

## Reading

Finish K&K Chapter 14, K&K Chapter 15.

## The Boltzmann Transport Equation

We can do a somewhat better job of evaluating transport phenomena with a technique developed by Boltzmann. The idea is to start from the distribution function. Recall that we describe the number of particles in a space volume  $d^3\mathbf{r}$  and a velocity volume  $d^3\mathbf{v}$  located at  $\mathbf{r}$  and  $\mathbf{v}$  at time  $t$  by

$$dN = f(t, \mathbf{r}, \mathbf{v}) d^3\mathbf{r} d^3\mathbf{v}.$$

We are dealing with a six dimensional space. In the case that the momenta and velocities are the same except for the mass, this is just phase space. Liouville's theorem which we'll demonstrate in a minute says that the phase space volume along a stream line in phase space is constant. This means that the distribution function must be constant along a stream line.

To see what this means, let's consider a two dimensional phase space, with coordinates  $q$  and  $p$ , which is described by a Hamiltonian, so

$$\dot{q} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial q}.$$

Consider the rectangular volume element  $\Delta q \Delta p$  with corners at  $(q, p)$ ,  $(q + \Delta q, p)$ ,  $(q, p + \Delta p)$ ,  $(q + \Delta q, p + \Delta p)$  at time  $t$ . If a particle has coordinates  $(q, p)$  at time  $t$ , where will it be at time  $t + dt$ ? This is determined by the Hamiltonian. The coordinates of the lower left corner of our rectangle move to

$$(q + \dot{q} dt, p + \dot{p} dt) = \left( q + \frac{\partial H(p, q)}{\partial p} dt, p - \frac{\partial H(p, q)}{\partial q} dt \right).$$

The lower right corner goes to

$$\begin{aligned} & (q + \Delta q + \dot{q} dt, p + \dot{p} dt) \\ &= \left( q + \Delta q + \frac{\partial H(q + \Delta q, p)}{\partial p} dt, p - \frac{\partial H(q + \Delta q, p)}{\partial q} dt \right), \\ &= \left( q + \Delta q + \frac{\partial H(q, p)}{\partial p} dt + \frac{\partial^2 H(q, p)}{\partial q \partial p} \Delta q dt, p - \frac{\partial H(q, p)}{\partial q} dt + \frac{\partial^2 H(q, p)}{\partial q^2} \Delta q dt \right). \end{aligned}$$

So the bottom side of the volume element is now the vector

$$\left( \Delta q + \Delta q \frac{\partial^2 H}{\partial q \partial p} dt, \Delta q \frac{\partial^2 H}{\partial q^2} dt \right).$$

Similarly, after time  $dt$ , the left side becomes

$$\left( \Delta p \frac{\partial^2 H}{\partial p^2} dt, \Delta p - \Delta p \frac{\partial^2 H}{\partial p \partial q} dt \right).$$

Now take the cross product of these two vectors to get the volume

$$dV = \Delta q \Delta p \left( 1 - \left( \frac{\partial^2 H}{\partial p \partial q} \right)^2 (dt)^2 - \frac{\partial^2 H}{\partial p^2} \frac{\partial^2 H}{\partial q^2} (dt)^2 \right) = \Delta q \Delta p,$$

where the last equality applies because all the first order terms in  $dt$  canceled leaving only the constant term and second and higher order terms. The upshot is that our original rectangle transformed into a parallelogram of the same phase space volume. Assuming particles are neither created nor destroyed, particles with coordinates in the original box at time  $t$  are in the transformed box at time  $t + dt$ . Since phase space trajectories can't cross, no particles moved into the box. The number of particles is the same and the area is the same. This means the phase space density of particles didn't change. This is the Liouville theorem. Of course, the phase space density is just  $f(t, \mathbf{r}, \mathbf{v})$ , modulo some factors of the mass.

In terms of  $f$ , what we've just shown is that

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_r f + \mathbf{a} \cdot \nabla_v f = 0,$$

when particles are neither created nor destroyed and we are dealing with a Hamiltonian system. Note that  $\mathbf{a}$  is the acceleration,  $\nabla_r$  indicates the spatial gradient and  $\nabla_v$  indicates the gradient with respect to velocity coordinates.

The idea behind the Boltzmann transport equation is to divide the interactions of the particles into two parts. One part, due to macroscopic forces and potentials, is described by a Hamiltonian. The other part is due to the microscopic interactions between particles—the collisions. The “external” interactions satisfy Liouville's theorem. The collisions “create” and “destroy” particles. That is, a particle undergoing a collision will “suddenly” disappear from its volume of phase space (it's been destroyed) and reappear (be created) in a different volume of phase space. In this case we write

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_r f + \mathbf{a} \cdot \nabla_v f = \left( \frac{\partial f}{\partial t} \right)_{\text{collisions}},$$

where the collision term is supposed to represent the net creation/destruction of particle density per unit time at that point in phase space. It will be greater than 0 if particles are entering the volume as a result of collisions. The trick to using this method is to make a guess for the collision term.

To make a guess, the first thing to assume is that the system is not too far from equilibrium. If  $f_0$  represents the equilibrium distribution the system would have if the constraints keeping the system out of equilibrium were removed (or if  $f_0$  is the distribution the system is trying to get to for equilibrium), then one guesses that if  $f > f_0$  in some volume of phase space, more particles will be scattered out of that volume than will be scattered in. (In equilibrium, the number scattered in and out must be the same, otherwise the number in the volume will change, and that's not equilibrium.) Since we're not too far from equilibrium, we guess that the net rate of scattering particles out of the volume will be proportional to the difference between the actual density and the equilibrium density. The proportionality constant must have dimensions of inverse time, so we just write it as one over a time which is called the *collision time* or *relaxation time*. The Boltzmann transport equation in the relaxation time approximation is,

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} f + \mathbf{a} \cdot \nabla_{\mathbf{v}} f = -\frac{f - f_0}{\tau_c},$$

where  $\tau_c$  is the collision/relaxation time, not the temperature, and the minus sign assures that particles leave the volume if the actual distribution is larger than the equilibrium density. Of course,  $\tau_c$  doesn't actually have to be a constant. It could depend on  $\mathbf{r}$  or  $\mathbf{v}$ .

### The Boltzmann Equation and Simple Diffusion

Suppose we have a steady state, so  $\partial f / \partial t = 0$  and suppose there are no external forces, so  $\mathbf{a} = 0$ . Let's suppose that  $f$  varies in the  $x$  direction. Then the Boltzmann equation becomes,

$$v_x \frac{df}{dx} = -\frac{f - f_0}{\tau_c}.$$

Since we want to be only mildly out of equilibrium, we expect that  $f - f_0$  is small (compared to  $f_0$ ) which means  $df/dx$  must be small. So we can use  $df_0/dx$  in place of  $df/dx$  and the error we make should be second order small. Then a first order approximation is

$$f = f_0 - \tau_c v_x \frac{df_0}{dx}.$$

Recall  $f$  is the density per unit volume per unit velocity volume. If we multiply by  $v_x$ , and integrate over velocity volume, we'll have the concentration flux density. In other words

$$J_{n,x} = \int v_x f d^3 \mathbf{v} = \int d^3 \mathbf{v} v_x \left( f_0 - \tau_c v_x \frac{df_0}{dx} \right).$$

For  $f_0$ , we should use the Maxwell velocity distribution times the concentration and the derivative of  $f_0$  will have the Maxwell velocity distribution times the concentration gradient. The first term will give 0 (no net  $v_x$ , but the second term will give a non-zero result,

$$J_{n,x} = -\tau_c \langle v_x^2 \rangle \frac{dn}{dx} = -\tau_c \frac{\tau}{m} \frac{dn}{dx}.$$

This calculation yields a diffusivity

$$D = \tau_c \frac{\tau}{m}.$$

Comparing with our earlier expression for the diffusivity, we find that the two will be the same if

$$\tau_c = \frac{8}{3\pi} \frac{\ell}{\bar{c}}.$$

The relaxation time is roughly the time it takes to go a mean free path at the average speed or roughly the time between collisions. This had to be: in our earlier derivation we assumed that one collision—the last one at a distance of one mean free path—was enough to randomize the velocity, energy, etc.

One might also assume that

$$\tau_c = \frac{\ell}{v},$$

that is, fast particles relax faster. Then our expression becomes

$$\begin{aligned} J_{n,x} &= - \int d^3\mathbf{v} \frac{\ell}{v} v_x^2 \frac{df_0}{dx}, \\ &= - \int d^3\mathbf{v} \frac{\ell}{v} \frac{1}{3} (v_x^2 + v_y^2 + v_z^2) \frac{df_0}{dx}, \\ &= - \int d^3\mathbf{v} \frac{1}{3} \ell v \frac{df_0}{dx}, \\ &= - \frac{1}{3} \ell \bar{c} \frac{dn}{dx}, \end{aligned}$$

and  $D = \ell \bar{c} / 3$  as before.

## Diffusion and the Fermi-Dirac Distribution

Up to now, we've been using the Maxwell-Boltzmann distribution function. Let's see what happens with the Fermi-Dirac distribution. This is important for describing the electrical conductivity of a conductor. So

$$f_0 = \frac{1}{e^{(\epsilon - \mu)/\tau} + 1}.$$

Note that this is normalized in a strange way—it's missing the density of states. So we'll have to multiply by the density of states. If we want to describe a situation where the temperature is constant but the concentration varies with position, it will be the chemical potential which varies.

Let's write down the diffusion integral

$$J_{n,x} = - \int d\epsilon v_x^2 \tau_c \frac{df_0}{dx} \mathcal{D}(\epsilon).$$

This is just like our earlier expression except that the density of states appears explicitly and the integral is over the energy rather than velocity volume. The density of states appearing here has to be the number of states per unit energy per unit volume. Recall in lecture 16, we used the same symbol for the number of states per unit energy. Now,

$$\frac{df_0}{dx} = \frac{df_0}{d\mu} \frac{d\mu}{dx}.$$

What is  $df_0/d\mu$ ? If we are at low temperatures (room temperature for a metal whose Fermi temperature is thousands of Kelvins), then  $f_0$  is flat at 0 almost up to  $\epsilon$ , then rises sharply to 1 and stays 1. This means that  $df_0/d\mu$  must be essentially 0 everywhere but very close to  $\mu$  where it must have a big spike. The area under the spike must be +1. You can see this, because integrating  $df_0/d\mu$  must produce the step of 1 in  $f_0$ . Note that  $df_0/d\mu = -df_0/d\epsilon$ , and  $f_0$  has a step of  $-1$  when  $\epsilon$  increases past  $\mu$ . Then

$$\begin{aligned} J_{n,x} &= - \frac{d\mu}{dx} \int d\epsilon v_x^2 \tau_c \frac{df_0}{d\mu} \mathcal{D}(\epsilon), \\ &= \frac{d\mu}{dx} \int d\epsilon v_x^2 \tau_c \frac{df_0}{d\epsilon} \mathcal{D}(\epsilon), \\ &= \frac{d\mu}{dx} \int d\epsilon \frac{1}{3} (v_x^2 + v_y^2 + v_z^2) \tau_c \frac{df_0}{d\epsilon} \mathcal{D}(\epsilon), \\ &= \frac{1}{3} \frac{d\mu}{dx} \int d\epsilon (v^2) \tau_c \frac{df_0}{d\epsilon} \mathcal{D}(\epsilon), \\ &= - \frac{1}{3} \frac{d\mu}{dx} (v_F^2) \tau_c \mathcal{D}(\epsilon_F), \end{aligned}$$

Where in the last line, we took  $\tau = 0$  so the energy and velocity are the Fermi energy and velocity. The density of states at the Fermi energy (lecture 16) is  $\mathcal{D}(\epsilon_F) = 3n/2\epsilon_F$ . The Fermi energy itself is

$$\mu(\tau = 0) = \epsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}.$$

Differentiate with respect to  $x$ ,

$$\frac{d\mu}{dx} = \frac{2}{3} \frac{\hbar^2}{2m} (3\pi^2)^{2/3} n^{-1/3} \frac{dn}{dx} = \frac{2}{3} \frac{\epsilon_F}{n} \frac{dn}{dx}.$$

Now we can put it all together,

$$J_{n,x} = -\frac{1}{3} v_F^2 \tau_c \frac{dn}{dx},$$

so the diffusivity for a cold Fermi gas is

$$D = \frac{1}{3} v_F^2 \tau_c = \frac{2}{3} \frac{\epsilon_F}{m} \tau_c.$$

### Electrical Conductivity

We can apply the result just obtained for diffusion with a Fermi-Dirac distribution to calculate the electrical conductivity. Everything is the same, except that we want the flux density of charge, so we need to multiply the above by  $-e$ . Also, the variation in chemical potential is not due to a variation in concentration but the variation in electric potential energy

$$\frac{d\mu}{dx} = \frac{d}{dx}(-e\Phi) = eE_x.$$

If we plug this in to our previous results, we have

$$J_{q,x} = -\frac{1}{3} (-e)(eE_x) v_F^2 \tau_c \frac{3n}{2\epsilon_F} = \frac{ne^2 \tau_c}{m} E_x.$$

We conclude the electrical conductivity is

$$\sigma = \frac{ne^2 \tau_c}{m}.$$

Note that  $\tau_c$  is to be evaluated for the electrons with energies near the Fermi energy.

When we were considering gases, we could make an estimate of the collision time by considering a simple model of the molecules as hard spheres and the collision time could be

calculated by considering the collisions of the spheres. In a metal, the relaxation time for the electrons is harder to calculate. (We're not going to calculate it!) The relaxation time is determined by interactions of the electrons with the lattice and especially impurities in the lattice.

An interesting point is that a classical treatment of the electrons gives the same expression for the conductivity (see K&K). So from studying electric conductivity, you might not have decided quantum effects are important in a metal. However, the Fermi-Dirac statistics reduce the contribution of the electrons to the heat capacity and so allow understanding of how a metal can have large electric and thermal conductivities due to the electrons, but very little electronic heat capacity. Note also that this is another clue that the electron relaxation time is determined by collisions with the lattice. Since the lattice "has the heat," the electrons must interact with the lattice in order to get the heat to transport it.

### Diffusion Equations

All of our transport equations had the generic form of a gradient of a quantity times a constant yielded a flux density of a related quantity. For example, consider heat conduction and temperature,

$$\mathbf{J}_u = -K\nabla\tau .$$

When we discussed transport we assumed a steady state. However, the main requirement for the above transport equation to be valid is that the system be not too far from equilibrium so that we need only consider a linear relation between flux density and driving force.

Suppose we consider the divergence of  $\mathbf{J}_u$ . What is the physical meaning of  $\nabla \cdot \mathbf{J}_u$ ? To find out, we'll integrate over a volume  $V$  bounded by a surface  $S$  and use the divergence theorem,

$$\int_V \nabla \cdot \mathbf{J}_u dV = \oint_S \mathbf{J}_u \cdot \mathbf{n} dA ,$$

where  $\mathbf{n}$  is the outward pointing unit normal to the surface  $S$  and  $dA$  is an element of area on the surface. Recall that the magnitude of  $\mathbf{J}_u$  is the energy per unit time that flows across a unit area perpendicular to  $\mathbf{J}_u$ . The integral above is the amount of energy that leaves the volume  $V$  by passing through the surface  $S$ . Assuming that any change in energy inside  $S$  must be the result of energy passing through  $S$ , we have

$$\int_V \nabla \cdot \mathbf{J}_u dV = -\frac{d}{dt} \int_V u dV ,$$

where  $u$  is the energy density. If we assume  $S$  is a fixed surface, then we can move the time derivative inside the integral where it must become a partial derivative. We have

$$\int_V \left( \nabla \cdot \mathbf{J}_u + \frac{\partial u}{\partial t} \right) dV = 0 .$$

This must be true for any volume, so the integrand must be zero and we have

$$\nabla \cdot \mathbf{J}_u + \frac{\partial u}{\partial t} = 0.$$

This is called a continuity equation. It simply says that the change in energy in a volume is due to energy passing through the boundaries of the volume. It can also be called an energy conservation equation. It's exactly analogous to the charge conservation equation in E&M; just replace  $\mathbf{J}_u$  with  $\mathbf{J}_q$  (electric current density) and  $u$  with  $\rho$  (charge density).

Now we consider the time rate of change of  $u$  in more detail. In our previous discussion, we took  $u = \hat{C}_V \tau$ , where  $\hat{C}_V$  is the heat capacity per unit volume at constant volume. This was motivated by considering an ideal gas. We will assume that volume changes can be ignored, and then we have

$$du = \hat{C} d\tau,$$

which is valid for systems other than an ideal gas provided  $\hat{C}$  can be treated as independent of temperature. Then the continuity equation becomes

$$\nabla \cdot \mathbf{J}_u + \hat{C} \frac{\partial \tau}{\partial t} = 0.$$

Finally we substitute from the transport equation to eliminate  $\mathbf{J}_u$  and we have

$$\nabla^2 \tau - \frac{1}{D_\tau} \frac{\partial \tau}{\partial t} = 0, \quad D_\tau = \frac{K}{\hat{C}}.$$

The constant  $D_\tau$  is the “diffusivity” of the temperature or internal energy (since  $du = \hat{C} d\tau$ ). The equation we've just derived, which has a second space derivative minus a constant times a first time derivative, is called a diffusion equation. You will notice it looks a little like the Schroedinger equation, except it's entirely real. This changes the character of the solutions from oscillations (for Schroedinger) to “spreading out” (for diffusion). It also looks a little like a wave equation except a wave equation has a second time derivative. Again, this changes the solutions from oscillations to diffusion.

The diffusion equation, like Schroedinger's equation and the wave equation, is one of the ubiquitous partial differential equations of physics. In the homework you are asked to derive the diffusion equation for particle diffusion.

Note that the diffusivity has the dimensions of a speed times a length, or length squared divided by time. For a gas, the order of magnitude is the the average velocity times the mean free path. For an insulating solid, one might guess it's the speed of sound times the mean distance between molecules. For a metallic solid, it's more complicated as energy is transported by electrons but stored in lattice vibrations.

The diffusion equation occurs with a magnetic field in a conducting medium. Starting from Ampere's law (Gaussian units), we have

$$\nabla \times \mathbf{B} = \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c} \mathbf{J}.$$

In a conducting medium,  $\mathbf{J} = \sigma \mathbf{E}$  where  $\sigma$  is the conductivity. Insert this in place of the current density and take the curl of Ampere's law.

$$\nabla \times (\nabla \times \mathbf{B}) = \frac{1}{c} \frac{\partial \nabla \times \mathbf{E}}{\partial t} + \frac{4\pi\sigma}{c} \nabla \times \mathbf{E}.$$

We expand the double curl with a vector identity,

$$\nabla \times (\nabla \times \mathbf{B}) = \nabla(\nabla \cdot \mathbf{B}) - \nabla^2 \mathbf{B} = -\nabla^2 \mathbf{B},$$

where we eliminated the first term since there is a Maxwell equation which says  $\nabla \cdot \mathbf{B} = 0$ . Substitute for  $\mathbf{E}$  from Faraday's law,

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t},$$

to get

$$-\nabla^2 \mathbf{B} = -\frac{1}{c^2} \frac{\partial^2 \mathbf{B}}{\partial t^2} - \frac{4\pi\sigma}{c^2} \frac{\partial \mathbf{B}}{\partial t}.$$

If the conductivity is larger than the characteristic frequency associated with the time variation of  $\mathbf{B}$ , in other words, for a good conductor, we can ignore the term with the second time derivative compared to the first and we have

$$\nabla^2 \mathbf{B} - \frac{1}{D_B} \frac{\partial \mathbf{B}}{\partial t} = 0, \quad D_B = \frac{c^2}{4\pi\sigma}.$$