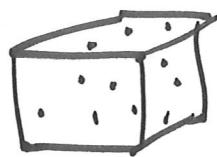


# KINETIC THEORY OF GASES

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Gas are fundamentally atoms & molecules



## PRINCIPLES

- ① A Gas is composed of a large number of molecules
- ② Molecules are small relative to separation
- ③ Molecules uniformly distributed & move randomly
- ④ Obey Newton's Laws of motion
- ⑤ No forces except in collisions with each other or the walls (hard spheres)
- ⑥ Collisions with walls are elastic

①, ③ & ⑥ are good approximations.

②, ⑤ break down at high density

④ molecules are really quantum objects

$$\lambda = \frac{h}{mv} \rightarrow \text{need } \lambda \ll \text{separation}$$

i.e. at high T, high v or low density

IDEAL GASES: are described by kinetic theory

# EMERGENT BULK PROPERTIES

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Volume  $V$

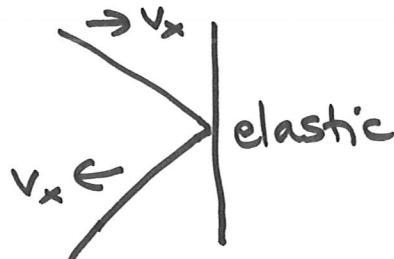
Density  $N$  molecules  $\Rightarrow n = N/V$   $\rho = \frac{Nm}{V}$   
can vary across volume.

Pressure

$$P = \frac{\text{Force}}{\text{area}}$$

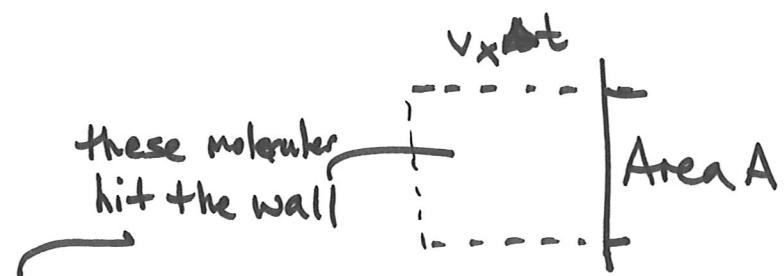
$$Pa = Nm^{-2}$$

Caused by collisions (assume some average  $v_x$ )



$$F = \frac{\cancel{\Delta m v}}{\Delta t} \sim 2Mv_x \text{ per collision}$$

In time  $\Delta t$



except 1/2 that were already travelling away

$$\# \text{ collisions in } \Delta t = \frac{1}{2} n \times (v_x \Delta t A)$$

$$\text{Force} = \frac{2Mv_x}{\Delta t} \times \frac{1}{2} n (v_x \Delta t A)$$

$$P = \frac{F}{A} = n M v_x^2$$

I've assumed all molecules have the same  $v_x^2 \dots$  so  $v_x^2 \rightarrow \bar{v}_x^2$  the mean squared velocity

Since motion is random

$$\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2 = \frac{1}{3} \bar{v}^2$$

We arrive at

$$P = \frac{1}{3} n m \bar{v}^2$$

EG] At standard temp. & pressure (stp)

$$T = 273K \quad (0^\circ C)$$

$$P = 101\ 000 \text{ Nm}^{-2} \quad (\text{atm})$$

$$\begin{aligned} v_{\text{root mean square}} &= \sqrt{\frac{3P}{nm}} \\ &= \sqrt{\frac{3P}{\rho}} \end{aligned}$$

e.g. air density is  $1.2 \text{ kg m}^{-3}$

$$\Rightarrow v_{\text{RMS}} \approx 500 \text{ ms}^{-1}$$

So an evacuated flask will fill in

$$\sim \frac{0.1 \text{ m}}{500 \text{ ms}^{-1}} \approx 0.25 \text{ ms}$$

## Internal Energy & Temperature

For an ideal gas the only energy is kinetic

$$U = \frac{1}{2} m \bar{v}^2 \times \text{number of molecules}$$

$$= \frac{1}{2} m \bar{v}^2 (n V) \quad m \bar{v}^2 n = \frac{2U}{V}$$

Remember  $P = \frac{1}{3} n m \bar{v}^2 = \frac{2}{3} U/V$

$$\Rightarrow U = \frac{3}{2} PV \quad \text{or} \quad PV = \frac{2}{3} U$$

This hopefully reminds you of the empirical

### EQUATION OF STATE :

$$PV = N k T_I$$

↑  
Boltzmann's constant

or

$$P = \frac{N k T_I}{V}$$

$$k = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

This gives us a link between temperature (here  $T_I$  for an ideal gas' temperature) and internal energy.

We have  $P = \frac{1}{3} n m \bar{v}^2 = \frac{1}{2} N k T_I$

$$\frac{3}{2} k T_I = \frac{1}{2} m \bar{v}^2$$

relation between KE & Temp.

&  $U = \frac{3}{2} N k T_I (= N \frac{1}{2} m \bar{v}^2)$

Aragadro's number:  $N_A = 6.02 \times 10^{23}$

This number of atoms/molecules weighs the atomic mass number in grams

$$N = n_m N_A \quad \begin{matrix} \leftarrow \\ \text{A. number} \end{matrix}$$

$\uparrow \quad \uparrow$   
number      number  
                of moles

$$PV = n_m N_A R T_I = n_m RT$$

$$\boxed{PV = n_m RT}$$

$$\begin{matrix} \uparrow \\ R = \cancel{k} N_A \end{matrix}$$

gas constant  $= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Q1) Volume of 1 mole at STP?

$$V_m = \frac{RT_I}{P} = \frac{8.314 \times 273}{101,000} = 0.0225 \text{ m}^3 = 22.5 \text{ l}$$

Q2) How many molecules in  $1 \text{ m}^3$  at 20°C?

$$N = \frac{PV}{RT_I} = \frac{101,000 \times 1 \text{ m}^3}{1.38 \times 10^{-23} \times 295} \approx 250 \times 10^{23}$$

## EQUIPARTITION OF ENERGY

We had for an ideal gas

$$\frac{1}{2}m\bar{v}^2 = \frac{1}{2}m(\bar{v_x}^2 + \bar{v_y}^2 + \bar{v_z}^2) = \frac{3}{2}kT$$

?

these are each "degrees of freedom" into which energy can be put

Equipartition Theorem: for a classical system in thermal equilibrium, the total energy is shared equally among all the degrees of freedom

& we can see each gets  $\boxed{\frac{1}{2}kT}$

### Monatomic Gases eg He

- three possible motions  $E = \frac{3}{2}kT$

$$\text{For a mole } U_{\text{mol}} = N_A k \underbrace{\frac{3}{2}T}_{R} = \frac{3}{2}RT$$

### Diatomlic Gases eg H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>

- 3 translations
- 2 axes of rotation



we neglect spinning on axis - I'll explain in a bit....

- 1 vibration



$$\frac{1}{2}mv^2 + \frac{1}{2}kx^2 = KE + PE$$

so counts as 2

$$U_{\text{mol}} = \frac{7}{2}RT$$

# MOTION DEGREES OF FREEDOM COUNTING

9<sup>1/2</sup>

If we ignore the bonds in a molecule there are  $3N$  movements of the  $N$  atoms



When we tie them with bonds some movements are different from others:



translations: 3 the whole structure can move in  $x, y, z$  rigidly...

rotations:

3



Rotations about 3 axes - rigid

2



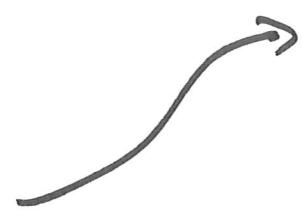
rotations about this axis doesn't move the atoms...

vibrations: the rest of the  $3N$  motions move one atom relative to another - this stresses the bond & needs potential as well as kinetic energy....

## CO<sub>2</sub>



- 3 translations
- 2 rotations
- 4 vibrations



$\overbrace{\text{O}=\text{C}=\text{O}}$  &  $\overbrace{\text{O}=\text{C}=\text{O}}$   
each has KE & PE

$$\Rightarrow U_{\text{mol}} = \frac{3+2+2\times 4}{2} RT$$

$$= \frac{13}{2} RT$$

## SOLIDS



KE & PE for each atom  
in each direction

$$U_{\text{mol}} = 6 \times \frac{1}{2} RT = 3RT$$

HEAT CAPACITIES : we can test the predictions

$$\Delta Q = C \Delta T$$

heat      heat      change in  
 in      capacity      temp

or

$$\Delta Q = n_m C \Delta T$$

Moles  
 ↓  
 specific heat  
 capacity

$$C = \frac{dQ}{dT}$$

monoatomic gas :  $C = 3R/2 = 12.5 \text{ JK}^{-1} \text{ mole}^{-1}$

diatomic gas :  $C = 7/2 R = 29 \text{ JK}^{-1} \text{ mole}^{-1}$

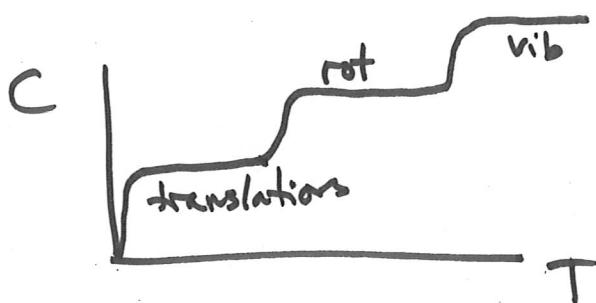
We find  $C_{\text{measured}} \leq C_{\text{predicted}}$

Why Equipartition Fails: this is one of the first signs of quantum mechanics

- classically - you can put any amount of energy into a degree of freedom
- QM - energy comes in lumps. If your  $kT$  is too small you can't excite the motion or vibration at all.

Typically  $\Delta E_{\text{trans}} \ll \Delta E_{\text{rot}} \ll \Delta E_{\text{vib}}$

so the modes switch on only as  $T$  goes through steps



So for example at room temp  $N_2$   $C = \frac{5}{2} R$   
 $= 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$

Incidentally this is why we ignore spin on axis  $KE = \frac{h^2}{2I} \propto I \sim mr^2 \propto r \rightarrow 0$

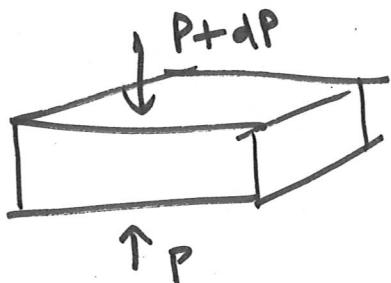
so the energy to excite is very, very large.

For ~~solids~~  $C$  is typically lower than predicted because harder to excite vibrations eg diamond !

Metals at room temp - prediction pretty good ... but at higher ~~temperatures~~ electron sea contributes  $3k_B/2$  per electron.

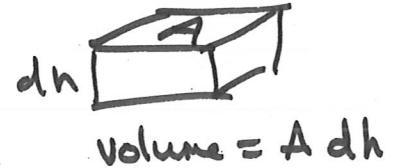
Boltzmann Factor : We've been pretending all particles at some T move at same v.... as conse they have a spread... to understand the spread better consider gas in the atmosphere:

### Hydrostatic Equilibrium



A lump of gas' weight is supported by a pressure gradient

$$\text{Weight} = mg = \rho (A dh) g$$



$$\text{Upward force} = PA - (P + dP)A = -A dP$$

(minus sign is because pressure goes down as go up)

$$\text{Balancing forces } \rho A g dh = -A dP$$

$$\frac{dP}{dh} = -\rho g$$

Eq'n of hydrostatic equilibrium

If  $\rho = \text{const}$  (eg in water) we can integrate

$$(dP = -\rho g dh) \quad "P = \rho gh"$$

For an ideal gas  $P = n k T_I$  &  $\rho = n M^{\frac{1}{3}}$   
 at const  $T_I$   $dP = k T_I dn$  ↑ number of pts/V

$$\frac{dn}{dh} = - \frac{P}{k T_I} g = - \frac{Mg}{RT_I}$$

$$\int_{n_0}^n \frac{dn}{n} = - \frac{Mg}{RT_I} \int_0^h dh$$

$$\ln \frac{n}{n_0} = - \frac{mgh}{k T_I}$$

$$\frac{n}{n_0} = e^{-mgh/k T_I} (= \frac{P}{P_0})$$

Pressure & number density fall off exponentially  
 e.g. on Earth  $m=30u$   $g=9.81 \text{ ms}^{-2}$   $T \sim 300\text{K}$

$$\text{At } h=5\text{km} \quad P/P_0 \approx 0.55$$

Pr. Interpretation: we have  $\frac{n}{n_0} = e^{-E_{GPE}/k T_I}$

Recast this as fraction or probability that one atom is at height  $h$  with  $E = mgh$

$$P(E) \propto e^{-E/kT}$$

BOLTZMANN  
FACTOR

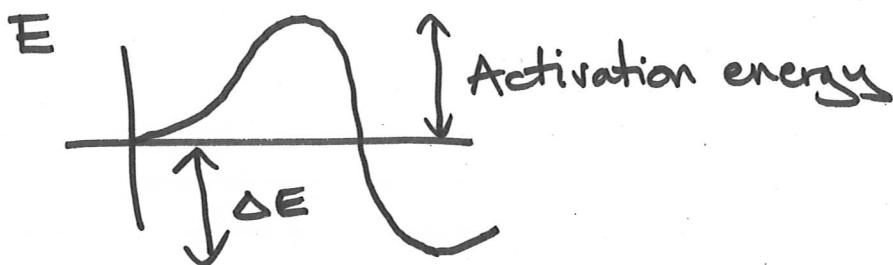
We won't prove this further here... or show it  
 leads to  $\langle E \rangle = \frac{1}{2} kT$  (next year!)

EXAMPLES • prob (pt in kinetic theory  
gas has speed  $v$ )  $\propto e^{-\frac{1}{2}mv^2/k}$

- Activation Energies



but you have to light a match!



The Boltzmann factor controls whether any atoms can get over the activation energy...  
...and it can be very T dependent

EG  $E_A = 100\text{kT}$   $T = 300\text{K}$

How does  $e^{-kT}$  change by  $\Delta T = 20\text{K}$ ?

$$P(300\text{K}) \propto e^{-100}$$

$$P(320\text{K}) \propto e^{-100(300/320)}$$

$$\text{ratio} \propto e^{100 - 93.75} = e^{6.25} = 518$$

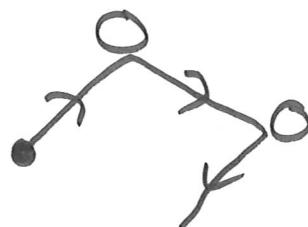
Using a bunsen burner in Chemistry can be a dangerous business!

## TRANSPORT IN KINETIC THEORY

Let's think about how transport (eg energy etc) happens in a gas where  $n$  depends on position. At base atoms/molecules move:

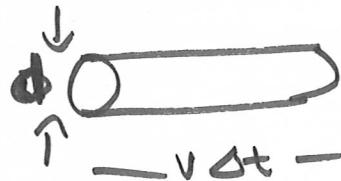
### Mean Free Path

particles ricochet about in the gas:



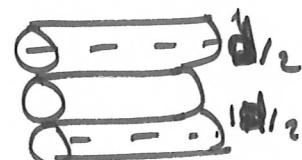
What is the "average distance between collisions"?

A particle, diameter  $d$  passes through a cylinder as it moves



It will hit another particle if it comes within  $d/2$  of the cylinder

So the number of collisions depends on how many pts are in a tube of radius =  $d$



$$\text{collisions/sec} = \underbrace{\pi d^2 v}_{\text{Volume}} n \sim N/V$$

I've assumed only one pt is moving here.

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A better job is to work out the average relative velocity of two particles

$$\vec{v}_{\text{rel}} = \vec{v}_A - \vec{v}_B$$

$$\vec{v}_{\text{rel}} \cdot \vec{v}_{\text{rel}} = v_A^2 + v_B^2 - 2 \vec{v}_A \cdot \vec{v}_B$$

$$v_{\text{rel}}^2 = v_A^2 + v_B^2 - 2 v_A v_B \cos \theta_{AB}$$

In a randomly moving gas every  $\theta_{AB}$  is equally likely  $\langle \cos \theta_{AB} \rangle = 0$

so  $v \rightarrow \langle v_{\text{rel}} \rangle \approx \sqrt{2} v$

The mean free path is then  $\frac{\text{speed}}{\text{collision rate}}$

which divides distance travelled by number of collisions

$$\Rightarrow \boxed{\lambda = \frac{1}{\sqrt{2} \pi d^2 n}}$$

EG air at STP  $P = n k T$

$$n = \frac{P}{k T} = \frac{1.01 \times 10^5 \text{ Pa}}{1.38 \times 10^{-23} \text{ J K}^{-1} \times 273 \text{ K}} = 2.7 \times 10^{25} \text{ m}^{-3}$$

$$\lambda = \frac{1}{\sqrt{2}} \times 3.142 \times (0.3 \text{ nm})^2 \times 2.7 \times 10^{25} \text{ m}^{-3}$$

$$\approx 10^{-9}$$

$$= 10^{-9} \text{ m}$$

## Distribution of Path lengths

$$P(\text{collision in } \delta r \text{ travel}) = \text{time of travel} \times \text{collision rate}$$

$$= \frac{\delta r}{v} \times \text{collision rate}$$

$\approx v/\lambda$

$$= \frac{\delta r}{\lambda}$$

This assumes an equal chance of collision through travelling  $\lambda$  rising to 1 when  $\delta r = \lambda$  ... good at small  $\delta r$ ...

Now

$$\begin{aligned} P(\text{travel } r + \delta r) &= P(\text{travel } r) P(\text{travel } \delta r) \\ &= P(\text{travel } r) (1 - P_{\text{collision}}(\delta r)) \\ &= P(\text{travel } r) (1 - \delta r/\lambda) \end{aligned}$$

$$\Rightarrow \frac{dP}{dr} = \frac{P(r+\delta r) - P(r)}{\delta r} = -\frac{P(r)}{\lambda}$$

$$\frac{dP}{P} = -\frac{dr}{\lambda}$$

integrate  $\int \frac{dP}{P} = -\frac{1}{\lambda} \int dr$

$$\ln P = -r/\lambda + \text{const}$$

$\uparrow$  zero since  
 $P(r=0) = 1$

$$P = e^{-r/\lambda}$$

$$P(\text{travel } \lambda) = e^{-1} = \frac{1}{e}$$

$$P(\text{travel } 10\lambda) = e^{-10} \quad \text{ie } 5 \text{ in } 100,000$$

# Distance Travelled On A Random Walk

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The particle is constantly scattered randomly

$$\vec{r} = \vec{s}_1 + \vec{s}_2 + \dots$$



$$r^2 = \vec{r} \cdot \vec{r} = s_1^2 + s_2^2 + \dots + \vec{s}_1 \cdot \vec{s}_2 + \vec{s}_2 \cdot \vec{s}_1 + \dots$$

As we saw before in a random environment

$$\langle \cos \theta_{1,2} \rangle = 0 \quad \vec{s}_1 \cdot \vec{s}_2 = 0$$

$$\Rightarrow r^2 = \sum_{i=1}^N s_i^2 \approx N \lambda^2$$

↑ assume go  $\lambda$  each step.

$$r = \sqrt{N} \lambda$$

This is much less than  $N\lambda$  - the total distance travelled.

EG Air molecules: previously we've computed  
 $v = 500 \text{ ms}^{-1}$  &  $\lambda = 10^{-7} \text{ m}$

In 1s it travels 500 m ...

But collides  $N = \frac{500}{10^{-7}} \sim 5 \times 10^9$  times

Total net distance is then  $\sqrt{N} \lambda = 7 \text{ mm}$

Note that since  $N \propto t^{1/2}$  (more collisions in more time)

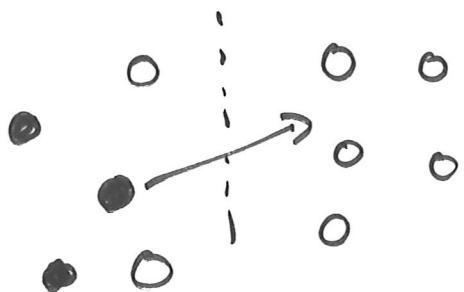
$$r \propto t^{1/2}$$

If one were to simulate a finite step walk particle by particle then  $\langle \cos \theta_{12} \rangle \neq 0$  precisely... one gets a distribution of distances travelled



As  $N \rightarrow \infty$  the Gaussian like peak narrows....

## Modelling Transport



black & white mix  
over time

movement of:  
identity  $\rightarrow$  diffusion  
energy  $\rightarrow$  thermal conductivity

momentum  $\rightarrow$  viscosity

We can do simple models of all these... assume particles move in  $\pm x, \pm y, \pm z$  only.

1/6<sup>th</sup> do each motion.

Ignore collisions - work in small st where pts cross line unimpeded

## Discussion

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### Fick's Law

number flowing across dotted line / sec

$$\frac{dN}{dt} = - DA \frac{dn}{dx}$$

↓      ↑      ↑

Area flowing over

spatial density gradient

this defines Diffusion Coefficient  $m^2/s$

Let's use kinetic theory to study the same process.

$$\text{Number flowing } L \rightarrow R = \frac{1}{6} n(x-\lambda) A \bar{v} \Delta t$$

↑  
1 in 6 go right way      ↓  
density to left by  $\lambda$       volume that can cross in  $\Delta t$  sec.

$$\text{Number flowing } R \rightarrow L = \frac{1}{6} n(x+\lambda) A \bar{v} \Delta t$$

so here's a net flow if the density is bigger on one side.

$$\text{Net flow } \frac{dN}{\Delta t} = \frac{1}{6} \left[ n(x-\lambda) - n(x+\lambda) \right] A \bar{v}$$

$n(x) - \frac{dn}{dx} \lambda$        $n(x) + \frac{dn}{dx} \lambda$

$$= \frac{1}{3} \lambda \bar{v} A \frac{dn}{dx}$$

$\Rightarrow$

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

# EG Evaporation from a test tube



$$\text{Flow rate} = - \frac{1}{3} \lambda \bar{J} A \frac{dn}{dx}$$

$\approx \frac{dN}{dt}$

Assume saturation density  $n_s$  just above surface; and zero at top

$$\frac{dn}{dx} = \frac{n_s}{h}$$

$$\text{Ideal gas: } P_s = n_s k T_I \quad = \frac{P_s}{h k T_I}$$

$$|\text{Flow rate}| = \frac{1}{3} \lambda \bar{J} A P_s \frac{1}{h k T_I}$$

$$\text{Mass loss} = \frac{M_{\text{mole}}}{N_A} \frac{\lambda \bar{J} A P_s}{3 h k T_I}$$

$$\uparrow M_{\text{mole}} = M_{\text{atom}} N_A$$

$$= \frac{M_{\text{mole}}}{R} \frac{\lambda \bar{J} A P_s}{3 h T_I}$$

$$\div \text{density} \quad \text{Volume loss} = \frac{M_{\text{mole}}}{R} \frac{\lambda \bar{J} A P_s}{3 h T_I \rho}$$

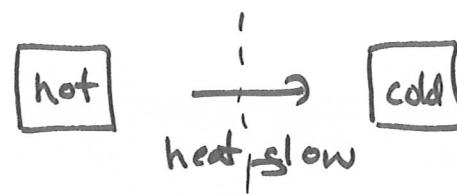
$$\div \text{area} \quad \text{Height loss} = \frac{M_{\text{mole}}}{R} \frac{\lambda \bar{J} P_s}{3 h T_I \rho}$$

$$T = 293K ; P_s = 1710 \text{ N m}^{-2} ; \rho = 1000 \text{ kg m}^{-3}$$

$$\text{If } h = 0.1 \text{ m}, \lambda = 10^{-7} \text{ m}, \bar{J} = 650 \text{ ms}^{-1} \text{ (here weights less than N<sub>2</sub>)}$$

$$\Rightarrow 0.24 \text{ mm/day}$$

# Thermal Conduction



Fourier's Law:

$$\frac{dQ}{dt} = -KA \frac{\downarrow \text{Area}}{\uparrow \text{thermal conductivity}} \frac{dT}{dx} \quad \begin{matrix} \text{K} \\ \text{temperature gradient} \end{matrix}$$

$\text{energy flow/s}$

As before assume  $\frac{1}{6} n A \bar{v}$  molecules glow/sec  
 ↑↑ assume don't change much

$$\text{So } L \rightarrow R \quad \frac{1}{6} n A \bar{v} E(x-\lambda) \Delta t \text{ energy flow} \\ \hookrightarrow \text{energy/molecule}$$

$$R \rightarrow L \quad \frac{1}{6} n A \bar{v} E(x+\lambda) \Delta t$$

$$\Rightarrow \frac{dQ}{dt} = \text{difference} = -\frac{1}{3} n A \bar{v} \lambda \frac{dE}{dx} \\ = -\frac{1}{3} n A \bar{v} \lambda \frac{dE}{dT} \frac{dT}{dx}$$

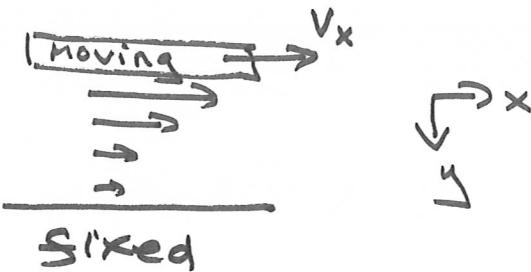
$$\text{Now } n \frac{dE}{dT} = \frac{dQ}{dT} \text{ for a unit volume} \\ = C \text{ specific heat capacity per volume}$$

$$\Rightarrow \boxed{\frac{dQ}{dt} = -\frac{1}{3} A C \bar{v} \lambda \frac{dT}{dx}}$$

$$\& \boxed{K = \frac{1}{3} \lambda \bar{v} C} \quad \text{which is } C \text{ times the result for D.}$$

## scosity

Molecules stick briefly to the surface & acquire x-momentum



This contradicts Ideal Gas rules!

i.e. there's a drag force in x, dependent on the velocity gradient in y

$$F_x = -\eta \frac{d}{dy} \left( \frac{v_x}{A} \right) \quad \begin{matrix} \text{now area of} \\ \text{moving surface} \end{matrix}$$

in opposite direction to  $v_x$

viscosity coefficient  $\text{Nm}^{-2} \text{s}^{-1}$

Consider a slice at some y & look at flow of x momentum across it

$$\frac{\Delta P}{dt} \text{ top to bottom} = \frac{1}{2} n A \bar{v} m v_x(y-1)$$

$$\frac{\Delta P}{dt} \text{ bottom to top} = \frac{1}{2} n A \bar{v} m v_x(y+1)$$

$$\text{net momentum flow} = -\frac{1}{3} n A \bar{v} \lambda m \frac{dv_x}{dy}$$

$n M = \text{mass/volume} = \text{density}$

$\Rightarrow$

$$\boxed{\eta = \frac{1}{3} \lambda \bar{v} \rho}$$

~~mass~~  
density  $\propto$  viscosity constant

note  $\frac{dv_x}{dy}$  is usually only large near e.g. an aeroplane

$$\text{Diffusion } D = \frac{1}{2} \lambda \bar{v}$$

$$\text{Thermal cond. } K = \frac{1}{2} \lambda \bar{v} C$$

$$\text{Viscosity } \eta = \frac{1}{2} \lambda \bar{v} \rho$$

$$\frac{\text{Concide } N/V}{M N/V} \sim \frac{K}{\rho} = \frac{C_{\text{mole}}}{M} = \frac{5k}{2m}$$

LT

$\hookrightarrow$   $\frac{5}{2}k$  diatomic molecules

$\text{eg } O_2 \sim 650 \text{ m s}^{-2} \text{ K}^2$   
order of magnitude OK....

## Maxwell Measures $N_A$ , 1865

$$\text{He noted } R/D = \rho$$

The  $D$  here is for slow of molecules - multiply by  $m$  to get slow rate of mass - this he could measure!

$$D_m = m D$$

$$\frac{R}{D_m} = \frac{P}{m} = n = \frac{N_A}{V_m}$$

So he could measure  $N_A$  via  $\eta$ ,  $D_m$ ,  $V_m$ ... he had to work out how to measure  $\eta$ ... but...

## Temperature Dependence

$$D: \frac{1}{2} m v^2 = \frac{3}{2} k T \quad \rightarrow v \sim T^{1/2}$$

$$\lambda = \frac{1}{\sqrt{2\pi d^2 n}} \sim \frac{1}{n} \stackrel{\text{ideal}}{\sim} \frac{kT}{P} \sim T$$

$$D \sim T^{3/2}$$

$$K: C \text{ is energy/volume & grows as } n \sim \frac{P}{kT} \sim \frac{1}{T}$$

$$K \sim T^{1/2}$$

$$\eta: \rho \sim n \text{ too } \rightarrow \eta \sim T^{1/2}$$

They all grow with temperature

## Pressure Dependence

$$\text{We had } \rho, C \sim n \quad \lambda \sim l/n \quad n = \frac{P}{RT_I}$$

$\Rightarrow \eta, K$  are predicted to be independent of  $P$ !

As the number of pts falls off... their mean free path grows...

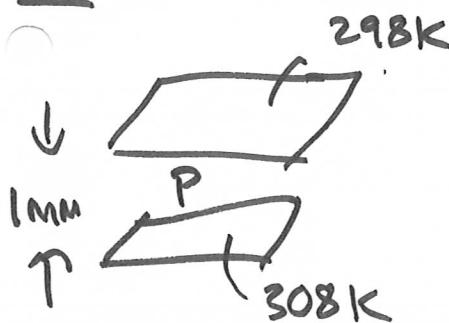
which matches data reasonably well.

BUT: surely as  $P \rightarrow 0$  transport should stop?

Point is  $\lambda$  can't be bigger than the container size. If  $\lambda$  saturates  $\eta, K \xrightarrow{P \rightarrow 0}$   
 "Knudsen low pressure regime"

ALSO  $P \rightarrow \infty$  intermolecular forces enter & mess up analysis...

EG conduction between two plates



$$d \approx 10^{-3} \text{ m} \ll d$$

$$K = \frac{1}{3} \lambda \bar{C}$$

$$\text{Heat capacity / unit volume } C = \frac{5}{2} k n = \frac{5P}{2T_I}$$

$$P = 10^5 \text{ Nm}^{-2} \rightarrow K = 0.014 \text{ Wm}^{-1} \text{ K}^{-1}$$

$$P = 0.1 \text{ Nm}^{-2} \quad \tilde{\lambda} \approx 0.1 \text{ m} \gg 1 \text{ mm}$$

$$K \text{ drops by } \frac{\tilde{\lambda}}{\lambda} = \frac{0.001}{0.001} \approx 100$$

## Dependence On Gas

Conduction grows with  $\lambda \sim \frac{1}{d^2} \Rightarrow$  small molecules good.

&  $D \sim \bar{v}$  so ~~small~~ light molecules are good too  
 $\frac{1}{2} M v^2 = \frac{3}{2} k T_I$

Thus  $H_2$  &  $He$  are better heat conductors than  $O_2$

## IMITATIONS OF KINETIC THEORY

MAINLY THAT IT ONLY DESCRIBES GASES!

No liquids or solids!

Hence no phase changes (boiling etc)!

Can't cope with interactions between molecules or quantum effects.

BUT we have learnt a gas is described by  $P, T (U), V, N$  (or  $n$ )

We will return at the end of the course to an improved gas model with interactions