Transport Theory #4

Boltzmann Formalism

We have seen how ionized-impurity scattering of charged particles is associated with a strong dependence of scattering time τ on the particle kinetic energy U^*_K. In addition we expect that τ and perhaps other aspects of the transport process, such as the number of particles involved, will depend on particle identity, i.e., classical (Maxwell-Boltzmann), Fermionic, etc. This leads us to the *Boltzmann transport* formalism, arguably the most important advancement of transport theory ever made because of its inherent ability to handle multiple physical effects automatically and self-consistently.[1]

At the foundation of Boltzmann are a set of three *axioms* each far more plausible than those of kinetic theory.

(1) First, each particle in the transport process can be described by a point in mechanical "phase space" spanned by position and momentum, $\vec{r}$ & $\vec{p}$. This phase space is *six* dimensional and is shared by all N particles of the population. In other words, at any moment in time, there are N points in this space, each designated by $\vec{r}_i$ & $\vec{p}_i$ where i is the particle index.

(2) The evolution of each particle point in time is given by the equations of motion which, in turn, depend on the external forces through the appropriate mechanical laws of motion. When Boltzmann developed the formalism, the only known laws where those of Newton, for which

$$\vec{p}_i = m\frac{d\vec{r}_i}{dt} \qquad (1) \qquad\qquad \vec{F}_i = \frac{d\vec{p}_i}{dt} \qquad (2)$$

where F is the external force and m is the particle mass.

[1] while we apply the Boltzmann transport only to solids, it is equally well suited to fluid transport, plasma transport, and even radiative (i.e., photonic) transport.

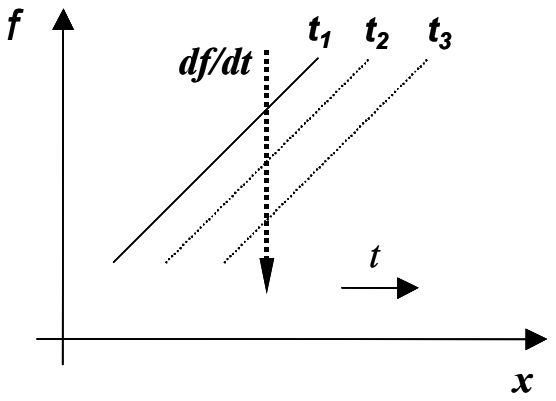

Fig. 1.

(3) The entire population of particles is described by a probability distribution function *f* that is the mean number of particles at each point in phase space at any given time. Mathematically we can write, f = $f[\vec{r}_i(t), \vec{p}_i(t)]$. So by the chain rule of elementary calculus,

$$\left.\frac{df}{dt}\right|_{ballistic} = -\frac{\partial f}{\partial \vec{r}_i}\frac{d\vec{r}_i}{dt} - \frac{\partial f}{\partial \vec{p}_i}\frac{d\vec{p}_i}{dt} \tag{3}$$

The first term is called the *diffusion* term since it is proportional to the gradient of the particle number in real space (i.e., with respect to r). The second term is called the drift term since from (2) it is proportional to the force on the particle. The subscript "ballistic" reminds us that there is nothing in (3) to account for the collisions (or scattering) of the particles necessary to maintain an equilibrium state in the solid.

The negative signs in (3) are important here and represent the fact that the particle transport always tends to go in the opposite direction to the gradient vs $\vec{r}$ or $\vec{p}$. To see this, we examine a specific example of (3), shown diagrammatically in Fig. 1, of one-dim diffusive (along x axis) transport in $\vec{r}$ space with v_x uniform (independent of x) and positive, and no applied forces. This implies

$$\Rightarrow \frac{df}{dr} = \frac{df}{dx} > 0; \frac{dr}{dt} = \frac{dx}{dt} \equiv v_x = \text{constant}.$$

Hence, $(\partial f/\partial x)(\partial x/\partial t)$ in (3) is positive and the second (drift) term in (3) is zero. Under these conditions and with evolving time, the distribution function will shift to the right as shown in Fig. 1 for three consecutive times, t_1 to t_3. This means that at any given value of x, $\left.\frac{df}{dt}\right|_x$ must be negative, as shown in Fig. 1. Clearly, the negative sign in (3) is needed to make makes this happen. A similar argument can be constructed for a nonzero drift term in (3), but without diffusion. Assuming one-dim drift along the x axis with more particles having high velocities than low values, $\left.\frac{df}{dt}\right|_{v_x}$ would always be opposite in sign to $(\partial f/\partial p_x)(\partial p_x/\partial t)$. Hence, the negative sign in the second term of (3) is needed.

A second advancement by Boltzmann was to add the effect of collisions into the same probability-functional formalism. He was guided by the following two physical considerations regarding the collisions (or scattering): (1) they have the fundamental role of returning the population of particles to a state of thermodynamic equilibrium when there are no external forces applied, and (2) they establish a steady-state in the non-equilibrium when external forces are applied. He thus added the following term to (3):

$$\left.\frac{df}{dt}\right|_{collision} = \frac{-\left(f - f_0\right)}{\tau\left(\vec{p}\right)} \tag{4}$$

where f is the non-equilibrium distribution function, f_0 is the equilibrium function. The quantity $\tau(p)$ is the *momentum-dependent* relaxation time, which has a broader meaning than in kinetic theory where it was defined as the mean time between collisions for all particles in the population. Now it is the relaxation time for the entire distribution function, averaged over all of particle "phase space". The subscript "collision" reminds us that this term should vanish in the

limit of no scattering, which is clear from (4) by taking the limit $\tau(p)\rightarrow\infty$. Historically, (4) has become known as the *relaxation-time approximation* and is ubiquitous in nearly all applications of transport theory. When added to (3), we get the full Boltzmann transport equation

$$\frac{df}{dt} = -\frac{\partial f}{\partial \vec{r}}\frac{d\vec{r}}{dt} - \frac{\partial f}{\partial \vec{p}}\frac{d\vec{p}}{dt} - \frac{\left(f - f_0\right)}{\tau\left(\vec{p}\right)} \tag{5}$$

To solve (5) under even the simplest conditions, boundary and initial conditions are always required. Perhaps the most useful condition, often true in solids, is that the total number of particles is conserved.

$$\int\int f\left(\vec{r},\vec{p}\right)d\vec{p}d\vec{r} = N$$

If the particles are uniformly distributed in real space, then the integral over space just yields V, the volume of the sample. Hence,

$$\int f\left(\vec{\mathrm{v}}\right)d\vec{\mathrm{v}} = \mathrm{N/V} = \mathrm{n} \tag{6}$$

Note that even when (6) it is not true, such as when *injection* of charge carriers is occurring in a semiconductor device, it can be included as one term in a carrier-balance equation, or rate equation, that conserves space charge neutrality. We will address this subject starting with the generation-recombination equation later on.

In the most common applications of (5) and (6) in solids, the particles are Fermions (electrons or holes) so can usually be described statistically by the Fermi-Dirac function,

$$f_0 = \frac{1}{\exp[(U_F - U)/k_B T] + 1}$$

where U_F is the Fermi energy and U is the total particle energy. It is important to realize here that U is the total particle energy per particle, kinetic plus potential, not just the kinetic energy as in kinetic transport theory. The potential energy is usually caused by external forces, but it might also arise from inhomogeneity of the solid.

In statistical mechanics or transport-theory courses, general solutions to (5) are studied. Here, we will look only at specific examples, especially electronic devices, where the transport is

usually just one- or two-dimensional. This solutions are then most easily obtained by a Cartesian decomposition of both $\vec{r}$ and $\vec{p}$, so that (5) becomes

$$\frac{df}{dt} = -\frac{\partial f}{\partial x}\mathrm{v}_x - \frac{\partial f}{\partial y}\mathrm{v}_y - \frac{\partial f}{\partial z}\mathrm{v}_z - \frac{F_x}{m}\frac{\partial f}{\partial \mathrm{v}_x} - \frac{F_y}{m}\frac{\partial f}{\partial \mathrm{v}_y} - \frac{F_z}{m}\frac{\partial f}{\partial \mathrm{v}_z} - \frac{f - f_0}{\tau(\vec{p})} \qquad (7)$$

and we have used the *Newtonian* relations:

$$\mathrm{v}_x = \frac{dx}{dt}, \mathrm{v}_y = \frac{dy}{dt}, \mathrm{v}_z = \frac{dz}{dt}; \qquad p_x = m\mathrm{v}_x, p_y = m\mathrm{v}_y, p_z = m\mathrm{v}_z;$$

$$F_x = \frac{dp_x}{dt}, F_y = \frac{dp_y}{dt}, F_z = \frac{dp_z}{dt}$$

Boltzman Transport for DC Electrical Current

Perhaps the simplest application of the Boltzmann transport equation is one-dimensional current flow of charged particles in a uniform electric field $\vec{E} = E_0\hat{z}$. The electric field is assumed to have been applied for a long enough time that steady-state exists in the solid, so that df/dt = 0. Furthermore, the electric field magnitude is assumed to be small enough that the particle density remains homogeneous at its equilibrium value so that,

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial y} = \frac{\partial f}{\partial z} = 0$$

So we get from (7)

$$0 = -\frac{qE_0}{m}\frac{\partial f}{\partial \mathrm{v}_z} - \frac{f - f_0}{\tau(m\vec{\mathrm{v}})}$$

or

$$f = f_0 - \tau(m\vec{\mathrm{v}})\frac{qE_0}{m}\frac{\partial f}{\partial \mathrm{v}_z} \qquad (8)$$

Next comes the most important assumption of all – that the applied force creates a significant difference between *f* and f_0, but an insignificant difference between $\partial f/\partial \mathrm{v}_z$ and $\partial f_0/\partial \mathrm{v}_z$. Mathematically we can then write,

$$\frac{df}{d\mathrm{v}_z} \approx \frac{df_0}{d\mathrm{v}_z} = \frac{df_0}{dU}\frac{dU}{d\mathrm{v}_z} = m\mathrm{v}_z \frac{df_0}{dU}$$

For *Fermi-Dirac* statistics, we get

$$\frac{df_0}{dU} = \frac{-e^{(U-U_F)/k_BT}(k_BT)^{-1}}{\left(e^{(U-U_F)/k_BT}+1\right)^2} = -\frac{1}{k_BT} f_0(1-f_0)$$

Therefore,
$$\frac{df}{d\mathrm{v}_z} \approx -\frac{m\mathrm{v}_z}{k_BT} f_0(1-f_0)$$

And (8) becomes
$$f \simeq f_0 + \frac{qE_0\mathrm{v}_z\tau\left(\vec{\mathrm{v}}\right)f_0(1-f_0)}{k_BT} \equiv f_0 + f' \qquad (9)$$

The next step which is applicable to many, but certainly not all, types of scattering is to assume that the scattering is isotropic,[2] meaning that $\tau\left(\vec{\mathrm{v}}\right) = \tau\left(|\,\vec{\mathrm{v}}\,|\right)$. This encourages us to write and solve (9) in spherical coordinates, $\mathrm{v}_z = \mathrm{v}_0\cos\theta$, leading to

$$f \approx f_0 + \frac{qE_0\mathrm{v}_0\cos\theta\cdot\tau\left(\mathrm{v}_0\right)f_0\left(1-f_0\right)}{k_BT} \qquad (10)$$

To proceed further we need a boundary condition, starting with the conservation of particles (6)

$$\int f\left(\vec{\mathrm{v}}\right)d\vec{\mathrm{v}} = \frac{N}{V} \equiv \mathrm{n} = \int f_0\left(\vec{\mathrm{v}}\right)d\vec{\mathrm{v}}$$

which leads to the important condition

$$\Rightarrow \int f'\left(\vec{\mathrm{v}}\right)d\vec{\mathrm{v}} = 0 \qquad (11)$$

To check this, we calculate from (10)

$$\int f'\left(\vec{\mathrm{v}}\right)d\vec{\mathrm{v}} = \int_0^{2\pi}\int_0^{\pi}\int_0^{\mathrm{v}_{max}} \frac{qE_0\mathrm{v}_0\cos\theta\cdot\tau\left(\mathrm{v}_0\right)f_0\left(1-f_0\right)\mathrm{v}_0^2\sin\theta\,d\mathrm{v}\,d\theta\,d\phi}{k_BT}$$

[2] This tends to be true for "point" scattering, such as ionized impurities, but must be applied very cautiously to scattering from extended defects, such as crystal dislocations.

The θ integral is $\int_0^{\pi} \cos\theta \sin\theta d\theta = \int_0^{\pi} \frac{\sin 2\theta}{2} d\theta = 0$. So, $\int f'(\vec{\mathrm{v}}) d\vec{\mathrm{v}} = 0$ as expected.

For the electrical current, we have

$$J_z = q < n\mathrm{v}_z >= qn < \vec{\mathrm{v}} >$$

where (< > denotes and an ensemble average over the nonequilibrium distribution function f)

$$< \mathrm{v}_z >= \frac{\int \mathrm{v}_z f \cdot d\vec{\mathrm{v}}}{\int f \cdot d\vec{\mathrm{v}}} = \frac{\int \mathrm{v}_z (f_0 + f') d\vec{\mathrm{v}}}{\int f \cdot d\vec{\mathrm{v}}}$$

But, $$\int \mathrm{v}_z f_0 d\vec{\mathrm{v}} = \iiint f_0 \mathrm{v}_0 \cos\theta \sin\theta \mathrm{v}^2 d\theta d\phi = 0$$

So, $$< \mathrm{v}_z >= \frac{\iiint (qE_0 / k_B T) \mathrm{v}_0^2 \tau(\mathrm{v}_0) f_0 (1 - f_0) \mathrm{v}_0^2 \cos^2\theta \sin\theta d\mathrm{v}_0 d\theta d\phi}{\iiint f_0(\vec{\mathrm{v}}) d\vec{\mathrm{v}}}$$

For θ integrals, we have $\int_0^{\pi} \cos^2\theta \sin\theta d\theta = -(\cos^3\theta / 3)\Big|_0^{\pi} = 2/3$ in numerator

$$\int_0^{\pi} f_0(\vec{\mathrm{v}}) d\theta = f_0(\mathrm{v}_0, \phi)(-\cos\theta)\Big|_0^{\pi} = 2 f_0(\mathrm{v}_0, \phi)$$

Similarly, ϕ integrals yield factor of 2π in numerator and denominator. Thus

$$< \mathrm{v}_z >= \frac{\frac{qE_0}{3k_B T} \int_0^{\infty} \mathrm{v}_0^4 \tau(\mathrm{v}_0) f_0 (1 - f_0) d\mathrm{v}_0}{\int_0^{\infty} f_0(\mathrm{v}_0) \mathrm{v}_0^2 d\mathrm{v}_0}$$

This can be regarded as a relationship between $<\mathrm{v}_z>$ and E_0

$$< \mathrm{v}_z >=< \mu > E = \frac{q < \tau >}{m} E \text{, where}$$

$$< \tau >= \frac{\frac{m}{3k_BT}\int_0^\infty \mathrm{v}_0^4 \tau(\mathrm{v}_0) f_0 (1-f_0) d\mathrm{v}_0}{\int_0^\infty f_0(\mathrm{v}_0)\mathrm{v}_0^2 d\mathrm{v}_0} \tag{12}$$

Note that the extra factor of v^2 (beyond the normal Jacobian factor in spherical coordinates) in the numerator comes from Boltzmann equation solution.

Botlzmann Transport in Semiconductors and other Non-degenerate Solids

In solids having a low carrier concentration compared to the atomic density, the Fermi-Dirac function reduces to the Maxwell distribution of velocities. As discussed earlier in our treatment of statistical mechanics, the Maxwell-Boltzmann (MB) distribution is a continuum form of the discrete Boltzmann pdf $P_i = C\exp(-U_i/k_BT)$ where C is the normalization constant, $C = \left(\sum_i e^{-U_i/k_BT}\right)^{-1}$. In principle U_i is the total energy of the particle. According to the MB approach, it is just the kinetic energy $(1/2)m(v_i)^2$, which is consistent with the assumption that the density of particles is homogeneous. Hence, we can write the MB density function as the r-independent function $P_0(\vec{r},\vec{\mathrm{v}})d^3rd^3\mathrm{v} = Ce^{-\frac{1}{2}m\mathrm{v}^2/k_BT}d^3rd^3\mathrm{v}$, and determine *C* by the conservation of particles: $\int\int P_0(\vec{r},\vec{\mathrm{v}})d^3rd^3\mathrm{v} = N$

or $$C\mathrm{V}\left(\int_{-\infty}^{\infty}\exp(-\frac{1}{2}m\mathrm{v}_x^2/k_BT)\,d\mathrm{v}_x\right)^3 = N$$

This is one of a well-known set of Gaussian integrals evaluated by the formulae:

$$\int_0^\infty \exp(-\alpha x^2)\,x^n dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \text{ for n=0 ; } = (2\alpha)^{-1} \text{ for n=1; } = \sqrt{\pi}\Big/\left(4\alpha^{3/2}\right) \text{ for n=2}$$

Thus, we can write

$$\int_{-\infty}^{\infty} \exp(-\tfrac{1}{2} m\mathrm{v}_x^2 / k_B T) d\mathrm{v}_x = \sqrt{2\pi k_B T / m}$$

and $C = n\left(\frac{m}{2\pi kT}\right)^{3/2}$. Thus the MB distribution can be written[3]

$$P_0(\vec{r}, \vec{\mathrm{v}}) = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp(-\frac{1}{2} m\mathrm{v}^2 / k_B T) \tag{13}$$

A benefit of using the MB distribution is the simplification it brings to the calculation of $<\tau>$ in (12). This occurs in part through the equipartition theorem: given one "degree-of-freedom" of each particle, such as $\mathrm{v_x}$. the mean value under (13) is clearly zero, but

$$<\mathrm{v}_x^2> = \frac{\mathrm{V}}{\mathrm{N}} \int_{-\infty}^{\infty} \mathrm{v}_x^2 f_0(\vec{\mathrm{v}}) d\vec{\mathrm{v}} = \frac{1}{n} \int_{-\infty}^{\infty} \mathrm{v}_x^2 n \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{1}{2} m\mathrm{v}^2 / k_B T} d\mathrm{v}_x d\mathrm{v}_y d\mathrm{v}_z$$

$$= \frac{k_B T}{m} \quad \text{since } \mathrm{v}^2 = \mathrm{v}_x^2 + \mathrm{v}_y^2 + \mathrm{v}_z^2$$

Therefore, $$<U> = \frac{1}{2} m \left\langle \mathrm{v}_x^2 \right\rangle = \frac{1}{2} k_B T$$

A second simplification is that f_0 in (12) becomes << 1 so that $1 - f_0 \approx 1$, and

$$<\tau> = \frac{m}{3k_B T} \int_0^{\infty} \frac{\mathrm{v}^2 \tau(\mathrm{v}) f_0 (1 - f_0) \mathrm{v}^2 d\mathrm{v}}{\int_0^{\infty} f_0(\mathrm{v}) \mathrm{v}^2 d\mathrm{v}} \approx \frac{m}{3k_B T} \int_0^{\infty} \frac{\mathrm{v}^2 \tau f_0 \mathrm{v}^2 d\mathrm{v}}{\int_0^{\infty} f_0 \mathrm{v}^2 d\mathrm{v}}$$

Since we have done integral in spherical coordinates, we can write

$$<\tau> = \frac{m}{3k_B T} <\mathrm{v}^2 \tau(\mathrm{v})> \equiv \frac{<\mathrm{v}^2 \tau(\mathrm{v})>}{<\mathrm{v}^2>}$$

[3] Note: the dimensions of P_0 are particles per unit volume per *velocity* cubed.

Aside on relationship between P_0 and a true probability density function:

P_0 is really a distribution function for the density of particles in real space and velocity space. In the Boltzmann equation, we need a distribution function for particles that, like the Fermi-Dirac function, is unitless. In mathematical terms,

$$P_0\left(\vec{r},\vec{\mathrm{v}}\right)d\vec{r}d\vec{\mathrm{v}} = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp(-\frac{1}{2}m\mathrm{v}^2 \Big/ k_B T)d\vec{r}d\vec{\mathrm{v}}$$

Integrating over $\vec{r}$, we get (assuming that P_0 is not a function of r)

$$P_0\left(\vec{\mathrm{v}}\right)d\vec{\mathrm{v}} = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp(-\tfrac{1}{2}m\mathrm{v}^2 \Big/ k_B T)d\vec{\mathrm{v}}\int d\vec{r}$$

$$= N\left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp(-\tfrac{1}{2}m\mathrm{v}^2 \Big/ k_B T)d\vec{\mathrm{v}}$$

With $U = \frac{1}{2}m\mathrm{v}^2$, we have $d\mathrm{v} = \mathrm{v}^2 \sin\theta d\mathrm{v}d\theta d\phi$ and $dU = m\mathrm{v}d\mathrm{v}$. So that by integrating over θ and ϕ we get $P_0\left(\mathrm{v}\right)d\mathrm{v} = N\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{1}{2}m\mathrm{v}^2 \Big/ k_B T}\left(4\pi\mathrm{v}^2\right)d\mathrm{v}$

Or in terms of the energy variable,

$$P_0\left(U\right)dU = \frac{2\pi N}{\left(\pi k_B T\right)^{3/2}}\sqrt{U}\, e^{-U/k_B T}dU$$

In general this can be written in product form

$$P_0\left(U\right) = f_0\left(U\right)g\left(U\right)$$

where $g(U)$ is the density of states. The density of states allows us to connect P_0 to quantum statistics for the particles. For example, if we assume the particles are "free" so k is a good quantum number, we have k = nπ/L (L being the width of the solid sample), $U = \frac{\hbar^2 k^2}{2m}$,

$$N(U) = \frac{V}{3\pi^2}\left(\frac{2mU}{\hbar^2}\right)^{3/2}$$ (includes a factor of 2 for spin degeneracy)

and $$g(U) \equiv \frac{dN(U)}{dU} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} U^{1/2} \Rightarrow g(U) = 8\pi V\sqrt{2}\,\frac{m^{3/2}}{\hbar^3}U^{1/2}$$

Therefore,

$$f_0 = \frac{P_0(U)}{g(U)} = \frac{2\pi N\sqrt{U}\ \exp(-U/k_BT)\left(h^3\right)}{\left(\pi k_BT\right)^{3/2}\left(8\pi V\sqrt{2}\,m^{3/2}\sqrt{U}\right)}$$

or $$f_0 = \frac{N}{V}\frac{h^3\exp(-U/k_BT)}{\left[2\left(2\pi m k_BT\right)^{3/2}\right]}$$

Note: For the purpose of doing problems, it is often acceptable to ignore the prefactor and write this as $f_0 = C\exp(-U/k_BT)$, since C ends up canceling out.

To compare directly to the Fermi-Dirac function we should drop the spin factor.

$$f_0 = \frac{nh^3e^{-U/kT}}{\left(2\pi m k_BT\right)^{3/2}} \rightarrow \frac{1}{e^{\left(U-U_F\right)/k_BT}+1}$$

where f_0 now means the mean number of particles in a state of given U and given spin.

This leads to an alternative derivation for the Fermi energy by recalling that to get classical behavior we must have $\frac{(U-U_F)}{k_BT} >> 1$ for all states.

$$\Rightarrow \frac{1}{e^{(U-U_F)/k_BT}+1} \approx \frac{1}{e^{(U-U_F)/k_BT}} = e^{U_F/k_BT}e^{-U/k_BT}$$

So we have

$$\frac{nh^3e^{-U/k_BT}}{(2\pi mk_BT)^{3/2}} \approx e^{\mu/k_BT}e^{-U/k_BT}$$

or

$$U_F \cong k_BT \ln\left[\frac{nh^3}{(2\pi mk_BT)^{3/2}}\right]$$
