

Semi-classical theory of conduction in metals

We have discussed so far how to get the ground-state (or good approximations for it) for electronic Hamiltonians. However, we cannot measure directly either the ground-state energy (we can only measure changes in energy) or its wavefunction, as such. What we do in practice is to perturb the system somehow, eg. by applying a small magnetic or electric field, let it get to a steady state (which is NOT the ground-state anymore), and measure its response to this perturbation, for example what density of current flows for a given applied electric field. If the external perturbation is weak enough, the response of the system is proportional to it; the ratio between the two, generically known as a **response function**, depends directly on the state of the system. For comparisons with experiments, we need to be able to calculate these response functions.

A couple of sections ago we discussed Linear Response Theory, which shows how one computes such quantities at $T = 0$ (the finite-T generalization is straightforward enough) as a ground-state matrix elements of certain commutators. The reason why the ground-state wavefunction appears is precisely because we assume that the system has not been perturbed too far away from it. So in principle, if we know the ground-state wavefunction we can do such calculations. However, as you saw, even for a simple Slater determinant the calculation can become rather complicated.

In practice, it is often convenient to use a simpler approach: a semi-classical calculation, which can be thought of as an intermediate between Drude's model (which is completely classical) and the full quantum mechanical calculation. We will now briefly discuss the key ideas behind this approximation for normal Fermi metals, where the concept of quasiparticles occupying states in single-electron bands is valid.

But first, let me define explicitly the specific response functions we will discuss. These are the transport coefficients characterizing the response of the system to applied electric fields and/or temperature gradients. There are many other quantities we could discuss, for example the response to magnetic fields, or combined electric and magnetic fields, but if you understand the general idea you can then figure out the specifics for any other case of interest.

We assume that we apply an external electric field of amplitude \vec{E} , and/or a uniform temperature gradient ∇T , across the material of interest. These will result in the appearance of a density of electric current \vec{j} and a heat current density \vec{j}_Q (this measures the density of energy that flows through the system). We assume that the system has arrived at steady-state, so these quantities are not time-dependent. Note that if the external perturbations oscillate with a frequency ω then so do these densities; in this case the quantities mentioned above represent the amplitudes multiplying the $e^{-i\omega t}$ time factors, and the response functions will depend on the frequency ω .

We define the transport coefficients as follows:

$$\vec{j} = \sigma[\vec{E} - S\nabla T] \tag{1}$$

defines the conductivity σ and the Seebeck coefficient S . The fact that a current should flow in response to an applied temperature gradient should not be a surprise: the current carried by electrons moving fast out of the hotter areas will not be fully compensated by the current carried by the slower electrons coming out of the colder areas. Another way to think of the Seebeck coefficient is as follows: consider a bar of metal of length L , with a temperature gradient $\nabla T = \frac{\Delta T}{L}$ applied between the ends. We also keep the ends isolated, so that no current flows through the sample. Because of the temperature imbalance a voltage $\Delta V = -EL$ appears between the ends of the sample, and the Seebeck coefficient is $S = -\Delta V/\Delta T$.

However, the system responds not just with a charge flow but also with a heat flow:

$$\vec{j}_Q = \sigma ST\vec{E} - K'\nabla T \tag{2}$$

where K' is the electron part of the thermal conductivity (in real life the lattice also contributes to such quantities but for the moment we continue to pretend that the lattice is frozen). We can rewrite this in another, probably more familiar, form, by using $\sigma\vec{E} = \vec{j} + \sigma S\nabla T$ from the first equation, and grouping together the terms proportional to ∇T to obtain:

$$\vec{j}_Q = ST\vec{j} - K\nabla T \tag{3}$$

The difference between the two is that K' is the value measured with no electric field in the sample, while K is measured when there is no charge current in the sample. The link is:

$$K = K' - \sigma TS^2$$

1 Boltzmann equation

Let us consider only the response of electrons (quasiparticles) from the band $E(\vec{k})$ which hosts the Fermi level (we are discussing metals). The reason for this is that we assume that the external perturbations are weak enough such that electrons cannot be excited from one band to another (this is an approximation, but usually a very good one because it can take many eV for such inter-band processes, so they can be avoided with suitably small perturbations). Then, each band responds and contributes independently of the others, and as we'll see soon, the response of any full band and of any empty band vanishes. So we can ignore all bands except the valence band which is partially filled.

We define the distribution function $f(\vec{r}, \vec{k}, t)$ such that $f(\vec{r}, \vec{k}, t)d\vec{r}d\vec{k}$ is the density of electrons that at time t are within a volume $d\vec{r}$ centered at \vec{r} and with momenta spread within $d\vec{k}$ of \vec{k} . Clearly this is a semi-classical concept because it assumes that location and momentum of electrons can be defined arbitrarily accurately, which is not true (Heisenberg's principle), but it is reasonable for a suitable coarse-graining.

When the system is in equilibrium, we have:

$$f(\vec{r}, \vec{k}, t) \rightarrow f_0(\vec{k}) = \frac{1}{e^{\beta(E(\vec{k})-\mu)} + 1}$$

i.e. the equilibrium Fermi-Dirac distribution.

We would like to find an equation of evolution for $f(\vec{r}, \vec{k}, t)$, the idea being that once we know this distribution, we can calculate the various currents (see below). To write this equation, consider the evolution of an electron wavepacket centered at \vec{r} and moving with average momentum \vec{k} . This is described by:

$$\dot{\vec{r}} = \vec{v}(\vec{k}) = \frac{1}{\hbar} \nabla_{\vec{k}} E(\vec{k})$$

and

$$\hbar \dot{\vec{k}} = e(\vec{E} + \frac{1}{c} \vec{v} \times \vec{B}) = \vec{F}_{ext}$$

This last equation is the analog of Newton's second law because $\hbar \vec{k} = \vec{p}/m$ is the quasi-momentum. However, also note that that on the rhs we have only the external force, not the total force experienced by the electrons, because the total force also includes the lattice contribution; this is why $\hbar \vec{k}$ is a quasi-momentum, not a momentum, and why it is restricted to the BZ and why $E(\vec{k})$ is periodic, etc.

We must have:

$$f(\vec{r}, \vec{k}, t) = f(\vec{r} - \vec{v}dt, \vec{k} - \frac{\vec{F}_{ext}}{\hbar}dt, t - dt) + \left(\frac{\partial f}{\partial t}\right)_{out} dt + \left(\frac{\partial f}{\partial t}\right)_{in} dt$$

because all electrons that were in the correct location and had the correct momentum at $t - dt$ will arrive at (\vec{r}, \vec{k}) at t , except some that will fail to arrive because they were scattered during dt (2nd term); but then there are some extra electrons that get there because of collisions that scatter them to the right place and with the right momentum (last term). Expanding this and keeping only terms linear in dt leads to **the Boltzmann equation**:

$$\frac{\partial f}{\partial t} + \vec{v} \nabla_{\vec{r}} f + \frac{\vec{F}_{ext}}{\hbar} \nabla_{\vec{k}} f = \left(\frac{\partial f}{\partial t}\right)_S$$

where

$$\left(\frac{\partial f}{\partial t}\right)_S = \left(\frac{\partial f}{\partial t}\right)_{out} + \left(\frac{\partial f}{\partial t}\right)_{in}$$

characterizes the scattering. Note that in some books this term is on the other side, i.e. it is defined with an overall - sign. You can use either definition so long as you are consistent.

We now proceed to simplify this equation by assuming that

$$f(\vec{r}, \vec{k}, t) = f_0(\vec{k}) + \delta f(\vec{r}, \vec{k}, t) \tag{4}$$

where δf is small, i.e. the system is not driven too far from equilibrium (a reasonable assumption if the applied fields are "small"). Considering only the linear terms (proportional to either δf , \vec{E} or ∇T) and ignoring anything else, the various contributions become:

$$\frac{\partial f}{\partial t} = \frac{\partial \delta f}{\partial t} = -i\omega \delta f$$

where ω is the frequency of the applied perturbations (again, I assume we're interested in the steady-state, not in the transient behavior while the system gets there. As discussed before, I will not write explicitly the $e^{-i\omega t}$ factors because all terms have it and they simplify out). Next:

$$\nabla_{\vec{r}} f = \nabla_{\vec{r}} f_0 + \nabla_{\vec{r}} \delta f$$

I will assume that the second term vanishes, which is reasonable if the applied perturbations are homogeneous, in which case f should not depend of \vec{r} . However, the first term is finite if there is a gradient of temperature, because we should consider the local temperature and this varies. As a result:

$$\nabla_{\vec{r}} f_0 = \frac{\xi}{T} \nabla T \left(-\frac{\partial f_0}{\partial \xi} \right)$$

where I will use the short-hand notation $\xi \equiv \xi_{\vec{k}} = E(\vec{k}) - \mu$. Finally,

$$\nabla_{\vec{k}} f \rightarrow \nabla_{\vec{k}} f_0 = \hbar \vec{v}_{\vec{k}} \frac{\partial f_0}{\partial \xi}$$

Here we ignore the δf contribution because this term is multiplied by the external fields, which are small, so this product would be small². Note that the $\vec{v} \times \vec{B}$ terms falls out of \vec{F}_{ext} , when multiplied by \vec{v} . So in the end, we get:

$$\left(\frac{\partial f}{\partial t} \right)_S + i\omega \delta f = \vec{v}_{\vec{k}} \left[e\vec{E} - \frac{\xi_{\vec{k}}}{T} \nabla T \right] \left(-\frac{\partial f_0}{\partial \xi} \right) \quad (5)$$

Now we need to know what is the scattering rate and how it is related to the distribution function. To calculate it properly, we need to do a quantum mechanical calculation – we will return to this later on. In practice, one often employs the **relaxation time approximation**:

$$\left(\frac{\partial f}{\partial t} \right)_S \approx -\frac{f(\vec{k}) - f_0(\vec{k})}{\tau_r(\vec{k})} = -\frac{\delta f(\vec{k})}{\tau_r(\vec{k})} \quad (6)$$

where $\tau_r(\vec{k})$ is a relaxation time. The explanation for this form is that in the absence of applied perturbations, scattering should help the system return back to equilibrium if somehow a perturbation occurred. With this approximation and no applied fields, the resulting Boltzmann equation is $\frac{\partial \delta f}{\partial t} = -\frac{\delta f(\vec{k})}{\tau_r(\vec{k})} \rightarrow \delta f \sim \exp(-t/\tau_r(\vec{k}))$. So the relaxation time characterizes how fast electrons with momentum \vec{k} thermalize back into equilibrium. As I said, we will discuss below how to calculate this scattering rate properly and then we will see when this approximation is valid. In practice, it is often customary to use this approximation and fit the relaxation times from experiments.

Putting everything together, the Boltzmann equation has now become:

$$-\frac{\delta f(\vec{k})}{\tau_r(\vec{k})} + i\omega \delta f = \vec{v}_{\vec{k}} \left[e\vec{E} - \frac{\xi_{\vec{k}}}{T} \nabla T \right] \left(-\frac{\partial f_0}{\partial \xi} \right) \rightarrow \delta f(\vec{k}) = \frac{\tau_r(\vec{k})}{1 - i\omega \tau_r(\vec{k})} \vec{v}_{\vec{k}} \left[e\vec{E} - \frac{\xi_{\vec{k}}}{T} \nabla T \right] \left(-\frac{\partial f_0}{\partial \xi} \right) \quad (7)$$

and we have our steady-state solution in terms of the applied perturbations.

We can now proceed to calculate the currents, defined as:

$$\vec{j} = 2e \int \frac{d\vec{k}}{(2\pi)^3} \vec{v}_{\vec{k}} f(\vec{k}) \quad \vec{j}_Q = 2 \int \frac{d\vec{k}}{(2\pi)^3} \vec{v}_{\vec{k}} \xi_{\vec{k}} f(\vec{k})$$

The factor of 2 is because of the spin, the rest is hopefully very reasonable.

First, note that in equilibrium these currents vanish, for the simple reason that the contribution from electrons with momentum \vec{k} is precisely canceled by that of the electrons with momentum $-\vec{k}$ because $f_0(\vec{k}) = f_0(-\vec{k})$ and $\vec{v}_{\vec{k}} = -\vec{v}_{-\vec{k}}$. We can therefore replace $f \rightarrow \delta f$ in the definitions above, and using the expression we obtained for δf in Eq. (7), for a cubic crystal (see below) the definition of the transport coefficients can be read off as:

$$\sigma(\omega) = \frac{2e^2}{3} \int \frac{d\vec{k}}{(2\pi)^3} \frac{\tau_r(\vec{k})}{1 - i\omega \tau_r(\vec{k})} v_{\vec{k}}^2 \left(-\frac{\partial f_0}{\partial \xi} \right)$$

$$\sigma S(\omega) = \frac{2e}{3T} \int \frac{d\vec{k}}{(2\pi)^3} \frac{\tau_r(\vec{k})}{1 - i\omega\tau_r(\vec{k})} \xi_{\vec{k}} v_{\vec{k}}^2 \left(-\frac{\partial f_0}{\partial \xi} \right)$$

$$K'(\omega) = \frac{2}{3T} \int \frac{d\vec{k}}{(2\pi)^3} \frac{\tau_r(\vec{k})}{1 - i\omega\tau_r(\vec{k})} \xi_{\vec{k}}^2 v_{\vec{k}}^2 \left(-\frac{\partial f_0}{\partial \xi} \right)$$

The formulae are very similar, they differ only through the power of e in front, and the power of ξ in the integrand. The factor of 3 is actually only valid in crystals with cubic symmetry. In general, these transport coefficients are matrices, for example if we only apply electric field we should have written $j_i = \sum_j \sigma_{ij} E_j$. The expression for σ_{ij} has the product $v_i v_j$ in the integrand. In a cubic crystal, the current flows in the direction of the field so only the diagonal matrix elements survive. Moreover, the three diagonal terms $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = \sigma$ because of the cubic symmetry, so we can replace $v_i v_j = \delta_{ij} \frac{1}{3} v_k^2$ and obtain the value of σ written above. In more complicated crystals we simply have to deal with the corresponding matrices. That can be done similarly to what we'll do now for the cubic case.

1.1 Evaluation of the transport coefficient in a metal

We will consider only the dc case $\omega = 0$.

To evaluate the integrals above, we need to make some approximations. The key point to remember is that $f_0(\xi_{\vec{k}})$ varies from 1 to 0 in a narrow interval $\delta\xi \sim k_B T \ll \mu$ centered around μ , so its derivative is strongly peaked at μ and falls off to zero very fast. Because of this fact, we only need good approximations for the various quantities close to μ .

(i) we take $E(k) = \xi_k + \mu \approx \frac{\hbar^2 k^2}{2m}$, where m would be fitted to the experimentally measured or analytically calculated dispersion. As a result $v_k = \frac{1}{\hbar} dE(k)/dk = \hbar k/m \rightarrow v_k^2 = \frac{2}{m}(\xi + \mu)$.

(ii) we assume that the relaxation time is a function of momentum only through the corresponding energy, i.e. $\tau_r(\vec{k}) = \tau(E(k))$. We'll see how we calculate this quantity later, and whether this is reasonable. Many times one takes this relaxation time to just be a constant, equal to its value at the Fermi energy.

With these two approximations we see that the integrand depends on the momentum only through the energy ξ_k . Introducing the density of state $N(\epsilon) = \frac{1}{V} \sum_{\vec{k}} \delta(\epsilon - E(\vec{k})) = \int \frac{d\vec{k}}{(2\pi)^3} \delta(\epsilon - E(k))$ we can rewrite any integral over momenta as an integral over energies: $\int \frac{d\vec{k}}{(2\pi)^3} F(\xi_k) = \int d\xi N(\xi + \mu) F(\xi)$ with $\xi = \epsilon - \mu$. For example, we now have:

$$\sigma = \frac{4e^2}{3m} \int d\xi N(\mu + \xi) \Sigma(\mu + \xi) \left(-\frac{\partial f_0}{\partial \xi} \right)$$

where we introduced $\Sigma(\epsilon) = \tau_r(\epsilon)\epsilon$ for simplicity. We now expand around the chemical potential, eg. $N(\mu + \xi) = N(\mu) + \xi N'(\mu) + \dots$, and then carry out the integrals over various powers of ξ . For this, we extend the limits of integral over all energies (remembering that only energies near μ contribute to the integral). The only combinations that appear are:

$$\int_{-\infty}^{\infty} d\xi \left(-\frac{\partial f_0}{\partial \xi} \right) = 1$$

(integrate by parts and remember that the occupation numbers change from 1 to 0 as you go from deep below to way above the chemical potential). By symmetry:

$$\int_{-\infty}^{\infty} d\xi \xi \left(-\frac{\partial f_0}{\partial \xi} \right) = 0$$

and finally, the last integral turns out to be:

$$\int_{-\infty}^{\infty} d\xi \xi^2 \left(-\frac{\partial f_0}{\partial \xi} \right) = \frac{\pi^2}{3} (k_B T)^2$$

(for this one you should be able to explain why it goes like T^2 , the constant in front is just a number).

Using these, we find:

$$\sigma = \frac{4e^2}{3m} [N(\mu)\Sigma(\mu) + \dots]$$

$$\sigma S = \frac{4e}{3mT} \frac{\pi^2}{3} (k_B T)^2 [N(\mu)\Sigma'(\mu) + N'(\mu)\Sigma(\mu) + \dots] = \frac{4\pi^2 k_B^2 e T}{9m} \frac{d}{d\mu} [\Sigma(\mu)N(\mu)] + \dots$$

and

$$K' = \frac{4}{3mT} \frac{\pi^2}{3} (k_B T)^2 \Sigma(\mu) N(\mu) + \dots = \frac{4\pi^2 k_B^2 T}{9m} \Sigma(\mu) N(\mu) + \dots$$

Note that this doesn't mean that the conductivity, for example, is necessarily independent of T (to first order) because Σ can be a function of T through the relaxation time.

From the first two equations, we get the Seebeck coefficient:

$$S = \frac{\pi^2 k_B^2 T}{3e} \frac{d}{d\mu} \ln [\Sigma(\mu) N(\mu)]$$

This is known as the **Mott formula for thermopower**, and shows that the Mott coefficient in metals should be roughly linear in T , which is the case for most metals except at very low temperatures.

Combining equations 1 and 3, we find that:

$$\frac{K'}{\sigma T} = L_0 = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2$$

is a universal constant, independent of the details of the metal. L_0 is known as the **Lorenz number** and this formula is known as the **Wiedemann-Franz law** and is widely used for normal metals. Note that here K' is only the component due to electrons. In real materials, the phonons (lattice vibrations, to be discussed soon) also carry energy and add to the total K , but the two contributions can usually be disentangled because they have different T -dependence.

One can go on and on about various other transport coefficients, and estimate their forms also in semiconductors, etc. I hope this short discussion suffices to give you a general idea of how this sort of thing is handled.

1.2 The scattering rate

Let us now consider how to calculate $\left(\frac{\partial f}{\partial t} \right)_S$, to get the full form of the Boltzmann equation and also to understand when the relaxation time approximation is acceptable.

Consider some scattering process whose scattering probability is $W_{\vec{k}, \vec{k}'}$ (I'll assume this to be spin-independent, for simplicity), meaning that $W_{\vec{k}, \vec{k}'} \frac{d\vec{k}'}{(2\pi)^3}$ is the probability that a particle with momentum \vec{k} will be scattered within $d\vec{k}'$ of \vec{k}' within time dt . This probability can be calculated using Fermi's Golden Rule (if the system isn't perturbed too much). For instance, if we're interested in scattering on impurities, then the scattering rate is:

$$W_{\vec{k}, \vec{k}'} = \frac{2\pi}{\hbar} n_i |T_{kk'}|^2 \delta(E(\vec{k}') - E(\vec{k})) \approx \frac{2\pi}{\hbar} n_i |\langle \vec{k} | \hat{V} | \vec{k}' \rangle|^2 \delta(E(\vec{k}') - E(\vec{k}))$$

Here n_i is the density of impurities and $T_{kk'}$ is the T -matrix. The second equality shows that for weak scattering, it equals the matrix element of the scattering potential and we recover Fermi's Golden Rule.

Knowing $W_{\vec{k}, \vec{k}'}$ we can calculate the scattering rates, for instance:

$$\left(\frac{\partial f}{\partial t} \right)_{out} = - \int \frac{d\vec{k}'}{(2\pi)^3} W_{\vec{k}, \vec{k}'} f(\vec{k}) [1 - f(\vec{k}')]]$$

where the sign $-$ is because this process is decreasing f (electrons are being lost from the state of interest), and the $f(\vec{k}) [1 - f(\vec{k}')]]$ factor is there because the initial state \vec{k} must be occupied whereas the final state \vec{k}' must be empty for this scattering process to happen. Note that $f(\vec{k}), f(\vec{k}')$ are the probability distribution we have been discussing so far and which we're trying to determine – they will not depend explicitly on t in the steady state of interest to us, and as mentioned above, they do not depend explicitly on \vec{r} if everything is homogeneous.

Similarly,

$$\left(\frac{\partial f}{\partial t} \right)_{in} = + \int \frac{d\vec{k}'}{(2\pi)^3} W_{\vec{k}', \vec{k}} f(\vec{k}') [1 - f(\vec{k})]$$

because this looks at electrons scattered from any other \vec{k}' into \vec{k} . Altogether, we have:

$$\left(\frac{\partial f}{\partial t} \right)_S = - \int \frac{d\vec{k}'}{(2\pi)^3} \left\{ W_{\vec{k}, \vec{k}'} f(\vec{k}) [1 - f(\vec{k}')]] - W_{\vec{k}', \vec{k}} f(\vec{k}') [1 - f(\vec{k})] \right\}$$

In principle now we're done, because if we plug this into Eq. (5) we have an integro-differential equation from which we can find f or δf , and then we can proceed to calculate various currents. Note that if we have several sources of scattering, we should just add up their contributions, each of which has its corresponding $W_{\vec{k}', \vec{k}}$.

Now we'd like to understand when can we replace this complicated term using the **relaxation time approximation**, like we did in the previous section. For this to be valid, the following conditions must hold:

(i) the scattering processes are (quasi)-elastic, i.e. such that the initial and final quasiparticle states have about the same energy $E(\vec{k}') = E(\vec{k}) \rightarrow f_0(\vec{k}) = f_0(\vec{k}')$. Since only quasiparticles near the Fermi energy will be scattered, in practice this means that the energy gained or lost in the scattering must be $\ll E_F$. Scattering on impurities is elastic, but for instance scattering on phonons (to be discussed later on) is not because energy is being transferred to or from the lattice. If that amount is small compared to E_F , then we call that scattering to be quasi-elastic, and that is sufficient for this purpose.

(ii) as already mentioned, we assume that a description in terms of independent quasiparticles is valid. Then the quasiparticles scatter independently, i.e. $W_{\vec{k}, \vec{k}'}$ do not themselves depend on $f(\vec{k}), f(\vec{k}')$.

(iii) we assume the **detailed balance condition** $W_{\vec{k}, \vec{k}'} = W_{\vec{k}', \vec{k}}$. This is also reasonable, see the Fermi Golden Rule above, and remember that \hat{V} must be hermitian.

Using (iii) and (i), we can simplify the scattering rate to:

$$\left(\frac{\partial f}{\partial t}\right)_S = - \int \frac{d\vec{k}'}{(2\pi)^3} W_{\vec{k}, \vec{k}'} [f(\vec{k}) - f(\vec{k}')] = - \int \frac{d\vec{k}'}{(2\pi)^3} W_{\vec{k}, \vec{k}'} [\delta f(\vec{k}) - \delta f(\vec{k}')]$$

Let us assume that in the steady-state, $\delta f(\vec{k}) = \vec{a} \cdot \vec{k}$, where \vec{a} depends on the applied external bias. This is based on the underlying assumption that in the steady-state, the distribution of occupied states changes from a Fermi sea centered at origin to one centered at some small \vec{G} . For instance, for an applied \vec{E} , this displacement \vec{G} is antiparallel with \vec{E} and shows that in average all electrons pick up some extra momentum due to the electric field (this is mirroring Drude's ideas). Then, $f(\vec{k}) = f_0(\vec{k} - \vec{G})$ and if we expand assuming a small \vec{G} we arrive to a form like the one above.

With this assumption:

$$\left(\frac{\partial f}{\partial t}\right)_S = -\vec{a} \cdot \int \frac{d\vec{k}'}{(2\pi)^3} W_{\vec{k}, \vec{k}'} [\vec{k} - \vec{k}']$$

Now we write \vec{k}' in terms of its components parallel and perpendicular to \vec{k} , i.e. $\vec{k}' = (\hat{k} \cdot \vec{k}')\hat{k} + \vec{k}'_{\perp}$, where $\hat{k} = \vec{k}/k$. We also assume that $W_{\vec{k}, \vec{k}'}$ depends only on the scattering angle between the two vectors, and therefore is independent of \vec{k}'_{\perp} . As a result,

$$\int d\vec{k}'_{\perp} W_{\vec{k}, \vec{k}'} \vec{k}'_{\perp} = 0$$

because positive and negative contributions precisely cancel each other out. So we're left with:

$$\left(\frac{\partial f}{\partial t}\right)_S = -\vec{a} \cdot \int \frac{d\vec{k}'}{(2\pi)^3} W_{\vec{k}, \vec{k}'} [\vec{k} - (\hat{k} \cdot \vec{k}')\hat{k}] = -\vec{a} \cdot \vec{k} \int \frac{d\vec{k}'}{(2\pi)^3} W_{\vec{k}, \vec{k}'} [1 - \cos \theta_{kk'}]$$

where $\cos \theta_{kk'} = \hat{k} \cdot \hat{k}'$ is the angle between the two vectors. Note that one more approximation was used, namely that $|\vec{k}'| \approx |\vec{k}|$ because we expect most scattering to occur at the Fermi surface where both magnitudes are close to k_F .

But $\vec{a} \cdot \vec{k} = \delta f(\vec{k})$ by definition, so indeed we find that when these approximations hold, the scattering rate is proportional to δf and we can define the relaxation time:

$$\frac{1}{\tau_r(\vec{k})} = \int \frac{d\vec{k}'}{(2\pi)^3} W_{\vec{k}, \vec{k}'} [1 - \cos \theta_{kk'}]$$

For instance, for scattering on impurities we have:

$$\frac{1}{\tau_r(\vec{k})} = n_i \frac{2\pi}{\hbar} \int \frac{d\vec{k}'}{(2\pi)^3} |T_{kk'}|^2 \delta(\epsilon_k - \epsilon_{k'}) [1 - \cos \theta_{kk'}]$$

which turns out to be independent of temperature, explaining why as $T \rightarrow 0$, the resistivity of metals becomes finite (instead of zero) and its value is controlled by n_i . Scattering on phonons, on the other hand, will result in

a $1/\tau_r(\vec{k}) \sim k_B T$ at high temperature, which simply comes from the fact that here the average number of phonons increases linearly with T , and the more phonons, the more scattering. That explains why the resistivity of metals increases linearly with T at large T (resistivity is inverse conductivity, but remember that in general, we're talking about matrices). And so on and so forth, in principle now we know how to calculate the scattering rate due to any process (the really complicated equation above), and how to estimate the corresponding relaxation time when that is a good approximation.

Final comment: do not confuse the relaxation time with the lifetime, i.e. the average time between two scattering processes. The latter is

$$\frac{1}{\tau(\vec{k})} = \int \frac{d\vec{k}'}{(2\pi)^3} W_{\vec{k},\vec{k}'}$$

so it is missing the $1 - \cos\theta$ factor. The reason is that any scattering contributes to decreasing the average lifetime, but the relaxation time only considers scattering far away from \vec{k} , i.e. to large angles θ (forward scattering, with $\vec{k}' \approx \vec{k}$, does not degrade currents so it does not contribute to transport coefficients).