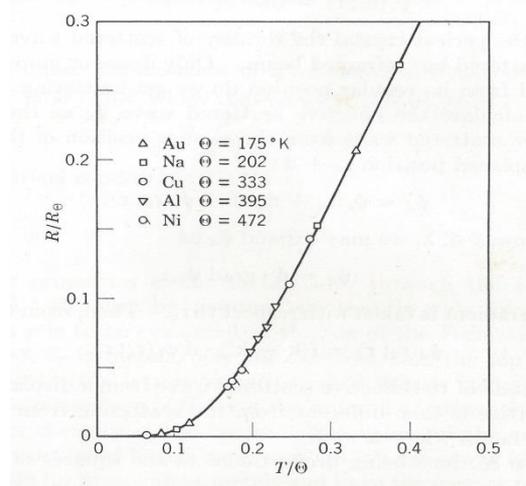


Figure 9. Theoretical (Grüneisen) temperature variation of the electrical resistance compared with experimental values for various metals.^[7]

It was found by Grüneisen that the observed temperatures dependence of the resistivity is quite well described at all temperatures by the semi-empirical formula

$$1/\Lambda_0 = N_a \langle \sigma_a \rangle (\hbar^2 q_D^2 k_B T / M k_B^2 \Theta^2) (T/\Theta)^4 \int_0^{\Theta/T} 4z^5 dz / \{[\exp(z) - 1][1 - \exp(-z)]\} \quad (6.21),$$

which has the same asymptotic behavior as (6.16) at high temperatures, that is, $\sim T$ and as (6.20) at low temperatures, that is, $\sim T^5$.

In Appendix C the resistivity $\rho_0(T)$ is calculated using the Second Quantization Theory.

Appendix A. *Effective Electron Mass.*

Let us suppose that an electron submitted to an electric field \mathbf{E} move in an allowed band with state vectors very close to \mathbf{k}_0 . Being $\epsilon(\mathbf{k}) = \hbar\omega(\mathbf{k})$ the electron energy as function of the momentum \mathbf{k} its group velocity at \mathbf{k}_0 is given by^[13]

$$\mathbf{v}_g(\mathbf{k}_0) = (d\omega(\mathbf{k})/d\mathbf{k})_0 = (d\epsilon(\mathbf{k})/d\mathbf{k})_0/\hbar \quad (A.1).$$

If the electron wave packet is accelerated in an electric field \mathbf{E} the work δW done on the electron in a time interval δt is written as^[7]

$$\delta W = eE v_g \delta t = (d\epsilon/dk) \delta k = \hbar v_g \delta k, \quad \text{that is,}$$

$$\delta k = (eE/\hbar) \delta t \quad \text{or} \quad dk/dt = (eE/\hbar).$$

We have further,

$$dv_g/dt = (dk/dt)(d^2\epsilon/dk^2)/\hbar, \quad \text{that is,}$$

$$dv_g/dt = (eE/\hbar^2)(d^2\epsilon/dk^2), \quad (A.2).$$

Comparing (A.2) with the classical equation for free electrons, $dv/dt = (eE/m)$ we verify that an electron in a periodic potential, accelerated by an electric field, has an effective mass m^* given by

$$m^* = \hbar^2 [d^2\epsilon(k)/dk^2]^{-1} \quad (\text{A.3}).$$

Experimental and theoretical values of effective mass ratios m^*/m for some metals are given in reference 7 (Table 13.1, pag.258).

Appendix B. Scattering Cross Section.

Let us remember how to obtain^[9,11] the scattering cross section $d\sigma(\epsilon, \theta)/d\Omega$ for the $i \rightarrow f$ transition taking into account the transition probability per unit time $dP(i \rightarrow f) = dP_{fi}$ due to a perturbation potential H_{int} .

In the first order Born approximation the probability per unit of time dP_{fi} between these states is given by the Fermi golden rule^[9,11]

$$dP_{fi} = (2\pi/\hbar) |\langle f | H_{int} | i \rangle|^2 \rho(E_f) \quad (\text{B.1}),$$

with the energy condition $E_f = E_i$ and where $\rho(E_f)$ is the number of final states per unit interval of energy E_f .

Let us assume that initial and final states $|i\rangle$ and $|f\rangle$ are described, respectively, by the plane waves $|i\rangle = \exp(i\mathbf{k}_i \cdot \mathbf{r})/\sqrt{V}$ and $|f\rangle = \exp(i\mathbf{k}_f \cdot \mathbf{r})/\sqrt{V}$. In this case the number of final states dN_k in the volume V with momentum within k and $k+dk$ and within a solid angle $d\Omega$ is given by the expressions^[9,11,16]

$$dN_k = V k_f^2 dk_f d\Omega \quad (\text{B.2}).$$

For massive particles $\epsilon = \mathbf{p}^2/2m$ and $\mathbf{p} = \hbar\mathbf{k}$ we get

$$dN_p = [V/(2\pi\hbar)^3] p_f^2 dp_f d\Omega \quad (\text{B.3}).$$

and

$$\rho(E_f) = dN_p/d\epsilon_f = [V/(2\pi\hbar)^3] m p_f d\Omega = [V/(2\pi\hbar)^3] m^2 v_f d\Omega$$

If P_{fi} is the total transition probability per unit of time, $(N/V) =$ density of atoms of the crystal, $|\mathbf{J}_i| = \hbar k_i/(mV) = p_i/(mV) = v_i/V$ the flux density of the incoming particles and σ the total scattering cross section ("effective scattering area") we must have

$$P_{fi} N = |\mathbf{J}_i| A_{total} = (v_i/V) N \sigma \quad \rightarrow \rightarrow \quad \sigma = P_{fi}/(v_i/V).$$

Consequently, using (B.1):

$$d\sigma = dP_{fi}/(v_i/V) = |\langle f | H_{int} | i \rangle|^2 [V^2/(2\pi\hbar^2)^2] m^2 (v_f/v_i) \quad (\text{B.4}).$$

Putting $|\psi\rangle = \exp(i\mathbf{k} \cdot \mathbf{r}) = \exp(i\mathbf{p} \cdot \mathbf{r}/\hbar)$ (normalized by unit of volume) Eq.(B.4) is written as

$$d\sigma/d\Omega = |\langle \psi_f | H_{int} | \psi_i \rangle|^2 [m/(2\pi\hbar^2)]^2 (v_f/v_i) \quad (\text{B.5}),$$

With these $|\psi\rangle$ functions the transition probability per unit time $dP_{fi}/d\Omega$ becomes, using (B.4) and (B.5):

$$dP_{fi}(\epsilon_i, \theta)/d\Omega = v_i (d\sigma(\epsilon_i, \theta)/d\Omega) \quad (\text{B.6}),$$

where ϵ_i and v_i are the incident energy and velocity, respectively.

Appendix C. Second Quantization Approach for the Electron-Phonon Interaction.

In Section 6 we have seen that classically, when only *acoustic modes* of the crystal are excited each atom is displaced from its ideal lattice site \mathbf{R}_ℓ by a very small dislocation $\mathbf{u}_\ell(t)$ given by (6.6)^[8]

$$\mathbf{R}_\ell(t) = \boldsymbol{\ell} + \mathbf{u}_\ell(t) = \boldsymbol{\ell} + \sum_{\mathbf{q}} [\mathbf{U}_\mathbf{q}(t)\exp(i\mathbf{q}\cdot\boldsymbol{\ell}) + \mathbf{U}_\mathbf{q}^*(t)\exp(-i\mathbf{q}\cdot\boldsymbol{\ell})] \quad (\text{C.1})$$

where $\mathbf{U}_\mathbf{q}(t) = \mathbf{U}_\mathbf{q} \exp(i\omega_\mathbf{q}t)$.

In order to use the second quantization formalism, putting generically $\boldsymbol{\ell} = \mathbf{r}$, the dislocations $\mathbf{u}_\ell(t) = \boldsymbol{\xi}(t)$ are preliminarily written as^[9]

$$\mathbf{u}_\ell(t) \equiv \boldsymbol{\xi}(t) = (\hbar/2MN)^{1/2} \sum_{\mathbf{q}} \mathbf{E}_\mathbf{q} [a_\mathbf{q}(t)\exp(i\mathbf{q}\cdot\mathbf{r}) + a_\mathbf{q}^*(t)\exp(-i\mathbf{q}\cdot\mathbf{r})]/\sqrt{\omega_\mathbf{q}} \quad (\text{C.2}),$$

where $\mathbf{E}_\mathbf{q} = (\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ are the three mutually perpendicular polarization unit vectors and $a_\mathbf{q}(t)$ are the wave amplitudes $a_\mathbf{q}(t) = a_\mathbf{q} \exp(i\omega_\mathbf{q}t)$. Each term in (B.2) describes a plane wave propagating in the direction of the wavevector \mathbf{q} . It can be shown that^[9] that classically the total energy H_{cl} of the atomic vibrations represented by (C.2) is given by

$$H_{cl} = (1/2) \sum_{\mathbf{q}} \hbar\omega_\mathbf{q} [a_\mathbf{q} a_\mathbf{q}^* + a_\mathbf{q}^* a_\mathbf{q}] \quad (\text{C.3}).$$

Replacing the complex amplitudes $a_\mathbf{q}$ and $a_\mathbf{q}^*$ by the *creation* and *annihilation* operators, $A_\mathbf{q}$ and $A_\mathbf{q}^+$ of *phonons* that satisfy the *bosonic* commutation relations

$$[A_\mathbf{q}, A_{\mathbf{q}'}] = [A_\mathbf{q}^+, A_{\mathbf{q}'}^+] = 0 \quad \text{and} \quad [A_\mathbf{q}, A_{\mathbf{q}'}^+] = \delta_{\mathbf{q}\mathbf{q}'} \quad (\text{C.4}),$$

the Hamiltonian operator H_{vib} in the second quantization approach becomes written as

$$H_{vib} = \sum_{\mathbf{q}} \hbar\omega_\mathbf{q} A_\mathbf{q}^+ A_\mathbf{q} + E_0, \quad (\text{C.5}),$$

where $E_0 = (1/2) \sum_{\mathbf{q}} \hbar\omega_\mathbf{q}$ is the energy of the ground state or the *vacuum state energy*, usually taken equal to zero. If $|0\rangle$ is the vacuum state wavefunction, the energy wave functions $|1_\mathbf{q}\rangle$ and $|n_\mathbf{q}\rangle$ are given, respectively, by $|1_\mathbf{q}\rangle = A_\mathbf{q}^+ |0\rangle$ and $|n_\mathbf{q}\rangle = (1/\sqrt{n_\mathbf{q}!})(A_\mathbf{q}^+)^n |0\rangle$. These states represent phonons with energy $n_\mathbf{q}\hbar\omega_\mathbf{q}$.

In the second quantization approach the displacements $\boldsymbol{\xi}$ are described by the formula^[9]

$$\boldsymbol{\xi} = (\hbar/2MN)^{1/2} \sum_{\mathbf{q}} \mathbf{E}_\mathbf{q} [A_\mathbf{q} \exp(i\mathbf{q}\cdot\mathbf{r}) + A_\mathbf{q}^+ \exp(-i\mathbf{q}\cdot\mathbf{r})]/\sqrt{\omega_\mathbf{q}} \quad (\text{C.6}).$$

Now, let us obtain the interaction between the conduction electrons and the quantized phonons. When there is no vibration of the atoms about their equilibrium positions the potential energy of an electron in a crystal is a periodic function of the lattice periods,

$V_o(\mathbf{r}) = \sum_{\boldsymbol{\ell}} V_a(\mathbf{r} - \mathbf{R}_\ell)$ where \mathbf{R}_ℓ is the position of the atom (or ion) at the lattice site $\boldsymbol{\ell}$, according to (6.1). Due to the atoms vibrations, their positions are changed, $\mathbf{R}_\ell \rightarrow \mathbf{R}_\ell + \boldsymbol{\xi}_\ell$. For small deviations from the equilibrium positions we can write the potential interaction energy $V(\mathbf{r})$, in a first order approximation,^[9]

$$V(\mathbf{r}) = V_o(\mathbf{r}) + \sum_{\boldsymbol{\ell}} (\boldsymbol{\xi}_\ell \cdot \text{grad}_\ell) V_a(\mathbf{r} - \mathbf{R}_\ell) \quad (\text{C.7}).$$

Thus the total Hamiltonian H_S of *nearly free* electrons + phonons can be written as

$$H_S = H_{el} + H_{vib} + H_{int} \quad (C.8),$$

where $H_{el} = \sum_i (\hbar^2 \mathbf{k}_i^2 / 2m^*) + V_o(\mathbf{r})$ ($i = 1, 2, \dots, N$), H_{vib} is defined by (C.5) and H_{int} given by

$$H_{int} = \sum_{\ell} (\xi_{\ell} \cdot \text{grad}_{\ell}) V_a(\mathbf{r} - \mathbf{R}_{\ell}) = \int (\xi_y(\mathbf{y}) \cdot \text{grad}_y) V_a(\mathbf{r} - \mathbf{y}) d^3y \quad (C.9),$$

defining $\xi_y(\mathbf{y}) = \sum_{\ell} \xi_{\ell} \delta(\mathbf{y} - \mathbf{R}_{\ell})$ and transforming the summation over the discrete ℓ atomic positions in an integral over the crystal volume where now \mathbf{y} are the atomic positions taken as a continuous variable.^[9]

When there is no interaction between the electron and the lattice vibrations the state of the electron in the conduction band is described, in the general case, by the Bloch function^[7,8,9]

$$|\psi_{\mathbf{k}}(\mathbf{r})\rangle = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}(\mathbf{r}) \quad (C.10).$$

For a nearly free electron $u_{\mathbf{k}}(\mathbf{r}) \approx 1$ (Section 3) and energy $E(\mathbf{k}) \approx \hbar^2 \mathbf{k}^2 / 2m^*$. The free vibrations of the lattice are determined by the wavefunction $|\dots n_q \dots\rangle$, that is, giving the number of phonons of different kinds in that state.^[9]

Let us assume for instance that one phonon is created in the collision represented by Figure (8.b). So, initial state $|i\rangle$ is described by the state function

$$|i\rangle = |n_q\rangle |\psi_{\mathbf{k}}(\mathbf{r})\rangle \quad (C.11)$$

and the final state $|f\rangle$ by

$$|f\rangle = |n_q + 1\rangle |\psi_{\mathbf{k}}(\mathbf{r})\rangle \quad (C.12).$$

According to the perturbation theory the transition probability (see Appendix B) $d\Pi_{\mathbf{k}'\mathbf{k}}/d\Omega$, per unit time, for a transition $|\mathbf{k}\rangle \rightarrow |\mathbf{k}'\rangle$ ($|\mathbf{k}_i\rangle \rightarrow |\mathbf{k}_f\rangle$), involving the interactions of conduction electrons with the lattice atoms with emission (or absorption) of phonons, is given by^[9,11]

$$d\Pi_{\mathbf{f}\mathbf{i}}/d\Omega = (2\pi/\hbar) |\langle f | H_{int} | i \rangle|^2 d\rho(E_f) \quad (C.13),$$

where $d\rho(E_f) = k_f^2 dk_f / (2\pi)^3$ is the *density of final states* of the scattered electrons, the total energy $E_f = E_i$, $E_i = \hbar^2 \mathbf{k}^2 / 2m^* + n_q \hbar \omega_q$ and $E_f = \hbar^2 \mathbf{k}'^2 / 2m^* + (n_q + 1) \hbar \omega_q$. Since $E_i - E_f = \hbar^2 (\mathbf{k}^2 - \mathbf{k}'^2) / 2m^* + \hbar \omega_q$ we see that the collision is not elastic.

Since

$$\langle f | H_{int} | i \rangle = \langle n_q + 1 | (\xi_y(\mathbf{y}) \cdot \text{grad}_y) F(\mathbf{y}) d^3y | n_q \rangle \quad (C.14),$$

where

$$F(\mathbf{y}) = \int \exp[(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] V_a(\mathbf{r} - \mathbf{y}) d^3r$$

and

$$\xi_y(\mathbf{y}) \cdot \text{grad}_y = -i(\hbar/2NM)^{1/2} \sum_{\mathbf{q}\ell} (\mathbf{q} \cdot \mathbf{C}_{\mathbf{q}}) \exp(-i\mathbf{q} \cdot \mathbf{R}_{\ell}) \mathbf{A}_{\mathbf{q}}^+ \delta(\mathbf{y} - \mathbf{R}_{\ell}) / \sqrt{\omega_{\mathbf{q}}}.$$

Performing an average over the three polarizations we obtain:

$$\langle f | H_{\text{int}} | i \rangle = -i(\hbar/2NM)^{1/2} q \langle n_q + 1 | \mathbf{A}_q^+ | n_q \rangle / \sqrt{\omega_q} \\ \cdot \sum_{\ell} \exp(-i\mathbf{q} \cdot \mathbf{R}_{\ell}) \int \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] u_{\mathbf{k}'}^*(\mathbf{r}) V_a(\mathbf{r} - \mathbf{R}_{\ell}) u_{\mathbf{k}}^*(\mathbf{r}) d^3\mathbf{r} \quad (\text{C.15}).$$

Putting $\mathbf{r} = \mathbf{R}_{\ell} + \boldsymbol{\rho}$ we can write the integral (C.15) as

$$\int (\dots) d^3\mathbf{r} = f_a \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_{\ell}]$$

where $f_a = f_a(\theta)$ is a function of the scattering angle θ between \mathbf{k} and \mathbf{k}' given by

$$f_a(\theta) = \int u_{\mathbf{k}'}^*(\boldsymbol{\rho}) V_a(\boldsymbol{\rho}) \exp[i(\mathbf{k} - \mathbf{k}') \cdot \boldsymbol{\rho}] u_{\mathbf{k}}(\boldsymbol{\rho}) d^3\boldsymbol{\rho}.$$

In this way, (B.15) becomes taking $\langle n_q + 1 | \mathbf{A}_q^+ | n_q \rangle = n_q + 1$,

$$\langle f | H_{\text{int}} | i \rangle = -i \{ \hbar (n_q + 1) / 2NM \}^{1/2} q f_a(\theta) \{ (1/N) \sum_{\ell} \exp[i(\mathbf{k} - \mathbf{k}' - \mathbf{q}) \cdot \mathbf{R}_{\ell}] \}.$$

The sum $\{ \dots \}$ vanishes unless $\mathbf{k} - \mathbf{k}' - \mathbf{q} = 2\pi\boldsymbol{\tau}$, where $\boldsymbol{\tau}$ is a reciprocal lattice vector. For N -processes (see Section 6) when $\boldsymbol{\tau} = 0$, $\mathbf{k} = \mathbf{k}' + \mathbf{q}$ we have $\sum_{\ell} \exp[i(\mathbf{k} - \mathbf{k}' - \mathbf{q}) \cdot \mathbf{R}_{\ell}] = N$. Giving, finally

$$\langle f | H_{\text{int}} | i \rangle = -i \{ \hbar (n_q + 1) / 2NM \}^{1/2} q f_a(\theta) \delta_{\mathbf{k}, \mathbf{k}' + \mathbf{q}} \quad (\text{C.16}).$$

Now, taking into account $\langle f | H_{\text{int}} | i \rangle$ defined by (C.16) and summing over all possible final $| \mathbf{q} \rangle$ states of the emitted phonons with momentum \mathbf{q} and energy $\hbar\omega_q$, the total transition probability per unit time Π_{if} for the *electron scattering* is given by

$$\Pi_{\text{if}} = (2\pi/\hbar) \iint |\langle f | H_{\text{int}} | i \rangle|^2 q^2 dq d\Omega / (2\pi)^3 \\ = [1/(2\pi)^2] (\hbar/2M) \iint \{ (n_q + 1) / \omega_q \} |f_a(\theta)|^2 q^3 dq d\Omega \quad (\text{C.17}). \\ = (1/16\pi^3) (\hbar^2/M) \iint \{ (n_q + 1) / \omega_q \} |f_a(\theta)|^2 q^3 dq d\Omega$$

Assuming that there are only acoustic modes, that is, putting $\omega_q = cq$ and writing $\omega_q = \omega$, (C.17) becomes

$$\Pi_{\text{if}} = (1/16\pi^3) (\hbar^2/Mv^4) \iint (n(\omega) + 1) |f_a(\theta)|^2 \omega^2 d\omega d\Omega \quad (\text{C.18}).$$

Note that there is an entanglement between the two functions in (C.18) due to the energy conservation relation $\mathbf{k}^2 = (\mathbf{k} - \mathbf{q})^2 + 2m^*\omega/\hbar$ and that $|f_a(\theta)|^2$ is a function of $\mathbf{K} = \mathbf{k} - \mathbf{k}'$ that depends on the scattering angle θ between \mathbf{k} and \mathbf{k}' . If in a first approximation we neglect this entanglement and put $|\mathbf{k}| \approx |\mathbf{k}'| \approx k_F$, as was done in Section 6, (C.18) is written as

$$\Pi(\theta) = (1/16\pi^3) (\hbar^2/Mv^4) \langle \sigma_a(\theta) \rangle \iint (n(\omega) + 1) \omega^2 d\omega d\Omega \quad (\text{C.19}),$$

where $\langle \sigma_a(\theta) \rangle = (m^*V/2\pi\hbar^2)^2 |f_a(\theta)|^2$ is the scattering cross-section of an isolated atom.^[11] Thus,

$$1/\Lambda_o = 2\pi N_a \int_0^{2\pi} \Pi(\theta) (1 - \cos\theta) \sin\theta d\theta \approx$$

$$= 2\pi N_a \langle \sigma_a \rangle (1/16\pi^3) (\hbar^2/Mc^4) \iint (n(\omega) + 1) \omega^2 d\omega d\Omega \quad (C.20),$$

where $\langle \sigma_a \rangle$ is the total scattering cross section of an isolated atom given by

$$\langle \sigma_a \rangle = 2\pi \int_0^{2\pi} \sigma_a(\theta) (1 - \cos\theta) \sin\theta d\theta .$$

Taking into account that $\langle n(\omega) \rangle = 1/[\exp(\hbar\omega/k_B T) - 1]$ and following the calculations used to deduce (6.18) we finally obtain

$$1/\Lambda_o = N_a \langle \sigma_a \rangle (\hbar^2 q_D^2 k_B T / M k_B^2 \Theta^2) (T/\Theta)^4 \int_0^{\Theta/T} 4z^4 dz / [\exp(z) - 1] \quad (C.21),$$

where $z = \hbar\omega/k_B T = (q/q_D)(\Theta/T)$, which is the same result given by (6.18).

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