Discussed Boltzmann equation in the limit $Kn \ll 1$ where evolution on large time scales is governed by Hilbert expansion

$$f = \underset{Kn^0}{f^{(0)}} + \underset{Kn^1}{f^{(1)}} + \ldots$$

$O(Kn^0)$: $\quad C[f^{(0)}] = 0 \Rightarrow f^{(0)}$ is local equilibrium distribution

$O(Kn^1)$: $\quad \left(\frac{\partial}{\partial t} + \frac{\vec{p}}{m}\vec{\nabla}_r + \vec{F}(\vec{r})\vec{\nabla}_p\right) f^{(0)}_{(t,\vec{r},\vec{p})} = \underbrace{\delta C[f^{(0)}, f^{(1)}]}_{\text{linearized collision operator}}(t,\vec{r},\vec{p})$

We obtain $f^{(1)}$ formally by inverting the linearized collision operator, which is difficult in practice and subtle due to the fact that $\delta C[f^{(0)}, f^{(1)}]$ has zero eigenvalues associated with conserved quantities

→ non-equilibrium corrections $f^{(1)}$ to local equilibrium distribution $f^{(0)}$ should not carry conserved quantities $e, \vec{p}, n$

Now if this is the case, we may approximate the linearized collision operator by the relaxation time approximation

$$\delta C[f^{(0)}, f^{(1)}] = -\frac{1}{\tau_R} f^{(1)}$$

resulting in an exponential relaxation towards local equilibrium on a time scale $\sim \tau_R$

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Calculation of transport coefficients

Q: What is a transport coefficient?

We encountered them in Chapter I as coefficients relating fluxes of conserved quantities $n, e, \vec{P}$ to affinities $\vec{\nabla}\left(\frac{1}{T}\right), \vec{\nabla}\left(-\frac{\mu}{T}\right), \vec{\nabla}\otimes\vec{v}$ which describe small deviations of the system from local equilibrium

e.g.
$$\vec{J}_N = \boxed{L_{NN}}\,\vec{\nabla}\left(-\frac{\mu}{T}\right) + \dots$$

Now for the treatment in Chapter I, we always treated the system as close to local equilibrium, which requires $Kn \ll 1$

$\rightarrow$ Can now employ BTE to calculate transport coefficients and look at the underlying dynamics from a micro cop'n perspective

Electrical conductivity σ_{el} (DC)

Defined as $J^i_{el} = \sigma^{ij}_{el} E^j$ in response to static electric field

Microscopic picture:

Dilute gas of charged particles subject to an static external electric field $\vec{E}$

experience Lorentz force $\vec{F}_L = q\vec{E}$

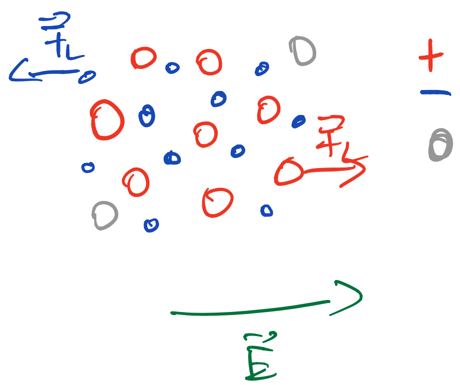
and two-body collisions described by BTE

If we have only one charged particle species the Lorentz force will be the same for all particles and the system as a whole will be accelerated; definitely not a small deviation from local equilibrium

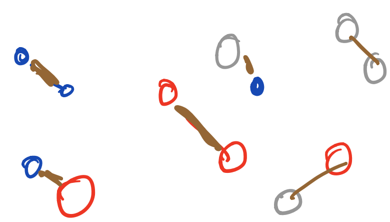
Shows that DC conductivity is physically quite different from AC conductivity (c.f. exercises)

Now in reality systems are usually charge neutral, as they consist of different microscopic degrees of freedom which are positively/negatively charged or charge neutral

Lorentz force:



Collision processes:



Need to account for different species (i) in the BTE

charge q_i

$$\left(\frac{\partial}{\partial t} + \frac{\vec p}{m_i}\vec\nabla_r + q_i \vec E\, \vec\nabla_p\right) f_i(t,\vec r,\vec p) = \sum_j C_{ij}\left[f_i,f_j\right](t,\vec r,\vec p)$$

mass m_i

collisions between particles i, j

where $\vec p = \vec p_{kin}$ is the kinetic momentum

Balance equation for momentum:

$$\vec{\mathcal{P}}(t,\vec{r}) = \int_{\vec{p}} \sum_i \vec{p}\, f_i(t,\vec{r},\vec{p})$$

$$\vec{P}(t) = \int d^3\vec{r}\; \vec{\mathcal{P}}(t,\vec{r})$$

$$\frac{d}{dt}\vec{P}(t) = \int d^3\vec{r} \left[\sum_i q_i\, n_i(t,\vec{r})\,\vec{E} + \sum_{ij} \int_{\vec{p}} \vec{p}\; C_{ij}[f_i,f_j](t,\vec{r},\vec{p}) \right]$$

Since microscopic collisions conserve the momenta of all participating particles

$$\frac{d}{dt}\vec{P}(t) = \int d^3\vec{r} \; \sum_i q_i\, n_i(t,\vec{r})\,\vec{E} = Q\,\vec{E}$$

$Q = \sum_i q_i \int d^3\vec{r}\; n_i(t,\vec{r})$ is the net charge

Since positive and negative charges will be accelerated in opposite directions, net momentum stays the same for charge neutral systems $(Q=0)$

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Now in the limit $\tau_e^{-1} \sim \frac{q_i E}{m_i v_{th}} \ll \tau_{mfp}^{-1}$

the response to the electric field is slow compared to the mean free time between collisions, such that the system stays close to local thermal equilibrium and we can find approximate solutions to BTE based on Hilbert expansion

$$O(Kn^0) \qquad \sum_j C_{ij}[f_i^{(0)}, f_j^{(0)}] = 0 \quad \forall i$$

$\Rightarrow f_i^{(0)}$ is local equilibrium distribution

$$f_i^{(0)} = n_i(t,\vec{r}) \left(\frac{2\pi\hbar^2}{m_i k_B T(t,\vec{r})}\right)^{3/2} \exp\left(-\frac{(\vec{p}-m\vec{V}(t,\vec{r}))^2}{2m_i k_B T(t,\vec{r})}\right)$$

with the <u>same</u> temperature T, velocity $\vec{V}$ for all species, as they can transfer energy and momentum between each others

Now if we specialize on a static and homogeneous system at rest, we have $T(t,\vec{r}) = T$ and $\vec{v} = 0$, $n_i(t,\vec{r}) = n_i$ such that $\partial_t f^{(0)} = \vec{\nabla}_r f^{(0)} = 0$

interactions between same species

$$\mathcal{O}(Kn^1) \qquad q_i \vec{E}\, \vec{\nabla}_p f_i^{(0)} = \delta C_{ii}\left[f_i^{(0)}, f_i^{(1)}\right]$$

$$+ \sum_{j \neq i} \left(\delta C_{ij}\left[f_i^{(0)}, f_j^{(1)}\right] + \delta C_{ij}\left[f_i^{(1)}, f_j^{(0)}\right] \right)$$

interactions between different species

Now to compute the electrical conductivity, we need to calculate

$$\vec{J}_{el} = \sum_i q_i \vec{J}_{n,i} = \sum_i q_i \int_p \frac{\vec{p}}{m_i} \left(f_i^{(0)}(t,\vec{r},\vec{p}) + f_i^{(1)}(t,\vec{r},\vec{p}) \right)$$

Since there are no equilibrium currents in the LRF $f_i^{(0)}(t,\vec{r},\vec{p})$ does not contribute

$$\vec{J}_{el} = \sum_i q_i \int_p \frac{\vec{p}}{m_i} f_i^{(1)}(t,\vec{r},\vec{p})$$

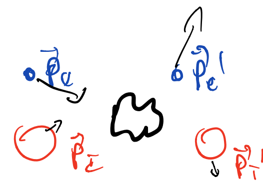
Electric field drives the system out of equilibrium which creating a current

We also observe that only charged particles ($q_i \neq 0$) contribute, and that light particles ($m_i \ll M_i$) contribute more significantly to the electric current

Specifically in conducting materials, we have loosely bound electrons m_e and atomic ions M_I with $m_e \ll M_I$, such that effectively only the electrons contribute

However, the dominant interaction is between e and I, i.e. if we focus on f_e, we have $C_{ee} \simeq 0$ but C_{eI} important. Now since the position of ions in a condensed matter system is fixed the structure, they are often treated as static scattering centers ($\vec{P}_I \simeq 0$)

Described by <u>Lorentz gas</u>:



$$\delta C_{eI} = \int_{\vec p_I} d\Omega_{\vec p_e \vec p_e'} \frac{d\sigma}{d\Omega_{\vec p_e \vec p_e'}} \left|\frac{\vec p_e}{m_e} - \frac{\vec p_I}{m_I}\right|$$

$$\left(f_e^{(1)}(\vec p_e')\, f_I(\vec p_I') - f_e^{(1)}(\vec p_e)\, f_I(\vec p_I)\right)$$

$$\vec p_I \simeq \vec p_I' \simeq 0 \quad \underset{\sim}{=} \quad \int_{\vec p_I} f_I(\vec p_I) \int d\Omega_{\vec p_e, \vec p_e'} \frac{d\sigma}{d\Omega_{\vec p_e, \vec p_e'}} \frac{|\vec p_e|}{m_e}$$

$$\left(f_e^{(1)}(\vec p_e') - f_e^{(1)}(\vec p_e)\right)$$

$$\boxed{\delta C_{eI}(t, \vec r_e, \vec p_e) = n_I(t, \vec r_e) \frac{|\vec p_e|}{m_e} \int d\Omega_{\vec p_e, \vec p_e'} \frac{d\sigma}{d\Omega_{\vec p_e, \vec p_e'}} \left(f_e^{(1)}(t, \vec r_e, \vec p_e') - f_e^{(1)}(t, \vec r_e, \vec p_e)\right)}$$

Note that due to the fact that e can transfer momentum (and in principle also energy) to I to the ions, the momentum of the electron can change in the scattering process, but the number of electrons is still conserved.

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Now to proceed with calculation of σ
w/o approximation

$$\vec{J}_{el} = \sum_i q_i \int_{\vec{p}} \frac{\vec{p}}{m_i} f_i^{(1)}(t,\vec{r},\vec{p}) \simeq q_e \int_{\vec{p}_e} \frac{\vec{p}_e}{m_e} f_e^{(1)}(t,\vec{r}_e,\vec{p}_e)$$

keeping only the contributions from e
and approximate their interactions as
Lorentz gas in the relaxation time
approximation

$$\delta C_{ii}[f_i^{(0)}, f_i^{(1)}] + \sum_{j\neq i}\left(\delta C_{ij}[f_i^{(0)}, f_j^{(1)}] + \delta C_{ij}[f_i^{(1)}, f_j^{(0)}]\right)$$

$$\underset{\text{Lorentz gas}}{\simeq} \delta C_{eI}[f_e^{(1)}] \underset{\text{RTA}}{\simeq} -\frac{f_e^{(1)}(t,\vec{r}_e,\vec{p}_e)}{\tau_R(T, n_I, \vec{p}_e)}$$

Such that the Hilbert expansion of BTE
for e takes the form

$$q_e \vec{E}\, \vec{\nabla}_p f_e^{(0)}(\vec{p}) = - \frac{f_e^{(1)}(t,\vec{r},\vec{p})}{\tau_R(T,n_I,\vec{p})}$$

By using $\vec{\nabla}_p f_e^{(0)}(\vec{p}) = \frac{-\vec{p}}{m_e k_B T} f_e^{(0)}(\vec{p})$

and inverting the equation, we find

$$f_e^{(1)}(t,\vec{r},\vec{p}) = + \frac{q_e \tau_R(T,n_I,\vec{p})}{m_e k_B T} (\vec{p}\vec{E}) f^{(0)}(\vec{p})$$

which is a stationary solution for $f^{(1)}$

Now to get the conductivity σ^{ij}, we need to plug the solution into the expression for the electric current

$$J_{el}^{i} = \underbrace{\frac{q_e^2}{m_e^2 k_B T} \int_{\vec{p}} \tau_R(T,n_I,\vec{p})\, p^i p^j f^{(0)}(\vec{p})}_{\sigma_{ee}^{ij}} E^j$$

Specifically for $\tau_R = \text{const}$, we get

$$\sigma_{el}^{ij} = \frac{q_e^2 \tau_R}{m_e^2 k_B T} \int \frac{d^3p}{(2\pi\hbar)^3} \; p^i p^j f^{(0)}_{(\vec{p})}$$

Since $f^{(0)}_{(\vec{p})}$ is rotationally symmetry

$$\int \frac{d^3\vec{p}}{(2\pi\hbar)^3} \; p^i p^j f^{(0)}_{(\vec{p})} = \int \frac{d^3\vec{p}}{(2\pi\hbar)^3} \; \delta^{ij} \frac{\vec{p}^2}{3} f^{(0)}(\vec{p})$$

So

$$\sigma_{el}^{ij} = \frac{2}{3} \frac{q_e^2 \tau_R}{m_e k_B T} \underbrace{\int \frac{d^3\vec{p}}{(2\pi\hbar)^3} \frac{\vec{p}^2}{2m_e} f^{(0)}(\vec{p})}_{\frac{3}{2} n k_B T} \delta^{ij}$$

$$\boxed{\sigma_{el}^{ij} = \frac{q_e^2 n \tau_R}{m_e} \delta^{ij}}$$

Note that Curie principle $\sigma_{el}^{ij} \propto \delta^{ij}$ emerges automatically from microscopic calculation in isotropic medium

Interestingly the result has a simple physical interpretation

$$\sigma_{ce} = \frac{q_e^2 n \tau_R}{m_e}$$

q_e : charge of particle creates force & current

n : density of particles

m_e : inertia of particle

τ_R : average time that particle can travel before colliding with $O(1)$ probability

and the same result can be obtained heuristically in terms of Drude model, where considering a statistical ensemble of particles

$$m \frac{d\langle\vec{v}\rangle}{dt} = q\vec{E} - m\frac{\langle\vec{v}\rangle}{\tau_R}$$

which gives terminal velocity

$$\langle\vec{v}\rangle_{\text{terminal}} = \frac{q\vec{E}\tau_R}{m}$$

Now current is given by

$$\vec{J} = qn\langle\vec{v}\rangle_{\text{forward}} = \frac{q^2 n \tau_R}{m}\vec{E}$$

yielding the same result.

Obviously a clear advantage of the Boltzmann equation is that it can be generalized to other kind of transport phenomena (next lectures) to more complicated/realistic interactions