

Fundamental of Statistical and Thermal
Physics by F. Reif
Chapter 12
**Elementary kinetic theory of transport
processes**

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Dec 2014

Pre-words

- Simply classical and sometimes crude
- Serves as very basis of studying non-equilibrium states
- More complex derivation will be done in coming chapters

How would you describe **diffusion**?

- Collision time τ
 - Probability that a molecule survives a time t without suffering a collision $P(t)$
- Collision rate w
 - probability per unit time that a molecule suffers a collision
 - *independent* of the past history
 - depend on particle speed v
- Probability that a molecule suffers a collision between time t and $t+dt$
 $w dt$

Derive the collision time

[P that a molecule survives a time $t+dt$ without suffering a collision]

= [P that this molecule survives a time t without suffering a collision]

* [P that it does not suffer a collision in the time interval dt]

$$P(t + dt) = P(t)(1 - wdt)$$

$$P(t) + \frac{dP}{dt}dt = P(t) - P(t)wdt$$

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

$$\ln P = -wt + \text{constant}$$

$$P = Ce^{-wt}$$

The constant of integration C can be determined by the condition that $P(0)=1$

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

Derive the collision time and Relating collision time to particle mean speed

[P that a molecule, after surviving without collisions for a time t , suffers a collision in the time interval dt]

$$\mathfrak{P}(t)dt = e^{-wt}w dt \quad \text{*Normalised to 1}$$

Define **collision time** to be the mean time between collisions

$$\begin{aligned} \tau \equiv \bar{t} &= \int_0^{\infty} \mathfrak{P}(t)dt \, t \\ &= \int_0^{\infty} e^{-wt}w \, dt \, t \\ &= \frac{1}{w} \int_0^{\infty} e^{-y}y \, dy = \frac{1}{w} \end{aligned}$$

Define **mean free path** to be the mean distance traveled by such a molecule between collisions

$$l(v) = v\tau(v)$$

Important to note

- That a gas of molecules can then be characterized by the average collision time, or the average mean free path, of the molecules traveling with a mean speed
- That we have linked our chosen description of diffusion to microscopic properties

Relating scattering cross section to particle radius

- Total scattering cross section

$$\sigma_0 = \pi(a_1 + a_2)^2 = \pi d^2$$

Relating scattering cross section to collision time

$$\tau^{-1} = \bar{V} \sigma_0 n$$

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

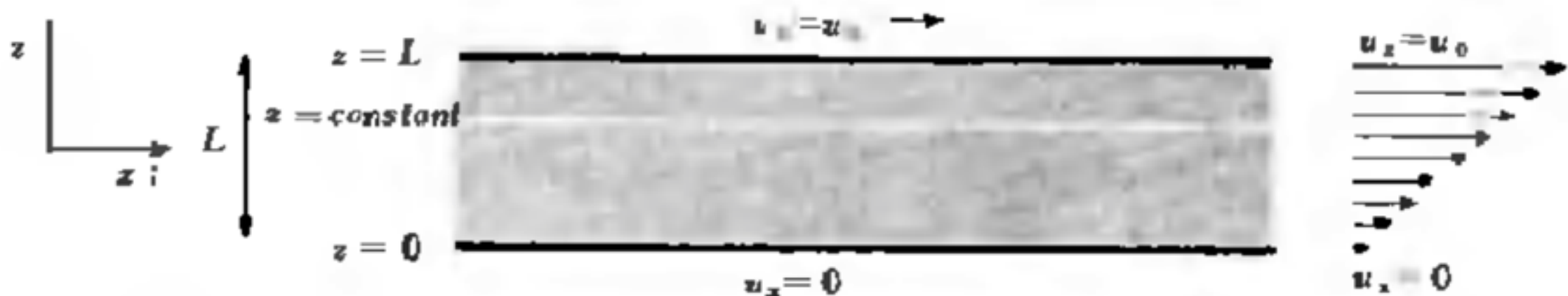
$$\bar{V} \approx \sqrt{2} \bar{v}$$

$$l \approx \frac{1}{\sqrt{2} n \sigma_0}$$

$$l \approx 3 \times 10^{-5} \text{ cm} \gg d$$

Before deriving viscosity

- Imagine we look at the diffusion inside a fluid in terms of plates
- What if a shear force is acting on one side of the container
- Tangential stress propagate down the container according to a gradient



Derive viscosity

We first define the constant of proportionality is called the
“coefficient of viscosity”

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

[the mean x component of momentum transported per unit time per unit area across the plane in the *upward* direction]

$$\left(\frac{1}{6}n\bar{v}\right)[mu_x(z-l)]$$

[the mean x component of momentum transported per unit time per unit area across the plane in the *downward* direction]

$$\left(\frac{1}{6}n\bar{v}\right)[mu_x(z+l)]$$

Derive viscosity

$$u_x(z + l) = u_x(z) + \frac{\partial u_x}{\partial z} l \dots$$

$$u_x(z - l) = u_x(z) - \frac{\partial u_x}{\partial z} l \dots$$

$$P_{zx} = \frac{1}{6} n \bar{v} m \left(-2 \frac{\partial u_x}{\partial z} l \right) \equiv -\eta \frac{\partial u_x}{\partial z}$$

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

The precise factor 1/3 is not to be trusted too much in this simplified calculation, but the dependence on the other parameters ought to be correct

Analogous to two men on two trains

- Two railroad trains move side by side along parallel tracks
 - the speed of one train being greater than that of the other
- Workers on each train constantly pick up sandbags from their train and throw them onto the other train
- There is a transfer of momentum between the trains so that the slower train tends to be accelerated and the faster train to be decelerated

Interesting predictions

- viscosity is independent of particle density

$$l \approx \frac{1}{\sqrt{2}n\sigma_0}$$

$$\eta = \frac{1}{3\sqrt{2}} \frac{m}{\sigma_0} \bar{v}$$

$$\bar{v} = \sqrt{\frac{8}{\pi} \frac{kT}{m}}$$

One paradox, two assumptions

- If the number of gas molecules is doubled, there are twice as many molecules available to transport momentum from one plate to the other;
- but the mean free path of each molecule is then also halved, so that it can transport this momentum only half as effectively

One paradox, two assumptions

- We assumed that
 - the gas is sufficiently dilute that there is negligible probability that more than two molecules come simultaneously so close together as to interact appreciably among themselves $l \gg d$
 - the gas is dense enough that the molecules collide predominantly with other molecules rather than with the walls of the container $l \ll L$
- Calm down. The range of densities where both assumptions are simultaneously satisfied is quite large $L \gg d$

Derive thermal conductivity

We first define the constant of proportionality is called the
“coefficient of thermal conductivity”

$$Q_z = -\kappa \frac{\partial T}{\partial z}$$

[the mean energy transported per unit time per unit area
across the plane in the *upward* direction]

$$\frac{1}{6}n\bar{v}\bar{\epsilon}(z - l)$$

[the mean energy transported per unit time per unit area
across the plane in the *downward* direction]

$$\frac{1}{6}n\bar{v}\bar{\epsilon}(z + l)$$

Derive thermal conductivity

$$Q_z = -\frac{1}{3}n\bar{v}l\frac{\partial\bar{\epsilon}}{\partial T}\frac{\partial T}{\partial z} \equiv -\kappa\frac{\partial T}{\partial z}$$

$$\kappa = \frac{1}{3}n\bar{v}l\frac{\partial\bar{\epsilon}}{\partial T} = \frac{1}{3}n\bar{v}lc$$

Other dependency of thermal conductivity

$$l \propto n^{-1}$$

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

$$\kappa \propto T^{\frac{1}{2}}$$

Comparison of viscosity and thermal conductivity

$$\kappa = \frac{2}{3\sqrt{\pi}} \frac{c}{\sigma_0} \sqrt{\frac{kT}{m}}$$

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

Experimentally found that it lies somewhere in the range between 1.3 and 2.5 instead of being unity

Application to nonclassical gases - metal

- Conduction electrons as nonclassical gases
- Scattering either by lattice vibration (phonon) or impurities

$$\kappa = \frac{1}{3} n \bar{v} l \frac{\partial \bar{\epsilon}}{\partial T} = \frac{1}{3} n \bar{v} l c$$

Derive Self-diffusion

We first define the constant of proportionality is called the
“coefficient of self-diffusion”

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

[the mean number of labeled molecules transported per unit
time per unit area across the plane in the *upward* direction]

$$\frac{1}{6} \bar{v} n_1(z + l)$$

[the mean number of labeled molecules transported per unit
time per unit area across the plane in the *downward* direction]

$$\frac{1}{6} \bar{v} n_1(z - l)$$

Derive Self-diffusion

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

$$D = \frac{1}{3}\bar{v}l$$

$$D = \frac{2}{3\sqrt{\pi}}\frac{1}{\bar{p}\sigma_0}\sqrt{\frac{(kT)^3}{m}}$$

$$\frac{D}{\eta} = \frac{1}{p}$$

Experimentally found that it lies in the range between 1.3 and 1.5 instead of being unity

It's elementary kinetic theory!

- Highly simplified discussion of non-equilibrium transport processes in dilute gases.
- Crude because no attempt whatever was made to take into account the distribution of molecular velocities

Looking forward to the
coming chapters