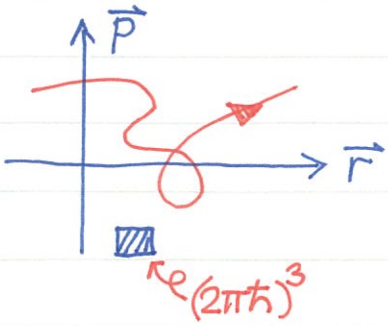
HH0048 Boltzmann Transport Equation

In the semiclassical regime, it's useful to introduce a distribution function $f(\vec{r},\vec{p},t)$ in the phase space

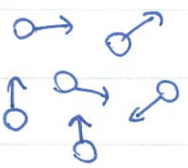


$$\boxed{f(\vec{r},\vec{p},t)\,\frac{d^3\vec{r}\,d^3\vec{p}}{(2\pi\hbar)^3} = \text{number of particles in } d^3\vec{r} \text{ and } d^3\vec{p}}$$

(1) You know the idea doesn't work in quantum world due to uncertainty principle.

(2) But! The factor $(2\pi\hbar)$ provides the natural normalization for the semiclassical approach.

<u>check.</u> The quantum Fermi gas can be discribed by



$$\boxed{f(\vec{r},\vec{p},t) = \frac{1}{e^{(\varepsilon-\mu)/\tau}+1}}$$

Let's check the normalization condition

Fermi gas $\displaystyle\int \frac{d^3\vec{r}\,d^3\vec{p}}{(2\pi\hbar)^3}\, f(\vec{r},\vec{p},t) = V\cdot \int \frac{d^3\vec{p}}{(2\pi\hbar)^3}\, f(\vec{r},\vec{p},t)$

At $\tau\to 0$ limit, spin $\frac{1}{2}$, $\longrightarrow V\cdot \dfrac{1}{(2\pi\hbar)^3}\cdot \underbrace{2}_{(2S+1)\text{ factor.}}\cdot \dfrac{4}{3}\pi p_F^3 = V\cdot \dfrac{p_F^3}{3\pi^2\hbar^3}$

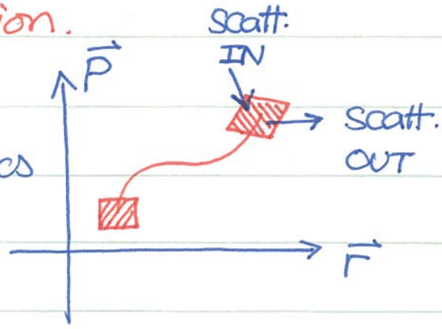
Making use of the relation $\varepsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{\frac{2}{3}}$, the integral equals

$$\boxed{\int \frac{d^3\vec{r}\,d^3\vec{p}}{(2\pi\hbar)^3}\, f(\vec{r},\vec{p},t) = V\cdot n = N}$$

This agrees with the definition of $f(\vec{r},\vec{p},t)$!!

⊘ Derivation of Boltzmann transport equation.

Follow a tiny element in the phase space. The Liouville theorem of classical mechanics tell us that $\frac{df}{dt} = 0$ because the volume of the element is constant!



But, collisions between molecules modify the equation.

$$\boxed{\frac{df}{dt} = \left(\frac{\partial f}{\partial t}\right)_{\text{collisions}} = (\text{rate of Scatt. IN}) - (\text{rate of scatt. OUT})}$$

According to partial differentiation: $\frac{d}{dt} = \frac{\partial}{\partial t} + \frac{d\vec{r}}{dt}\cdot\vec{\nabla}_r + \frac{d\vec{p}}{dt}\cdot\vec{\nabla}_p$

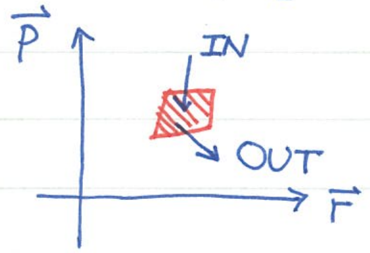
Thus, the previous equation becomes

$$\boxed{\frac{\partial f}{\partial t} + \frac{\vec{P}}{M}\cdot\vec{\nabla}_r f + \vec{F}_{ex}\cdot\vec{\nabla}_p f = \left(\frac{\partial f}{\partial t}\right)_c}$$

The famous Boltzmann transport equation

In above, we have used the relations, $\vec{v} \equiv \frac{d\vec{r}}{dt} = \vec{P}/M$ and $\vec{F}_{ex} = d\vec{P}/dt$. Rember – the dynamics is classical!

Relaxation time approximation: In general, $(\partial f/\partial t)_c$ can be computed from microscopic quantum transitions (mainly by Fermi's golden rule). But, if $f(\vec{r},\vec{p},t)$ is not far away from a thermal equilibrium $f_0 = f_0(\vec{r},\vec{p})$, one can assume the scattering rate is constant, $\gamma_c = 1/\tau_c$, independent of $\vec{r}$ and $\vec{p}$.



$$\boxed{\left(\frac{\partial f}{\partial t}\right)_c = f_0\cdot\gamma_c - f\cdot\gamma_c = -\frac{f-f_0}{\tau_c}}$$

The Boltzmann equation is greatly simplified.

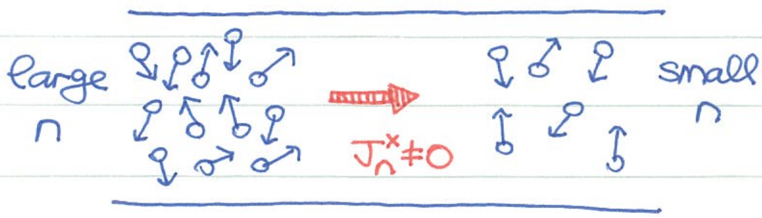
Consider a homogeneous system without any external force. $f=f(\vec{p},t)$ $\rightarrow$ $\vec{\nabla}_r f = 0$ and $\vec{F}_{ex}\cdot\vec{\nabla}_p f = 0$. The Boltzmann transport eq. is

$$\frac{\partial f}{\partial t} = -\frac{f-f_0}{\tau_c} \quad \rightarrow \quad \boxed{f(\vec{p},t) = f_0(\vec{p}) + \left[f(\vec{p},0)-f_0(\vec{p})\right]e^{-t/\tau_c}}$$

The distribution function goes from $f(\vec{p},0)$ to $f_0(\vec{p})$ within the time scale of relaxation time τ_c. Again, collisions between molecules are important to explain why most systems thermalize.

Diffusion explained by Boltzmann theory: Suppose the system is inhomogeneous with $n=n(x)$. Naively, we may guess the local thermal equilibrium gives

$$\boxed{f_0(x,\vec{p}) = \frac{1}{e^{[\varepsilon-\mu(x)]/\tau}+1}}$$



In the steady state, $f = f(x, \vec{p})$ does not change with time,

$$\cancelto{0}{\frac{\partial f}{\partial t}} + v_x \frac{\partial f}{\partial x} + \cancelto{0}{\vec{0} \cdot \vec{\nabla}_p f} = -\left(\frac{f - f_0}{\tau_c}\right)$$

The collision term is balanced by gradient.

$$\rightarrow \boxed{f = f_0 - \tau_c v_x \frac{\partial f}{\partial x} \approx f_0 - \tau_c v_x \frac{\partial f_0}{\partial x}}$$

solution to the linear order

We can now evaluate the flux density J_n^x of transported particles,

$$J_n^x = \frac{1}{V} \int \frac{d^3\vec{r}\, d^3\vec{p}}{(2\pi\hbar)^3} f(x, \vec{p}) \cdot v_x = \frac{1}{V} \int \frac{d^3\vec{r}\, d^3\vec{p}}{(2\pi\hbar)^3} \cdot \left(-\tau_c v_x \frac{\partial f_0}{\partial x}\right) \cdot v_x$$

The equilibrium dist. $f_0(x, \vec{p}) = f_0(x, -\vec{p})$ and gives no contribution to J_n^x. The derivative can be computed by chain rule,

$$\boxed{\frac{\partial f_0}{\partial x} = \frac{\partial f_0}{\partial \mu} \frac{d\mu}{dx} \approx \delta(\varepsilon - \mu) \frac{d\mu}{dx}}$$

for degenerate Fermi gas.

$$\rightarrow J_n^x = \frac{1}{V} \int d^3\vec{r} \left(-\tau_c \frac{d\mu}{dx}\right) \int \frac{d^3\vec{p}}{(2\pi\hbar)^3} v_x^2\, \delta(\varepsilon - \mu)$$

Now need to change variables

Recall that, for spin $\frac{1}{2}$ electrons, the sum-integral relation is

$$\boxed{\frac{1}{V} \sum_n = \frac{1}{V} \int_0^\infty d\varepsilon\, D(\varepsilon) = \int \frac{d^3\vec{p}}{(2\pi\hbar)^3} \cdot 2}$$

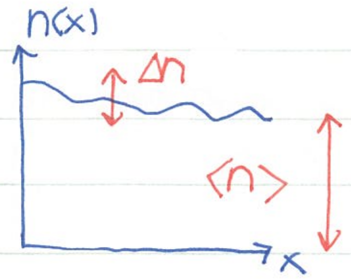
a factor of 2 should be here for spin degeneracy.

Thus, it is more convenient to introduce $d(\varepsilon) \equiv D(\varepsilon)/V$ and the flux density can be expressed as

from angular average

$$\boxed{\begin{aligned} J_n^x &= \frac{1}{V} \int d^3\vec{r} \left(-\tau_c \frac{d\mu}{dx}\right) \int_0^\infty d\varepsilon\, d(\varepsilon) \cdot \frac{1}{3} v^2\, \delta(\varepsilon - \mu) \\ &= \frac{1}{V} \int d^3\vec{r} \left[-\frac{1}{3} \tau_c v_F^2\, d(\varepsilon_F)\right] \frac{d\mu}{dx} \end{aligned}}$$

We still need to handle the spatial integral.



If the density variations are small, $\Delta n / \langle n \rangle \ll 1$, the spatial integral just gives V, canceling the $\frac{1}{V}$ factor in front.

$$\boxed{J_n^x = -\frac{1}{3} \tau_c v_F^2\, d(\varepsilon_F) \cdot \frac{d\mu}{dx}}$$

① $d(\varepsilon_F) = \dfrac{3n}{2\varepsilon_F}$

② $\mu = \dfrac{\hbar^2}{2M} (3\pi^2 n)^{\frac{2}{3}}$

$$\frac{d\mu}{dx} = \frac{2\varepsilon_F}{3n} \cdot \frac{dn}{dx} = \frac{1}{d(\varepsilon_F)} \cdot \frac{dn}{dx}$$

Substitute into the above relation

The flux density of particles is $\boxed{J_n^x = -\frac{1}{3}\tau_c v_F^2 \cdot \frac{dn}{dx}}$

By comparison, the diffusion constant D is $D = \frac{1}{3}\tau_c v_F^2$ One can also work out the same route of calculations for a non-degenerate Fermi gas (i.e. ideal gas). The Fick's law takes the same form except the Diffusion constant is different,

$$\boxed{D = \frac{1}{3}\tau_c\langle v^2\rangle = \frac{1}{\cancel{3}}\tau_c\cdot\frac{\cancel{3}\tau}{M} = \frac{\tau\tau_c}{M}}$$

linear dependence on temperature.

(II) Conductivity tensor and mobility: Now consider the system with uniform density but with applied external electric field.

$$\cancel{\frac{\partial f}{\partial t}}^{\,0} + \vec{v}\cdot\cancel{\vec{\nabla}_r f}^{\,0} + q\vec{E}\cdot\vec{\nabla}_p f = -\left(\frac{f-f_0}{\tau_c}\right), \quad f_0 = \frac{1}{e^{\varepsilon-\mu/\tau}+1}$$

Following similar steps, the electric current density is

$$J_a = \frac{q}{V}\int d^3\vec{r}\int\frac{d^3\vec{p}}{(2\pi\hbar)^3}\cdot 2\cdot f\cdot v_a, \quad \text{where } f = f_0 - q\tau_c\sum_b E_b\frac{\partial f}{\partial p_b}$$

$$= q^2\tau_c\sum_{b=1}^{3}E_b\int\frac{d^3\vec{p}}{(2\pi\hbar)^3}\cdot 2\left(-\frac{\partial f}{\partial p_b}\right)v_a$$

$$-\frac{\partial f}{\partial p_b} = -\frac{\partial f}{\partial \varepsilon}v_b \approx \delta(\varepsilon-\mu)v_b$$

$$= \sum_{b=1}^{3}E_b\cdot(q^2\tau_c)\int\frac{d^3\vec{p}}{(2\pi\hbar)^3}\cdot 2\; v_a v_b\,\delta(\varepsilon-\mu)$$

The conductivity tensor is defined as $J_a = \sum_{b=1}^{3}\sigma_{ab}E_b$

By comparison, it's easy to see that

$$\boxed{\sigma_{ab} = q^2\tau_c\int\frac{d^3\vec{p}}{(2\pi\hbar)^3}\cdot 2\; v_a v_b\,\delta(\varepsilon-\mu)}$$

What's the physical meaning of $\delta(\varepsilon-\mu)$?

It's quite clear that $\langle v_a v_b\rangle = 0$ for $a\neq b$ $\longrightarrow$ $\sigma_{ab} = \delta_{ab}\sigma$

$$\sigma = q^2\tau_c\int\frac{d^3\vec{p}}{(2\pi\hbar)^3}\cdot 2\; v^2\cos^2\theta\,\delta(\varepsilon-\mu) = q^2\tau_c\int_0^\infty d\varepsilon\, d(\varepsilon)\cdot\frac{1}{3}v^2\,\delta(\varepsilon-\mu)$$

Finally, the conductivity is $\boxed{\sigma = \frac{1}{3}q^2\tau_c v_F^2\cdot d(\varepsilon_F)}$

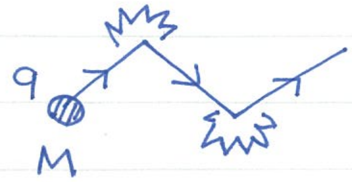
Let's try to get rid of $d(\varepsilon_F) = 3n/2\varepsilon_F$. The conductivity tensor is

$$\boxed{\sigma_{ab} = \delta_{ab}\,\frac{1}{3}\,q^2 \tau_c v_F^2 \left(3n/2\varepsilon_F\right) = \delta_{ab}\,\frac{nq^2\tau_c}{M}}$$

Drude conductivity

The mobility $\tilde{\mu}$ is defined as $\langle u \rangle = \tilde{\mu} E$ where $\langle u \rangle$ is drift velocity and E is the electric field.

$J = \sigma E \longrightarrow nq\langle u \rangle = \sigma E$ Thus, $\boxed{\tilde{\mu} = \frac{\sigma}{nq} = \frac{q\tau_c}{M}}$



mobility $\tilde{\mu}$

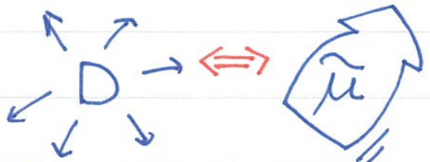
$= \frac{q}{M} \times$ (mean free time)

$\ell \sim v_F \tau_c$ linking MFP and relaxation time together

In the high temperature limit (ideal gas), the diffusion constant $D = \frac{1}{3}\tau_c\langle v^2 \rangle = \tau\tau_c/M$ is related to the mobility $\tilde{\mu} = q\tau_c/M$

$$\longrightarrow \boxed{D = \left(\frac{\tilde{\mu}}{q}\right)\tau}$$

This is the celebrated Einstein relation. It is the simplest version of the fluctuation-dissipation theorem. We shall encounter this relation in later lectures as well.



diffusion from fluctuations ⇔ dissipative drift

Q: What's the quantum version of Einstein relation?

⊘ Equilibrium v.s. steady state: In the previous examples, we illustrate the steady states in diffusion and electrical conduction. Now come back and ask the criterion for equilibrium in Boltzmann transport equation. In the presence of external force $\vec{F} = -q\vec{\nabla}V$, we expect the equilibrium is described by

$$\boxed{f_0(\vec{r},\vec{p}) = \frac{1}{e^{(\varepsilon + qV - \mu)/\tau} + 1}}, \quad \text{where } \varepsilon = p^2/2M$$

The Boltzmann transport equation for equilibrium state is

$$\cancel{\frac{\partial f_0}{\partial t}}^{\,0} + \frac{\vec{p}}{M}\cdot\vec{\nabla}_r f_0 + \vec{F}_{ex}\cdot\vec{\nabla}_p f_0 = -\cancel{\frac{f_0 - f_0}{\tau_c}}^{\,0}$$

This will give us equilibrium conditions.

Define $z = (\varepsilon + qV - \mu)/\tau$, the derivatives are

$$\vec{\nabla}_r f_0 = \frac{df_0}{dz}\vec{\nabla}_r z = \frac{df_0}{dz}\left[\frac{1}{\tau}(q\vec{\nabla}V - \nabla\mu) - \frac{1}{\tau^2}(\varepsilon+qV-\mu)\vec{\nabla}\tau\right]$$

$$\vec{\nabla}_p f_0 = \frac{df_0}{dz}\vec{\nabla}_p z = \frac{df_0}{dz}\cdot\frac{\vec{p}}{M}\frac{1}{\tau}$$ Substitute into Boltzmann eq.

$$\rightarrow \frac{df_0}{dz}\left[\cancel{\frac{q}{\tau}\nabla V} - \frac{1}{\tau}\vec{\nabla}\mu - \frac{1}{\tau^2}(\varepsilon+qV-\mu)\vec{\nabla}\tau\right]\cdot\frac{\vec{p}}{M} + \cancel{\frac{df_0}{dz}\frac{\vec{p}}{M\tau}\cdot\vec{F}_{ex}} = 0$$

Because df_0/dz and τ are not zero, the above equation is

$$\boxed{\vec{\nabla}\mu + \left(\frac{\varepsilon+qV-\mu}{\tau}\right)\vec{\nabla}\tau = 0}$$

← hold for all momenta and all positions !!

The only way to make the above equation true for all $\vec{p}$ & $\vec{F}$ is

$\vec{\nabla}\mu = 0$, $\vec{\nabla}\tau = 0$ That is to say, $\boxed{\mu(\vec{r}) = \mu, \quad \tau(\vec{r}) = \tau}$

Let us apply the equilibrium condition to derive the Einstein relation again. Consider a system in the presence of external force $\vec{F}_{ex} = -q\vec{\nabla}V$. The equilibrium distribution is

$$\boxed{f_0(\vec{r},\vec{p}) = \frac{1}{e^{[\varepsilon(\vec{p})+qV(\vec{r})-\mu]/\tau}+1}}$$

To simplify the calculations, let's consider the high temperature limit

$$f_0(\vec{r},\vec{p}) = e^{-(\varepsilon+qV-\mu)/\tau}$$

In equilibrium, the total current should be zero. The current due to density gradient is

$$q\cdot\vec{J}_n = -qD\vec{\nabla}n$$

Note that $\mu - qV(\vec{r}) = \tau\log(n/n_Q)$

$\rightarrow -q\vec{\nabla}V = (\tau/n)\vec{\nabla}n$

Thus, the diffusive current is $\boxed{\vec{J}_D = -qD\vec{\nabla}n = \frac{nq^2D}{\tau}\vec{\nabla}V}$

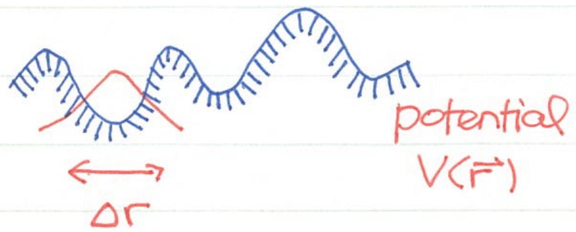
The drift current is $\vec{J}_d = \sigma \vec{E} = -nq\tilde{\mu}\,\vec{\nabla}V$. In equilibrium, we expect $\vec{J}_D + \vec{J}_d = 0 \longrightarrow \boxed{qD = \tilde{\mu}\,\tau}$ Einstein relation, again!

It is rather nice that the balance between diffusive and drift currents is implicitly embedded in Boltzmann transport eq..

⊘ Validity of Boltzmann transport equation: Because it's just semiclassical, quantum effects will invalidate BTE.

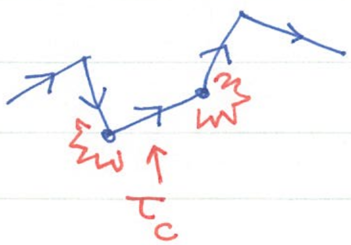
① $\Delta r \Delta p \gg \hbar$, The momentum variance $\Delta p \sim \sqrt{2M\tau}$

$$\longrightarrow \frac{\hbar}{\Delta p} \sim \frac{h}{\sqrt{2M\tau}} \equiv \lambda_T \quad \text{thermal wavelength.}$$



Therefore, the particle cannot be too localized... $\boxed{\Delta r \gg \lambda_T}$ smooth potential

② $\Delta t \Delta E \gg \hbar$, $\Delta E \sim \tau$ and $\Delta t \sim \tau_c$ (life time for definite momentum). Thus, the mobility cannot be too bad, $\boxed{\tau_c \gg \frac{\hbar}{\tau}}$



In addition to the above criteria, BTE does not include correlations between particles and fails for strongly correlated systems.

Doh!

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