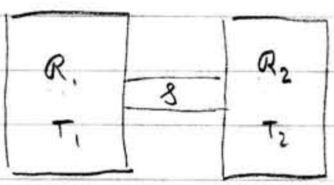
Lecture 25 - Kinetic theory

So far we've dealt with systems at equilibrium (ex: two systems in thermal contact), but said very little about how equilibrium is reached, especially how long it takes.

Ex: 2 reservoirs at $T_1 \neq T_2$. How is heat transfered?

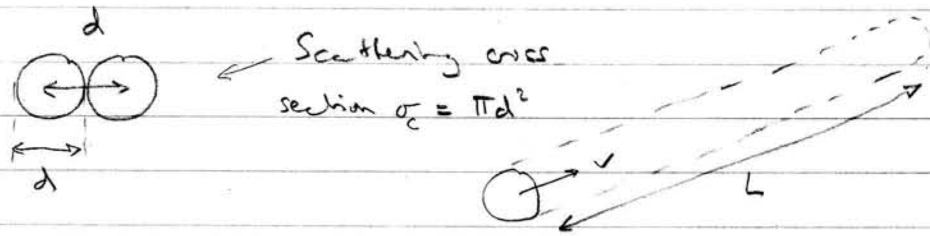


3 Mechanisms:
- Radiation - lectures 8+9
- Convection - bulk motion of fluid
- Conduction - heat transfer through molecular collisions*

* In solids, thermal conduction occurs through lattice vibrations
In metals, through electrons

Collisions

How often do molecular collisions occur?
Treat molecules as hard spheres - they collide when spacing $= d$



A molecule moving in space will sweep out a volume $\pi d^2 L$
If $n =$ concentration of other molecules, then there will be $n \pi d^2 L$ molecules in that volume. This is the # of collisions

Average distance between collisions
"Mean free path" $= \ell = \dfrac{L}{n \pi d^2 L} = \dfrac{1}{n \pi d^2}$

average collision rate $\equiv \frac{1}{\tau_c} = \frac{v_{rms}}{\ell}$

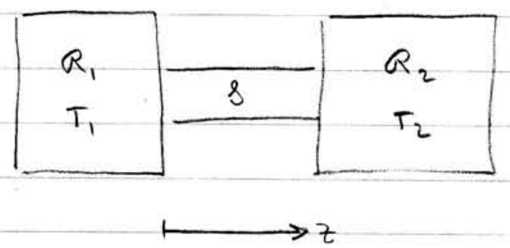
For a typical gas at room T, atmospheric p:

$\ell \sim 3\times10^{-5}$ cm $\gg d$

$1/\tau_c \sim 10^9 - 10^{10}\,s^{-1}$ $\qquad v_{rms} \sim 5\times10^4$ cm/s (Maxwell velocity distribution)

Thermal conductivity

Consider non-equilibrium situation with 2 reservoirs at $T_1 > T_2$

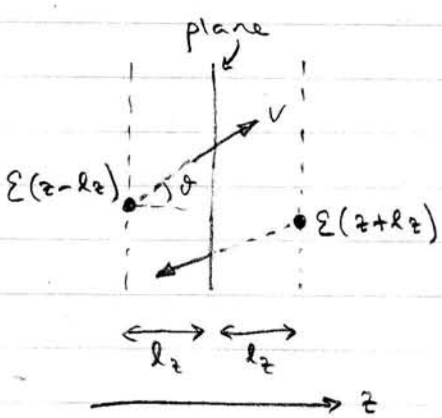


Energy flows from $R_1 \rightarrow R_2$ along $+z$ direction
$\therefore$ $\mathcal{E}$ depends on z

Define flux density J_u = net quantity of energy transported across unit area in unit time

Consider a plane at constant z

Net flux $J_u = J_u^{(R)} - J_u^{(L)}$ = flux to right − flux to left



$J_u^{(R)}$ comes from particles moving right that last had a collision some distance $\ell_z = \ell\cos\vartheta$ to the left and carry energy $\mathcal{E}(z-\ell_z)$

$J_u^{(L)}$ comes from particles moving left that last had a collision some distance ℓ_z to the right and carry energy $\mathcal{E}(z+\ell_z)$

$\therefore \quad J_u^{(R)} = \frac{1}{2} n v_z \mathcal{E}(z - l_z)$

$J_u^{(L)} = \frac{1}{2} n v_z \mathcal{E}(z + l_z)$

only v_z move in correct direction ↑ # density

v_z = speed along z

$$\therefore \quad J_u = J_u^{(R)} - J_u^{(L)} = \frac{1}{2} n v_z \left[\mathcal{E}(z - l_z) - \mathcal{E}(z + l_z) \right] \approx -n v_z l_z \frac{\partial \mathcal{E}}{\partial z}$$

Note: there is no net flux of particles only energy

This is valid for particles moving along particular direction ϑ
$\Rightarrow$ average over all orientations in hemisphere (2π solid angle)

$$\langle v_z l_z \rangle = \bar{v} l \frac{\cancel{2\pi} \int_0^{\pi/2} \cos^2\vartheta \sin\vartheta \, d\vartheta}{\cancel{2\pi}} = \frac{1}{3} \bar{v} l$$

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

Define heat capacity per unit volume

$$\hat{C}_V = n \frac{\partial \mathcal{E}}{\partial T}$$

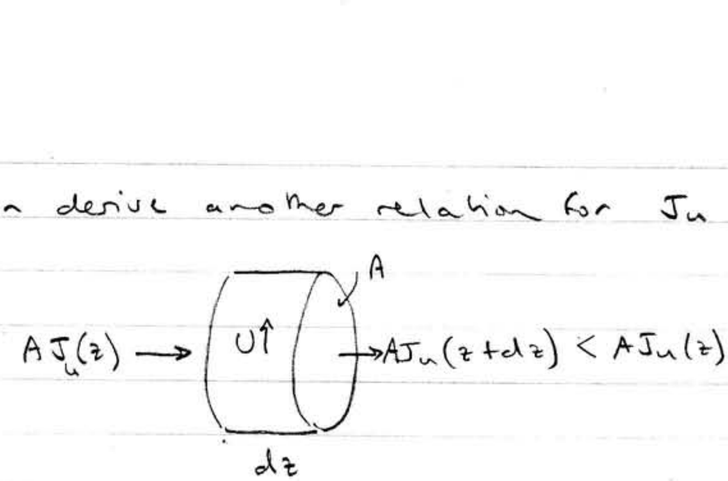
In 3-D, get Fourier Law:

$$\boxed{\bar{J}_u = -K \bar{\nabla} T}$$

$K = \frac{1}{3} \bar{v} l \hat{C}_V$ "thermal conductivity"

"Flux $\propto$ gradient in temperature"

Can derive another relation for J_u based on energy conservation



Consider volume $A\,dz$. If $J_u(z) > J_u(z+dz)$ then U in volume V must increase with time

$$\therefore \quad \frac{\partial U}{\partial t} = \frac{\partial}{\partial t}\left(\rho_u \cdot A\,dz\right) = A\,J_u(z) - A\,J_u(z+dz)$$

$\uparrow$ energy density $= n\varepsilon$

$$\Rightarrow \quad \frac{\partial \rho_u}{\partial t}\cancel{A\,dz} \approx -\cancel{A}\frac{\partial J_u}{\partial z}\cancel{dz}$$

$$\boxed{\frac{\partial \rho_u}{\partial t} + \bar{\nabla}\cdot \bar{J}_u = 0}$$

Continuity equation

Combined with Fourier Law:

$$\frac{\partial \rho_u}{\partial t} = +K\,\nabla^2 T = \underbrace{\frac{\partial \rho_u}{\partial T}}_{\hat{c}_V}\frac{\partial T}{\partial t}$$

$$\therefore \quad \boxed{\frac{\partial T}{\partial t} = D_T\,\nabla^2 T} \qquad D_T = \frac{K}{\hat{c}_V}$$

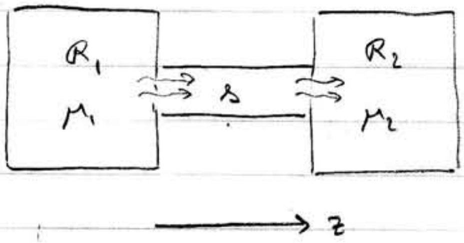
"thermal diffusivity"

Heat conduction equation or diffusion equation

Next lecture we will see how to solve this equation

Particle diffusion

Consider 2 reservoirs with $\mu_1 > \mu_2$. Particles will flow $R_1 \to R_2$



Can use similar arguments as for heat conduction except here particles are flowing (not energy)

Analog to Fourier Law is called Fick's law:

$$\boxed{\bar{J}_n = -D\bar{\nabla}n}$$

$D = \frac{1}{3}\bar{v}\ell$ "diffusivity" or "diffusion coefficient"

Continuity eq'n is $\frac{\partial n}{\partial t} + \bar{\nabla}\cdot\bar{J}_n = 0$

Diffusion eq'n : $\boxed{\frac{\partial n}{\partial t} = D\nabla^2 n}$ Same form as heat conduction eq'n

Boltzmann transport eq'n

General formalism for non-equilibrium processes

Consider distribution function $f(\bar{r}, \bar{v}, t)$ such that

$f(\bar{r}, \bar{v}, t)\, d^3\bar{r}\, d^3\bar{v}$ = number of particles with position in range $x \to x+dx$, $y \to y+dy$, $z \to z+dz$ and velocity in range $v_x \to v_x + dv_x$, $v_y \to v_y + dv_y$, $v_z \to v_z + dv_z$

Ex: ideal classical gas with no external forces at equilibrium

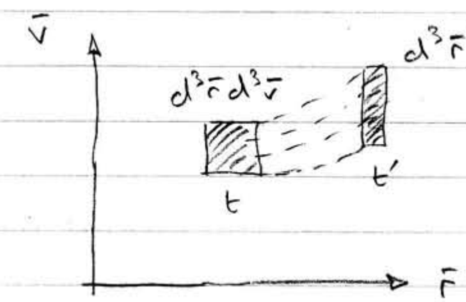
$f_{eq}(\bar{v})$ is related to Maxwell velocity distribution:

$$f_{eq}(\bar{v}) = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT}$$

$$\int d^3\bar{r} \int d^3\bar{v}\ f_{eq}(\bar{v}) = \underbrace{\int n\, d^3\bar{r}}_{nV = N} \underbrace{\int d^3\bar{v} \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT}}_{1} = N$$

Want to generalize this to situations in which there is an external force $\bar{F}$ (ex: $\bar{E}$-field, gravity) and in which things depend on time t

Let's see how $f(\bar{r},\bar{v},t)$ would evolve in time $t \to t' = t + dt$



$$\bar{r} \to \bar{r}' = \bar{r} + \frac{d\bar{r}}{dt}\, dt = \bar{r} + \bar{v}\, dt$$

$$\bar{v} \to \bar{v}' = \bar{v} + \frac{d\bar{v}}{dt}\, dt = \bar{v} + \frac{\bar{F}}{m}\, dt$$

Same # of particles at t and t', so by number conservation

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

Also, to lowest order $d^3\bar{r}' d^3\bar{v}' = d^3\bar{r}\, d^3\bar{v}$
(correction is $O(dt^2)$) $\Rightarrow$ "volumes in phase space are preserved"

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

In classical mechanics this is called the <u>Liouville theorem</u>

Expand to lowest order:

$$f(\bar{r}',\bar{v}',t') = f\left(\bar{r} + \bar{v}\,dt,\ \bar{v} + \frac{\bar{F}}{m}dt,\ t + dt\right)$$

$$= f(\bar{r},\bar{v},t) + dt\ \bar{v}\cdot\bar{\nabla}_{\bar{r}} f + dt\ \frac{\bar{F}}{m}\cdot\bar{\nabla}_{\bar{v}} f + dt\ \frac{\partial f}{\partial t}$$

$$\therefore \quad \frac{\partial f}{\partial t} + \bar{v} \cdot \bar{\nabla}_{\bar{r}} f + \frac{\bar{F}}{m} \cdot \bar{\nabla}_{\bar{v}} f = 0$$

This assumed that particles do not undergo collisions. If they do, some # will leave phase space volume $d^3\bar{r}\, d^3\bar{v}$ and some # will enter from outside.

This is captured with an extra "source" term:

$$\boxed{\frac{\partial f}{\partial t} + \bar{v} \cdot \bar{\nabla}_{\bar{r}} f + \frac{\bar{F}}{m} \cdot \bar{\nabla}_{\bar{v}} f = \left.\frac{\partial f}{\partial t}\right|_{collision}}$$

Boltzmann transport eq'n

Collision term is very complicated in general.
A very simple assumption is that f relaxes to local equilibrium distribution $f_0(\bar{r}, \bar{v})$ with time constant τ_c = time between collisions

$$\left.\frac{\partial f}{\partial t}\right|_{collision} = \frac{-(f - f_0)}{\tau_c}$$

"Relaxation time approximation"

To see how to solve this eq'n, use example
Ex: Imagine we have a gradient in particle density in z (i.e. connecting system to 2 reservoirs with $\mu_1 > \mu_2$)
Let $\bar{F} = 0$, and system is in steady state so $\frac{\partial f}{\partial t} = 0$

$$\therefore \quad \bar{v} \cdot \bar{\nabla}_{\bar{r}} f = v_z \frac{\partial f}{\partial z} = \frac{-(f - f_0)}{\tau_c}$$

with f_0 = local equilibrium distribution (assume ideal classical gas)

$$= n(\bar{r}) \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT}$$

Solve for f: $\quad f = f_0 - \tau_c v_z \frac{\partial f}{\partial z}$

We can solve iteratively by plugging f into $\frac{\partial f}{\partial z}$.

To first order:

$$f_1 \approx f_0 - v_z \tau_c \frac{\partial f_0}{\partial z}$$ Usually this is enough

(To second order: $f_2 \approx f_0 - v_z \tau_c \frac{\partial f_0}{\partial z} + (v_z \tau_c)^2 \frac{\partial^2 f_0}{\partial z^2}$ etc...)

$$\frac{\partial f_0}{\partial z} = \frac{\partial n}{\partial z} \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT} \quad \Rightarrow \text{ get } f_1$$

Consider the flux of particles. If all the particles moved at the same velocity $\bar{J} = n\bar{v}$. With a distribution:

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

$$\therefore\ J_z \cong \int d^3\bar{v}\ f_1 v_z = \underbrace{\int d^3\bar{v}\ f_0 v_z}_{=0} - \int d^3\bar{v}\ \tau_c v_z^2 \frac{\partial f_0}{\partial z}$$

f_0 is even

$$J_z = -\tau_c \frac{\partial n}{\partial z} \int dv_x \int dv_y \int dv_z\ v_z^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT}$$

$$= -\tau_c \frac{\partial n}{\partial z} \cancel{\left(\frac{m}{2\pi k_B T}\right)^{3/2}} \underbrace{\int_{-\infty}^{\infty} dv_x\ e^{-mv_x^2/2k_BT}}_{\left(\frac{2\pi k_B T}{m}\right)^{1/2}} \underbrace{\int_{-\infty}^{\infty} dv_y\ e^{-mv_y^2/2k_BT}}_{\left(\frac{2\pi k_B T}{m}\right)^{1/2}} \underbrace{\int_{-\infty}^{\infty} dv_z\ v_z^2\ e^{-mv_z^2/2k_BT}}_{\left(\frac{2\pi k_B T}{m}\right)^{1/2} \frac{k_B T}{m}}$$

$$J_z = -\tau_c \frac{k_B T}{m} \frac{\partial n}{\partial z}$$

This is just Fick's law again: $\bar{J} = -D\bar{\nabla} n$

$$D = \tau_c \frac{k_B T}{m} = \tau_c \langle v_z^2 \rangle = \frac{1}{3}\langle v^2 \rangle \tau_c = \frac{1}{3} v_{rms}\, l$$

same as before!