3. Boltzmann equation :

Differential eq. for the distribution function $f(\vec{r}, \vec{v}, t)$

(in nonequilibrium situations)

⊙ distribution function

$f(\vec{r}, \vec{v}, t)\, d^3\vec{r}\, d^3\vec{v}$ $\equiv$ the mean # of molecules whose center of mass at time t has a position $\in [\vec{r}, \vec{r}+d\vec{r}]$ and a velocity $\in [\vec{v}, \vec{v}+d\vec{v}]$

→ nonequilibrium cases

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

(density)

⇒ average of any function $\chi(\vec{r}, \vec{v}, t)$

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

(ex) 1. mean velocity $\vec{u}(\vec{r}, t)$ of a molecule at $(\vec{r}, t)$

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

$$\vec{U} \equiv \vec{v} - \vec{u}$$

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

2. flux of χ through a plane moving with $\vec{u}(\vec{r}, t)$

$F_{\hat{n}}(\vec{r}, t)$ $\equiv$ the net amount of χ which is transported per unit time per unit area of an element of area (normal direction $/\!/\ \hat{n}$) from its $(-)$ to its $(+)$ side.

$$F_{\hat{n}}(\vec{r}, t) = \left[\int_{\hat{n}\cdot\vec{U} > 0} d^3\vec{v}\ f(\vec{r}, \vec{v}, t) \left(dt\, |\hat{n}\cdot\vec{U}| \right) \chi\, dA \right.$$

$$\left. - \int_{\hat{n}\cdot\vec{U} < 0} d^3\vec{v}\ f(\vec{r}, \vec{v}, t) \left(dt\, |\hat{n}\cdot\vec{U}| \right) \chi\, dA \right] \Big/ dt\, dA$$

$$= \int d^3\vec{v}\ f\,\hat{n}\cdot\vec{U}\,\chi$$

$$= n\langle \hat{n}\cdot\vec{U}\,\chi\rangle$$

$$\begin{cases} F_{\hat{n}} = \hat{n}\cdot\vec{F} \\ \vec{F} = n\langle \vec{U}\chi\rangle \end{cases}$$

(ex) viscosity

$$P_{zx} = n\langle U_z\cdot m v_x\rangle \quad \sim \text{ flux of momentum.}$$

$$= mn\langle U_z\cdot(u_x + U_x)\rangle$$

$$= \underbrace{mn\langle U_z u_x\rangle}_{= mn\langle \cancel{U_z}\rangle u_x} + mn\langle U_z U_x\rangle$$

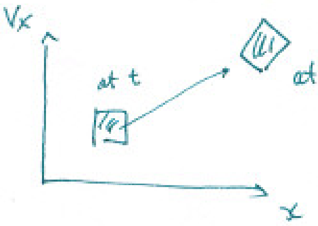
◎ Boltzmann eq. in the absence of collisions

$$\begin{cases} \text{each molecule with mass } m \\ \text{external force } \vec{F}(\vec{r},t) \end{cases}$$

at t, $(\vec{r},\vec{v}) \longrightarrow$ at $t+dt$ $(\vec{r}',\vec{v}')$

$$\boxed{\begin{aligned} \vec{r}' &= \vec{r} + \dot{\vec{r}}\,dt = \vec{r} + \vec{v}\,dt \\ \vec{v}' &= \vec{v} + \dot{\vec{v}}\,dt = \vec{v} + \frac{\vec{F}}{m}dt \end{aligned}}$$

no collision $\Rightarrow$ $f(\vec{r}',\vec{v}',t')\,d^3\vec{r}'\,d^3\vec{v}' = f(\vec{r},\vec{v},t)\,d^3\vec{r}\,d^3\vec{v}$



and $d^3\vec{r}'d^3\vec{v}' = |J|\,d^3\vec{r}\,d^3\vec{v}$

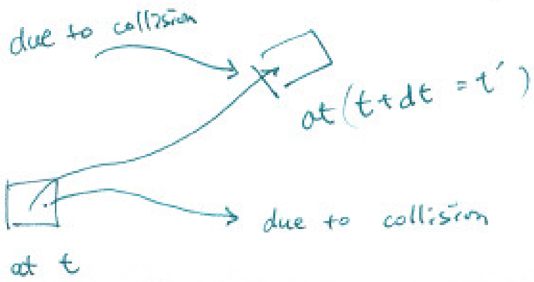
$J = 1 + O(dt^2)$

$\Rightarrow f(\vec{r}',\vec{v}',t') = f(\vec{r},\vec{v},t)$

$$\Rightarrow Df = \left[\frac{\partial f}{\partial t} + \dot{\vec{r}}\cdot\frac{\partial f}{\partial \vec{r}} + \dot{\vec{v}}\cdot\frac{\partial f}{\partial \vec{v}}\right] \Rightarrow \boxed{\frac{\partial f}{\partial t} + \vec{v}\cdot\frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{m}\cdot\frac{\partial f}{\partial \vec{v}} = 0}$$

Boltzmann eq. without collisions.

① Boltzmann equation in the presence of collisions



$$f(\vec{r}+\dot{\vec{r}}dt,\ \vec{v}+\dot{\vec{v}}dt,\ t+dt)\ d^3\vec{r}'d^3\vec{v}'$$

$$= f(\vec{r},\vec{v},t)\ d^3\vec{r}\,d^3\vec{v} + \underbrace{D_c f\ d^3\vec{r}\,d^3\vec{v}\,dt}_{\text{caused by collisions}}$$

Explicit expression of $D_c f$ will be given later

(see Reif chapter 14.3).

Here, we will find an approximation for $D_c f$, based on the assumptions:

(i) collisions will restore a local equilibrium situation described by

$$f^{(0)}(\vec{r},\vec{v},t) = n\left(\frac{m\beta}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m(\vec{v}-\vec{u})^2}$$

Maxwell - Boltzmann distribution

$$n = n(\vec{r},t),\quad \beta = \beta(\vec{r},t),\quad \vec{u} = \vec{u}(\vec{r},t)$$

(ii) if $f \neq f^{(0)}$, f goes to $f^{(0)}$ exponentially rapidly with a relaxation time τ_0 (mean free time) due to collisions.

$$\to\ D_c f = -\frac{f-f^{(0)}}{\tau_0}$$

"relaxation-time approximation"

$$\boxed{Df \equiv \frac{\partial f}{\partial t} + \vec{v}\cdot\frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{m}\cdot\frac{\partial f}{\partial \vec{v}} = -\frac{f-f^{(0)}}{\tau_0}}$$

check: for fixed $\vec{r}$ and $\vec{v}$, $f(t)-f^{(0)}(t) = [f(0)-f^{(0)}(0)]\,e^{-t/\tau_0}$

$D_c f = 0$ if $f = f^{(0)}$

⊙ Alternative approach for $f(\vec{r}, \vec{v}, t)$ in the presence of collisions

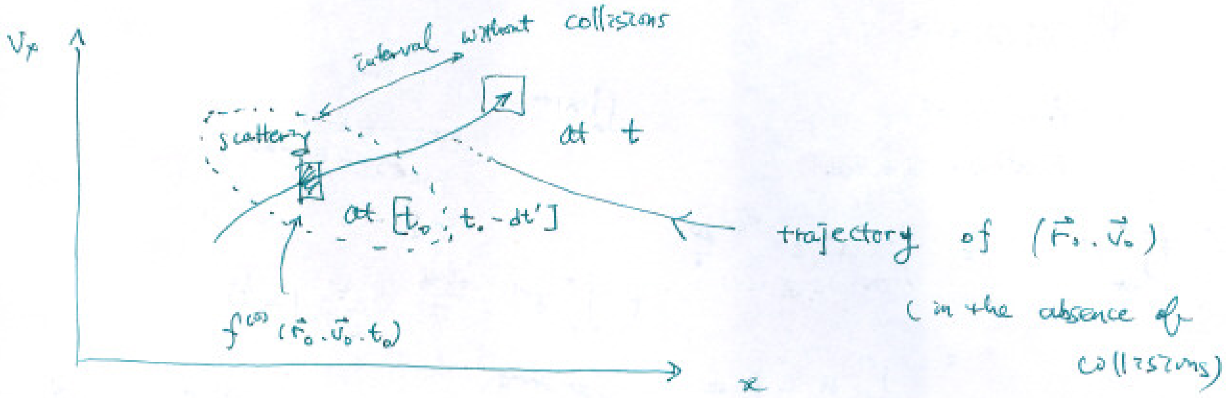
$$\begin{cases} \text{at ~~t~~ time } t, \text{ a molecule has } (\vec{r}, \vec{v}). \\ \text{at time } t_0 \ (<t), \text{ it has } (\vec{r}_0, \vec{v}_0). \end{cases}$$

$(\text{or } t_0 = t - t', \ t' > 0)$

If there is no collision, one can find $(\vec{r}_0, \vec{v}_0)$ in terms of $(\vec{r}, \vec{v})$, by ~~...~~ solving eq. of motion under the influence of $\vec{F}$.

$$\begin{cases} \vec{r}_0 = \vec{r}_0(t'; \vec{r}, \vec{v}) \\ \vec{v}_0 = \vec{v}_0(t'; \vec{r}, \vec{v}) \end{cases}$$

Now consider the effect of collisions



$$\begin{cases} \text{Collisions at } t_0 \Rightarrow \text{We assume that } f \to \underbrace{f^{(0)}}_{\text{local equilibrium distribution}} \text{ due to collision} \\ \text{We also assume:} \end{cases}$$

probability that a molecule suffered a collision in $[t_0, t_0 - dt']$, and then had no further collision during the time t'

$$= \frac{dt'}{\tau} e^{-t'/\tau}$$

$$\Rightarrow f(\vec{r}, \vec{v}, t) = \int_0^\infty f^{(0)}(\vec{r}_0(t'), \vec{v}_0(t'), t - t') \, e^{-t'/\tau} \frac{dt'}{\tau}$$

"path-integral" formulation

⊙ Equivalence of (Boltzmann eq ⊕ relaxation-time approximation
path integration approach

$$f(\vec{r},\vec{v},t) = \int_0^\infty f^{(0)}(\vec{r}_0,\vec{v}_0,t-t')\, e^{-t'/\tau}\, dt'/\tau$$

$$- \left(f(\vec{r}+\dot{\vec{r}}dt,\ \vec{v}+\dot{\vec{v}}dt,\ t+dt) = \int_0^\infty f^{(0)}(r_0,v_0,t+dt-t')\, e^{-t'/\tau}\, dt'/\tau \right.$$

$$f(\vec{r}+\dot{\vec{r}}dt,\vec{v}+\dot{\vec{v}}dt,t+dt) - f(\vec{r},\vec{v},t)$$

$$= \int_0^\infty \frac{\partial f^{(0)}(\vec{r}_0,\vec{v}_0,t-t')}{\partial t} dt\ e^{-t'/\tau}\frac{dt'}{\tau}$$

$$\Rightarrow Df = \int_0^\infty \frac{\partial f^{(0)}}{\partial t} e^{-t'/\tau}\frac{dt'}{\tau}$$

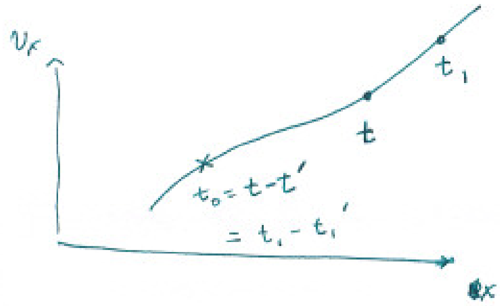
$$= -\frac{1}{\tau}\int_0^\infty \frac{\partial f^{(0)}(\vec{r}_0,\vec{v}_0,t-t')}{\partial t'} e^{-t'/\tau}\, dt'$$

$$= -\frac{1}{\tau}\left[f^{(0)}(\vec{r}_0,\vec{v}_0,t-t')e^{-t'/\tau}\right]_0^\infty - \frac{1}{\tau}\int_0^\infty f^{(0)}(\vec{r}_0,\vec{v}_0,t-t')\, e^{-t'/\tau}\, dt'/\tau$$

$$= -\frac{1}{\tau}\left[0 - f^{(0)}(\vec{r},\vec{v},t)\right] - \frac{1}{\tau} f(\vec{r},\vec{v},t)$$

$$= \frac{1}{\tau}(f^{(0)} - f)$$

→ Boltzmann eq. ⊕ relaxation time approximation alternative proof :



at t, $(\vec{r}, \vec{v})$

at t_0, $(\vec{r}_0, \vec{v}_0)$

at t_1, $(\vec{r}_1, \vec{v}_1)$

$$f(\vec{r}, \vec{v}, t) = \int_0^\infty f^{(0)}(\vec{r}_0(t'), \vec{v}_0(t'), t - t')\, e^{-t'/\tau} \frac{dt'}{\tau}$$

$$f(\vec{r}_1, \vec{v}_1, t_1) = \int_0^\infty f^{(0)}(\vec{r}_{0,1}(t_1'), \vec{v}_{0,1}(t_1'), t_1 - t_1')\, e^{-t_1'/\tau} \frac{dt_1'}{\tau}$$

change of variable $t_1' \to t'$ by using $t_0 = t - t' = t_1 - t_1'$

$$t_1' = (t_1 - t) + t'$$

$\Rightarrow$ $\left(\begin{array}{l} \vec{r}_{0,1}(t_1') \to \vec{r}_0(t') \\ \vec{v}_{0,1}(t_1') \to \vec{v}_0(t') \end{array} \right.$

$$f(\vec{r}_1, \vec{v}_1, t_1) = \int_{-(t_1 - t)}^\infty f^{(0)}(\vec{r}_0(t'), \vec{v}_0(t'), t - t')\, e^{-\frac{t' + (t_1 - t)}{\tau}} \frac{dt'}{\tau}$$

Now, let's put $t_1 = t + dt$. $\Rightarrow$ $\vec{r}_1 = \vec{r} + \vec{v}\,dt$, $\vec{v}_1 = \vec{v} + \frac{\vec{F}}{m} dt$

$$f(\vec{r} + \vec{v}\,dt, \vec{v} + \tfrac{\vec{F}}{m} dt, t + dt) = \int_{-dt}^\infty f^{(0)} e^{-\frac{t'}{\tau}} e^{-\frac{dt}{\tau}} \frac{dt'}{\tau}$$

$$= \int_{-dt}^\infty f^{(0)} e^{-\frac{t'}{\tau}} \frac{dt'}{\tau} \left(1 - \frac{dt}{\tau}\right)$$

$$= \underbrace{\int_{-dt}^\infty f^{(0)} e^{-\frac{t'}{\tau}} \frac{dt'}{\tau}} - \frac{dt}{\tau} \underbrace{\int_{-dt}^\infty f^{(0)} e^{-\frac{t'}{\tau}} \frac{dt'}{\tau}}$$

$$= f(\vec{r}, \vec{v}, t) + \underbrace{\int_{-dt}^0 f^{(0)} e^{-\frac{t'}{\tau}} \frac{dt'}{\tau}}_{= \frac{f^{(0)}}{\tau} dt} \qquad = f(\vec{r}, \vec{v}, t) + \boxed{}\, dt$$

$\left(\because \int_{b-\delta}^b g\, dx = G(b) - G(b - \delta) \right.$

$\delta \to 0$ $\left. = \frac{dG(b)}{db} \cdot \delta = g(b)\, \delta \right)$

$$\Rightarrow f(\vec{r} + \vec{v}\,dt, \vec{v} + \tfrac{\vec{F}}{m} dt, t + dt) = f(\vec{r}, \vec{v}, t)$$

$$+ \frac{f^{(0)}}{\tau} dt - \frac{f}{\tau} dt - \cancel{\frac{\boxed{}}{\tau} (dt)^2}$$

(as $dt \to 0$)

$$\Rightarrow Df \cdot dt = f(\vec{r} + \vec{v}\,dt, \vec{v} + \tfrac{\vec{F}}{m} dt, t + dt) - f(\vec{r}, \vec{v}, t)$$

$$= -\frac{f - f^{(0)}}{\tau} \cdot dt$$

//

① applications

- $f = f^{(0)}$

   $\Rightarrow \; Df = 0$ ~ a special case of Liouville's theorem.

- a situation slightly removed from equilibrium

   $f = f^{(0)} + f^{(1)}$, $f^{(1)} \ll f^{(0)}$

① ~~Electrical~~ Electrical conductivity

$\vec{\mathcal{E}} \parallel \hat{z}$. (electric field)

($\vec{\mathcal{E}}$ ~ spatially uniform , time-independent. , $\left(\frac{e|\vec{\mathcal{E}}|}{m}\right)\tau \ll \bar{v}$ mean thermal velocity

constant density $n(\vec{r},t) = n$ ($\vec{\mathcal{E}}$ ~ small enough)

$\Rightarrow f(\vec{r},\vec{v},t)$ ~ independent of $\vec{r}$ and t .   ($\mathcal{E}$ ~ small enough. → linear response)

$$\Rightarrow \underbrace{\frac{e\vec{\mathcal{E}}}{m}\frac{\partial f}{\partial v_z}} = -\frac{f-f^{(0)}}{\tau} = -\frac{f^{(1)}}{\tau}$$

ex. $f^{(0)} = n\left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} e^{-\beta\epsilon}$, $\epsilon = \frac{1}{2}mv^2$

$$= \frac{e}{m}\mathcal{E}\left(\frac{\partial f^{(0)}}{\partial v_z} + \underbrace{\frac{\partial f^{(1)}}{\partial v_z}}_{\text{negligible}}\right)$$

($f = f^{(0)} + f^{(1)}$, $f^{(0)} \gg f^{(1)}$)

($\underset{\text{small}}{\mathcal{E}} \times \underset{\text{small}}{\frac{\partial f^{(1)}}{\partial v_z}}$)

$$\Rightarrow f^{(1)} = -\frac{e\mathcal{E}\tau}{m}\frac{\partial f^{(0)}}{\partial v_z}$$

$$= -e\mathcal{E}\tau v_z \frac{df^{(0)}}{d\epsilon}$$

(check : $e\mathcal{E}\tau v_z\beta \ll 1$ should be required to achieve $f^{(0)} \gg f^{(1)}$)

current density j_n in the $\hat{n}$ direction

$$j_z = e\int f v_z \, d^3\vec{v}$$

(check : $f \to f^{(0)}$ $\Rightarrow j_n = 0$)

$$= e\int(\cancel{f^{(0)}} + f^{(1)})\, v_z \, d^3\vec{v}$$

$$= e\int f^{(1)} v_z \, d^3\vec{v} = -e^2\mathcal{E}\int \tau v_z^2 \frac{df^{(0)}}{d\epsilon} d^3\vec{v}$$

$$\Rightarrow \sigma_{el} = \frac{J_z}{\varepsilon} = -e^2 \int d^3\vec{v}\, \frac{df^{(0)}}{d\epsilon}\, \tau v_z^2$$

$$f^{(0)} = ⓐ e^{-\beta\epsilon} \to \frac{df^{(0)}}{d\epsilon} = -\beta f^{(0)}$$

$$\Rightarrow \sigma_{el} = \beta e^2 \int d^3\vec{v}\, f^{(0)} \tau v_z^2$$

neglect $\tau = \tau(v)$ and use $\bar{\tau}$ (mean value)

$$\cong \beta e^2 \bar{\tau} \int d^3\vec{v}\, f^{(0)} v_z^2$$

$$= \beta e^2 \bar{\tau} \left(n \overline{v_z^2} \right)$$

$$= \frac{n e^2 \bar{\tau}}{m}$$

$\frac{1}{2} m \overline{v_z^2} = \frac{1}{2} kT$

② Viscosity

when $\frac{\partial u_x}{\partial z} = 0$. $\Rightarrow f = f^{(0)} = f^{(0)}(v_x - u_x,\ v_y,\ v_z)$

$$= f^{(0)}(U_x,\ U_y,\ U_z)$$

$$U_i = v_i - \bar{v}_i = v_i - u_i \qquad (i = x, y, z)$$

When $\frac{\partial u_x}{\partial z} \neq 0$,

f depends on z via $u_x(z)$

Since f does not depend on t and $\vec{F} = 0$ (no external force)

$$v_z \frac{\partial f}{\partial z} = -\frac{f - f^{(0)}}{\tau}$$

$\frac{\partial u_x}{\partial z}$ ~ small enough $\Rightarrow f^{(1)} = f - f^{(0)} \ll f^{(0)}$

$$\Rightarrow v_z \frac{\partial f^{(0)}}{\partial z} = -\frac{f^{(1)}}{\tau}$$

$$\Rightarrow f^{(1)} = -\tau v_z \frac{\partial f^{(0)}}{\partial z} = -\tau U_z \frac{\partial f^{(0)}}{\partial U_x} \frac{\partial U_x}{\partial z} = \tau U_z \frac{\partial f^{(0)}}{\partial U_x} \frac{\partial u_x}{\partial z}$$

$$P_{zx} = m\int d^3\vec{u}\ f\ u_z u_x$$

$$= m\int d^3\vec{u}\ f_0 u_z u_x + m\int d^3\vec{u}\ u_z^2 u_x \frac{\partial f_0}{\partial u_x}\tau\frac{\partial u_x}{\partial z}$$

$$\left(f = f_0 + \tau v_z \frac{\partial f^{(0)}}{\partial u_x}\frac{\partial u_x}{\partial z} \quad \text{and} \quad v_z = u_z \right)$$

$$= m\int d^3\vec{u}\ u_z^2 u_x \frac{\partial f_0}{\partial u_x}\tau\frac{\partial u_x}{\partial z} \qquad \left(\because \int d^3\vec{u}\ f_0\ u_z u_x = 0\right)$$

$$= -\eta\frac{\partial u_x}{\partial z}$$

$$\eta = -m\int d^3\vec{u}\ u_z^2 u_x \frac{\partial f_0}{\partial u_x}\tau$$

$$\simeq -m\bar{\tau}\int d^3\vec{u}\ u_z^2\ u_x \frac{\partial f_0}{\partial u_x}$$

$$\int u_x\, du_x \frac{\partial f_0}{\partial u_x} = \cancel{u_x f_0 \Big|_{-\infty}^{+\infty}}^{\,0} - \int du_x f_0$$

$$= m\bar{\tau}\int d^3\vec{u}\ u_z^2 f_0$$

$$= m\bar{\tau}\, n\, \overline{u_z^2}$$

$$= n\bar{\tau}kT \qquad \therefore\ \frac{1}{2}m\overline{u_z^2} = \frac{1}{2}kT$$

$$= \frac{1}{3}n\bar{\tau}\cdot m\overline{u^2}$$

$$\simeq \frac{1}{3}n\bar{\tau}\, m\, \bar{u}^2$$

$$\simeq \frac{1}{3}nm\,l\,\bar{u}$$

$$\simeq \frac{1}{3}nm\,l\,\bar{v}$$