Boltzmann Transport Equation
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Now, we are moving towards the topic about nonequilibrium thermal dynamics. But we don't yet plan to go too far away. Assuming there is a situation that slightly differs from equilirium, our task is to find out the time evolution of the situation, or more simply, to find out the steady state. **One will be amazed by the result that steady state $\neq$ equilibrium state.** And that's the key point why diffusion, current, viscosity occur. All these can be classified as transportation, which make up the fancy thermal dynamic world!

We start with some conceptions. Consider a box of gas. There all collsions between them all the time. So for each of the particles, the time evolution can be viewed as a stochastic process

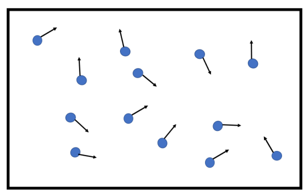

Figure 1: semiclassical stochastic process

In order to discribe it more detailly, we introduce the phase space, or sometimes called the μ space. A phase space is a six-dimention space, whose coordinates are $\vec{q}$ and $\vec{p}$, the generalized coodinates of **one** particle. The time evolution of a particle is represented as a line with orirentation in the phase space.

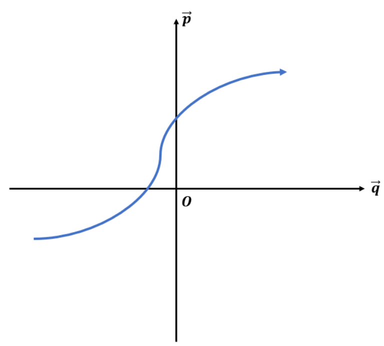

Figure 2: phase space and trajectory

However, the key concept in our discussion is that we are in "semi-classical" world. Classical world is just a limit of quantum rule. So "trajectory" is a vague concept in quantum world due to Heisemberge uncertainty principle. If we want to know the distribution of particles of a system in phase space, the smallest block, or unit, we can use is planck constant h. That's the semiquantum part.

Then it is safe to derive the distribution function $f(\vec{p},\vec{q},t)$, which are defined as:

$f(\vec{p},\vec{q},t)\cdot\frac{d^3\vec{p}d^3\vec{p}}{h^3}$ =the number of partialces within $(\vec{p},\vec{p}+d\vec{p})$, $(\vec{q},\vec{q}+d\vec{q})$

Hence,

$$\int_\mu \frac{d^3\vec{p}d^3\vec{p}}{h^3}f(\vec{p},\vec{q},t)=N \tag{1}$$

- **Validity of distribution function**

Using Dirac-Ferimion distribution at $\tau=0$ to check if this relation is correct:

$$f_{F.D.}(\vec{p})=\frac{1}{exp(\frac{\varepsilon-\mu}{\tau})+1}=\Theta(\varepsilon_F-\varepsilon)$$

Where $\varepsilon_F=\frac{\hbar^2}{2m}(3\pi^2n)^{2/3}$

$$\int_\mu \frac{d^3\vec{p}d^3\vec{p}}{h^3}f(\vec{p},\vec{q},t)=\frac{V}{h^3}\cdot 2\cdot\frac{4}{3}\pi {p_F}^3=V\cdot n=N$$

Which coincides with the definition of f

- **Collison Correction**

In classical mechanics, we know that a small piece of "area" in phase space remains the same value when it is evolving with time. The proof is rather simple: time-evolution can be considered as a canonical transformation mapping $q_i(t_1),p_j(t_1)$ to $q_i(t_2),p_j(t_2)$. Let x_i be a coordinate in phase space. According to canonical transformation:

$$\vec{x}(t_2)=M\vec{x}(t_1), dA(t_2)=|det(M)|dA(t_1) \tag{2}$$

Where M is a symplectic matrix, satisfying M^TM =J. $J=\begin{pmatrix} 0 & E_s \\ -E_s & 0\end{pmatrix}$ is the standard metric matrix of sympletic space.

It is easy to derive that $|det(M)|=1$. So the "area" is not changed.

And if the particle numbers within this area is conserved, then this can also be the proof of Liouville theorm. In our notation, it is equivalent to $\frac{df}{dt}=0$.

However, the particles within the area $(\vec{p},\vec{p}+d\vec{p})$, $(\vec{q},\vec{q}+d\vec{q})$ are not conserved owning to collisons between particles. Some will scatter in and some will scatter out. So the collison correction is now very important.

$$\frac{df}{dt}=(\frac{\partial f}{\partial t})_{collison} \tag{3}$$

Expanding the left-hand-side, we get the prototype of Boltzmann transport equation:

$$\frac{\partial f}{\partial t}+\vec{v}\cdot\nabla_q f+\vec{F}_{ex}\cdot\nabla_p f=(\frac{\partial f}{\partial t})_{collison} \tag{4}$$

Where F_{ex} is equal to $\dot{\vec{p}}$.

How to quantitatively express $(\frac{\partial f}{\partial t})_{collison}$? That's a difficlut task. And the main assumption that the system is not too far away from equilibrium will soon shows its power.

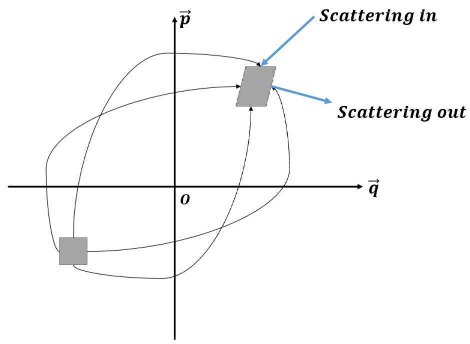

Figure 3: collison correction

- **Relaxation Time Approximation**

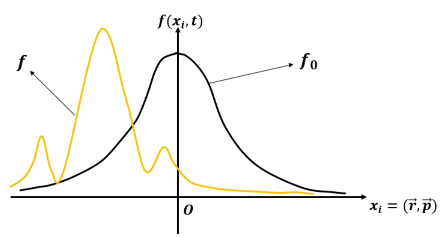

Figure 4: slightly variation distribution

For a system that is closed to equilibrium, $\frac{f-f_0}{f_0} << 1$ holds.
Boltzmann assumes that:

the rate of scattering in=$f_0 \cdot \gamma_c$
the rate of scattering out=$-f \cdot \gamma_c$

Hence,

$$(\frac{\partial f}{\partial t})_{collison} = -(f - f_0) \cdot \gamma_c = -\frac{f - f_0}{\tau_c} \tag{5}$$

Where $\tau_c = \gamma_c$. τ_c has more clear physical meaning: it is the relaxation time scale for f to varify near f_0.

If there is no external force and the system remains homogenous(uniform). Then $F_{ex} = 0, \nabla_r f = 0$.

$f = f(\vec{p}, t)$ satisfies:

$$(\frac{\partial f}{\partial t}) = -\frac{f - f_0}{\tau_c} \tag{6}$$

This gives the exact soulution :

$$f(\vec{p}, t) = f_0(\vec{p}) + [f(0) - f_0]exp(-\frac{t}{\tau_c})$$

As $t \to \infty$, $f \to f_0$. The steady state here is the same as equilbrium state. Again collisons between molecules are important to explain why mosy system thermalize.

- **Diffusion**

It is worthwhile to tell the micorscopic scenario of diffusion from conducting current (such as eletric current). In pure diffusion, there's no external force. The only variation from equilibrium is caused by the gradient of particle density ∇n. The amazing result is that now the steady state is no longer the equilibrium state!!

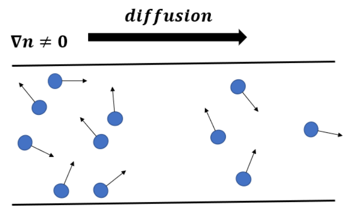

Figure 5: diffusion caused by density gradient

First, we make a wild guess: the local thermal equilibrium

$$f_0(\vec{r}, \vec{p}) = \frac{1}{exp(\frac{\varepsilon - \mu(\vec{r})}{\tau}) + 1} \tag{7}$$

Secondly, for steady state without external field, $F_{ex} = 0, \frac{\partial f}{\partial t} = 0$. The Boltzmann transport equation gives:

$$\frac{\vec{p}}{M} \nabla_r f = -\frac{f - f_0}{\tau_c} \tag{8}$$

$$\Rightarrow f = f_0 - \tau_c v_x \frac{\partial f}{\partial x}$$

It is still hard to solve f. Considering it is slightly variant from f_0. Leaving to the first term approximation,

$$f \approx f_0 - \tau_c v_x \frac{\partial f_0}{\partial x} \neq f_0 \tag{9}$$

The diffusion current J_n^x is the average of the whole μ- space:

$$J_n^x = n\langle v_x\rangle = \frac{1}{V}\int \frac{d^3\vec{r}d^3\vec{p}}{h^3} f(\vec{r},\vec{p})v_x = \frac{1}{V}\int \frac{d^3\vec{r}d^3\vec{p}}{h^3}(f_0 - \tau_c v_x \frac{\partial f_0}{\partial x})v_x \tag{10}$$

Note that the equilibrium distribution $f_0(\vec{r},\vec{p}) = f_0(\vec{r},\vec{-p})$
By chain rule (in low temperature limit f is a step function):

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

$$\Rightarrow J_n^x = \frac{-\tau_c}{V}\int d^3\vec{r}\int \frac{d^3\vec{p}}{h^3}v_x^2\delta(\varepsilon-\mu)\frac{d\mu}{dx} = \frac{-\tau_c}{V}\int d^3\vec{r}\int \frac{d^3\vec{p}}{h^3}v^2 cos^2\theta\delta(\varepsilon-\mu)\frac{d\mu}{dx}(x) \tag{11}$$

Take degeneracy of Fermion into account, choosing $2s+1=2$

$$J_n^x = \frac{-\tau_c}{V}\int d^3\vec{r}\int 2\frac{d^3\vec{p}}{h^3}v^2 cos^2\theta\delta(\varepsilon-\mu)\frac{d\mu}{dx}(x)$$

Now, it's time change variables from momentum to energy. Using the identities: $\varepsilon = \frac{p^2}{2m}, p = \hbar k$

$$2\int \frac{d^3\vec{p}}{2\pi\hbar} = \int \frac{d\varepsilon D(\varepsilon)}{V} = \int d\varepsilon d(\varepsilon) \tag{12}$$

Where $D(\varepsilon)d\varepsilon = \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\sqrt{\varepsilon}d\varepsilon$, $d(\varepsilon) = \frac{D}{V} = \frac{4\pi}{h^3}(2m)^{\frac{3}{2}}\sqrt{\varepsilon}$

$$\Rightarrow J_n^x = \frac{-\tau_c}{V}\int d^3\vec{r}\int d\varepsilon\delta(\varepsilon-\mu)\cdot\frac{1}{3}v^2\frac{d\mu}{dx}(x) = \frac{-\tau_c}{V}\int d^3\vec{r}\frac{1}{3}v_F^2 d(\varepsilon_F)\frac{d\mu}{dx} \tag{13}$$

Chain Rule again:

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

Finally:

$$J_n^x = -\int \frac{d^3\vec{r}}{V}\cdot\frac{1}{3}\tau_c v_F^2\frac{dn}{dx} = -\langle\frac{1}{3}\tau_c v_F^2\frac{dn}{dx}\rangle \approx -\frac{1}{3}\tau_c v_F^2\frac{dn}{dx} \tag{14}$$

The last approximation comes from the assumption that we are consider a small area $(\vec{r},\vec{r}+\Delta\vec{r})$.

Comparing with Fick's law:

$$\vec{J_n} = -D\nabla n$$

The diffusion constant D at not low temperature is:

$$\Rightarrow D = \frac{1}{3}\tau_c v_F^2 \tag{15}$$

What about high temperature limit? Consider ideal gas approximation.

$$f_0 = exp(-\frac{\varepsilon - \mu}{\tau}), \mu(x) = \tau log(\frac{n(x)}{n_Q}), n_Q = (\frac{m\tau}{2\pi\hbar^2})^{\frac{3}{2}}$$

Equation (10) changes to:

$$J_n^x = -\frac{\tau_c}{m^2 h^3 n_Q}\int dp_x dp_y dp_z p_x^2 exp(-\frac{p_x^2 + p_y^2 + p_z^2}{2m})\frac{dn}{dx} = -\frac{\tau_c \tau}{m}\frac{dn}{dx}$$

$$\Rightarrow D = \frac{\tau_c \tau}{m} \tag{16}$$

Note that pure diffusion is caused by collisons only.

- **Conducting Current**

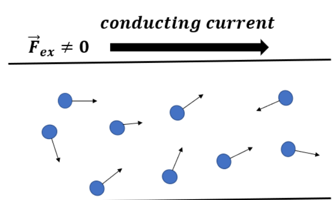

Figure 6: Conducting Current

A pure eletric current is caused by external field (such as electrimagnetic field). So we may assume that it is homogenous, ∇n=0.

Use J_a to represent one component of the current, J_a =(charge density)×(drift velocity)

$$J_a = \frac{q}{V}\int \frac{d^3\vec{r}d^3\vec{p}}{(2\pi\hbar)^3}(2s+1)f(\vec{p})\cdot v_a \approx q\int \frac{d^3\vec{p}}{(2\pi\hbar)^3}(2s+1)f(\vec{p})\cdot v_a \tag{17}$$

BTE:

$$\vec{F_{ex}} \cdot \nabla_p f = -\frac{f - f_0}{\tau_c} \tag{18}$$

$$\Rightarrow f \approx f_0 - q\tau_c \nabla_p f_0 \cdot \vec{E}$$

The same as we have done before:

$$J_a = -q^2\tau_c \sum_{b=1}^{3} \int \frac{d^3\vec{p}}{(2\pi\hbar)^3}(2s+1)\frac{\partial f_0}{\partial p_b} E_b v_a \tag{19}$$

Comparing with :

$$J_a = \sum_{b=1}^{3} \sigma_{ab} E_b$$

$$\Rightarrow \sigma_{ab} = -q^2\tau_c \sum_{b=1}^{3} \int \frac{d^3\vec{p}}{(2\pi\hbar)^3}(2s+1)\frac{\partial f_0}{\partial p_b} v_a$$

Again, we will consider low temperature limit first:

$$-\frac{\partial f_0}{\partial p_b} = -\frac{\partial f_0}{\partial \varepsilon}\frac{\partial \varepsilon}{\partial p_b} = \frac{\partial f_0}{\partial \mu} v_b \approx \delta(\varepsilon - \varepsilon_F) v_a v_b$$

Substitude into σ_{ab}

$$\sigma_{ab} = q^2\tau_c \int \frac{d^3\vec{p}}{h^3}(2s+1)\delta(\varepsilon - \varepsilon_F) v_a v_b \tag{20}$$

Which tells us some properties coincides with ohm's law.

Ohm's Law:

- Symmetric $\sigma_{ab} = \sigma_{ba}$
- Diagonalized $\sigma_{ab} = \delta_{ab}\sigma$

Futher calculation is similar to what we have done before:

$$\int \frac{d^3\vec{p}}{h^3}(2s+1)(...) = \int d\varepsilon d(\varepsilon)(...)$$

Angular average: $\int d\theta cos^2\theta = \frac{1}{3}$
Finally:

$$\sigma = q^2\tau_c \int d\varepsilon d(\varepsilon)\delta(\varepsilon - \varepsilon_F)\frac{1}{3}v^2 = \frac{1}{3}q^2\tau_c v_F^2 d(\varepsilon_F) \tag{21}$$

$d(\varepsilon_F) = \frac{3n}{2\varepsilon_F}$ will cancel the quantum quantity v_F^2, making it seem classical.

$$\sigma_{ab} = \delta_{ab}\frac{nq^2\tau_c}{M} \tag{22}$$

Which gives us the famous Drude conductivity derived from classcial assumptions.

It's worthwhile to pay attention to the meaning of $\delta(\varepsilon-\varepsilon_F)$. The delta function tells us only the Fermions(eletrons) close to the Fermi surface contributes to conducting, which really converses with the classical thought of all eletrons are contributing to the current with a relatively slow velocity v_e. This can be checked also by the Ferimion velocity v_F in σ.

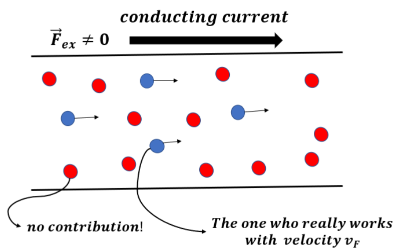

Figure 8: the correct understanding of current

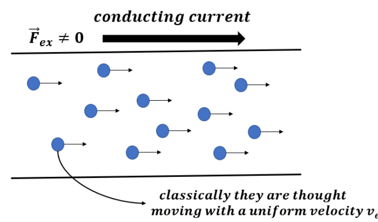

Figure 9: classical understanding

Now let's try to compute one more quantity, mobility $\tilde{\mu}$.

$$\tilde{\mu} = \frac{\langle u \rangle}{E} \tag{23}$$

But we know that :

$$qn\langle u \rangle = J = \sigma E$$

Hence,

$$\tilde{\mu} = \frac{q}{M} \times \tau_c \tag{24}$$

This can be a method to attain τ_c. Experimentally, one is easy to get the ratio of a charged particle by mass spectrometer and $\tilde{\mu}$ is also availabel.

***High temperature limit:**

$$\sigma_{ab} = \delta_{ab} \cdot \frac{n}{3\tau} q^2 \tau_c \langle v^2 \rangle = \frac{nq^2\tau_c}{M}\delta_{ab} \tag{25}$$

Which gives the same result as in low temperature limit!!

- **Fluctuation and Dissipation Theorem**

We all really know that D(high temperature)=$\frac{\tau\tau_c}{M}$, which is proportional to thermal fluctuation.

$$\Rightarrow \frac{D}{\tilde{\mu}} = \frac{\tau}{q}$$

$$qD = \tilde{\mu}\tau \tag{26}$$

The right-hand-side is related to dissipation with factor $\frac{1}{\sigma}$

Consider the criterion for equilibrium f_0.

If $f = f_0 = \frac{1}{exp(\frac{\varepsilon + qV - \mu}{\tau}) + 1}$, then:

$$\vec{v} \cdot \nabla_r f + \vec{F} \cdot \nabla_p f = 0 \tag{27}$$

Substitue into (27), we obtain:

$$\vec{v} \cdot [\nabla\mu + (\frac{\varepsilon + qV - \mu}{\tau})\nabla\tau] = 0 \tag{28}$$

holds for arbitrary $\vec{v}$.

$\Rightarrow \nabla\mu = 0, \nabla\tau = 0$. i.e. $\mu = const, \tau = const$

The same as we have discussed in thermal dynamics.

The last part of our story will be Einstein relation. Consider high temperature limit. When we have external field as well as gradient of density, what will happen? The answer is: if it reaches equilibrium, (diffusion)+(drift current)=0

Equilibrium distribution is:

$$f_0 \approx exp(-\frac{\varepsilon + qV - \mu}{\tau})$$

In previous lecture, we know that:

$$\mu - qV(\vec{r}) = \tau log(\frac{n}{n_Q}) \tag{29}$$

Taking gradien on both side of (29).

$$-q\nabla V = \tau\frac{1}{n}\nabla n \tag{30}$$

$$J_D = q\vec{J_n} = -qD\nabla n = \frac{q^2 nD}{\tau}\nabla V \tag{31}$$

Which gives us the diffusion part.

As for the drift part:

$$\vec{J_d} = nq\langle\vec{u_d}\rangle = -nq\tilde{\mu}\nabla V \tag{32}$$

From $\vec{J_d} + \vec{J_D} = 0$, we get:

$$nq(\frac{qD}{\tau} - \tilde{\mu})\nabla V = 0 \tag{33}$$

Again, the diffusion-dissipation relation is embeded in BTE:

$$qD = \tilde{\mu}\tau \tag{34}$$