\[ N = \text{total number} \]
\[ N = \text{number of moles} \]
\[ \hat{N} = \text{Avogadro's} \]
\[ \hat{R} = \text{universal gas constant} \]
\[ n = \frac{N}{V} = \text{number density} \]

\[ E_{\text{ke}} = \text{total translational Energy (kinetic energy)} \]
\[ = \sum_{i=1}^{N} m_i v_i^2 \]

\[ \bar{E}_{\text{ke}} = \frac{E_{\text{ke}}}{N} \]

\[ \bar{E}_{\text{ke}} = \text{average kinetic energy (translational energy) per particle} \]

\[ \bar{E}_{\text{ke}} \approx \tilde{E}_{\text{ke}} = \text{actual kinetic per particle} \]

\[ \bar{E}_{\text{ke}} \approx \tilde{E}_{\text{ke}} = \text{assumed with on a per mole basis} \]

\[ e_{\text{sp}} = \text{specific kinetic energy} \]

\[ k = \text{Boltzmann constant} = \frac{\hat{R}}{N} \]

\[ \tilde{E}_{\text{ke}} = \frac{k}{m} \]

From last time:

\[ PV = \frac{1}{3} \sum_{i=1}^{N} m_i v_i^2 = \frac{2}{3} \sum_{i=1}^{N} m_i v_i^2 = \frac{2}{3} E_{\text{ke}} \]

\[ \Rightarrow PV = \frac{2}{3} E_{\text{ke}} = \gamma \hat{R} T \]

\[ \Rightarrow E_{\text{ke}} = \frac{3}{2} \gamma \hat{R} T \]

\[ \tilde{E}_{\text{ke}} = \frac{E_{\text{ke}}}{N} = \frac{3}{2} \hat{R} T \]

\[ E_{\text{ke}} = \frac{E_{\text{ke}}}{N} = \frac{3}{2} \frac{\hat{R} T}{M} \]

\[ \hat{R} = \frac{\hat{R}}{M} \]

\[ \Rightarrow \hat{R} = \frac{3}{2} \frac{R}{M} T = \frac{3}{2} \frac{RT}{M} \text{ average molecular weight} \]

\[ \Rightarrow \hat{R} = \frac{3}{2} \frac{R}{M} \text{ gas constant} \]
why do we need this? - because we want the specific heat.

Assume $e$ (internal energy) = $e_{\text{Br}}$

$$\frac{\partial e}{\partial T} \bigg|_v = C_v = \frac{\partial}{\partial T} \left( \frac{3}{2} RT \right)$$

A gas which has only kinetic energy

$\Rightarrow$ calorically perfect also perfect in that

$$e = f(T)$$

$\Rightarrow C_v = \frac{n}{2} R$

$$H = E + PV$$

$$h = \frac{E}{m} + \frac{PV}{m} = \frac{3}{2} RT + \frac{\hat{M} \hat{R} T}{m}$$

$$= \frac{3}{2} RT + \frac{\hat{R} T}{M}$$

$$h = \frac{3}{2} RT + RT$$

$$C_p = \frac{\partial h}{\partial T} \bigg|_P = \frac{3}{2} R + R$$

$$C_p - C_v = R$$

$$C_p = \frac{5}{2} R$$

very close to monatomic gas at ordinary temps

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2} R}{\frac{3}{2} R} = \frac{5}{3} = 1.6667$$

ratio of specific heats

Equation of state - Vague notion of this point

$$\frac{1}{2} m \left( C_1^2 + C_2^2 + C_3^2 \right)^3$$

Each squared term or degree of freedom contributes $\frac{1}{2} RT$ to the internal energy
Number of degrees of freedom depend on whether or not the degree is
1) Possible – no rotation
   
   two degrees of freedom

2) fully excited
   Rotate ok
   
   but vibrational & electronic are not normally excited at ordinary temperatures

See p. 133 Eqn (12.6)

\( \gamma = \frac{3}{2} \) p. 136 Fig 6.

If this is the case then

\[ \gamma = \frac{3}{2} \]

\[ \frac{3}{2} (\frac{1}{2}RT) = \frac{3}{2} RT \implies C_v = \frac{3}{2} R \]

\[ C_p = \frac{3}{2} R + R = \frac{3}{2} R + \frac{5}{2} R \]

\[ \implies \gamma = \frac{3 + 2}{\frac{5}{2}} \]

Air (for example) which is diatomic

3 - translational
2 - rotational
\[ \implies 5 = \frac{3}{2} \]

\[ \implies \gamma = \frac{\frac{3}{2} + 2}{\frac{3}{2}} = \frac{7}{3} = 1.4 \]

We can also get average speed of particles

\[ \frac{\sum m_i v_i^2}{\sum m_i} \]

\[ \frac{1}{\gamma} \]

all particles

(This result does not result to thermodynamics)
Note that in a similar way an average could be defined for each type of particle as follows:

\[ \sum_{i=1}^{N} m_i c_i^2 = \sum_{i=1}^{N_A} m_{A_i} c_{A_i}^2 + \sum_{i=1}^{N_B} m_{B_i} c_{B_i}^2 + \ldots \]

\[ M_A = \sum_{i=1}^{N_A} m_{A_i} \text{ etc.} \]

\[ \Rightarrow \bar{c}_A^2 = \frac{\sum_{i=1}^{N_A} m_{A_i} c_{A_i}^2}{\sum_{i=1}^{N_A} m_{A_i}} \text{ etc.} \]

Note that

\[ \sum_{i=1}^{N} m_i c_i^2 = N_A m_A \bar{c}_A^2 + N_B m_B \bar{c}_B^2 + \text{ etc.} \]

Let us return to the average squared velocity for all particles \( \bar{c}^2 \)

\[ PV = \frac{1}{3} \sum_{i} m_i v_i^2 \]

\[ \Rightarrow \sum_{i} m_i v_i^2 = 3PV \]

\[ \Rightarrow \bar{c}^2 = \frac{\sum_{i} m_i v_i^2}{N} = 3PV \frac{1}{M} = 3PV \frac{P}{\rho} = RT \]

or \( \frac{P}{3} = \frac{1}{3} \bar{c}^2 \)

\[ \Rightarrow \sqrt{\bar{c}^2} = \sqrt{\frac{3P}{\rho}} \geq 486 \text{ m/s} \]

\[ \bar{c}_{\text{rms}} \text{ velocity of particle} \]

Note that the speed of sound is \( 332 \text{ m/s} \) – same conditions

\[ \Rightarrow \text{speed of sound is } 68\% \text{ of } \bar{c}^2 \]

makes sense.
we can also derive Dalton's law of partial pressures

\[ P = \frac{1}{3V} \sum m_i V_i^2 = \frac{1}{3V} \sum \left( \frac{N_A}{v} \frac{m_A V_A^2}{v} + \frac{1}{3V} \sum \frac{N_B}{v} \frac{m_B V_B^2}{v} \right) \]

\[ \Rightarrow P_A = P_B + P_C + \ldots \cdots = \sum \frac{p}{v} \]

Further,

\[ P_A V = \frac{2}{3} \frac{E_A V}{v} \frac{N_A}{v} \]

\[ \sum v = \frac{1}{2} \sum m_i V_i^2 \]

\[ \Rightarrow E_A V = \frac{2}{3} \frac{N_A}{v} \frac{\hat{R} T}{v} \]

\[ \frac{E_A}{v} = \frac{N_A}{v} \frac{\hat{R} T}{v} \]

\[ \Rightarrow \frac{\hat{E}_A}{v} = \frac{N_A}{v} \frac{\hat{R} T}{v} \]

\[ \Rightarrow \text{all species have same average translational energy per particle (again Equipartitioning of Energy)} \]

\[ \rightarrow \text{Read in Jeans p. 2042!} \]

Next time we will take up the collision events on the simplest model.
Let's move on to properties associated with fluid mechanics.

Collisions

Let's say we have a gas all made up of the same type particles of diameter $d$.

Notice that the "Collision Cross Section" has a diameter $= 2d$.

So collisions take place when the particles are $d$ apart.

We will focus on a single particle of "radius" $d$ and all other particles as point sources.

We want to compute the number of collisions with other particles per unit time.

Again let the particle be moving around at its average speed

(Note this is $\bar{C}$ not $\sqrt{\bar{C}^2}$)

Also we will ignore the fact that other particles are also moving.

Swept Volume/Time

$$\frac{\pi d^2 \bar{C} t}{4}$$
if \( n \) is the number density, i.e., \( \frac{\text{# particles}}{\text{Volume}} \)

\[ \Rightarrow \text{number of collisions/s} = \frac{\text{Volume Swept}}{\text{time}} \times \frac{\text{# particles}}{\text{Volume}} \]

\[ \Rightarrow \Theta = \frac{1}{\pi d^2} \pi n \]

\text{Mean Free Path = Average Distance between Collisions, } \lambda

\[ \lambda = \frac{\text{distance/\text{collision}}}{\text{time/\text{Collisions}}} \times \frac{\text{distance}}{\text{time}} \]

\[ \Rightarrow \lambda = \frac{\Theta}{\Theta} = \frac{1}{\pi d^2} \pi \frac{1}{\pi d^2} \pi n = \frac{1}{\pi d^2} \pi n \]

\[ \Rightarrow \lambda = \frac{1}{\pi \sqrt{2} d^2 n} \]

(\text{relative motion which modifies the relative speed in collisions})

\( \text{Really a profound result} \)

\( \text{Since } \Theta = f(T) \Rightarrow \text{mean free path is independent of Temp!} \)

\( \text{Could mention that } d \text{ is a function of } T \text{ to some extent.} \)

\( \text{Can write in terms of density, } \rho, \text{ mass/Volume} \)

\[ \Rightarrow \rho = m n \]

\[ \Rightarrow \lambda = \frac{m}{\sqrt{2} \pi d^2 \rho} \]

\( \rho = 1.288 \times 10^{-3} \text{ g/m}^3 \text{ from } \text{at STP} \) \[ m = 30 \text{ g/mole} \Rightarrow m = \frac{1}{N} = \frac{32}{6.02252 \times 10^{23}} = 4.98 \times 10^{-23} \text{ g} \]
So for air (at STP)
\[ \lambda = \frac{4.98 \times 10^{-23} \text{ g m}}{\sqrt{\frac{2 \pi}{1}} \left(3.7 \times 10^{-8}\right)^{2} \text{ (cm)}^{2} \cdot 1.288 \times 10^{-4} \text{ g m}^{-1} \text{ cm}^{-3}} \]
\[ d \sim 3.7 \times 10^{-8} \text{ cm} \]
From liquid air
\[ \approx 6.36 \times 10^{-6} \text{ cm} \approx 10^{-5} \text{ cm} \approx \frac{1}{10} \mu \text{m} \]
(1 μm = 10^{-6} m = 10^{-4} cm)

Finally!

Transport Phenomena

\[ \begin{align*}
\text{Apples} & \quad \text{Oranges} \\
\text{Blind Person} & \quad \text{(with gloves on)}
\end{align*} \]

For transport to take place:

1. a gradient must exist
2. mechanism

Velocity gradient \(\Rightarrow\) momentum transport - Viscous
Temperature gradient \(\Rightarrow\) \(mv^{2}\) transport - Heat Conduction
Composition gradient \(\Rightarrow\) mass transport - Diffusion
Momentum Law

\[ \tau = \frac{d\mathbf{v}}{dy} \]

Newton's
\[ \frac{p}{m} = \gamma \quad \{ \text{m}^2 \text{s}^-1 \} \]

Heat
\[ \frac{q}{A} = -k \frac{dT}{dy} \]

Fourier's
\[ \frac{p}{\rho c_p} = \alpha \quad \{ \text{m}^2 \text{s}^-1 \} \]

Mass
\[ \frac{T_A}{A} = -D \frac{\partial n_A}{\partial y} \]

Fick's
\[ pD = \beta \quad \{ \text{m}^2 \text{s}^-1 \} \]

In this course we are interested in viscosity.
So the required gradient is a velocity gradient.
But what is the "mechanism"? what is the blind man?

\[ \rightarrow \text{Collisions} \]

So let's see if the little Kinetic theory we have derived can give us a theoretical basis for Newton's shear-stress law.

In this case we will assume that the particles are identical, but differ only in the "information" they carry. In the general case we will just call it a quantity \( \tilde{a} \) (i.e., per particle) and there is a gradient in it in the \( y \) direction.

The mechanism for transporting \( \tilde{a} \) is the "random" motion of the particles passing through the plane, \( y_0 \).
Further, let's say that the information that the particle carries, $a_0$, is reminiscent of the macroscopic manifestation of that property at the location of the particle's last collision.

With this in mind, then, information crossing the $y_0$ plane from below is reminiscent of $a(y_0 - S_{tr})$ and from above $a(y_0 + S_{tr})$. $S_{tr}$ is the "average" distance above or below $y_0$ of the last collision. Clearly this is related to $a$, but

\[ \frac{1}{S_{tr}} \frac{1}{\lambda_2} \frac{1}{\lambda_3} \frac{1}{\lambda_4} \cdot \text{etc.} \]

It may be even related to the property itself, i.e., if the property is $T$ (\(1/2 m c^2\)), the further away the C's would bias $S_{tr}$.

This being considered and under the assumption of random distributions, it is clear that an integration on a purely kinetic model would yield a multiplier which may be dependent on the property being transported.

Let's assume

\[ S_{tr} = \alpha \cdot \lambda \]

Now we can consider the number flux crossing the plane $y_0$.

Recall the meaning of mass flux

\[ \text{Flux} = \frac{\dot{m}}{\text{Area}} \Rightarrow \dot{m} = \rho A V \]

\[ \frac{\dot{m}}{A} = \rho V \frac{\dot{z}}{5.0} \]
So a Volume Flux would just be \( V/A = \frac{\text{Volume}}{\text{time}\cdot\text{Area}} \)

we can obtain mass flux from volume flux by

\[
\frac{\text{Volume}}{\text{time}\cdot\text{Area}} \cdot \frac{\text{mass}}{\text{Volume}} = \rho V
\]

similarly we can obtain number flux by

\[
\frac{\text{Volume}}{\text{time}\cdot\text{Area}} \cdot \frac{\#}{\text{Volume}} = n V
\]

what \( V \) do we use?

Certainly it is related to \( \tilde{c} \) with the same geometric cavities so let it be \( \eta \tilde{c} \) but rather \( \eta \tilde{c} \)

where this constant results from proper integrations of the speed distributions.

Now we can calculate/model the flux of property \( \tilde{a} \)

First, from below going up through \( y_0 \)

\[
\bigwedge \tilde{a}_{up} \sim \text{property } \tilde{a}(y_0 - \Delta x_2) \times \text{number of part crossing from below}
\]

\[
= \eta \tilde{c} \tilde{a}(y_0 - \Delta x_2)
\]

and similarly from above going down through \( y_0 \)

\[
\bigwedge \tilde{a}_{down} = \eta \tilde{c} \tilde{a}(y_0 + \Delta x_2)
\]
so the net transport of $\check{a}$ (positive up), reminiscent of location $y_0$

\[
\Lambda \check{a} = \Lambda \check{a}_{up} - \Lambda \check{a}_{down} = \eta \eta \frac{\partial}{\partial y} [\check{a}(y_0 - \alpha \lambda) - \check{a}(y_0 + \alpha \lambda)]
\]

Now we will get $\check{a}(y_0 - \alpha \lambda)$ using a Taylor expansion, where $\lambda$ is small compared to the macroscopic measure of $\check{a}$ as a continuum

\[
\Rightarrow \check{a}(y_0 - \alpha \lambda) = \check{a}(y_0) - \alpha \lambda \frac{\partial \check{a}}{\partial y} + \ldots
\]

Truncate at "=-" term

\[
\Rightarrow \check{a}(y_0 - \alpha \lambda) - \check{a}(y_0 + \alpha \lambda) = \check{a}(y_0) - \alpha \lambda \frac{\partial \check{a}}{\partial y} - [\check{a}(y_0) + \alpha \lambda \frac{\partial \check{a}}{\partial y}]
\]

("-" terms cancel; squared terms also cancel so)

\[
\Rightarrow \check{a}(y_0 - \alpha \lambda) - \check{a}(y_0 + \alpha \lambda) = -2\alpha \lambda \frac{\partial \check{a}}{\partial y}
\]

\[
\Rightarrow -\lambda \check{a} = -((2\alpha \eta) \eta) \bar{c} \lambda \frac{\partial \check{a}}{\partial y}
\]

\[
\Rightarrow -\lambda \check{a} = -\beta \check{a} \eta \bar{c} \lambda \frac{\partial \check{a}}{\partial y}
\]

\[
\Rightarrow \Lambda \check{a} = -\beta \check{a} \eta \bar{c} \lambda \frac{\partial \check{a}}{\partial y} \quad \text{← General Form}
\]

so $\check{a}$ could be momentum, temperature, or species.
Now let's get specific and look at the transport of momentum due to a velocity gradient (on the macroscopic scale).

![Graph showing velocity gradient](image)

- \( u_x \) - component of velocity in the x-direction
- Property being transported is momentum (x-component), \( \mu \)
- \( \lambda \mu \) - mass of one particle

\[ \Lambda \mu = \text{rate of transport of momentum per unit area, per unit time} \]

\( \zeta \) - apparent force per unit area due to momentum transport.

**Note:** with a positive gradient in \( u \), momentum transported up gives rise to a negative stress on the layer above, or if \( u \) larger above gives a positive stress on the layer below.

\[ \Lambda \mu = \zeta = -\beta \mu n \bar{c} \lambda \frac{\partial \mu}{\partial y} \]

\[ \Rightarrow \zeta = \beta \mu n \bar{c} \lambda \frac{\partial \mu}{\partial y} \text{ (compare to Newton's Law)} \]

\[ \Rightarrow \mu = \beta \mu n \bar{c} \lambda = \beta \mu n \bar{c} \lambda \text{ (nm)} \]
Recall \( \lambda = \frac{m}{\sqrt{2} \pi d^2 \rho} = \frac{1}{\sqrt{2} \pi d^2 n} \)

\[ \Rightarrow \mu = \beta \frac{m \bar{c}}{\sqrt{2} \pi d^2 n} \]

\[ \Rightarrow \mu = \beta \frac{m \bar{c}}{\sqrt{2} \pi d^2} \left\{ \begin{array}{l} \text{1. \mu independent of } p \text{ & Pressure.} \\
\text{2. since } \bar{c} \sim \sqrt{T} \\
\Rightarrow \mu \sim \sqrt{T} \end{array} \right. \]

Maxwell was the first to do this and he "discovered" that this implied several consequences that surprised him:

1. Larger \( m \) \( \Rightarrow \) Larger \( \mu \)
2. \( T \) goes up \( \mu \) goes up by \( \sqrt{T} \)

At the time based on experience with liquids, the presumption was that if \( T \) goes up \( \mu \) goes down.

This prompted experimentalists to measure \( \mu = f(T) \) for air & almost exactly \( \mu \sim \sqrt{T} \), but not quite.

1st experimental evidence that air is not a continuum but rather a collection of gas "particles."
a last comment about why \( \eta = f(T) \)
which eventually reconciled \( \mu \) not being
exactly proportional to \( \sqrt{T} \)

As "particles" are really not solid spheres

so the collision cross-section depends
on the average \( \bar{D} \) so as \( T \) goes up,
def \( \text{eff} \) goes down.

At least we now have a basis
for Newton's viscosity law & how one
might be able to compute it rather
than measuring it.