**Kinetic Transport Theory #2**

**Clarification of kinetic theory**

A gradient of temperature in a solid generally creates a flux of kinetic energy, often called thermal current or heat transfer. Often this heat transfer occurs by charged particles, so there can also be electrical current from the temperature gradient, depending on the boundary conditions. As we will see shortly, thermal current is considerably more complicated in the kinetic formalism than electrical current because particles having different velocity directions contribute differently to the final result. So thermal current forces us to take a deeper look at the foundation of kinetic theory, particularly the nature of the particles.

We have stated previously that kinetic theory treats all the particles as statistically independent and interacting with the temperature “bath” through randomizing collisions that occur at a rate $\tau^{-1}$, where $\tau$ is the relaxation time. If the collision rate is fast enough that sample-dependent boundary or shape effects do not matter, then the distribution of particles velocity vectors in space must be purely random. Furthermore, if we neglect the fact that some collisions are elastic (i.e., conserve kinetic energy) and others are inelastic, we can adopt an “average kinetic velocity”, $v_0$, for every particle in the solid. This velocity (magnitude) is assumed to be constant until an external force is applied.

These points can be expressed by writing the velocity of any given particle as

$$\vec{v} = v_0 \hat{r} = v_0 (\hat{x} \sin \theta \cos \phi + \hat{y} \sin \theta \sin \phi + \hat{z} \cos \theta) \quad (1)$$

where $\hat{r}$ is the radial unit vector in spherical coordinates. Geometrically, the velocity vectors of all particles in a population would terminate on a sphere of radius $v_0$, all directions of the velocity vector being equally probable.
Energy Flux and Charge Flux: One Dimensional Analysis

Besides the charge flux, or electrical current, the second important particle flux in kinetic theory (and transport theories, in general) is the energy flux $\mathbf{J}_U = n \cdot [(1/2)mv^2] \mathbf{v}$.

Since all energy is assumed to be kinetic, and kinetic energy comprises heat, this is also the heat flux and is often designated as $\mathbf{J}_K$. For the simple geometry shown in Fig. 1(a) of transport of charged particles in a uniform electric field and homogeneous temperature $T$, there is a simple relationship between the heat flux and the charge flux. The electric field is assumed uniform along the $z$ axis so that

$$J_{q,z} = n \cdot q \cdot v_z = n \cdot q \cdot \mu E_z$$

But because the particles carry both charge and heat, the kinetic velocities are the same, so that

$$J_{U,z} \equiv J_{K,z} = n \cdot [(1/2)mv^2] \cdot v_z = n \cdot [(1/2)mv^2] \cdot \mu E_z$$

Thus the ratio of heat flux to electrical flux is given by

$$\frac{J_K}{J_q} \equiv \Pi = \frac{(1/2)mv^2}{q} \equiv \frac{U^*_K}{q}$$

where $U^*_K$ is the kinetic energy per particle, and $\Pi$ is the Peltier coefficient – an important quantity in solids whenever electrical and thermal transport are occurring simultaneously.

Motion in a Temperature Gradient: One-Dimensional Analysis

Given these clarifications, we can also proceed to analyze the electrical and thermal effects together for the special geometry of a parallelepiped in which heat and charge are restricted to flowing in one end, and out the other. We assume that the long axis of the parallelepiped is the $z$ axis, as shown in the cross-sectional views of Fig. 1(b) and (c). The
temperature at one end is assumed to be $T_2$ and the opposite end $T_1$, where $T_2 > T_1$. We examine the relevant physical quantities in any plane perpendicular to the $z$ axis. The analysis is carried out in two extreme cases: (1) with a metal wire (“short circuit”) connecting both ends so that there is no difference in electrostatic potential between them, and (2) no metal wire (“open circuit”) connecting the two ends so that an electrostatic potential difference can build up in response to the temperature difference.

**Short-Circuit Conditions**

In the short-circuit case represented by Fig. 1(b), the heat flux along the $z$ axis is given by the (scalar) expression

$$J_{K,z}^L = n_z \cdot v_z \cdot U^*_K$$  \hspace{1cm} (5)$$

where $n_z$ and $v_z$ are the $z$ components of the density and velocity, respectively. We assume that the temperature difference $T_2 - T_1 = \Delta T$ is small compared to $T_1$ and $T_2$ so that $n$ remains
approximately constant throughout the sample, and the kinetic behavior remains isotropic about any point. Intuitively we then expect that the left-going heat flux in Fig. 1(a) \( J^L_Q \) is greater than the right going flux \( J^R_Q \) because \( J^L_Q \) is associated with particles coming from a hotter region \( (T_2 > T_1) \) and, therefore, having higher kinetic energy. This guides us to calculate the difference \( \Delta J_{K,z} \), also called the net heat flux, by a judicious application of the chain rule of differential calculus:

\[
\Delta J_{Q,z} = J^L_{Q,z} - J^R_{Q,z} \approx -\frac{dJ_Q}{dU_K} \frac{dU^*_K}{dU^*_K} \frac{dT}{dz} \Delta z
\]

where the minus sign is added to account for the fact that kinetic energy flows from high-T regions to low-T regions. From (5), we calculate

\[
\frac{dJ_{Q,z}}{dU_K} = nV_z
\]

Furthermore, all kinetic energy contributes to heat, but \( U^*_K \) is only one-third of the total since the fundamental kinetic assumption of (1) is an isotropically directed velocity. In other words

\[
\frac{dU^*_K}{dT} = \frac{1}{n} C'_v
\]

where \( C'_v \) is the specific heat capacity. Thus (6) becomes

\[
\Delta J_{K,z} \approx -\nu_z C'_v \frac{dT}{dz} \Delta z
\]

The next and most subtle step is to estimate \( \Delta z \), the seemingly arbitrary spatial differential. Presumably, \( \Delta z \) should be much less than the length of the parallelapiped, but larger than the atomic dimension so that it makes sense to be using macroscopic
thermodynamic quantities like temperature and heat capacity. In most cases a reasonable distance is the “mean-free-path”,

\[ \Delta z = v_z \tau \]  

(8)

Substitution of this into (7) yields,

\[ \Delta J_{K,z} \approx -v_z C'_v \frac{dT}{dz} \tau = -\kappa \frac{dT}{dz} \]  

(9)

where the last step defines the thermal conductivity:

\[ \kappa = v_z^2 \tau C'_v \]  

(10)

This is a very useful expression for the thermal conductivity of many different types of independent particles, quasiparticles, or quantized collective excitations. Good examples are electrons, phonons, and magnons.

The last step is to spatially average over the isotropic kinetic distribution represented by (1). The average is taken over just the hemisphere for which the z axis is the polar axis and all directions being equally weighted:

\[ \langle v_z^2 \rangle = \frac{2 \pi}{\int_0^{\pi/2} \int_0^{\pi/2} (v_z \cdot z)^2 \sin \theta d\theta d\phi} \frac{\int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta}{\int_0^{\pi/2} \sin \theta d\theta} = \frac{-v_0^2 (\cos^3 \theta / 3)_{\pi/2}^{\theta_0}}{-\cos \theta_{\pi/2}^{\theta_0}} = \frac{1}{3} v_0^2 \]  

(11)

So (10) become

\[ \kappa = (1/3)v_0^2 \tau C'_v \]  

(12)

Open-Circuit Conditions

We now consider the open-circuit case of Fig. 1(c) whereby a temperature gradient leads to the motion of charged particles and the creation of an internal electric field.

Historically, this is called a thermoelectric effect. Electric current flows along with the thermal
current until enough charge builds up at the ends of the sample to stop the flow. This condition is defined in general by an internal electric field

$$\vec{E} = \Sigma \cdot \hat{\nabla} T$$

where $\Sigma$ is called the thermopower, or Seebeck coefficient. Naturally the direction of the electric field in the bar geometry of Fig. 1(b) is along the $z$ axis, $E_z = \Sigma (dT/dz)$.

To calculate $\Sigma$ we can inspect in any plane perpendicular to the $z$ axis. First we write the net velocity difference at a point $z_0$

$$\nu_L - \nu_R = \Delta \nu_z = -\frac{d\nu_z}{dT} \frac{dT}{dz} \Delta z$$

where again, the length scale is the “mean-free-path” $\Delta z = v_z \tau$, and the negative sign is added to account for the fact that kinetic energy transfers from high-T to low-T regions. Therefore,

$$\Delta \nu_z = -v_z \tau \frac{d\nu_z}{dT} \frac{dT}{dz} = -\frac{\tau}{2} \frac{d\nu_z^2}{dT} \frac{dT}{dz}$$

and

$$\Delta \nu_z = -\frac{\tau}{m} \frac{d}{dT} \left( \frac{1}{2} m v_z^2 \right) \frac{dT}{dz}$$

Now we spatially average (designated by an overbar) with respect to the isotropic kinetic distribution of (1),

$$\overline{\Delta \nu_z} = -\frac{\tau}{m} \frac{d}{dT} \left( \frac{1}{2} m v_z^2 \right) \frac{dT}{dz} = -\frac{\tau}{3m} \frac{d}{dT} \left( \frac{1}{2} m v_0^2 \right) \frac{dT}{dz}$$

But since $(1/2)mv_0^2 = U_k^*$, we can write

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1 after Thomas Seebeck, an early-19th century German physicist
In steady state and for the open-circuit conditions, the thermal $\Delta v_z$ will spatially separate the particles, creating an internal electric field when they have charge. This internal field will induce the “drift” velocity effect derived earlier for purely electrical transport,

$$v_z^e \equiv \mu E_z = \frac{q\tau}{m} E_z.$$  \hspace{1cm} (14)

A steady state will be reached when the thermally-induced velocity difference from (13) is equal and opposite to the drift velocity (12). That is

$$\frac{q\tau}{m} E_z = -\Delta v_z = \frac{+\tau C'_v}{3m \cdot n} \frac{dT}{dz}$$

or,

$$E_z = \frac{C'_v}{3n \cdot q} \frac{dT}{dz}$$

$$\Rightarrow \Sigma = \frac{E}{dT/dz} = \frac{+C'_v}{3qn} = \frac{-C'_v}{3en} \text{ (for electrons)}.$$  \hspace{1cm} (15)

**Specification of kinetic theory results with Maxwell Boltzmann distribution: Transport Laws**

With relatively little work, kinetic theory predicts several important quantities, $\sigma$, $\Pi$, $K$, and $\Sigma$. All off them represent linear response to non-equilibrium conditions. (gradient in temperature, electrostatic potential, or both). But to relate the thermally-related quantities to experiment, we need to know the values of the kinetic velocity $v_0$ or the related kinetic energy per particle $U'_K$. The simplest and most popular approach is to use the Maxwell-Boltzmann distribution:

\footnote{This is the big advantage of kinetic theory over all other transport formalisms – capturing multiple physical effects with the greatest possible simplicity.}

distribution of velocities derived much earlier in the coverage of statistical mechanics. A key result of the Maxwell-Boltzmann distribution was the *equipartition theorem*, for which the mean energy of the particle is \( \frac{1}{2} k_B T \) per “degree-of-freedom.” In kinetic theory, there are three degrees of freedom, \( v_x \), \( v_y \), and \( v_z \), in total, each with equal value (\( v_0 \)) and weighting. Thus,

\[
< (1/2) m v_0^2 > = < (1/2) m (v_x^2 + v_y^2 + v_z^2) > = (3/2) k_B T \]

\[
C'_V \equiv \frac{n d < U_K^* >}{dT} = (3/2) nk_B \tag{16}
\]

where the < > brackets denote statistical averaging.

For the Peltier coefficient of (2), (16) leads to

\[
\Pi = \frac{(3/2) k_B T}{q} = -3 k_B T / 2 e \tag{17}
\]

where the last step applies to electrons. For the thermal conductivity of (12), (16) yields

\[
K = \frac{3 k_B T}{3m} \tau \cdot \frac{3}{2} nk_B = \frac{3nk_B^2 T \tau}{2m} \tag{18}
\]

For the Seebeck coefficient (15), (16) yields

\[
\Sigma = \frac{C'_V}{3 q n} = \frac{nk_B}{2qn} = \frac{-k_B}{2e} \tag{19}
\]

where the last step applies to electrons.

It is interesting and historic to take the ratio of \( K \) to \( \sigma \) using (16):

\[
\frac{K}{\sigma} = \frac{(1/3) C'_V v_0^2 \tau}{nq^2 \tau / m} = \frac{3}{2} \left( \frac{k_B}{q} \right)^2 \cdot \frac{T}{\left( \frac{k_B}{e} \right)^2 \cdot T} \tag{20}
\]
where the last step pertains to the particles being electrons. This linear dependence of $K/\sigma$ on $T$ was discovered in metals during the mid-19th century and called the \textit{Wiedemann Franz Law}.

The ratio of the Peltier to Seebeck coefficients, (15)/(18), is simply given

$$\frac{\Pi}{\Sigma} = \frac{(3/2)k_B T}{(1/2)k_B / q} = 3T,$$

a result known as Kelvin’s law, and a cornerstone of the rather esoteric field of irreversible thermodynamics.

\textit{Comparison of Kinetic Theory and Transport Laws with Experiment}

The linear relation of $K/\sigma$ to $T$ of the Wiedemann-Franz law forms an important comparison with experiment. The proportionality constant, $K/\sigma T$, is called the Lorenz number, and according to (20) has the value

$$L = (3/2) (k_B/e)^2 = 1.11 \times 10^{-8} \text{ [MKSA]}$$

A few experimental values for common metals are listed in Table 1 below. Note that the experimental values are just over two-times larger than the kinetic-theory prediction of (14). Not bad agreement for (14) considering the low level of effort expended at deriving it!

Most metals have Lorenz numbers in the range shown and display the linear dependence $K/\sigma = L \cdot T$ over a wide temperature range. But semiconductors do not generally display this behavior.

<table>
<thead>
<tr>
<th>Material</th>
<th>$L \times 10^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2.23</td>
</tr>
<tr>
<td>Au</td>
<td>2.35</td>
</tr>
<tr>
<td>Pb</td>
<td>2.47</td>
</tr>
</tbody>
</table>
The reason, as might be expected, is that the thermal current and electrical current are not carried by the same particle type in semiconductors. The electrical current is carried by free carriers, as in metals, but the thermal current is carried primarily by phonons.

To understand the discrepancy between (22) and Table 1, we recall that in metals, semimetals, or “degenerate” semiconductors, the Pauli exclusion principle allows only those electrons near or above the Fermi energy to change their kinetic energy significantly in response to a significant change of temperature. This was quantified in the coverage of the heat capacity for the Fermi model of free electrons:

\[ C_v \cong \frac{\pi^2}{2} n k_B \frac{T}{T_F}, \]

which is generally much smaller than the kinetic theory result \((3/2)n k_B\). To illustrate this point, we recall that the typical Fermi temperature in good metals is \(T_F = 5 \times 10^4 K\), for which \(C_v \cong 0.01(\frac{3}{2} n k_B)\) at \(T \cong 300 K\). In addition, \(\frac{1}{2} m v^2 \neq \frac{3}{2} k_B T\) in the Fermi model, but instead,

\[ \frac{1}{2} m v^2 \equiv k T_F. \]

Adding these corrections to (13), we get

\[
\frac{K}{\sigma} = \frac{m}{3} C_v \frac{m}{nq^2} = \frac{m \pi^2}{3} \frac{n k_B}{T_F} \frac{T}{m} = \frac{\pi^2}{3} \frac{k_B^2}{q^2} \cdot T = \frac{\pi^2}{3} \frac{k_B^2}{e^2} \cdot T
\]  

(23)

where the last step pertains to the particles being electrons.

The difference between (23) and the kinetic theory prediction is stated by

\[
\frac{(K/\sigma)_{\text{corrected}}}{(K/\sigma)_{\text{kinetic}}} = \frac{\pi^2}{3} = 2.19
\]

So the corrected Lorenz number becomes

\[ \Rightarrow \]
This is now in good agreement with the experimental values in Table I. And indeed, this agreement was one of the early triumphs of the Fermi model of the free electrons in metals.

For the Seebeck coefficient of (19), we get the evaluation

$$\Sigma = \frac{C_v}{3qn} = \frac{k_B}{2q} = -4.3 \times 10^{-5} V / K$$

(24)

where the last step pertains to electrons. This is to be compared to the experimental values listed in Table II. Clearly, the magnitude deviates from experiment for all materials except the semimetals, antimony and bismuth.

<table>
<thead>
<tr>
<th>Material</th>
<th>Seebeck Coefficient [x10^{-6} V/K](@273 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>6.5</td>
</tr>
<tr>
<td>Iron</td>
<td>19</td>
</tr>
<tr>
<td>Aluminum</td>
<td>3.5</td>
</tr>
<tr>
<td>Silicon</td>
<td>440</td>
</tr>
<tr>
<td>Antimony</td>
<td>47</td>
</tr>
<tr>
<td>Bismuth</td>
<td>-72</td>
</tr>
</tbody>
</table>

To explain the discrepancy with gold and the other common metals, we resort to the Fermi model once again, noting that

$$C_v' = \frac{\pi^2}{2} nk_B \frac{T}{T_F} \ll \frac{3}{2} nk_B$$

So,

$$\Sigma = \frac{(-\pi^2 / 2)nk_B T / T_F}{3ne} = \frac{-\pi^2}{6} \frac{k_B T}{e T_F}$$

(25)

For example, gold has $T_F \approx 6.4 \times 10^4 \text{K}$ @ T=273K, so that

$$\Rightarrow \Sigma \approx -0.6 \times 10^{-6} V / K$$

still in poor agreement with the experimental value of $Q = 6.5 \times 10^{-6}$.
In addition, semiconductors display poor agreement between the experimental and theoretical Seebeck coefficient, even though no correction is needed by the Fermi model. In intrinsic silicon, for example, the experimental thermopower is $Q \sim 4.4 \times 10^{-4} V/K$. This is over ten-times higher than kinetic prediction of (24). The reason for this is the same as for the inaccuracy in predicting the Lorenz number: the electrical and thermal currents in semiconductors are carried primarily by two different particle types: electrons (or holes) for electrical and phonons for thermal. From (16), the heat capacity of phonons remains high even when the density $n$ of free carriers becomes low.

In conclusions, the Seebeck coefficient and other thermoelectric metrics are amongst the most difficult quantities to predict theoretically in all of transport theory. As we shall see later, they are strongly sensitive to the band structure and, therefore, are best addressed with a more sophisticated treatment we will develop later called *semiclassical transport*. 