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BOLTZMANN TRANSPORT EQUATION AND THE ELECTRICAL AND THERMAL CONDUCTIVITIES OF METALLIC BULKS

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# BOLTZMANN TRANSPORT EQUATION AND THE ELECTRICAL AND THERMAL CONDUCTIVITIES OF METALLIC BULKS 

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#### Abstract

. Our goal is to write a didactical article to graduate and postgraduate students of Physics showing first how to deduce the Boltzmann transport equation and second how these equations can be used to predict the thermal and electrical conductivities of metallic bulks. This formalism is also applied to explain the Thermoelectric Effects known as Seebeck, Thomson and Peltier effects.


## I) Introduction.

To analyze the electrical and thermal conductivities of an aggregate we need first to deduce the Boltzmann transport equation (BTE) which is the basic tool to study the non-equilibrium phenomena. To obtain this equation is necessary first to deduce the Liouville theorem. This is done in Section 1. In Section 2 we deduce, using the Liouville theorem, the BTE. In Section 3, as an application of the BTE, we calculate the electric and thermal conductivities of metallic bulks. In Section 4 we estimate the thermo-electric effects named Seebeck, Thomson $t$ and Peltier effects.

## 1) Liouville Theorem.

There are many excellent basic texts where the students can find the deduction of the Liouville theorem and of the Boltzmann transport equations and the application of these to study the thermoelectric conduction. However, with the intention to give only a few number of references, articles and books, we will mention here only three classical books written by Sommerfeld, ${ }^{1}$ Huang ${ }^{2}$ and Kubo. ${ }^{3}$ However, to pay tribute to Prof. Jun'ichi Osada the above mentioned problems will be developed following the lectures ${ }^{4}$ on Statistical Physics ministered at 1970 by this professor at the Institute of Physics of the USP.

So, let us consider a system composed by a very large number N of "almost free" particles. By "almost free" we mean that: (1) there is an external force field that changes very slowly with the time in a such a way that the particles orbits do not change abruptly; (2) Besides the external field there are some centers of intense forces called "scattering centers". The interaction range with these centers is very short and the centers density is so small that between two collisions with these centers the
particles can move freely being under the influence only of the external forces mentioned above.

For equilibrium states, according to the Statistical Mechanics, ${ }^{1-3}$ the number dN of free particles with linear momentum between $\mathbf{p}$ and $\mathbf{p}+\mathrm{d} \mathbf{p}$ and $g$ internal degrees of freedom, in a box with volume $V$ at the temperature T is given by

$$
\begin{equation*}
\mathrm{dN}(\mathbf{p}, \mathbf{q})=\mathrm{g}(\mathrm{Vd} \mathbf{p} / 2 \pi \hbar)^{3} \mathrm{f}_{\mathrm{o}}(\mathbf{p}, \mathbf{q}) \tag{1.1}
\end{equation*}
$$

where $\mathrm{f}_{\mathrm{o}}(\mathbf{p}, \mathbf{q})=\mathrm{f}_{\mathrm{o}}(\mathbf{p})=\mathrm{f}_{\mathrm{o}}(\varepsilon)=[\exp (\varepsilon-\mu) / \mathrm{kT} \pm 1]^{-1}$ is the equilibrium distribution function for fermions ( + ) and bosons ( - ), $\varepsilon=\mathbf{p}^{2} / 2 \mathrm{~m}, \mathrm{~m}$ the particle mass and $\mu$ the chemical potential of the system. According to (1.1) the number of particles in a small region of space $d \boldsymbol{q}$ is

$$
\begin{equation*}
\mathrm{dN}(\mathbf{p}, \mathbf{q})=\mathrm{g}(\mathrm{~d} \mathbf{q} \mathrm{~d} \mathbf{p} / 2 \pi \hbar)^{3} \mathrm{f}_{0}(\mathbf{p}, \mathbf{q}) \tag{1.2}
\end{equation*}
$$

where $\mathrm{d} \mathbf{q} \mathbf{d} \mathbf{p} /(2 \pi \hbar)^{3}$ is the number of cinematic quantum states inside the element of volume $d \mathbf{q d} \mathbf{p}$ of the phase space ${ }^{4}$ and $f_{o}(\mathbf{p}, \mathbf{q})$ is the average number of particles by quantum states. The total number N of particles is, using (1.2), given by $\mathrm{N}=\mathrm{g} \iint \mathrm{d} \mathbf{q d} \mathbf{p} \mathrm{f}_{\mathrm{o}}(\mathbf{p}, \mathbf{q}) /(2 \pi \hbar)^{3}$.

When the external field is non-uniform and time dependent the distribution function is now written as $\mathrm{f}(\mathbf{p}, \mathbf{q}, \mathrm{t})$ and (1.1) becomes given by

$$
\begin{equation*}
\mathrm{dN}(\mathbf{p}, \mathbf{q}, \mathrm{t})=\mathrm{g}(\mathrm{~d} \mathbf{q} \mathrm{~d} \mathbf{p} / 2 \pi \hbar)^{3} \mathrm{f}(\mathbf{p}, \mathbf{q}, \mathrm{t}) \tag{1.3}
\end{equation*}
$$

Let us show that the phase space element of volume is time independent, that is, $(\mathrm{d} \mathbf{q} d \mathbf{p})_{\mathrm{t}}=(\mathrm{d} \mathbf{q} \mathrm{d} \mathbf{p})_{\mathrm{t}+\mathrm{dt}}$. Indeed, putting

$$
\begin{align*}
(\mathrm{d} \mathbf{q} \mathbf{d} \mathbf{p})_{t+\mathrm{dt}} & =\prod_{\mathrm{i}=\mathrm{x}, \mathrm{y}, \mathrm{z}}\left\{\left(\mathrm{dq}_{\mathrm{i}} \mathrm{dp}_{i}\right)_{\mathrm{t}}+\left(\mathrm{dq}_{\mathrm{i}}^{*} \mathrm{dp}_{\mathrm{i}}+\mathrm{dq}_{\mathrm{i}} \mathrm{dp}_{\mathrm{i}}^{*}\right) \mathrm{dt}\right\} \\
& =\prod_{\mathrm{i}=\mathrm{x}, \mathrm{y}, \mathrm{z}}\left(\mathrm{dq}_{\mathrm{i}} \mathrm{~d} \mathrm{p}_{\mathrm{i}}\right)_{\mathrm{t}}\left\{1+\left(\partial \mathrm{q}_{\mathrm{i}}^{*} / \partial \mathrm{q}_{\mathrm{i}}+\partial \mathrm{p}_{\mathrm{i}}{ }^{*} \partial \mathrm{p}_{\mathrm{i}}\right)_{\mathrm{t}} \mathrm{dt}\right\} \tag{1.4}
\end{align*}
$$

where $q^{*}=d q / d t$ and $p^{*}=d p / d t$. Taking into account the Hamilton's
equations ${ }^{4} p_{i}{ }^{*}=-\partial H / \partial q_{i}$ and $q_{i}{ }^{*}=\partial H / \partial p_{i}$ we get $\partial q_{i}{ }^{*} / \partial q_{i}+\partial p_{i} * / \partial p_{i}=0$. In this way, from (1.4) we verify that

$$
(\mathrm{d} \mathbf{q} \mathrm{~d} \mathbf{p})_{\mathrm{t}}=(\mathrm{d} \mathbf{q} \mathrm{~d} \mathbf{p})_{\mathrm{t}+\mathrm{d} \mathrm{t}} .
$$

which is a result known as "Liouville theorem"(LT): "the phase space volume is time invariant" (see also Goldstein").

## 2) Boltzmann Transport Equation.

Combining the LT with a plausible fact, the conservation of the number of particles of the system, we can write:

$$
\mathrm{f}_{\mathrm{t}}=\mathrm{f}_{\mathrm{t}+\mathrm{dt}}=\mathrm{f}_{\mathrm{t}}+\mathrm{dt}\left\{\Sigma_{\mathrm{i}} \mathrm{p}_{\mathrm{i}}^{*}\left(\partial \mathrm{f} / \partial \mathrm{p}_{\mathrm{i}}\right)+\Sigma_{\mathrm{i}} \mathrm{q}_{\mathrm{i}}^{*}\left(\partial \mathrm{f} / \partial \mathrm{q}_{\mathrm{i}}\right)+\partial \mathrm{f} / \partial \mathrm{t}\right\}_{\mathrm{t}}
$$

from which we obtain $\partial \mathrm{f} / \partial \mathrm{t}$ due to the temporal variation of the external force:

$$
\begin{equation*}
(\partial \mathrm{f} / \partial \mathrm{t})_{\text {external force }}=-(\mathrm{d} \mathbf{p} / \mathrm{dt}) \cdot \mathrm{grad}_{\mathrm{p}} \mathrm{f}-(\mathrm{d} \mathbf{q} / \mathrm{dt}) \cdot \operatorname{grad}_{\mathrm{q}} \mathrm{f} \tag{2.1}
\end{equation*}
$$

Let us assume that besides the external field, there are intense centers of force, localized in very small regions of the space. Due to collisions with these centers the $(\mathbf{p}, \mathbf{q})$ values of the particles in the phase space are abruptly changed, that is, $(\mathbf{p}, \mathbf{q}) \rightarrow\left(\mathbf{p}^{\prime}, \mathbf{q}^{\prime}\right)$ and vice-versa. The distribution function modifications $\partial \mathrm{f} / \partial \mathrm{t}$ due to these collisions is expressed in terms of the transition probabilities $\omega\left(\mathbf{p} \rightarrow \mathbf{p}^{\prime}\right)$ per unit of time from the quantum state $\mathbf{p}$ to the state $\mathbf{p}^{\prime}$ as follows:

$$
\begin{equation*}
(\partial \mathrm{f} / \partial \mathrm{t})_{\text {collisions }}=\mathrm{A}-\mathrm{B} \tag{2.2}
\end{equation*}
$$

where

$$
\mathrm{A}=\Sigma_{\mathbf{p}^{\prime}} \omega\left(\mathbf{p}^{\prime} \rightarrow \mathbf{p}\right) \mathrm{f}\left(\mathbf{p}^{\prime}\right)[1-\gamma \mathrm{f}(\mathbf{p})]
$$

and

$$
\mathrm{B}=\Sigma_{\mathbf{p}^{\prime}} \omega\left(\mathbf{p} \rightarrow \mathbf{p}^{\prime}\right) \mathrm{f}(\mathbf{p})\left[1-\gamma \mathrm{f}\left(\mathbf{p}^{\prime}\right)\right],
$$

with $\gamma=0$ for bosons and $\gamma=1$ for fermions. In (2.2) we have written for simplicity $\mathrm{f}(\mathbf{p}, \mathbf{q}, \mathrm{t})=\mathrm{f}(\mathbf{p})$. So, the total time variation df/dt due to the external force and the scattering centers is given by

$$
\begin{align*}
\mathrm{df} / \mathrm{dt} & =(\partial \mathrm{f} / \partial \mathrm{t})_{\text {external force }}+(\partial \mathrm{f} / \partial \mathrm{t})_{\text {collisions }} \\
& =-(\mathrm{d} \mathbf{p} / \mathrm{dt}) \cdot \operatorname{grad}_{\mathrm{p}} \mathrm{f}-(\mathrm{d} \mathbf{q} / \mathrm{dt}) \cdot \operatorname{grad}_{\mathrm{q}} \mathrm{f}+\mathrm{A}-\mathrm{B} \tag{2.3}
\end{align*}
$$

Equation (2.3) is called Boltzmann Transport Equation (BTE). For stationary systems, $\mathrm{df} / \mathrm{dt}=0$, we get

$$
\begin{equation*}
(\mathrm{d} \mathbf{p} / \mathrm{dt}) \cdot \operatorname{grad}_{\mathrm{p}} \mathrm{f}+(\mathrm{d} \mathbf{q} / \mathrm{dt}) \cdot \mathrm{grad}_{\mathrm{q}} \mathrm{f}=\mathrm{A}-\mathrm{B} \tag{2.4}
\end{equation*}
$$

Note that (2.4) does not take into account the mutual interactions between the N particles. However, this effect can be included, if we want, in the $\omega\left(\mathbf{p} \rightarrow \mathbf{p}^{\prime}\right)$ calculation.

## 3) Electrical and Thermal Conductivities of Metals.

Let us calculate the electrical $(\sigma)$ and thermal $(\chi)$ conductivities of metal in bulk assuming the simple model: (a) it is composed by a large number N of almost-free electrons and by a rigid crystalline array; (b) the electrons move independently one of the other and being only under the influence of the external field; (c) when they came very close to one point of the array ("scattering center") they are scattered elastically. The N electrons are in the conducting band ${ }^{6}$ with energy $\varepsilon$ between $\varepsilon=0$ and $\varepsilon=$ $\varepsilon_{\mathrm{F}}$, where $\varepsilon_{\mathrm{F}}=3^{2 / 3} \pi^{4 / 3}\left(\hbar^{2} / 2 \mathrm{~m}\right)(\mathrm{N} / \mathrm{V})^{2 / 3}$ is the Fermi energy of the electrons in the volume V . Note that $\mu=\varepsilon_{\mathrm{F}}$ and that $\mathrm{p}_{\mathrm{F}}^{2}=2 \mathrm{~m} \varepsilon_{\mathrm{F}}$.

Now, let us assume that the electric field and that the temperature gradient is along the x -axis, that is, $\mathbf{E}=\mathrm{E} \boldsymbol{i}$ and $\operatorname{grad}_{\mathrm{q}} \mathrm{f}=(\partial \mathrm{T} / \partial \mathrm{x})(\partial \mathrm{f} / \partial \mathrm{T}) \boldsymbol{i}$ where $\boldsymbol{i}$ is the unit vector along the x -axis. Assuming also that the system is in a stationary state, putting $\mathrm{d} \mathbf{p} / \mathrm{dt}=-\mathrm{eE} \boldsymbol{i}$ the first and the second terms of (2.4), are given by $-\mathrm{eE}\left(\partial \mathrm{f} / \partial \mathrm{p}_{\mathrm{x}}\right)$ and $\left(\mathrm{p}_{\mathrm{x}} / \mathrm{m}\right)(\partial \mathrm{T} / \partial \mathrm{x})(\partial \mathrm{f} / \partial \mathrm{T})$, respectively.

To write the right hand side of $(2.4)$ we must take into account the electronic scattering produced by the $\mathrm{N}^{*}$ fixed points of the crystalline array. Assuming that the scattering are elastic the transition probabilities $\omega$ per unit of time are given by $^{7}$

$$
\begin{equation*}
\omega\left(\mathbf{p}^{\prime} \rightarrow \mathbf{p}\right)=\omega\left(\mathbf{p} \rightarrow \mathbf{p}^{\prime}\right)=(\mathrm{p} / \mathrm{m})\left(\mathrm{N}^{*} / \mathrm{V}\right)(\mathrm{d} \sigma / \mathrm{d} \Omega) \mathrm{d} \Omega \tag{3.1}
\end{equation*}
$$

$|\mathbf{p}|=\left|\mathbf{p}^{\prime}\right|$ and $\mathrm{d} \sigma / \mathrm{d} \Omega=\mathrm{d} \sigma(\varepsilon, \theta) / \mathrm{d} \Omega$ is the elastic electron scattering cross section due to collisions with the fixed points of the crystalline array; $\theta$ is the scattering angle between $\mathbf{p}$ and $\mathbf{p}^{\prime}$ and $\mathrm{d} \Omega=\sin \theta \mathrm{d} \theta \mathrm{d} \varphi$. Since the collision are elastic we have $\left|\mathbf{p}-\mathbf{p}^{\prime}\right|=2 \mathrm{p} \sin (\theta / 2)$. The electron diffraction described by $\operatorname{d} \sigma(\varepsilon, \theta) / \mathrm{d} \Omega$ is due, for instance, to phonons, impurities and bulk imperfections. ${ }^{6}$

Taking into account (2.4) we see that $\mathrm{A}-\mathrm{B}$ given by (2.2) for fermions, that is, with $\gamma=1$, is written as

$$
\begin{align*}
\Sigma_{\mathbf{p}^{\prime}} \omega\left(\mathbf{p}^{\prime} \rightarrow \mathbf{p}\right) & \mathrm{f}\left(\mathbf{p}^{\prime}\right)[1-\mathrm{f}(\mathbf{p})]-\Sigma_{\mathbf{p}^{\prime}} \omega\left(\mathbf{p} \rightarrow \mathbf{p}^{\prime}\right) \mathrm{f}(\mathbf{p})\left[1-\mathrm{f}\left(\mathbf{p}^{\prime}\right)\right] \\
= & (\mathrm{p} / \mathrm{m})\left(\mathrm{N}^{*} / \mathrm{V}\right) \int \mathrm{d} \Omega(\mathrm{~d} \sigma / \mathrm{d} \Omega)\left[\mathrm{f}\left(\mathbf{p}^{\prime}\right)-\mathrm{f}(\mathbf{p})\right] \tag{3.2}
\end{align*}
$$

As the external field $\mathbf{E}=\mathrm{E} \boldsymbol{i}$ and temperature gradient $\operatorname{grad} \mathrm{T}=(\partial \mathrm{T} / \partial \mathrm{x}) \boldsymbol{i}$ are along the x -axis we put

$$
\begin{equation*}
\mathrm{f}(\mathbf{p})=\mathrm{f}_{\mathrm{o}}(\varepsilon)+\mathrm{p}_{\mathrm{x}} \chi(\varepsilon) \text { and } \mathrm{f}\left(\mathbf{p}^{\prime}\right)=\mathrm{f}_{\mathrm{o}}(\varepsilon)+\mathrm{p}_{\mathrm{x}}^{\prime} \chi(\varepsilon) \tag{3.3}
\end{equation*}
$$

where $\mathrm{p}^{\prime}=\mathrm{p}_{\mathrm{x}}$ and $\mathrm{p}_{\mathrm{x}}{ }^{\prime}=\mathrm{p}^{\prime} \cos \theta=\mathrm{p}_{\mathrm{x}} \cos \theta$. In this way, substituting (3.3) at (3.2) the right member of (3.2) is written as

$$
\begin{equation*}
-\left(\mathrm{pp}_{\mathrm{x}} / \mathrm{m} \ell(\varepsilon)\right) \chi(\varepsilon) \tag{3.4}
\end{equation*}
$$

where

$$
\ell(\varepsilon)^{-1}=\left(2 \pi \mathrm{~N}^{*} / \mathrm{V}\right) \int \mathrm{d}(\cos \theta)(1-\cos \theta)[\mathrm{d} \sigma(\varepsilon, \theta) / \mathrm{d} \Omega]
$$

The parameter $\ell(\varepsilon)$ which has length dimension is named "mean free path". Finally, taking into account the above results the BTE (2.4) becomes

$$
\begin{equation*}
-\mathrm{eE}\left(\partial \mathrm{f} / \partial \mathrm{p}_{\mathrm{x}}\right)+\left(\mathrm{p}_{\mathrm{x}} / \mathrm{m}\right)(\partial \mathrm{f} / \partial \mathrm{T})(\partial \mathrm{T} / \partial \mathrm{x})=-\left(\mathrm{pp}_{\mathrm{x}} / \mathrm{m} \ell(\varepsilon)\right) \chi(\varepsilon) \tag{3.5}
\end{equation*}
$$

When E and $\partial \mathrm{f} / \partial \mathrm{T}$ are small perturbations we can solve (3.5) in a first order approximation putting $f=f_{o}$ at the left side of the (3.5) obtaining

$$
\begin{equation*}
\chi(\varepsilon)=(\ell / \mathrm{p})\{\mathrm{eE}+[\varepsilon / \mathrm{T}-(\mu / \mathrm{T}-\partial \mu / \partial \mathrm{T})](\partial \mathrm{T} / \partial \mathrm{x})\}\left(\partial \mathrm{f}_{0} / \partial \varepsilon\right) \tag{3.6}
\end{equation*}
$$

Since for electrons $g=2$ the electric flux $J_{x}\left(\right.$ charge $\left./ \mathrm{m}^{2} \mathrm{~s}\right)$ and the thermal flux $Q_{x}$ (kinetic energy $/ \mathrm{m}^{2}$ s) along the x -axis are given, respectively, by

$$
\begin{equation*}
\mathrm{J}_{\mathrm{x}}=-2 \mathrm{e} \int \mathrm{~d} \mathbf{p} /(2 \pi \hbar)^{3}\left(\mathrm{p}_{\mathrm{x}} / \mathrm{m}\right) \mathrm{f}(\mathbf{p}, \mathbf{q}) \tag{3.7}
\end{equation*}
$$

and

$$
\begin{equation*}
\mathrm{Q}_{\mathrm{x}}=2 \int \mathrm{~d} \mathbf{p} /(2 \pi \hbar)^{3} \varepsilon\left(\mathrm{p}_{\mathrm{x}} / \mathrm{m}\right) \mathrm{f}(\mathbf{p}, \mathbf{q}) \tag{3.8}
\end{equation*}
$$

Substituting (3.3) and (3.6) into (3.7) and (3.8) we obtain, respectively,

$$
\begin{align*}
& \mathrm{J}_{\mathrm{x}}=\mathrm{e}[\mathrm{eE}-(\mu / \mathrm{T}-\partial \mu / \partial \mathrm{T})(\partial \mathrm{T} / \partial \mathrm{x})] \mathrm{D}^{(1)}+(\mathrm{e} / \mathrm{T})(\partial \mathrm{T} / \partial \mathrm{x}) \mathrm{D}^{(2)}  \tag{3.9}\\
& \mathrm{Q}_{\mathrm{x}}=-[\mathrm{eE}-(\mu / \mathrm{T}-\partial \mu / \partial \mathrm{T})(\partial \mathrm{T} / \partial \mathrm{x})] \mathrm{D}^{(2)}-(1 / \mathrm{T})(\partial \mathrm{T} / \partial \mathrm{x}) \mathrm{D}^{(3)} \tag{3.10}
\end{align*}
$$

where

$$
\begin{equation*}
\mathrm{D}^{(\mathrm{s})}=-\mathrm{C} \int_{0}^{\infty} \mathrm{d} \varepsilon \varepsilon^{\mathrm{s}} \ell(\varepsilon)\left(\partial \mathrm{f}_{\mathrm{o}} / \partial \varepsilon\right) \tag{3.11}
\end{equation*}
$$

$C=\left[16 \pi \mathrm{~m} / 3(2 \pi \hbar)^{3}\right]$ and $s=1,2$ and 3 . The functions $\mathrm{D}(\mathrm{s})$ are given by (see Appendix of ref.4)

$$
\begin{aligned}
& \mathrm{D}^{(1)}=\mathrm{C}\left[\mu \ell+\left(\pi^{2} / 6\right)(\mathrm{kT})^{2}\left(2 \ell^{\prime}+\mu \ell^{\prime \prime}\right)\right] \varepsilon=\varepsilon_{\mathrm{F}} \\
& \mathrm{D}^{(2)}=\mathrm{C}\left[\mu^{2} \ell+\left(\pi^{2} / 6\right)(\mathrm{kT})^{2}\left(2 \ell+4 \mu \ell^{\prime}+\mu^{2} \ell^{\prime \prime}\right)\right] \varepsilon=\varepsilon_{\mathrm{F}} \\
& \mathrm{D}^{(3)}=\mathrm{C}\left[\mu^{3} \ell+\left(\pi^{2} / 6\right)(\mathrm{kT})^{2}\left(6 \mu \ell+6 \mu^{2} \ell^{\prime}+\mu^{3} \ell^{\prime \prime}\right)\right] \varepsilon=\varepsilon_{\mathrm{F}},
\end{aligned}
$$

where $\ell, \ell^{\prime}=\mathrm{d} \ell / \mathrm{d} \varepsilon$ and $\ell^{\prime \prime}=\mathrm{d}^{2} \ell / \mathrm{d} \varepsilon^{2}$, seen above, are calculated at $\varepsilon=\mu=\varepsilon_{\mathrm{F}}$.

In many cases ${ }^{1-4}$ we can put, in a good approximation, $\mathrm{D}^{(1)} \approx \mathrm{C} \mu \ell\left(\varepsilon_{\mathrm{F}}\right)$, $\mathrm{D}^{(2)} \approx \mathrm{C} \mu^{2} \ell\left(\varepsilon_{\mathrm{F}}\right)$ and $\mathrm{D}^{(3)} \approx \mathrm{C} \mu^{3} \ell\left(\varepsilon_{\mathrm{F}}\right)$. In these conditions putting $\partial \mathrm{T} / \partial \mathrm{x}=0$ in (3.9) the electrical conductivity $\sigma$, defined by $\mathrm{J}_{\mathrm{x}}=\sigma \mathrm{E}$, is given by

$$
\begin{equation*}
\sigma=\mathrm{J}_{\mathrm{x}} / \mathrm{E}=\mathrm{e}^{2} \mathrm{D}^{(1)} \approx \mathrm{e}^{2} \mathrm{C} \mu \ell\left(\varepsilon_{\mathrm{F}}\right)=\mathrm{e}^{2} \mathrm{n} \ell\left(\varepsilon_{\mathrm{F}}\right) / \mathrm{p}_{\mathrm{F}} \tag{3.12}
\end{equation*}
$$

taking into account that $p_{\mathrm{F}}^{2}=2 \mathrm{~m} \varepsilon_{\mathrm{F}}, \varepsilon_{\mathrm{F}}=3^{2 / 3} \pi^{4 / 3}\left(\hbar^{2} / 2 \mathrm{~m}\right)(\mathrm{N} / \mathrm{V})^{2 / 3}$ and that n is the density of free electrons $n=N / V=2 \mathrm{p}_{\mathrm{F}}^{3} /\left(3 \pi^{2} \hbar^{3}\right)$. Similarly, the thermal conductivity $\kappa$ defined by $\mathrm{Q}_{\mathrm{x}}=-\kappa(\partial \mathrm{T} / \partial \mathrm{x})$ is obtained first extracting $E$ from (3.9) putting $J_{x}=0$ and substituting it in (3.10). In this way we get

$$
\begin{equation*}
\kappa=-\mathrm{Q}_{\mathrm{x}} /(\partial \mathrm{T} / \partial \mathrm{x})=\left[\mathrm{D}^{(3)} \mathrm{D}^{(1)}-\mathrm{D}^{(2) 2}\right] / \mathrm{D}^{(1)} \mathrm{T} \approx\left(\pi^{2} / 3\right) \mathrm{k}^{2} \operatorname{Tn} \ell\left(\varepsilon_{\mathrm{F}}\right) / \mathrm{p}_{\mathrm{F}} \tag{3.13}
\end{equation*}
$$

From (3.12) and (3.13) we get the Wiedman-Franz law ${ }^{8}$

$$
\begin{equation*}
\kappa / \sigma=\left(\pi^{2} / 3\right)(\mathrm{k} / \mathrm{e})^{2} \mathrm{~T} \tag{3.14}
\end{equation*}
$$

which gives a good agreement with the experimental results. ${ }^{8}$

## 4) Thermoelectric Metallic Bulk Effects.

The thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice-versa ${ }^{9}$. A thermoelectric device creates a voltage when there is a different temperature on each side. Conversely, when a voltage is applied to it, it creates a temperature difference. At the atomic scale, an applied temperature gradient or an applied voltage cause charged carriers to diffuse in the material. These effects can be used to generate electricity, measure temperature or change the temperature of objects. Because the direction of heating and cooling is determined by the polarity of the applied voltage, thermoelectric devices are efficient temperature controllers. The term "thermoelectric effect" encompasses three separately identified effects: the Seebeck effect, Peltier effect and Thomson effect.

These effects will be studied taking into account (3.9) and (3.10) that will be written as

$$
\begin{equation*}
\mathrm{J}=\mathrm{e}^{2} \mathrm{ED}^{(1)}-\mathrm{e}\left[(\mu / \mathrm{T}-\partial \mu / \partial \mathrm{T}) \mathrm{D}^{(1)}+\mathrm{D}^{(2)} / \mathrm{T}\right](\partial \mathrm{T} / \partial \mathrm{x}) \tag{4.1}
\end{equation*}
$$

and

$$
\begin{equation*}
\mathrm{Q}=-\mathrm{eED}^{(2)}-\left[(\mu / \mathrm{T}-\partial \mu / \partial \mathrm{T}) \mathrm{D}^{(2)}+\mathrm{D}^{(3)} / \mathrm{T}\right](\partial \mathrm{T} / \partial \mathrm{x}) \tag{4.2}
\end{equation*}
$$

## 4.1) Seebeck Effect.

The Seebeck effect is the conversion of temperature differences directly into electricity and is named for discovered in 1821 by the German physicist Thomas Johann Seebeck in 1821. It will be described using the Figure 1 where is shown an electric circuit known as a thermo-electric pair, formed by two different metals, A and B, where there is no current, that is, $\mathrm{J}=0$ and where the junctions b and c are maintained at different temperatures $\mathrm{T}_{\mathrm{b}}$ and $\mathrm{T}_{\mathrm{c}}$, respectively. A voltmeter is placed between the points $a$ and $d$ that are maintained at the same temperature $T_{0}$.


Figure 1. Diagram of the circuit with two different metals A and B with voltmeter between a and b of the metal $\mathrm{B} .{ }^{9}$ The junctions b and c are maintained at the temperatures $\mathrm{T}_{\mathrm{b}}$ and $\mathrm{T}_{\mathrm{c}}$, respectively.

So, putting J = 0 in (4.1) we obtain the electric field E created by the temperature gradient $\mathrm{dT} / \mathrm{dx}$ between the junctions c and d :

$$
\begin{equation*}
\mathrm{E}=(1 / \mathrm{e})\left[\mu / \mathrm{T}-\partial \mu / \partial \mathrm{T}-(1 / \mathrm{T})\left(\mathrm{D}^{(2)} / \mathrm{D}^{(1)}\right)\right](\mathrm{dT} / \mathrm{dx}) \tag{4.3}
\end{equation*}
$$

In this way, putting $G=\mu / T-\partial \mu / \partial T-(1 / T)\left(D^{(2)} / D^{(1)}\right)$, the voltage measured by the voltmeter between a and d must be given by $\mathrm{V}=\mathrm{V}_{\mathrm{ad}}=\int_{\mathrm{a}}^{\mathrm{d}} \mathrm{E} d \mathrm{dx}$, that is,

$$
\int_{a}{ }^{d} G(d T / d x) d x=\int_{a}{ }^{b} G_{A} d T+\int_{b}{ }^{c} G_{B} d T+\int_{c}{ }^{d} G_{A} d T
$$

where $G_{A}$ and $G_{B}$ are the $G$ values for the metals $A$ and $B$, respectively. Since the temperatures at the junctions $a$ and $d$ is $T_{o}$, at $b$ is $T_{b}$ and at $c$ is $T_{c}$ we see that (3.4) is written as

$$
\begin{equation*}
\int_{\mathrm{a}}^{\mathrm{d}} \mathrm{G}(\mathrm{dT} / \mathrm{dx}) \mathrm{dx}=\int_{\mathrm{Tb}}^{\mathrm{Tc}}\left(\mathrm{G}_{\mathrm{B}}-\mathrm{G}_{\mathrm{A}}\right) \mathrm{dT} \tag{4.5}
\end{equation*}
$$

Since $\mu_{\mathrm{A}}(\mathrm{T})=\mu_{\mathrm{B}}(\mathrm{T})$ at the metal junction due to the equilibrium condition for the electron gases we see that only the term $(1 / T)\left(\mathrm{D}^{(2)} / \mathrm{D}^{(1)}\right)$ will give a non-null contribution to (4.5). This term can be put in a first approximation using (3.11),

$$
\begin{align*}
(1 / \mathrm{T})\left(\mathrm{D}^{(2)} / \mathrm{D}^{(1)}\right) & \approx(1 / \mathrm{T})\left\{\left[\mu^{2} \ell+\left(\pi^{2} / 6\right)(\mathrm{kT})^{2}\left(2 \ell+4 \mu \ell^{\prime}\right)\right] /(\mu \ell)\right\} \\
& =\mu / \mathrm{T}+\left(\pi^{2} \mathrm{k}^{2} \mathrm{~T} / 3 \mu\right)\left(1+2 \ell^{\prime} / \ell\right) \tag{4.6}
\end{align*}
$$

Defining $\Lambda=1+2 \mu \ell^{\prime} / \ell$ we verify that $\mathrm{V}_{\mathrm{ad}}$ between the junctions a and d is given by

$$
\begin{equation*}
\mathrm{V}_{\mathrm{ad}}=\mathrm{V}=\left(\pi^{2} \mathrm{k}^{2} / 3 \mathrm{e}\right) \int_{\mathrm{Tb}} \mathrm{Tc}^{\mathrm{Tc}} \mathrm{dTT}\left[(\Lambda / \mu)_{\mathrm{B}}-(\Lambda / \mu)_{\mathrm{A}}\right) \tag{4.7}
\end{equation*}
$$

Defining the Thomson coefficient $\tau=\pi^{2} \mathrm{k}^{2} \Lambda \mathrm{~T} /(3 \mu \mathrm{e})$, (4.7) becomes

$$
\begin{equation*}
\mathrm{V}=\int_{\mathrm{Tb}}{ }^{\mathrm{Tc}} \mathrm{dT}\left(\tau_{\mathrm{B}}-\tau_{\mathrm{A}}\right) \tag{4.8}
\end{equation*}
$$

For a small temperature difference $\mathrm{T}_{\mathrm{c}}-\mathrm{T}_{\mathrm{b}}=\delta \mathrm{T}$, (4.8) can be written as

$$
\delta \mathrm{T} \approx \mathrm{~V} /\left(\tau_{\mathrm{B}}-\tau_{\mathrm{A}}\right)
$$

The voltage created by this effect is on the order of several microvolts per Kelvin difference. One such combination, copper-constantan has a Seebeck coefficient of 41 microvolts per Kelvin at room temperature. The Seebeck effect is used in the thermocouple to measure a temperature difference; absolute temperature may be found by setting one end to a known temperature. A metal of unknown composition can be classified by its thermoelectric effect if a metallic probe of known composition, kept at a constant temperature, is held in contact with it. In a recent paper ${ }^{10}$ we have shown that for very thin metallic films, with thickness $\mathrm{d} \leq 20 \mathrm{~nm}$, due to quantum size effects there appears a "Quantum Seebeck Effect".

## 4.2) Peltier Effect.

The Peltier effect is the presence of heat at an electrified junction of two different metals A and B. It was discovered in 1834 by the French physicist Jean-Charles Peltier. Let us assume now that, in Figure 1, instead of a voltmeter there is a battery with voltage V . In these conditions an electrionic current flows through the circuit in the counter clockwise sense. Let us also assume that the junctions b and c are maintained almost at the same temperature in such a way that $\mathrm{dT} / \mathrm{dx}=0$ in the circuit. In this case, as $\mathrm{dT} / \mathrm{dx}=0$ we get from (4.1) and (4.2): $\mathrm{J}=\mathrm{e}^{2} \mathrm{ED}^{(1)}$ and $\mathrm{Q}=\mathrm{eED}^{(2)}$, that
is, $Q=\left(D^{(2)} / \mathrm{eD}^{(1)}\right) J$. Since $\left(\mathrm{D}^{(2)} / \mathrm{eD}^{(1)}\right) \approx \mu / \mathrm{e}+\tau \mathrm{T}$, where $\tau=\pi^{2} \mathrm{k}^{2} \Lambda \mathrm{~T} /(3 \mu \mathrm{e})$ is the Thomson coefficient defined by (4.8), the heat flux is written as $\mathrm{Q}=$ $\Pi \mathrm{J}$, where $\Pi=\mu / \mathrm{e}+\tau \mathrm{T}$ is named Peltier coefficient. So, the heat flux in the counter clockwise sense along the branch A and B are given, respectively, by $\mathrm{Q}_{\mathrm{A}}=\Pi_{\mathrm{A}} \mathrm{J}$ and $\mathrm{Q}_{\mathrm{B}}=\Pi_{\mathrm{B}} \mathrm{J}$, respectively. In this way, at the junction $b$ there is a heat production $Q_{b}=\left(\Pi_{A}-\Pi_{B}\right) J$ and at the junction $c$ a heat absorption $\mathrm{Q}_{\mathrm{c}}=\left(\Pi_{\mathrm{B}}-\Pi_{\mathrm{A}}\right) \mathrm{J}=-\mathrm{Q}_{\mathrm{b}}$.

## 4.3) Thomson Effect.

The Thomson effect describes the heating or cooling of a currentcarrying conductor with a temperature gradient. Let us assume that along a conductor (non superconductor) submitted to a temperature gradient dT/dx passes a current density J . It can be shown that heat production $q$ per unit of volume in the circuit is given by ${ }^{9}$

$$
\begin{equation*}
\mathrm{q}=\rho \mathrm{J}^{2}-\tau \mathrm{J}(\mathrm{dT} / \mathrm{dx}) \tag{4.9}
\end{equation*}
$$

where $\rho$ is the resistivity of the material and $\tau$ is the Thomson coefficient. The first term is the Joule heating which does not change in sign; the second term is the Thomson heating, which follows J changing sign.

In metals such as zinc and copper, whose temperature is directly proportional to their potential, when current moves from the hotter end to the colder end, there is a generation of heat and the positive Thomson effect occurs. Conversely, in metals such as cobalt, nickel, and iron, whose temperature is inversely proportional to their potential, when current moves from the hotter end to the colder end, there is a heat absorption and the negative Thomson effect occurs.

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