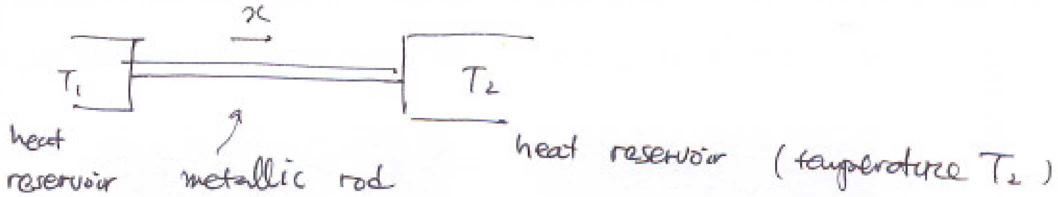
Course 5. Kinetic Theory

※ steady-state situation : (not isolated
nonequilibrium but
all of its parameters are time-independent.

(ex)



$\Rightarrow$ $T(x)$ ~ steady-state

How to deal such a nonequilibrium situation ?

— the aim of Kinetic theory.

※ We will use classical trajectories.

Reif ch. 12 {
- collisions
- Examples of nonequilibrium situations

viscosity, thermal conductivity, diffusion,
electrical conductivity.

Reif ch. 13 - Boltzmann equation ⊕ relaxation-time approximation

Reif ch. 14 - Boltzmann equation without relaxation-time approximation

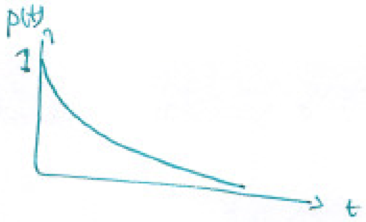
※ discuss the role of collision in kinetic theory

1. Collisions (scatterings)

A molecule with velocity $\vec{v}$ ⊕ (other molecules, impurities, ...) scattering centers

$P(t) \equiv$ probability that such a molecule survives a time t without suffering a collision

$$\begin{cases} P(t=0) = 1 \\ P(t\to\infty) = 0 \end{cases}$$



$w\,dt \equiv$ the probability that a molecule suffers a collision between t and $t+dt$

$w \sim$ collision rate

· evaluate $P(t)$

assume: $\begin{cases} w \text{ is independent of the past history of the molecule.} \\ w = w(|\vec{v}|) \end{cases}$

$$P(t+dt) = \underbrace{P(t)}_{\text{no scattering in } [0,t]} \; (1 - \underbrace{w\,dt}_{\text{no scattering in } [t,\, t+dt]})$$

$$\Rightarrow \frac{dP}{dt} = -wP \quad \to \quad P(t) = e^{-wt} \qquad (P(t=0) = 1)$$

$Q(t)dt \equiv$ the probability that a molecule suffers a collision in $[t, t+dt]$, after surviving without collision for a time t

$$Q(t)\,dt = P(t)\cdot w\,dt$$

a molecule will collide at some time t.

$$\Rightarrow \int_0^\infty Q(t)\,dt = 1$$

· mean free time τ (collision time, relaxation time)

$\tau \equiv \overline{t}$. mean time between collisions.

$$\tau = \int_0^\infty Q(t)\, t\, dt = \int_0^\infty e^{-\omega t} \omega t\, dt = \frac{1}{\omega}$$

$$\rightarrow \boxed{Q(t)\, dt = e^{-t/\tau} \frac{dt}{\tau}}$$

· mean free path l

$$l(|\vec{v}|) = |\vec{v}|\, \tau(|\vec{v}|)$$

⊙ Scattering cross section σ_0

$$N = F \sigma_0(\vec{v})$$

N: # of molecules scattered per unit time

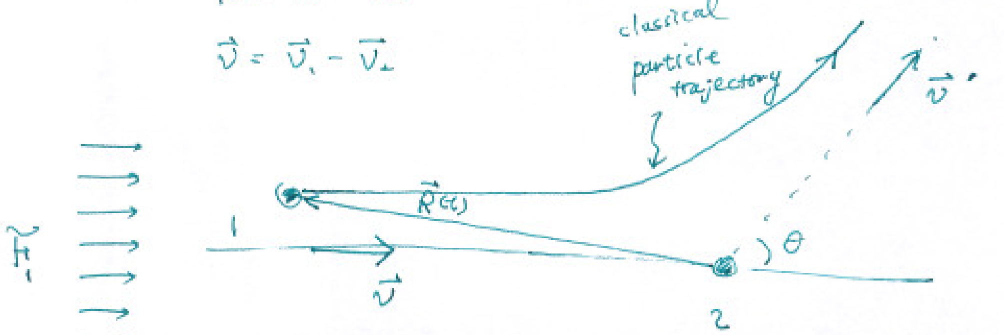
F: flux, # of incident particles with $\vec{v}$ per unit time, per unit area

σ_0 : it has dimension of area.

Consider two particles (mass, position, velocity) = $(m_1, \vec{r}_1, \vec{v}_1)$
$(m_2, \vec{r}_2, \vec{v}_2)$

$\vec{R} = \vec{r}_1 - \vec{r}_2$

$\vec{v} = \vec{v}_1 - \vec{v}_2$



incident flux of particles $\underbrace{}_{\text{type-1}}$

$\vec{v}'$: relative velocity after collision

Assume: $|\vec{v}'| = |\vec{v}|$. elastic scattering

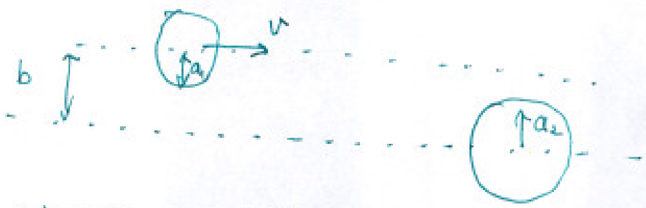
dN : # of particles with $\vec{v}'$ (solid angle $\in [\Omega', \Omega'+d\Omega']$) after scattering

$$dN = F_1 \underbrace{\sigma}_{\text{differential scattering cross section}} d\Omega'$$

$$\boxed{\begin{aligned} N &= \int dN = \int_{\Omega'} F_1 \sigma \, d\Omega' \equiv F_1 \sigma_0 \\ \sigma_0 &\equiv \int_{\Omega'} \sigma(\vec{v}\,; |\vec{v}'|)\, d\Omega' \end{aligned}}$$

To evaluate σ_0, one needs to know the interaction potential between particles.

(Example) hard sphere



→ interaction potential $V(R) = \begin{cases} 0 & R > (a_1+a_2) \\ \infty & R < (a_1+a_2) \end{cases}$

$$\sigma_0 = \pi (a_1+a_2)^2 = N/F$$

⊙ collision time ⟷ scattering cross section

a gas of a single kind of molecule : $\begin{cases} \text{density } n \\ \text{mean speed } \bar{v} \\ \text{relative mean speed } \bar{v}_{rel} \\ \text{mean total cross section } \sigma_0 \end{cases}$

Focus on the particular type of molecules in the gas (denoted by type 1) with $\begin{cases} \text{velocity near } \vec{v}_1 \\ \text{density } n_1 \\ \text{collision rate } \tau^{-1} \end{cases}$

$$\underbrace{\tilde{F}_1}_{} = \frac{n_1 (dt \cdot \bar{V}_{rel}) \cdot dA}{dt\, dA} = n_1 \bar{V}_{rel}$$

relative flux of type-1 molecules

$N = n_1 \bar{V}_{rel} \sigma_0$ ~ # of type 1 particles scattered by a given particle (target)

$\downarrow$

$N_{tot} = N \cdot n\, d\vec{r}^3$ " by all particles in $d\vec{r}^3$

$$\tau^{-1} = \frac{N_{tot}}{n_1 d\vec{r}^3}$$ by definition

$$\Rightarrow \boxed{\tau^{-1} = n \sigma_0 \bar{V}_{rel}}$$

$$l = \tau \bar{v} = \frac{\bar{v}}{\bar{V}_{rel}} \frac{1}{n\sigma_0}$$

$$\vec{v}_{rel} = \vec{v}_1 - \vec{v}_2 \Rightarrow \overline{|\vec{v}_{rel}|^2} = \overline{|\vec{v}_1|^2} + \overline{|\vec{v}_2|^2} - \cancel{\overline{2\vec{v}_1 \cdot \vec{v}_2}}$$

due to randomness of relative direction

$$\Rightarrow \overline{V_{rel}} \simeq \sqrt{2}\, \bar{v}$$

$$\Rightarrow l \simeq \frac{1}{\sqrt{2}\, n \sigma_0}$$

※ one can check the validity of initial assumption

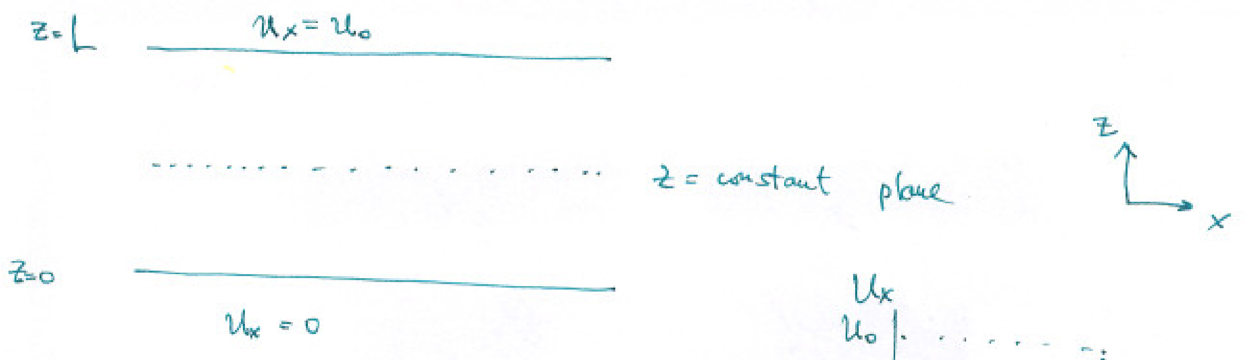
$l \gg d$. (d: diameter of particle)

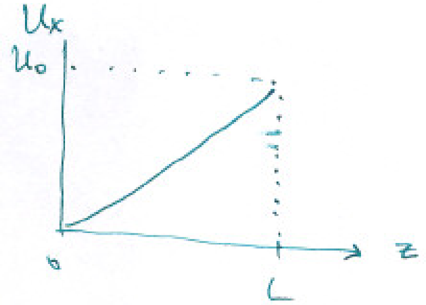
→ see Ref Eqs. (12.2.14), (12.2.15)

2. Examples of nonequilibrium situations

- Viscosity

Consider the following nonequilibrium situation :





(cf.) corresponding equilibrium case : $u_x(z)$ = constant.

viscosity (η) : a measure of the diffusion of momentum parallel to the flow velocity and transverse to the gradient of the flow velocity.

$$P_{zx} = -\eta \frac{\partial u_x(z)}{\partial z}$$

(linear response regime : $\frac{\partial u_x}{\partial z}$ ~ small enough)

$\eta > 0$

($\because$ $\frac{\partial u_x}{\partial z} > 0$. and the fluid below z=constant plane exerts on the fluid above z=const. a force in the $-x$ direction)

$P_{\alpha\gamma}$: pressure tensor

(cf) $\boxed{\text{pressure} \rightarrow \text{Reif. See section 7.13}}$

(α : normal direction of (unit) plane
γ : direction of flow

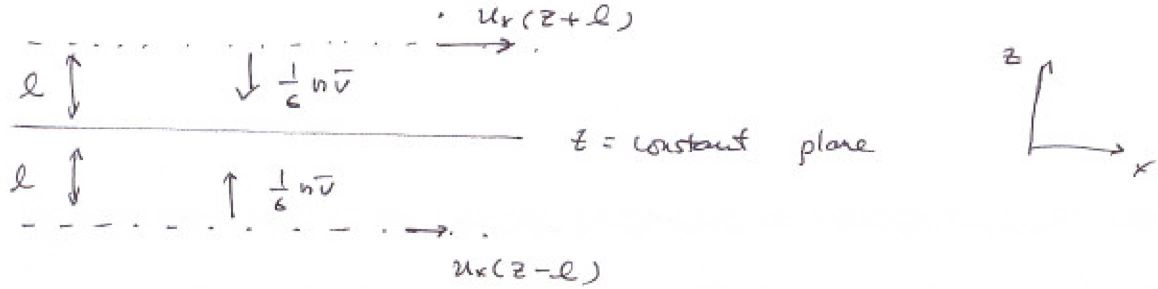
※ Origin of momentum transfer { (i) particle transport (gas, liquid)
(ii) direct forces between molecules (~~gas~~, liquid)

(ii) → negligible in dilute gas

5-6

$d_0 \simeq \sqrt{\sigma_0}$ gas is dense enough. ⇒ neglect the collisions at the boundary of the system

- Calculation of η for a dilute gas ($\underbrace{d \ll l}_{\text{"dilute"}} \ll L$)



l: mean free path

\# of molecules moving $+\hat{z}$ direction : $\frac{1}{6} n$
(per unit volume)

\# of molecules crossing a unit area of z=constant plane : $\frac{1}{6} n\bar{v}$
in unit time

P_{zx} = mean increase of the x component of momentum of gas above the plane per unit time per unit area

$$= \frac{1}{6} n\bar{v} \left[\underline{m u_x(z-l)} - m u_x(z+l) \right]$$

mean momentum (x component) of molecules crossing the z= constant plane from z < constant to z > constant.
($\because$ the molecules have been scattered roughly at $z-l$.)

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

$$\eta = \frac{1}{3} n \bar{v} m l$$

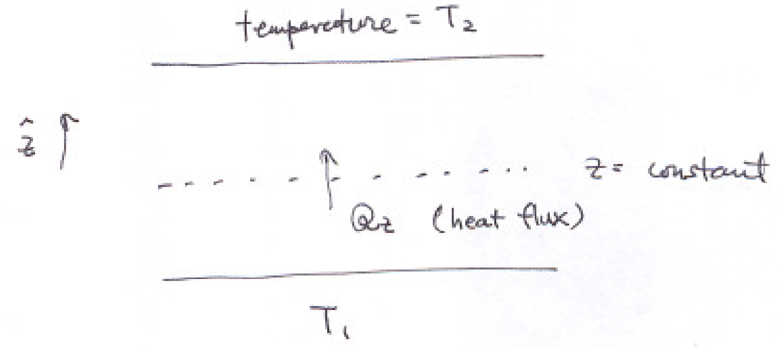
Note : 1. the factor $1/3$ is not necessarily correct.
(i) For example, we have not taken into accont of the distributi of velocity
(ii) We use crude ~~app~~ argument of mean free path.
2. $l \simeq \frac{1}{\sqrt{2}\, n \sigma_0}$ ⇒ $\eta = \frac{1}{3\sqrt{2}} \frac{m\bar{v}}{\sigma_0}$ ~ independent of n
($\eta \propto \sqrt{T}$
$\because \bar{v} = \sqrt{\frac{8kT}{\pi m}}$ see Reif Eq. (7.10.13)

※. the case of Liquid :

One should take into account of the momentum transfer by direct forces between molecules near the z = constant plane as well as particle transfer across the plane.

($\because$ In liquid, the density is dense.)

⊙ Thermal conductivity κ



Q_z : the heat crossing unit area of a plane normal to $\hat{z}$ per unit time

$$Q_z = -\kappa \frac{\partial T}{\partial z} \quad \text{(linear response)}$$

$\kappa > 0$ ($\because \frac{\partial T}{\partial z} > 0 \Rightarrow$ heat flows to small z)

- evaluation of Q_z for a dilute gas ($d \ll l \ll L$)

$$Q_z = \frac{1}{6} n \bar{v} \left(\bar{E}(z-l) - \bar{E}(z+l) \right)$$

$\bar{E}$: mean energy per molecule

$$= -\frac{1}{3} n \bar{v} l \frac{\partial \bar{E}}{\partial T} \frac{\partial T}{\partial z}$$

$\frac{\partial \bar{E}}{\partial T} = c$: specific heat per molecule

$$\rightarrow \kappa = \frac{1}{3} n \bar{v} c l$$

$$\simeq \frac{1}{3\sqrt{2}} \frac{c \bar{v}}{\sigma_0}$$

- relation between viscosity and thermal conductivity

$$\kappa/\eta = \frac{c}{m}$$

experimentally, $\kappa/\eta \cdot \frac{m}{c} \in [1.3, 2.5] \neq 1$

($\because$ we have not taken into account of the distribution of molecular velocities.)

※ κ in metals

$\kappa \propto \underline{n\bar{v}}\ \underline{c}\ \ell$ ← impurity scattering is dominant at low temperature → independent of T

$n\bar{v}$: v_F

c: $C \propto T$ (remember the effective # of electrons contributing heat capacity $\propto kT/\mu$)

$\Rightarrow \kappa \propto T$ at low temperature

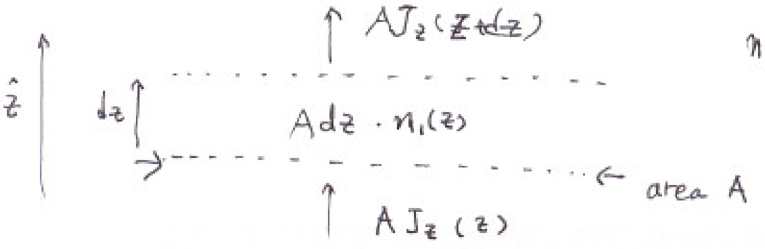
$\ell \propto \frac{1}{n_{ph}}$, $n_{ph} \propto T^3$ ($\because$ $n_{ph} \propto \int_0^\infty \frac{\rho(\omega)d\omega}{e^{\beta\hbar\omega}-1}$, $\rho(\omega) \propto \omega^2$ $\Rightarrow n_{ph} \propto T^3$)

$\Rightarrow \kappa \propto T \cdot \frac{1}{T^3} \propto T^{-2}$

$C \propto T$

generally, $\frac{1}{\kappa} = \underbrace{\frac{1}{\kappa_i}}_{\text{impurity scattering}} + \underbrace{\frac{1}{\kappa_p}}_{\text{phonon scattering}} = \frac{a}{T} + bT^3$

○ diffusion (D : diffusion constant)



$n_1(z)$ ~ the density of a given type of molecule is not uniform.

$$J_z = -D \frac{\partial n_1}{\partial z}$$

(J_z : mean particle current (per unit area) through a plane)

$$J_z = \frac{1}{6} \bar{v}\, n_1(z-l) - \frac{1}{6} \bar{v}\, n_1(z+l)$$

$$= -D \frac{\partial n_1}{\partial z}, \qquad D = \frac{1}{3} \bar{v}\, l$$

$$l = \frac{1}{\sqrt{2}\, n \sigma_0} = \frac{1}{\sqrt{2}\, \sigma_0} \frac{kT}{\bar{p}}, \qquad \bar{v} = \sqrt{\frac{8}{\pi} \frac{kT}{m}}$$

$$\Rightarrow \quad D \propto T^{3/2}. \qquad D \propto \frac{1}{\bar{p}}$$

- diffusion equation

equation of continuity : $\dfrac{\partial n_1}{\partial t} = -\nabla J$

$$\left(\because \quad \frac{\partial (n_1 A\, dz)}{\partial t} = A J_z(z) - A J_z(z+dz) \right)$$

$$\Rightarrow \boxed{\frac{\partial n_1}{\partial t} = -\frac{\partial J}{\partial z} = D \frac{\partial^2 n_1}{\partial z^2}}$$

- random walk

(ζ_i : $\hat{z}$ component of the displacement of molecule

molecule starts at $z=0$

$z = \sum_{i=1}^{N} \zeta_i$ after N steps

$$\Rightarrow \overline{z^2} = \sum_i \overline{\xi_i^2} + \cancel{\sum_i \sum_{\substack{j \\ i \neq j}} \overline{\xi_i \xi_j}}$$

$\because$ ξ_i and ξ_j are statistically independent.

$$= N \overline{\xi^2}$$

$$\xi = v_z t$$

$$\overline{\xi^2} = \overline{v_z^2}\, \overline{t^2} \quad , \quad \overline{v_z^2} = \frac{1}{3} \overline{v^2}$$

$$\overline{t^2} = \int_0^\infty Q(t)\, t^2\, dt = \int_0^\infty e^{-t/\tau}\, t^2 \frac{dt}{\tau}$$

$$= 2\tau^2$$

$$\Rightarrow \overline{\xi^2} = \frac{2}{3} \overline{v^2} \tau^2$$

$$\rightarrow \overline{z^2}(t) = \frac{2}{3} \overline{v^2} \tau^2 N$$

$N = \frac{t}{\tau}$. # of collisions

$$= \left(\frac{2}{3} \overline{v^2} \tau\right) t .$$

On the other hand,

$$\overline{z^2}(t) = \frac{1}{N_1} \int_{-\infty}^{\infty} z^2 n_1(z,t)\, dz . \quad , \quad N_1 = \int_{-\infty}^{\infty} n_1(z,t)\, dz$$

$= \text{constant}$.

Diffusion eq.

$$\frac{\partial n_1}{\partial t} = D \frac{\partial^2 n_1}{\partial z^2} \quad \Big) \otimes z^2$$

$$\underbrace{\int_{-\infty}^{\infty} z^2 \frac{\partial n_1}{\partial t} dz}_{} = D \underbrace{\int_{-\infty}^{\infty} z^2 \frac{\partial^2 n_1}{\partial z^2} dz}_{}$$

$$= \frac{\partial}{\partial t}\left(N_1 \overline{z^2}\right) = N_1 \frac{\partial \overline{z^2}}{\partial t}$$

$$= \cancel{z^2 \frac{\partial n_1}{\partial z}\Big|_{-\infty}^{\infty}} - 2\int_{-\infty}^{\infty} z \frac{\partial n_1}{\partial z} dz$$

$$= -2 \cancel{\left[z n_1\right]_{-\infty}^{\infty}} + 2\int_{-\infty}^{\infty} n_1 dz$$

$$= 2N_1$$

$$\Rightarrow \frac{\partial}{\partial t} \overline{z^2} = 2D$$

$$\Rightarrow \overline{z^2} = 2Dt$$

$$\Rightarrow D = \frac{1}{3} \overline{v^2} \tau \simeq \frac{1}{3} \bar{v} l \qquad (l = \bar{v}\tau)$$

⊙ Electrical conductivity σ_{el}

$j_z \equiv$ mean electric current ~~cross~~ through a unit area (normal to $\hat{z}$)

$$j_z = \sigma_{el} \underset{\sim}{E} \qquad \text{(Linear response)}$$

(electric field // $\hat{z}$)

$$j_z = ne\bar{v}_z$$

$$m\frac{dv_z}{dt} = eE \Rightarrow v_z = \frac{eE}{m}t + v_z(0)$$

$$\bar{v}_z = \frac{eE}{m}\bar{t} + \cancel{\overline{v_z(0)}}$$

($\vec{v}(0)$: random direction)

$$\bar{t} = \int_0^\infty t\, e^{-t/\tau}\frac{dt}{\tau} = \tau$$

$$\Rightarrow j_z = \frac{ne^2\tau}{m}E.$$

$$\Rightarrow \sigma_{el} = \frac{ne^2}{m}\tau$$