***Transport Theory #5***

***Boltzmann Transport in Uniform Electric Field (cont)***

We have seen how the solution to the classical Boltzmann transport equation in a uniform electric field has the form

$$< \tau >= \frac{m}{3k_B T} \frac{\int_0^\infty v^4 \tau(v) f_0 (1 - f_0) dv}{\int_0^\infty v^2 f_0(v) dv} \tag{1}$$

where $f_0$ is the equilibrium distribution function, the Fermi-Dirac function in the most general case. The product $f_0(1-f_0)$ has deeper meaning than might first appear. From statistical mechanics we know $f_0$ is the mean number of charge carriers (assumed to be fermions), or mean "occupancy", of any space-spin state quantum state. So $1-f_0$ is the mean "de-occupancy" of that same state. This reflects an important principle in transport theory at all levels, including fully quantum mechanical. Which is, transport requires the presence of a particle occupying a state, *and* it requires an available state for that particle to transfer into.

In the limit of low carrier concentration (i.e., non-degenerate population) covered in the previous section, $f_0$ approaches zero for most particles in the population so the "de-occupancy" factor can be assumed to be unity. This is primarily what makes the calculation of (1) tractable with the Maxwell-Boltzmann function – a very common and useful exercise with semiconductors. In the intermediate case of moderate carrier concentration, $0 < f_o < 1$ and $0 < 1 - f_0 < 1$, so that neither factor can be ignored and the calculation of (1) becomes much more complicated than the low-concentration case.

In the limit of high carrier concentration, $f_o$ is approaching 1 for most particles in the population and the "de-occupancy" factor approaches zero, but clearly can not be ignored. Fortunately, the calculation of (1) gets simple again in this "degenerate" limit because of the behavior of the behavior of the Fermi-Dirac function, $f(U) = \{\exp[(U - U_F)/k_B T] + 1\}^{-1}$. Plotted in Fig. 1 are $f_0$, $1-f_0$ and the product $f_0 (1 - f_0)$. The only place where $f_0$ and $1-f_0$ are not nonzero is in the region around $U_F$, which makes the product display a narrow symmetric peak.

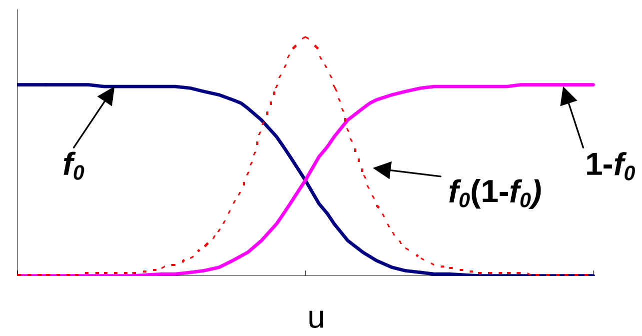


Fig. 1.

To a good approximation that is best in metals, the product looks like a Dirac delta function: $f_0\left(1-f_0\right)\approx A\delta\left(U-U_F\right)$. We find the coefficient A by definition of $f_0$ and its derivative with respect to U:

$$\int_0^\infty f_0\left(U\right)\left[1-f_0\left(U\right)\right]du=\int_0^\infty -k_BT\frac{df_0}{dU}dU=\left.\frac{-k_BT}{1+\exp[(U-U_F)/k_BT]}\right|_0^\infty\cong k_BT$$

$\Rightarrow A = k_BT$

So, $$f_0\left(1-f_0\right)\cong k_BT\delta\left(U-U_F\right)\leftarrow \textit{Dirac Delta function} \qquad (2)$$

---

Aside on Dirac Delta function:

Normalization property: $\int_{-\infty}^{\infty}\delta\left(x-x'\right)dx=1$

"Sifting" property $\int_{-\infty}^{\infty}f\left(x\right)\delta\left(x-x'\right)dx=f\left(x'\right)$

Derivative sifting property: $\int f\left(x\right)\frac{d\delta\left(x-x'\right)}{dx}dx=-\left.\frac{df}{dx}\right|_{x=x'}$

Symmetry and factor properties: $\delta\left(-x\right)=\delta\left(x\right)$, $\delta\left(\pm ax\right)=\frac{1}{a}\delta\left(x\right)$ $a>0$

To utilize these properties, we go back and re-write *(1)* in terms of energy using $U = \frac{1}{2}m\mathrm{v}^2$,

$$dU = m\mathrm{v}d\mathrm{v} = \sqrt{2Um}\,d\mathrm{v}\,; \qquad \mathrm{v}^2 d\mathrm{v} = \mathrm{v}^2\frac{dU}{m\mathrm{v}} = \frac{\mathrm{v}}{m}dU = \frac{\sqrt{2Um}}{m}dU = \frac{\sqrt{2U}}{m^{3/2}}dU$$

$$m\int \mathrm{v}^4 d\mathrm{v} = 2\int u\mathrm{v}^2 dv = 2\int \frac{U\sqrt{2U}}{m^{3/2}}dU\,, \quad \text{and} \quad \frac{m\int \mathrm{v}^4 d\mathrm{v}}{\int \upsilon^2 d\mathrm{v}} = \frac{2\int U^{3/2}dU}{\int U^{1/2}dU}$$

This leads to $$<\tau> = \frac{2\int U^{3/2}\tau(U)\,f_0(U)\left[1-f_0(U)\right]dU}{3k_BT\int U^{1/2}f_0(U)\,dU}$$

Given the expression for $<\tau(U)>$, we can now apply the delta function approximation of (2) in the numerator and the following Heaviside unit step function approximation in the denominator

$$f(U) = \frac{1}{\exp[(U-U_F)/k_BT]+1} \approx \theta(U)\cdot\theta(U_F - U)$$

This leads to

$$<\tau> \approx \frac{2}{3k_BT}\frac{\int_0^\infty U^{3/2}\tau(U)k_BT\delta(U-U_F)\,dU}{\int_0^{U_F}U^{1/2}dU}$$

$$<\tau> \approx \frac{2}{3}\frac{U_F^{3/2}\tau(U_F)}{\frac{2}{3}U^{3/2}\Big|_0^{U_F}} = \frac{2}{3}\frac{U_F^{3/2}\tau(U_F)}{\frac{2}{3}U_F^{3/2}} = \tau(U_F)$$

This is a very important result: the non-equilibrium ensemble average <τ(U)> can be taken as value at Fermi energy. This leads to the adage often use in the transport theory of metals: "all the action is a the Fermi energy" (or more accurately, the *Fermi surface*).

***Boltzmann Equation with Concentration Gradient***

Going back to the time-dependent Boltzmann equation, we can establish another solution that is essentially opposite to transport in a uniform electric field. We suppose that ∂f/∂v is zero for all velocity components, but ∂f/∂z is nonzero. This represents the case of a concentration gradient that, as in the case of kinetic theory, can be created by injection of carriers at one point of an otherwise homogeneous semiconductor. To simplify the analysis we assume the concentration gradient occurs only along one direction of space, z. Then the time-dependent Boltzmann equation (in the relaxation approximation) can be written

$$\frac{df}{dt} = -\frac{dz}{dt}\frac{\partial f}{\partial z} - \frac{f - f_0}{\tau(\mathrm{v})} \tag{3}$$

As in the case of electrical drift, we assume $\frac{\partial f}{\partial z} \approx \frac{\partial f_0}{\partial z}$. And then we expand by the chain rule,

$\frac{\partial f_0}{\partial z} = \frac{\partial f_0}{\partial n}\frac{dn}{dz}$, so that in the steady state (3) becomes

$$\Rightarrow f = f_0 - v_z \tau(\mathrm{v})\frac{\partial f_0}{\partial n}\frac{dn}{dz} = f_0 + f' \tag{4}$$

The particle current $J_n = nv_z$, which has a (transport) ensemble average,

$$< J_n >= n < \mathrm{v}_z >= \frac{n\int \mathrm{v}_z f d\vec{\mathrm{v}}}{\int f d\vec{\mathrm{v}}} = \frac{n\int \mathrm{v}_z f' d\vec{\mathrm{v}}}{\int f_0 d\vec{\mathrm{v}}}$$

Substitution of (4) yields

$$< J_n >= -n\frac{dn}{dz}\frac{\int \mathrm{v}^4 \tau(\mathrm{v})\frac{\partial f_0}{\partial n}\cos^2\theta \sin\theta d\mathrm{v} d\theta d\phi}{\int f_0 \mathrm{v}^2 \sin\theta d\mathrm{v} d\theta d\phi} = -\frac{n}{3}\frac{dn}{dz}\frac{\int_0^\infty \mathrm{v}^4 \tau(\mathrm{v})\frac{\partial f_0}{\partial n} d\mathrm{v}}{\int_0^\infty \mathrm{v}^2 f_0 d\mathrm{v}} \equiv -D\frac{dn}{dz}$$

where the diffusivity is defined by: $$D = \frac{n}{3}\frac{\int_0^\infty \mathrm{v}^4 \tau(\mathrm{v})\frac{\partial f_0}{\partial n} d\mathrm{v}}{\int_0^\infty \mathrm{v}^2 f_0 d\mathrm{v}}$$

For special case of the *Maxwell Boltzmann* distribution

$$f_0 = nC(T)e^{-U/k_BT} = nC(T)e^{-m\mathrm{v}^2/2k_BT}$$

$$\Rightarrow \frac{\partial f_0}{\partial n} = \frac{f_0}{n}$$

and

$$D = \frac{1}{3}\frac{\int_0^\infty \mathrm{v}^4\tau(\mathrm{v})\, f_0 d\mathrm{v}}{\int_0^\infty \mathrm{v}^2 f_0 d\mathrm{v}} = \frac{1}{3} < \mathrm{v}^2\tau(\mathrm{v}) > \tag{5}$$

Now we recall that for the Maxwell-Boltzmann statistics,

$$<\tau> = <\mathrm{v}^2\tau>/<\mathrm{v}^2> = <\mathrm{v}^2\tau> m/3k_BT \tag{6}$$

Substitution of (6) into (5) results in the expression:

$$D = \frac{1}{3}\frac{3k_BT<\tau>}{m} = \frac{k_BT<\tau>}{m} = \frac{k_BT}{e}<\mu> \tag{7}$$

which is Einstein's relation yet again. It turns out that there is a similar Einstein's relation valid in the opposite limit of high particle concentration, and everywhere in between. This makes the Einstein relation one of the most universal results in all of transport theory.

***Importance of Diffusion in Semiconductors***

- Diffusion is a process that tends to drive the solid back to equilibrium after excitation by non-uniform external forces. By contrast, drift in an electric field is a process that tends to drive the solid away from equilibrium. So naturally, the two are often co-operating in semiconductor devices, leading to the drift-diffusion formalism developed after semiclassical transport.

***Boltzmann Equation with Temperature Gradient (Optional Material for ECE215B. 2008)***

The last topic we address on the classical Boltzmann equation is transport in a temperature gradient, assumed to occur along the z axis. And as in kinetic theory, we must consider two difference electrical conditions: open circuit, and short circuit, to fully describe the subtle coupling between temperature and electrical effects. We will limit the analysis to thermal transport by charge carriers, assumed to be Fermions having well-defined Fermi energy $U_F$ (T).

Open-Circuit Conditions

We allow for a nonzero electric field along the same axis to accommodate the Seebeck or other possible thermoelectric effects. The Boltzmann equation can be written

$$\frac{df}{dt} = -\frac{dz}{dt}\frac{\partial f}{\partial z} - \frac{d\mathrm{v}_z}{dt}\frac{\partial f}{\partial \mathrm{v}_z} - \frac{f - f_0}{\tau(\mathrm{v})}$$

and we assume $\frac{\partial f}{\partial z} \cong \frac{\partial f_0}{\partial z}$ ; $\frac{\partial f}{\partial \mathrm{v}_z} = \frac{\partial f_0}{\partial \mathrm{v}_z}$ as before.

So we get in steady state:

$$0 = -\mathrm{v}_z \frac{\partial f_0}{\partial z} - \frac{qE}{m}\frac{\partial f_0}{\partial \mathrm{v}_z} - \frac{f - f_0}{\tau(\mathrm{v})}$$

$$\Rightarrow f = f_0 - \tau(v)\left[\frac{qE}{m}\frac{\partial f_0}{\partial v_z} + \frac{\partial f}{\partial z} v_z\right] \tag{8}$$

As with electrical drift, by operating on the Fermi-Dirac function for $f_0$, we get

$$\frac{\partial f_0}{\partial \mathrm{v}_z} = \frac{-m\mathrm{v}_z}{k_B T} f_0(1 - f_0)$$

We expand the spatially-dependent term as

$$\frac{\partial f_0}{\partial z} = \left(\frac{\partial f_0}{\partial T}\right)\left(\frac{\partial T}{\partial z}\right)$$

or
$$\frac{\partial f_0}{\partial T} = \frac{e^{(U-U_F)/k_BT}}{\left(e^{(U-U_F)/k_BT}+1\right)^2}\frac{\partial}{\partial T}\left(\frac{U-U_F}{k_BT}\right)\frac{\partial T}{\partial z} = f_0\left(1-f_0\right)\left[\frac{1}{k_BT}\frac{\partial U_F}{\partial T}+\frac{U-U_F}{k_BT^2}\right]$$

Therefore,
$$\frac{\partial f_0}{\partial T}\frac{\partial T}{\partial z} = \frac{f_0\left(1-f_0\right)}{k_BT}\left[\frac{\partial U_F}{\partial T}+\frac{U-U_F}{T}\right]\frac{\partial T}{\partial z} \tag{9}$$

Finally we recall that

$$\frac{\partial f_0}{\partial \mathrm{v}_z} = \frac{-m\mathrm{v}_z f_0\left(1-f_0\right)}{k_BT}qE \qquad \text{and} \qquad \mathrm{v}_z = \mathrm{v}\cos\theta$$

Substitution of these into (8) along with (9) yields

$$f = f_0 + \frac{\tau(\mathrm{v})\mathrm{v}\cos\theta}{k_BT}f_0(1-f_0)\left[qE-\left(\frac{\partial U_F}{\partial T}+\frac{U-U_F}{T}\right)\frac{\partial T}{\partial z}\right] \tag{10}$$

The most useful quantity to average over this nonequilibrium distribution function is the z component of the velocity
$$<\mathrm{v}_z> = \frac{\int \mathrm{v}_z f d\vec{\mathrm{v}}}{\int f d\vec{\mathrm{v}}}$$

By substitution of (10), this becomes

$$<\mathrm{v}_z> = \frac{1}{k_BT}\frac{\iiint \tau(\mathrm{v})\mathrm{v}^2\cos\theta f_0(1-f_0)\left[qE-\left(\frac{\partial U_F}{\partial T}+\frac{U-U_F}{T}\right)\frac{\partial T}{\partial z}\right]\mathrm{v}^2\sin\theta d\mathrm{v}d\theta d\phi}{\iiint (f_0+f')\mathrm{v}^2\sin\theta d\mathrm{v}d\theta d\phi}$$

(11)

It is easy to see that the denominator integral over f' vanishes since $\int_0^{\pi}\cos\theta\sin\theta d\theta = 0$

We can also integrate the numerator over θ and ϕ to get $\int_0^{\pi} \cos^2\theta \sin\theta d\theta = -\left.\frac{\cos^3\theta}{3}\right|_0^{\pi} = 2/3$

and $\int_0^{2\pi} d\phi = 2\pi$ , and do the same integrals in the denominator to get $\int_0^{\pi} \sin\theta d\theta = 2$ and

$\int_0^{2\pi} d\phi = 2\pi$ . So in total, (11) becomes

$$< \mathrm{v}_z >= \frac{1}{3k_B T}\frac{\int \tau(\mathrm{v}) f_0(1-f_0)\left[qE - \left(\frac{\partial U_F}{\partial T} + \frac{U-U_F}{T}\right)\frac{\partial T}{\partial z}\right]\mathrm{v}^4 d\mathrm{v}}{\int f_0 \mathrm{v}^2 d\mathrm{v}}$$

The only terms that depend on velocity are τ and U (to first order, $U_F$ is independent of v). So if we assume a Maxwell-Boltzmann distribution,

$$< \mathrm{v}_z >= \frac{1}{m}\left\{\left[qE - \left(\frac{\partial U_F}{\partial T} - \frac{U_F}{T}\right)\frac{\partial T}{\partial z}\right] < \tau > - \frac{1}{T}\frac{\partial T}{\partial z} < U\tau >\right\} \tag{12}$$

where
$$< \tau >= \frac{m}{3k_B T}\frac{\int \mathrm{v}^4 f_0(\mathrm{v}) d\mathrm{v}}{\int \mathrm{v}^2 f_0(\mathrm{v}) d\mathrm{v}} = \frac{m}{3k_B T} < \mathrm{v}^2\tau(\mathrm{v}) >= \frac{< \mathrm{v}^2\tau(\mathrm{v}) >}{< \mathrm{v}^2 >}$$

Eqn (12) is very useful in describing various thermal effects such as the thermopower, Σ, i.e., Seebeck coefficient. This is obtained by setting $<v_z>$ equal to zero in (12), consistent with zero electrical current under open-circuit conditions. Then solving for E, we get

$$E_z = \frac{1}{q}\left\{\left[\left(\frac{\partial U_F}{\partial T} - \frac{U_F}{T}\right)\right] - \frac{< U\tau >}{T < \tau >}\right\}\frac{\partial T}{\partial z} \equiv \frac{\Sigma}{q}\frac{\partial T}{\partial z} \tag{13}$$

which means that

$$\Sigma = \left[\left(\frac{\partial U_F}{\partial T} - \frac{U_F}{T}\right)\right] + \frac{< U\tau >}{T < \tau >} \tag{14}$$

With an electrical field and the thermal gradient present, there will be a heat flux

$$\langle J_Q \rangle = n\langle U_K v_z \rangle \tag{15}$$

From (12), we can write

$$< U\mathrm{v}_z >= \frac{1}{m}\left\{\left[qE - \left(\frac{\partial U_F}{\partial T} - \frac{U_F}{T}\right)\frac{\partial T}{\partial z}\right] < U\tau > - \frac{1}{T}\frac{\partial T}{\partial z} < U^2\tau >\right\} \tag{16}$$

But we know the open-circuit E from (13), and substitution leads to

$$< U\mathrm{v}_z >= \frac{1}{m}\left\{\left[\left(\frac{\partial U_F}{\partial T} - \frac{U_F}{T} + \frac{< U\tau >}{T < \tau >}\right)\frac{\partial T}{\partial z} - \left(\frac{\partial U_F}{\partial T} - \frac{U_F}{T}\right)\frac{\partial T}{\partial z}\right] < U\tau > - \frac{1}{T}\frac{\partial T}{\partial z} < U^2\tau >\right\}$$

or

$$< U\mathrm{v}_z >= \frac{1}{m}\left\{\left(\frac{< U\tau >^2}{T < \tau >}\right) - \frac{1}{T} < U^2\tau >\right\}\frac{\partial T}{\partial z} \equiv \mathrm{K}\frac{\partial T}{\partial z}$$

Therefore, the thermal current has the form

$$< J_Q >= n < U\mathrm{v}_z >= \frac{n}{m}\left\{\left(\frac{< U\tau >^2}{T < \tau >}\right) - \frac{1}{T} < U^2\tau >\right\}\frac{\partial T}{\partial z} \equiv \mathrm{K}\frac{\partial T}{\partial z}$$

and the thermal conductivity is given by the rather elegant expression:

$$\mathrm{K} = \frac{n}{mT < \tau >}\left(< U\tau >^2 - < U^2\tau >< \tau >\right)$$

## Short-Circuit Conditions

When the ends of the sample are connected by a metal wire so the internal electric field of (13) is zero, then (11) becomes

$$< v_z >= \frac{1}{m}\left\{\left[\left(\frac{\partial U_F}{\partial T} - \frac{U_F}{T}\right)\frac{\partial T}{\partial z}\right] < \tau > - \frac{1}{T}\frac{\partial T}{\partial z} < U\tau >\right\}$$

and an electrical current will flow:

$$\langle J_q \rangle = nq\langle v_z \rangle \ .$$