11/24

Kinetic Theory of Transport Processes.

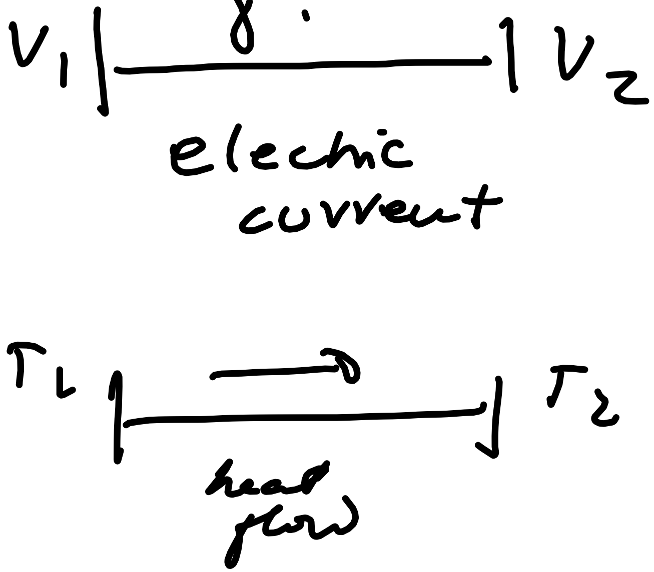
Up to now we have considered equilibrium situations:

- Equilibrium: Observables are time independent in an isolated system.

Now we will consider steady state problems:

- Observables time independent in a system that is not isolated.

$\bar{j}$:



The system that provides $T_1 \neq T_2$ or $V_1 \neq V_2$ is not in equilibrium (its observables are time dependent).

- Equilibrium is achieved due to interactions: usually collisions.

We will gases.

Interaction: collisions between molecules.

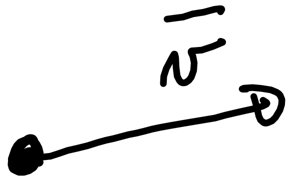
- Dilute system.
- Separation between molecules is much larger than their de Broglie wavelengths.

$l \ll \lambda$

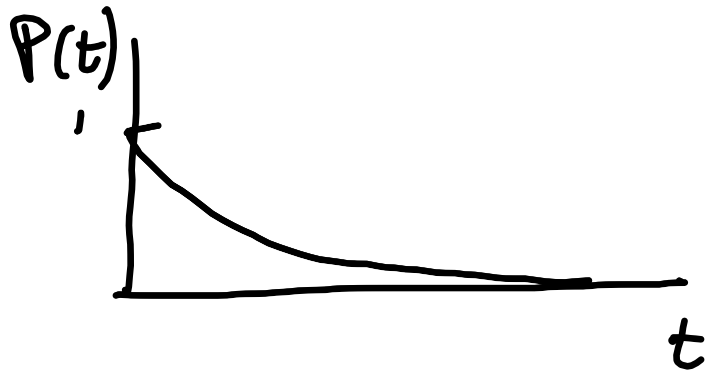
Assumptions:

- The molecules are traveling free most of the time.
- Collisions are between two molecules (three or more mol. col. are very unlikely).

Collision Time: (it is much shorter than the time that the molecules travel free).



$P(t)$: probability that a molecule survives a time t without a collision.



The longer you wait the most likely the molecule will collide so less survival chances (like in Russian roulette).

$w\,dt$: probability that a molecule collides in the time interval $t - t+dt$.

w: collision rate (it can be a function of v).

$$\underbrace{P(t+dt)}_{\text{prob that the particle survives up to time } t+dt} = \underbrace{P(t)}_{\text{prob that it survives up to time } t} \overbrace{(1 - w\,dt)}^{\text{prob that it survives for } dt \text{ after time } t}$$

$\downarrow$ Taylor

$$\cancel{P(t)} + \frac{dP}{dt}\cancel{dt} = \cancel{P(t)} - w\,P(t)\,\cancel{dt}$$

Then

$$\frac{1}{P}\frac{dP}{dt} = -w$$

If $w(v) = \text{constant}$

$$\int_{P_0}^{P} \frac{dP}{P} = -w\int_0^t dt$$

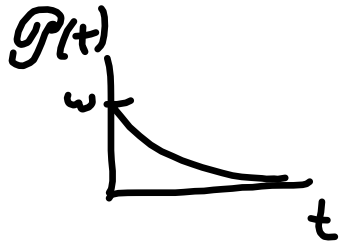
$$\ln P - \ln P_0 = -wt$$

$$P = P_0 e^{-wt}$$

but $P_0 = P(t=0) = 1$

$$\therefore P(t) = e^{-wt}$$

$$\therefore \quad \mathcal{P}(t)\,dt = \underbrace{e^{-wt}}_{P(t)} \; \underbrace{w\,dt}_{\text{prob that it collides at } t+dt.}$$



probability that the molecule collides at time $t+dt$ after surviving from $t=0$ to t.

$$\int_0^\infty \mathcal{P}(t)\,dt = 1$$

$wt = y$
$w\,dt = dy$

$$\int_0^\infty \mathcal{P}(t)\,dt = \int_0^\infty e^{-wt}\, w\,dt = \int_0^\infty e^{-y}\,dy = -e^{-y}\Big|_0^\infty = 1$$

$\tau = \bar{t}$ mean time between collisions

collision time or relaxation time. $\omega t = y$

$$\tau = \langle t \rangle = \int_0^\infty t\, \mathcal{P}(t)\, dt = \int_0^\infty t\, e^{-\omega t} \omega\, dt =$$

$$= \int_0^\infty \frac{y}{\omega} e^{-y} dy = \frac{1}{\omega} \underbrace{\int_0^\infty y e^{-y} dy}_{1} = \frac{1}{\omega}$$

$\int_0^\infty y^n e^{-y} dy = n!$

$$\therefore \boxed{\tau = \frac{1}{\omega}}$$

If $w = w(\bar{v})$ then $\tau = \tau(\bar{v})$.

Then

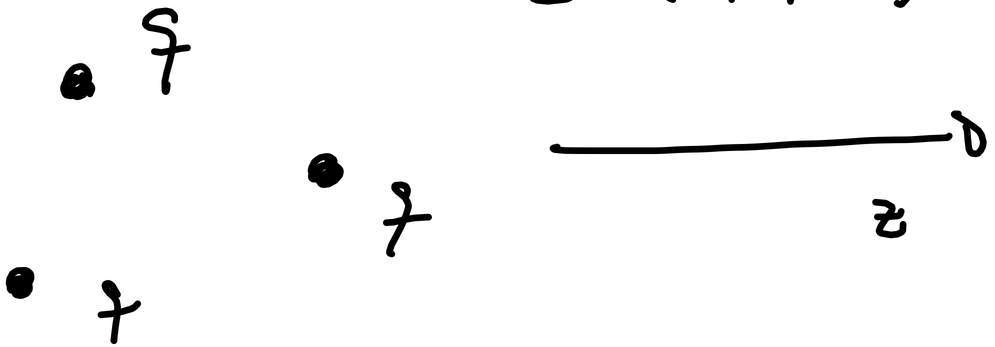
$$\mathcal{P}(t)\,dt = e^{-t/\tau}\,\frac{dt}{\tau}$$

Mean distance traveled between collisions, mean free path, is given by:

$$\ell(\bar{v}) = v\,\tau(\bar{v}).$$

Electric Conductivity

$\bar{\mathcal{E}} = (0,0,\mathcal{E})$ Electric field.



constant current
not an equilibrium situation
steady state.

electrons, ions
or other
charged
particles

j_z : mean electric charge crossing a unit of area perpendicular to $\tilde{z}$ per unit time (current density).

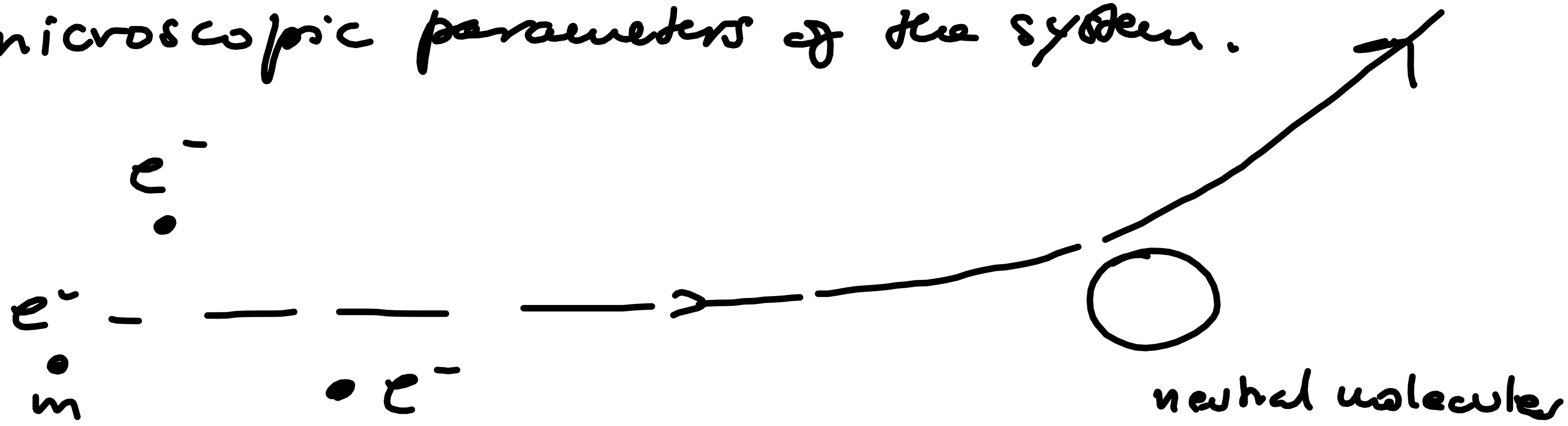
If $\mathcal{E}$ is small $\underbrace{\text{(linear response)}}_{j_z \propto \mathcal{E}}$

$$j_z = \sigma_{el}\, \mathcal{E}$$

constant of proportionality

σ_{el} : electric conductivity

We want to obtain σ_{el} in terms of microscopic parameters of the system.



If $\bar{\mathcal{E}} = \mathcal{E}_z \neq 0$ then $\langle v_z \rangle \neq 0$.

$n \langle v_z \rangle$: mean number of charged particles per unit volume that go through a unit area per unit time :

$j_z = e\, n \langle v_z \rangle$ we multiply the above by the charge e of the particles

We have to estimate $\langle v_z \rangle$.

In between collisions the charged particles follow the following equation of motion:

$$\underbrace{m \frac{dv_z}{dt}}_{m\bar{a}} = \underbrace{e \mathcal{E}}_{\bar{F}}$$

$$\therefore \; dv_z = \frac{e\mathcal{E}}{m} dt$$

$$\int_{v_z(0)}^{v_z(t)} dv_z = \frac{e\mathcal{E}}{m} \int_0^t dt' \quad \Rightarrow \quad v_z(t) = \frac{e\mathcal{E}}{m} t + v_z(0) \qquad (1)$$

Assumption: as a result of the collisions the particles are on average restored to thermal (Maxwell-Boltzmann) equilibrium $\Rightarrow$ $\langle v_z(0) \rangle = 0$ (random).

Averaging (1):

$$\langle v_z(t) \rangle = \frac{e\mathcal{E}}{m} \langle t \rangle = \frac{e\mathcal{E}}{m} \int_0^\infty t \, \mathcal{P}(t) \, dt =$$

$$= \frac{e\mathcal{E}}{m} \int_0^\infty t \, e^{-t/\tau} \frac{dt}{\tau} = \frac{e\mathcal{E}}{m} \tau \qquad (2)$$

$-t/\tau = y$

Then

$$j_z = \frac{n e^2 \mathcal{E}}{m} \tau = \sigma_{ee} \mathcal{E}$$

$$\Rightarrow \boxed{\sigma_{ee} = \frac{n e^2}{m} \tau}$$

This expression works very well for ions in a dilute gas.

We will see that for electrons in a metal the Pauli statistics plays a role.

Transport processes and distribution functions:

Non-equilibrium: assume that

$$\underbrace{f(\bar{r},\bar{v},t)}_{\text{molecular distribution}} \text{ is known}$$

$f(\bar{r},\bar{v},t)\, d^3r\, d^3v$: mean number of molecules at time t with center of mass at $\bar{r} - \bar{r} + d^3r$ and its velocity between $\bar{v} - \bar{v} + d^3v$

Define

$n(\bar{r},t)\,d^3r$: mean number of molecules at time t with center of mass at $\bar{r} - \bar{r}+d^3r$ regardless of their velocity.

$$n(\bar{r},t) = \int d^3v \; f(\bar{r},\bar{v},t)$$

Define:

$\chi(\bar{r},\bar{v},t)$: some property of a molecule (such as energy, momentum, etc.) at $\bar{r}$ with velocity $\bar{v}$ at time t.

Then

$$\langle \chi(\bar{r}, t) \rangle = \frac{1}{n(\bar{r}, t)} \int d^3v \, f(\bar{r}, \bar{v}, t) \, \chi(\bar{v}, \bar{r}, t)$$

then:

$$\langle \underbrace{u(\bar{r}, t)}_{\substack{\text{mean velocity} \\ \bar{u}(\bar{r}, t)}} \rangle = \langle \bar{v}(\bar{r}, t) \rangle = \frac{1}{n(\bar{r}, t)} \int d^3v \, f(\bar{r}, \bar{v}, t) \, \bar{v}$$

$\bar{u} = 0$ for a system in equilibrium.

$\bar{u}(\bar{r}, t)$: describes the "flow" of a gas at a given point. It is the hydrodynamic velocity described by macroscopic hydrodynamics.

Let's define the "peculiar" velocity $\bar{U}$ for a molecule as its velocity with respect to $\bar{u}$:

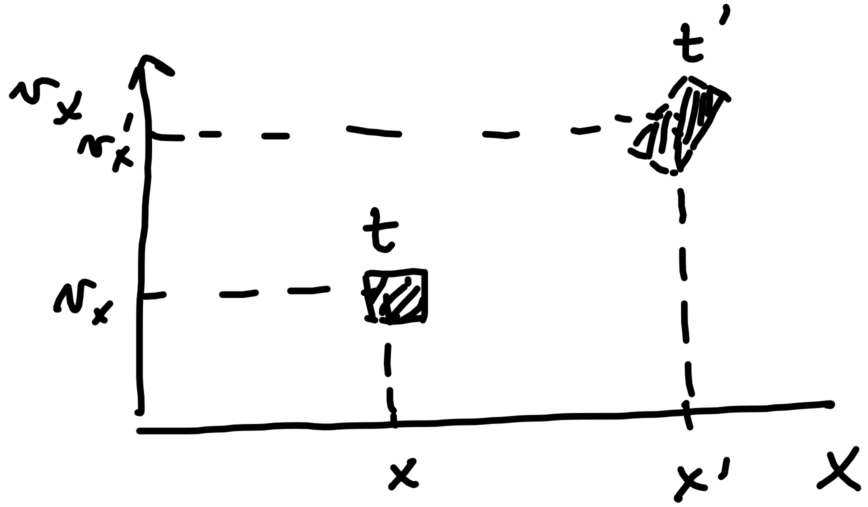
$$\bar{U} = \bar{v} - \bar{u}$$

$$\therefore \langle \bar{U} \rangle = \langle \bar{v} \rangle - \bar{u} = \bar{u} - \bar{u} = 0$$

Boltzmann's equation in the absence of collisions:

- We want to obtain $f(\bar{r}, \bar{v}, t)$ knowing $f(\bar{r}_0, \bar{v}_0, t_0)$ if the molecules do not suffer collisions.

- Assume that there is an external force $\bar{F}(\bar{r}, t)$ (independent of $\bar{v}$) such as gravity or an electric field, so that the system is not in equilibrium.



We want to obtain f' in terms of f (# of molecules in each volume):

At $t' = t + dt$ what happens with the molecules at (x, v_x, t)?

$$\left.\begin{aligned}\bar{r}' &= \bar{r} + \dot{\bar{r}}\,dt = \bar{r} + \bar{v}\,dt \\ \bar{v}' &= \bar{v} + \dot{\bar{v}}\,dt = \bar{v} + \frac{\bar{F}}{m}\,dt\end{aligned}\right\} \quad (1)$$

All the molecules at t' will be in the range $\bar{r}' - \bar{r}' + d^3r'$ and $\bar{v}', \bar{v}' + d^3v'$

$$\therefore \quad f(\bar{r}, \bar{v}, t)\, d^3r\, d^3v = f(\bar{r}', \bar{v}', t')\, d^3r'\, d^3v'$$

Notice that (1) represents a change of coordinates and then

$$d^3r'\, d^3v' = |J|\, d^3r\, d^3v$$

$$|J| = \left| \frac{\partial\{\bar{x}',\bar{v}'\}}{\partial\{\bar{x},\bar{v}\}} \right| = \left| \begin{array}{ccc|ccc} 1 & 0 & & dt & 0 & \\ 0 & 1 & & 0 & dt & \\ & & 1 & & & dt \\ \hline \sim dt & & & 1 & & 0 \\ & \sim dt & 0 & & 1 & \\ 0 & & \sim dt & 0 & & 1 \end{array} \right| \approx 1$$

if $dt \ll 1$

$$\frac{\partial x'_\alpha}{\partial x_\gamma} = \delta_{\alpha\gamma}$$

$$\frac{\partial x'_\alpha}{\partial v_\gamma} = \delta_{\alpha\gamma}\, dt$$

$$\frac{\partial v'_\alpha}{\partial x_\gamma} = \frac{1}{m}\frac{\partial F}{\partial x_\gamma}\, dt\, \delta_{\alpha\gamma}$$

$$\frac{\partial v'_\alpha}{\partial v_\gamma} = \delta_{\alpha\gamma}$$

then

$$d^3r'\, d^3v' \approx d^3r\, d^3v$$

then

$$\boxed{f(\bar{r}', \bar{v}', t') = f(\bar{r}, \bar{v}, t)}$$

3

③ can be rewritten as:

$$f(\bar{r}', \bar{v}', t') - f(\bar{r}, \bar{v}, t) = 0$$

$$f(\bar{r} + \dot{\bar{r}}\,dt,\ \bar{v} + \dot{\bar{v}}\,dt,\ t+dt) - f(\bar{r}, \bar{v}, t) = 0$$

or by components:

$$\left[\left(\frac{\partial f}{\partial x}\dot{x} + \frac{\partial f}{\partial y}\dot{y} + \frac{\partial f}{\partial z}\dot{z}\right) + \left(\frac{\partial f}{\partial v_x}\dot{v}_x + \frac{\partial f}{\partial v_y}\dot{v}_y + \frac{\partial f}{\partial v_z}\dot{v}_z\right) + \frac{\partial f}{\partial t}\right]dt = 0$$

or $\boxed{Df = 0}$ Boltzmann's equation without collisions

$$Df = \frac{\partial f}{\partial t} + \dot{\bar{r}} \cdot \frac{\partial f}{\partial \bar{r}} + \dot{\bar{v}} \cdot \frac{\partial f}{\partial \bar{v}} =$$

$$= \frac{\partial f}{\partial t} + \bar{v} \cdot \frac{\partial f}{\partial \bar{r}} + \frac{\bar{F}}{m} \cdot \frac{\partial f}{\partial \bar{v}}$$

$$\frac{\partial f}{\partial \bar{r}} = \bar{\nabla}_r f$$

$$\frac{\partial f}{\partial \bar{v}} = \bar{\nabla}_v f$$

$\therefore$ f remains unchanged if one moves along with the molecules in phase space in the absence of collisions.

Next time:

- Effect of collisions.
- Calculation of σ_{el}.

- Start working on HW #12.
  Solutions will be provided on 12/1.

- Take-home final will be given on 12/1.