

## Lecture 25 – Thermal conduction

LAST TIME: we discussed radiation as a mechanism of heat transfer between systems

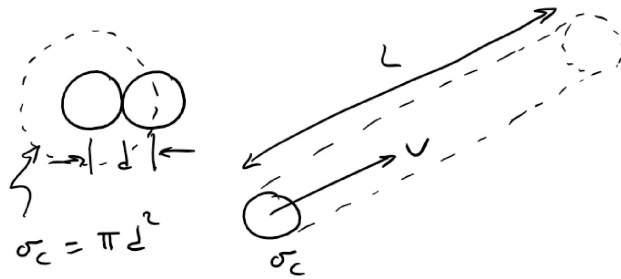
TODAY: thermal conduction

In a gas, the transfer of heat within a system or between systems occurs through molecular collisions (Note: in solids, thermal conduction occurs through lattice vibrations; in metals through electrons as well.)

KEY CONCEPT: Mean free path

How often do molecular collisions occur?

Treat molecules as hard spheres of diameter  $d$  – they collide when spacing  $< d$



Scattering cross section of hard sphere is  
 $\sigma_c = \pi d^2$

A molecule moving in space sweeps out a volume  $\sigma_c L = \pi d^2 L$

If the density of molecules is  $n$ , then there are  $n\sigma_c L = n\pi d^2 L$  molecules in that volume = the number of collisions

The mean free path  $\ell$  is defined as the average distance travelled between collisions:

$$\ell = \frac{L}{n\sigma_c L} = \frac{1}{n\sigma_c} = \frac{1}{n\pi d^2}$$

The mean collision rate is then:

$$\frac{1}{\tau_c} = \frac{\bar{v}}{\ell} = n\sigma_c \bar{v} = n\pi d^2 \bar{v}$$

Putting in some numbers, for a typical gas at room  $T$ , atmospheric  $p$ :

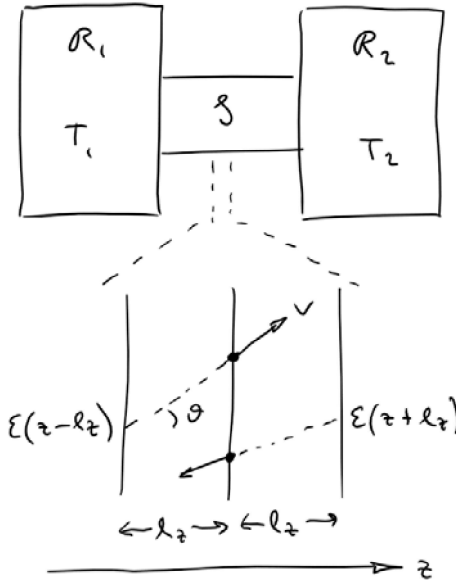
$$\ell \sim 3 \times 10^{-5} \text{ cm} \gg d, \quad \bar{v} \sim 5 \times 10^4 \text{ cm/s}, \quad \frac{1}{\tau_c} \sim 10^{9-10} \text{ s}^{-1}$$

(Note:  $\bar{v} = \langle v \rangle \approx v_{rms} = \sqrt{\langle v^2 \rangle}$  comes from the Maxwell velocity distribution, Lect. 6)

KEY CONCEPT: Thermal conductivity & the Fourier law

Consider a non-equilibrium situation with 2 reservoirs  $\mathcal{R}_1$  and  $\mathcal{R}_2$  at  $T_1 > T_2$  connected to a system  $\mathcal{S}$

Energy flows from  $\mathcal{R}_1$  to  $\mathcal{R}_2$  along +z direction –  $\varepsilon(z)$  is a function of  $z$



Look at the flow of energy along  $z$ , energy flux density  $J_u$  (energy per time per unit area)

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  $\ell_z = \ell \cos \theta$  to the left of the plane, and that carry energy  $\varepsilon(z - \ell_z)$

$J_u^{(L)}$  comes from particles moving left that last had a collision some distance  $\ell_z = \ell \cos \theta$  to the right of the plane, and that carry energy  $\varepsilon(z + \ell_z)$

Therefore,

$$J_u^{(R)} = \frac{1}{2} n v_z \varepsilon(z - \ell_z) \quad (\text{1/2 of the molecules move in the correct direction})$$

$$J_u^{(L)} = \frac{1}{2} n v_z \varepsilon(z + \ell_z)$$

Note: there is no net flux of particles, only energy, so the number density  $n$  is homogeneous. In the limit that  $\ell$  is small compared to the size of the system

$$J_u = J_u^{(R)} - J_u^{(L)} = \frac{1}{2} n v_z [\varepsilon(z - \ell_z) - \varepsilon(z + \ell_z)] \approx -n v_z \ell_z \frac{\partial \varepsilon}{\partial z}$$

This is just for particles moving along one particular direction  $\theta$ .

We need to average over all orientations in hemisphere ( $2\pi$  solid angle):

$$\langle v_z \ell_z \rangle = v \ell \underbrace{\frac{1}{2\pi} \int_0^{2\pi} d\phi}_{2\pi} \underbrace{\int_0^{\pi/2} d\theta \cos^2 \theta \sin \theta}_{1/3} = \frac{1}{3} v \ell$$

This is for particles moving at the same speed. If there is a distribution of speeds, we can replace  $v$  with the mean  $\bar{v}$ :

$$J_u = -\frac{1}{3} n \bar{v} \ell \frac{\partial \varepsilon}{\partial z} = -\frac{1}{3} n \bar{v} \ell \frac{\partial \varepsilon}{\partial T} \frac{\partial T}{\partial z} = -\frac{1}{3} \bar{v} \ell \hat{c}_v \frac{\partial T}{\partial z}$$

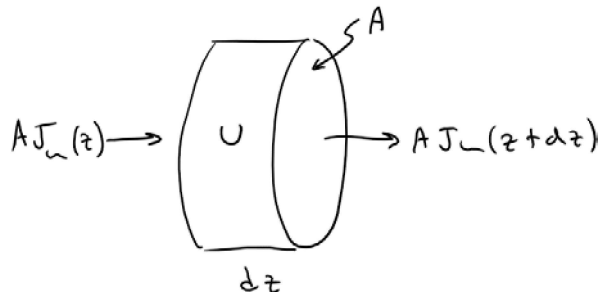
where we defined the heat capacity per volume  $\hat{c}_v \equiv n \frac{\partial \varepsilon}{\partial T}$ .

In 3-D, this is called the Fourier law  $\vec{J}_u = -\kappa \vec{\nabla} T$  where  $\kappa = \frac{1}{3} \bar{v} \ell \hat{c}_v$  is the thermal conductivity.

KEY CONCEPT: The heat conduction equation

Another relation for  $J_u$  is based on energy conservation

Consider volume  $V = Adz$ . If  $J_u(z) > J_u(z + dz)$  then  $U$  inside  $V$  must be increasing with time:



$$\frac{\partial U}{\partial t} = \frac{\partial}{\partial t} (uA dz) = A \underbrace{(J_u(z) - J_u(z + dz))}_{-\frac{\partial J_u}{\partial z} dz}$$

where  $u$  is the energy density

In 3-D, we have the continuity equation:

$$\frac{\partial u}{\partial t} + \vec{\nabla} \cdot \vec{J}_u = 0$$

Combined with the Fourier law, we get the heat conduction equation (or diffusion equation):

$$\frac{\partial u}{\partial t} = \frac{\partial u}{\partial T} \frac{\partial T}{\partial t} = +\kappa \nabla^2 T \quad \text{or} \quad \frac{\partial T}{\partial t} = D_T \nabla^2 T$$

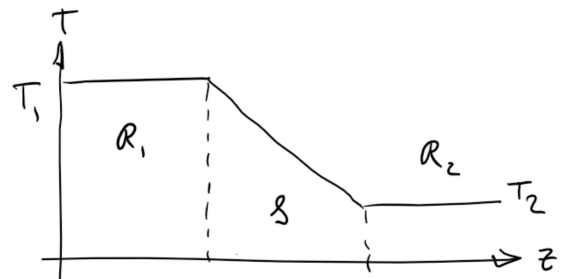
$\hat{c}_v$

where  $D_T = \kappa / \hat{c}_v = \frac{1}{3} \bar{v} \ell$  is the thermal diffusivity

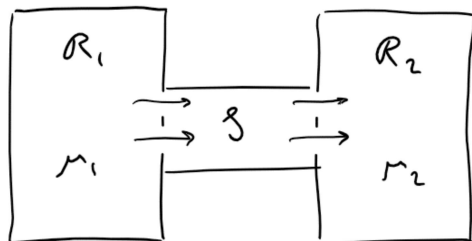
**Question 1: Sketch the temperature distribution in the system  $\mathcal{S}$  at steady-state**

In 1-D:  $\frac{\partial T}{\partial t} = 0 = D_T \frac{\partial^2 T}{\partial z^2}$  so  $T(z) = Az + B$ , with  $A$  and  $B$  determined by the boundary conditions

i.e. the temperature varies linearly between the two reservoirs  $\mathcal{R}_1$  and  $\mathcal{R}_2$



KEY CONCEPT: Particle diffusion



Consider a non-equilibrium situation with 2 reservoirs  $\mathcal{R}_1$  and  $\mathcal{R}_2$  at  $\mu_1 > \mu_2$  connected to a system  $\mathcal{S}$

Particles flows from  $\mathcal{R}_1$  to  $\mathcal{R}_2$  along  $+z$  direction –  $n(z)$  is a function of  $z$

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**Question 2: Letting  $J_n$  be the particle flux density, derive the equivalent of the Fourier law for particle flow**

We can use similar arguments as for heat conduction, except here particles are flowing, not energy. So, we replace  $n\epsilon(z)$  above with  $n(z)$ . In 1-D we get:

$$J_n = -\frac{1}{3}\bar{v}\ell \frac{\partial n}{\partial z}$$

This is called Fick's law. In 3-D, this is generally written as

$$\vec{J}_n = -D\vec{\nabla}n$$

where  $D = \frac{1}{3}\bar{v}\ell$  is the diffusivity or diffusion coefficient. Note that  $D = D_T$ .

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Also, the continuity equation for particle flow is now  $\frac{\partial n}{\partial t} + \vec{\nabla} \cdot \vec{J}_n = 0$ . Combined with Fick's law:

$$\frac{\partial n}{\partial t} = D\nabla^2 n$$

which is called the diffusion equation and has the same form as the heat conduction equation. We'll learn how to solve this equation next lecture.

**KEY CONCEPT:** Boltzmann transport equation – a general formalism for non-equilibrium processes

We will use distribution function  $f(\vec{r}, \vec{v}, t)$  defined such that

$$f(\vec{r}, \vec{v}, t) d^3\vec{r} d^3\vec{v} = \begin{array}{l} \text{number of particles with position } \vec{r} \text{ in} \\ \text{range } \vec{r}, \vec{r} + d\vec{r} \text{ and with velocity } \vec{v} \text{ in} \\ \text{range } \vec{v}, \vec{v} + d\vec{v} \text{ at time } t \end{array}$$

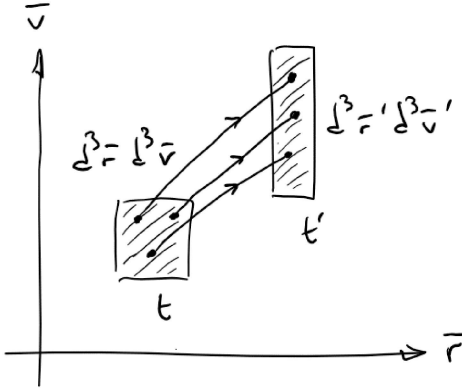
Ex: consider a classical ideal gas at equilibrium.  $f(\vec{r}, \vec{v}, t)$  is related to the Maxwell velocity distribution (Lect. 6):

$$f(\vec{r}, \vec{v}, t) = f_{eq}(\vec{v}) = n \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T}$$

which integrates to give the total number of particles  $N$

$$\int d^3\vec{r} \int d^3\vec{v} f(\vec{r}, \vec{v}, t) = \underbrace{\int d^3\vec{r} n}_N \underbrace{\int d^3\vec{v} \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T}}_1 = N$$

We want to generalize this distribution to non-equilibrium situations with an external force (e.g.  $E$ -field, gravity, etc.) and that are time dependent.



Let's see how  $f(\vec{r}, \vec{v}, t)$  would evolve in time:

$$t \rightarrow t' = t + dt$$

$$\vec{r} \rightarrow \vec{r}' = \vec{r} + \frac{d\vec{r}}{dt} dt = \vec{r} + \vec{v} dt$$

$$\vec{v} \rightarrow \vec{v}' = \vec{v} + \frac{d\vec{v}}{dt} dt = \vec{v} + \frac{\vec{F}}{m} dt$$

The number of particles at  $t$  and  $t'$  are the same, so

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

Also, a well-known property from classical mechanics is that volumes in phase space are preserved:  $d^3\vec{r} d^3\vec{v} = d^3\vec{r}' d^3\vec{v}'$  to lowest order (correction is  $\mathcal{O}(dt^2)$ ). Therefore,

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

(In classical mechanics, this is called the Liouville theorem)

Expanding to lowest order:

$$f(\vec{r}', \vec{v}', t) = f\left(\vec{r} + \vec{v} dt, \vec{v} + \frac{\vec{F}}{m} dt, t + dt\right) = f(\vec{r}, \vec{v}, t) + dt \vec{v} \cdot \vec{\nabla}_{\vec{r}} f + dt \frac{\vec{F}}{m} \cdot \vec{\nabla}_{\vec{v}} f + dt \frac{\partial f}{\partial t}$$

which yields

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

This is an equation of motion for the distribution of particles if there is an explicit time dependence, spatial gradients, and external forces.

This does not include situations where particles undergo collisions. If they do, some number will leave and some will enter the phase space volume  $d^3\vec{r} d^3\vec{v}$ . This is captured by including a "source term":

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \vec{\nabla}_{\vec{r}} f + \frac{\vec{F}}{m} \cdot \vec{\nabla}_{\vec{v}} f = \left( \frac{\partial f}{\partial t} \right)_{\text{collision}}$$

This is the Boltzmann transport equation

In general, the collision term can very complex. A very simple assumption is that  $f$  relaxes to a local equilibrium distribution  $f_0(\vec{r}, \vec{v})$  with time constant  $\tau_c$  = time between collisions

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

This simple model of collisions is called the relaxation time approximation

Generally, the Boltzmann transport equation is difficult to solve exactly; usually it is solved iteratively. Let's use an example to see how this is done.

Ex: Take previous situation –  $\mathcal{R}_1$  and  $\mathcal{R}_2$  with  $\mu_1 > \mu_2$  filled with an ideal gas surround  $\mathcal{S}$

We have  $\vec{F} = 0$  and assume the system has reached a steady state so  $\partial f / \partial t = 0$ :

$$v_z \frac{\partial f}{\partial z} = \left( \frac{\partial f}{\partial t} \right)_{\text{collision}} = -\frac{f - f_0}{\tau_c}$$

with  $f_0(\vec{r}, \vec{v}) = n(\vec{r}) \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T}$

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

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

To first order,  $f_1 \approx f_0 - v_z \tau_c \frac{\partial f_0}{\partial z}$  (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.)

Usually first order is enough.

Consider the flux of particles. If all the particles moved at the same velocity,  $\vec{J} = n\vec{v}$ . If there is a distribution of velocities, then:

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

In 1-D, and using the first order solution to the Boltzmann transport equation:

$$J_z \approx \int d^3\vec{v} f_1 v_z = \int d^3\vec{v} f_0 v_z - \int d^3\vec{v} v_z^2 \tau_c \frac{\partial f_0}{\partial z}$$

### Question 3: Evaluate $J_z$ using $f_0$ above

The first integral  $\int d^3\vec{v} f_0 v_z$  is simply  $n \langle v_z \rangle = 0$  by symmetry ( $f_0$  is even in  $v_z$ ).

For the second integral

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

This is just Fick's law again  $\vec{J}_n = -D \vec{\nabla} n$  with

$$D = \langle v_z^2 \rangle \tau_c = \frac{1}{3} \langle v^2 \rangle \tau_c \approx \frac{1}{3} \bar{v} \ell$$

Same as before. Note higher orders yield corrections to Fick's law.