14 December 2018

Thermal Physics

↳ What is it about?

— almost everything

the world around us
— room
— weather
— climate
— refrigetor
— furnace
— stars
— big bang.

Systems of many particles (atoms, molecules, making up gas, liquid, solid) are found to exhibit "universal behaviour"

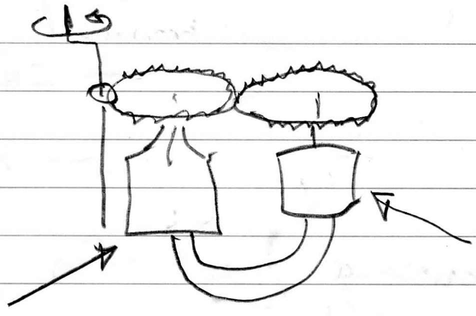
↳ you can predict a lot of the behaviour of system, without knowing the detailed internal structure.

Emperically Thermal Physics originated in the 19th century with the INDUSTRIAL REVOLUTION

PRACTICAL QUESTIONS, LIKE:

→ Can we build a perpetual motion machine 1st kind

I thought you could when I was a kid.



Runs forever

My Dad (an engineer) said it would never work

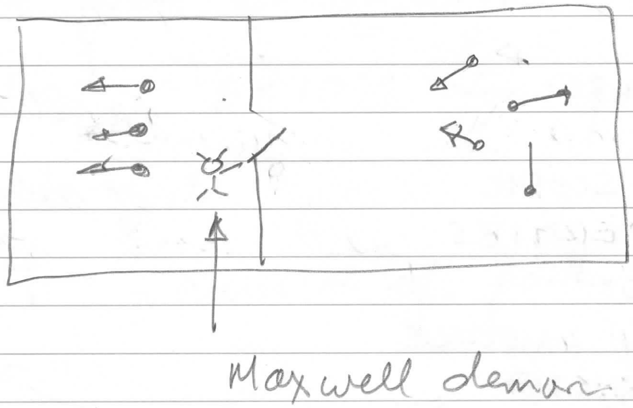
free energy

1st Law of thermodynamics

Conservation of Energy

→ Perpetual motion 2ND kind

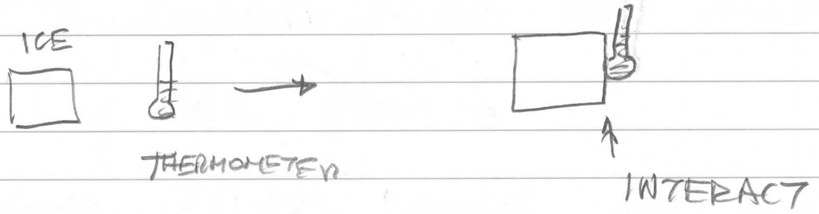
useful energy from rectifying random motion of air molecules



2ND Law of Thermodymanics

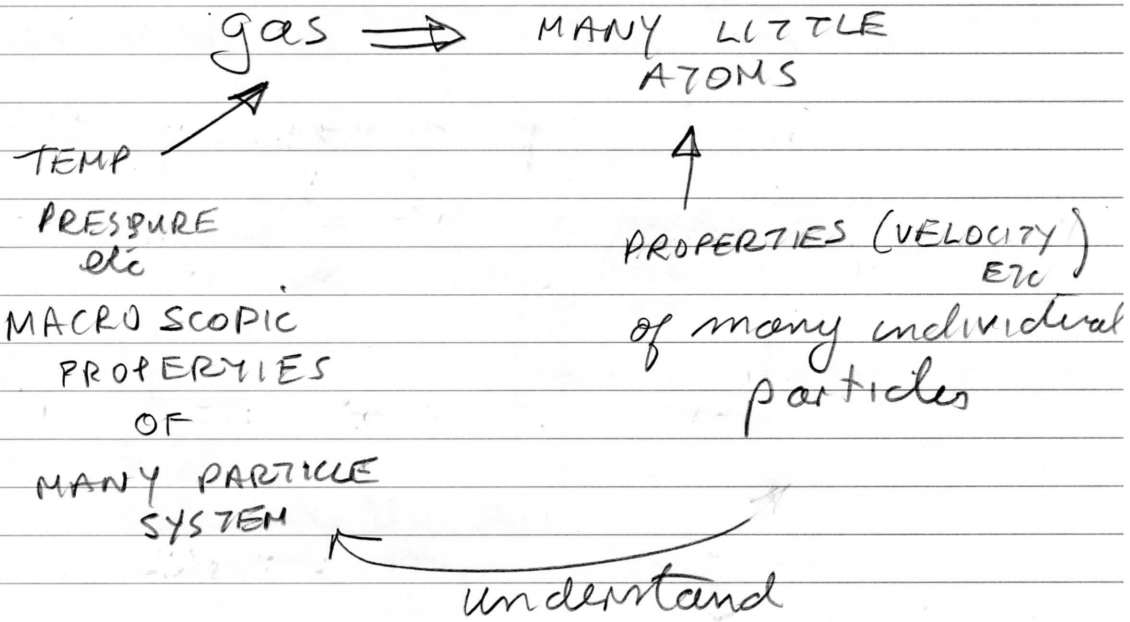
↳ Increase of Entropy

1) THERMODYNAMIC — study of general properties of systems of MANY PARTICLES which can INTERACT WITH EACH OTHER



2) STATISTICAL MECHANICS

Make a MICROSCOPIC model



Statistical Mechanics offers a way to derive thermodynamics from FIRST PRINCIPLES.

How many particles are "a MANY"?

$$m_{H\text{-atoms}} \approx 10^{-27}\,\mathrm{kg}$$

so one gram of hydrogen ~ 10^{24} atoms

Avogadro — 6×10^{23} atoms per mole

$$N \sim 10^{24}$$

↳ number of particles in a system

How do you describe a system of ~10^{24} particles?

Use classical mechanics?

$$m\ddot{\vec{r}}_i = \vec{F}(\vec{r}_1, \dots \vec{r}_n, \dot{\vec{r}}_1 \dots \dot{\vec{r}}_n)$$

$$i = 1 \dots N = 10^{24}$$

$$\hookrightarrow 3\times 10^{24} \text{ equations.}$$

Presently supercomputers can model motion of 10^{12} stars.

But even if we could do that computation → it would be 6×10^{24} numbers for every moment in time

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How could you possibly make sense of that?

For a system of so many particles the individual behaviour of particles is of no real interest

Epirically you "feel" the "average action" of many particles in the air.

M MACROSCOPIC QUANTITIES → pressure P average force / unit area

→ N particles

→ Volume V

→ Temperature → quantity measured by a thermometer

As opposed to MICROSCOPIC QUANTITIES

$\bar{r}_i(t) \quad \dot{\bar{r}}_i(t)$

$i = 1 \dots 10^{10^4}$

6×10^3 position and velocities

SUMMARY:

- Description of a system via MACROSCOPIC QUANTITIES is the subject of THERMODYNAMICS

"COURSE GRAINED"

- Mechanics (classical or quantum) uses MICROSCOPIC QUANTITIES to describe a system — DETAILED FINE GRAINED
- STATISTICAL MECHANICS, relates the two of them

Concrete example of a SYSTEM

↳ IDEAL GAS

will define what
we mean by this

↳ obeys IDEAL GAS LAWS

Important concept for any thermodynamic System is THERMODYNAMIC EQUILIBRIUM

Experimentally a gas (N particles in volume V) is left on its own for a sufficiently long time it will

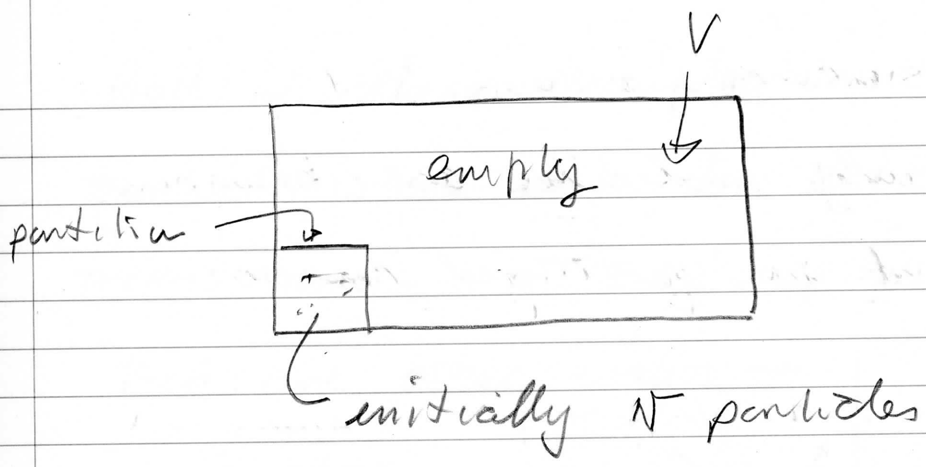
THERMODYNAMIC EQUILIBRIUM.

1) be uniform, have same density, throughout the volume V

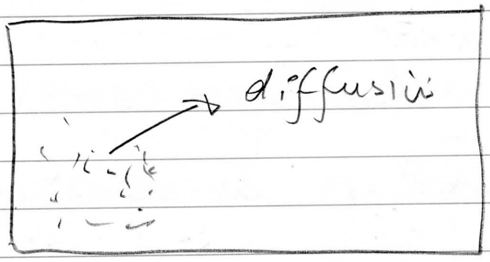
2) PRESSURE + TEMPERATURE will not change with time, and will be uniform throughout the volume

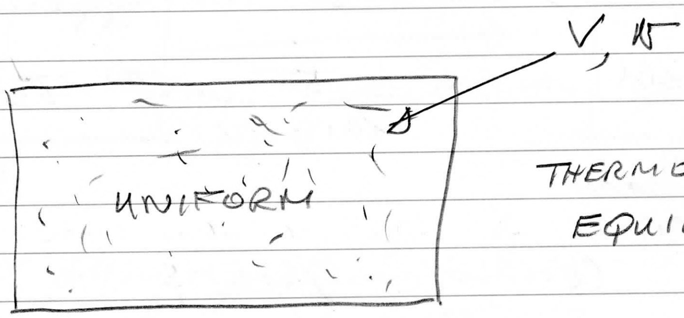
3) No microscopic fluxes currents/winds

↳ individual particles will still be bouncing around but in no preferred direction



then remove PARTITION



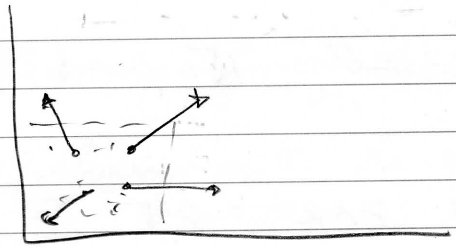


THERMODYNAMIC EQUILIBRIUM.

- GAS uniformly fills box
- pressure and temperature and density are all UNIFORM IN SPACE
  CONSTANT IN TIME

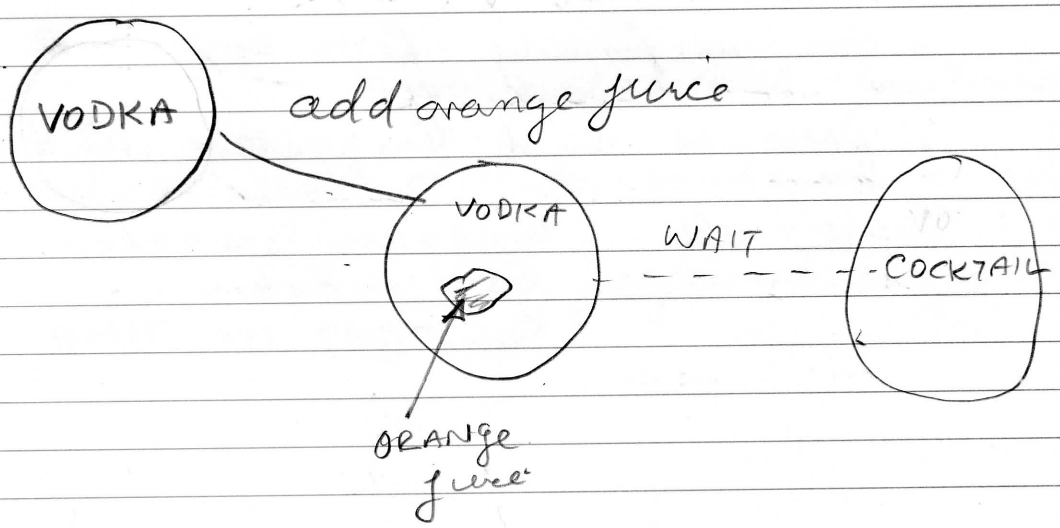
DIFFUSION

initially molecules are bouncing around in partitioned corner.



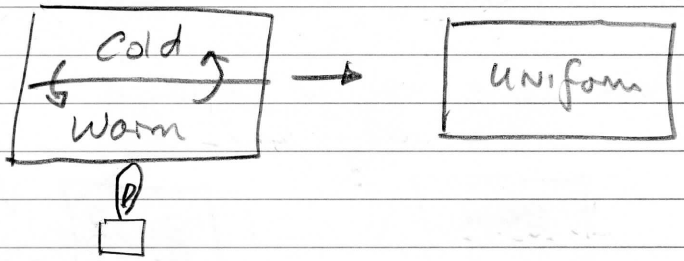
Initially there were some molecules with velocities directed outwords when there is no partition, they will move out into the empty volume

More COMPLEX SYSTEMS



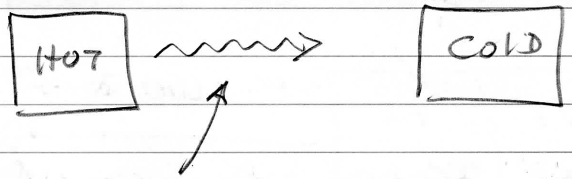
other mechanisms leading to THERMODYNAMIC EQUILIBRIUM

CONVECTION



Heating water, warmer rises, colder falls

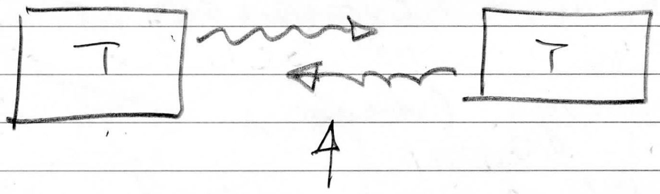
RADIATION



electromagnetic radiation carries

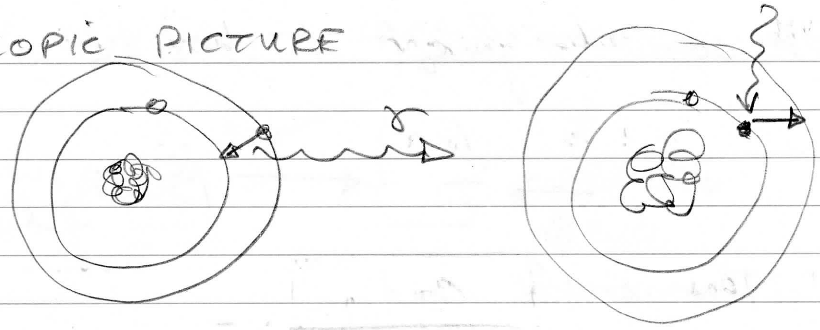
carries energy from HOT to COLD

eventually temperatures equalize



each is producing same energy from radiation

MICROSCOPIC PICTURE



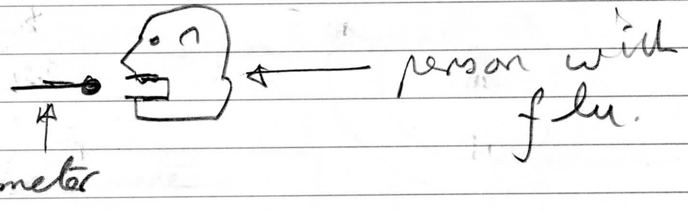
In thermodynamics and statistical mechanics we are usually not concerned with the detailed microscopic mechanism leading to the establishment of thermodynamic Equilibrium

↳ should be aware of the general nature of the processes which lead to equilibrium

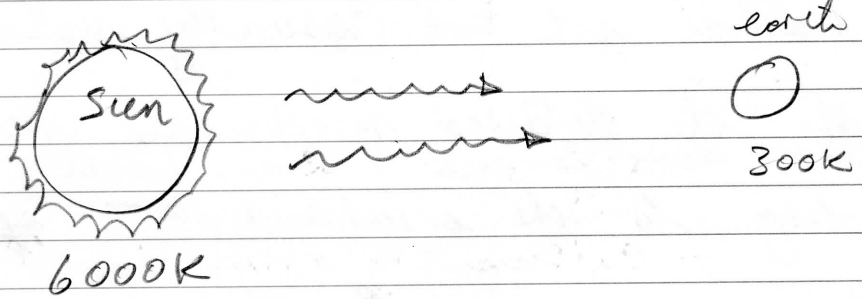
↳ heat exchange, diffusion, convection radiation - - - .

Also question of how long it takes to equalize pressure, density, temperature is not trivial — depends on mechanisms involved

It can be fast



very slow



not in equilibrium, luckily

PHYSICAL KINETICS studies rates of diffusion, heat exchange, radiation etc

→ Section 1-7 Schröder.

Concrete System — IDEAL CLASSICAL GAS

$N \sim 10^{24}$

obeys ideal gas laws

point like particles

IT is a <u>striking fact</u> that any gas which is

- sufficiently hot
- sufficiently dilute

} obeys ideal gas law.

to great accuracy

$$PV = kNT$$

pressure $= \frac{\text{force}}{\text{area}}$

$= \frac{N}{m^2}$

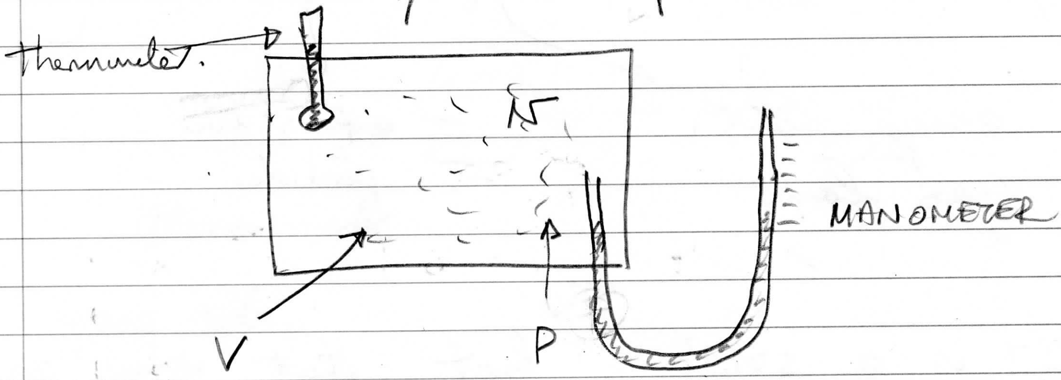
volume m^3

Boltzman $= 1.381 \times 10^{-23} \frac{J}{K}$

particles

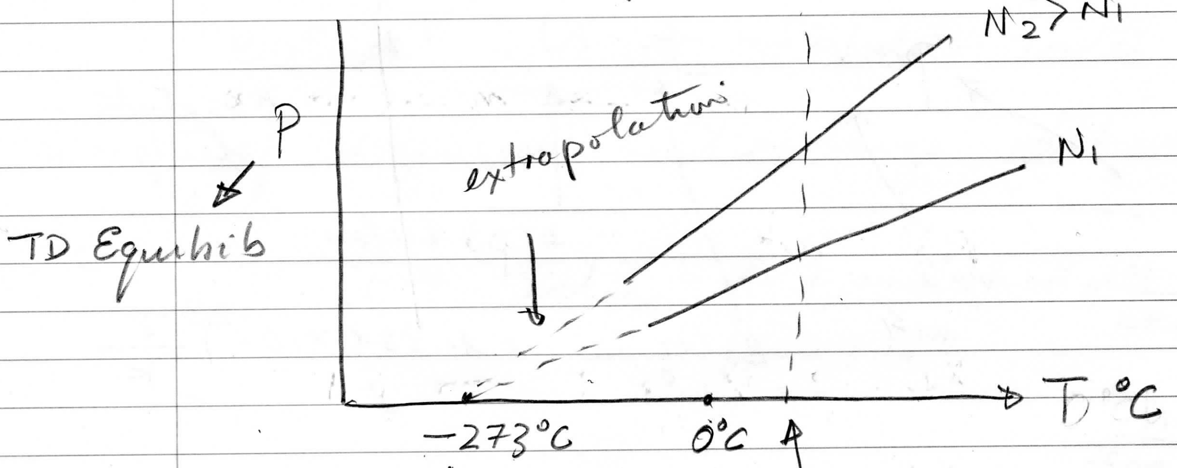
Absolute temp in K

This is an experimental fact (18th → 19th century?)



pressure ~ 1 atm ~ $10^5 \frac{N}{m^2}$

put, at fixed V, different amounts of molecules and measure pressure at different temperatures



Absolute zero

at fixed T doubling N doubles pressure

$$pV = nRT$$

$\nearrow$ # of mols of gas

1 Mole = $N_A = 6.02 \times 10^{23}$ molecules or atoms

eg N_A = # of atoms in 12g of ^{12}C carbon

Comparing with $pV = NkT$

$$R = N_A \cdot k = 8.31 \frac{J}{mol\,K}$$

$$nR = N_A k$$

$$R = \frac{N_A \cdot k}{n} \rightarrow n = 1 \rightarrow \text{per mole}$$

$pV = nkT$ simple!

at fixed V, if T ↑ → P ↑

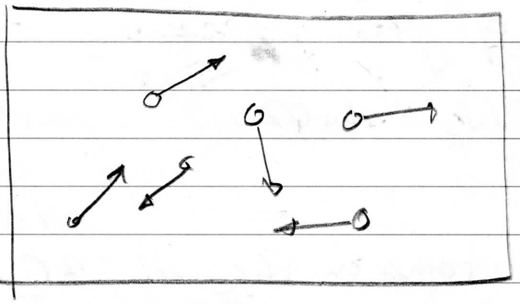
at fixed T, if V ↑ → P ↓

→ common sense → or is it experience

↓

see JP441!

Can deduce from SIMPLE MOLECULAR MODEL OF GAS



~ 10^{24} molecules randomly bouncing around.

→ uniformly distributed

→ velocities isotropically distributed

in any given volume containing a large number of molecules, the number having a given direction of $\vec{v}$ is the same

↳ if this were not true would have a macroscopic flow in direction $\vec{v}$ → this would not be thermodynamic Equilibrium

Important assumption is that there is some AVERAGE SPEED

Call average velocity $\bar{v}_x$, because vs are isotropically distributed

$$\underset{\text{average}}{\bar{v}_x} = \bar{v}_y = \bar{v}_z = c$$

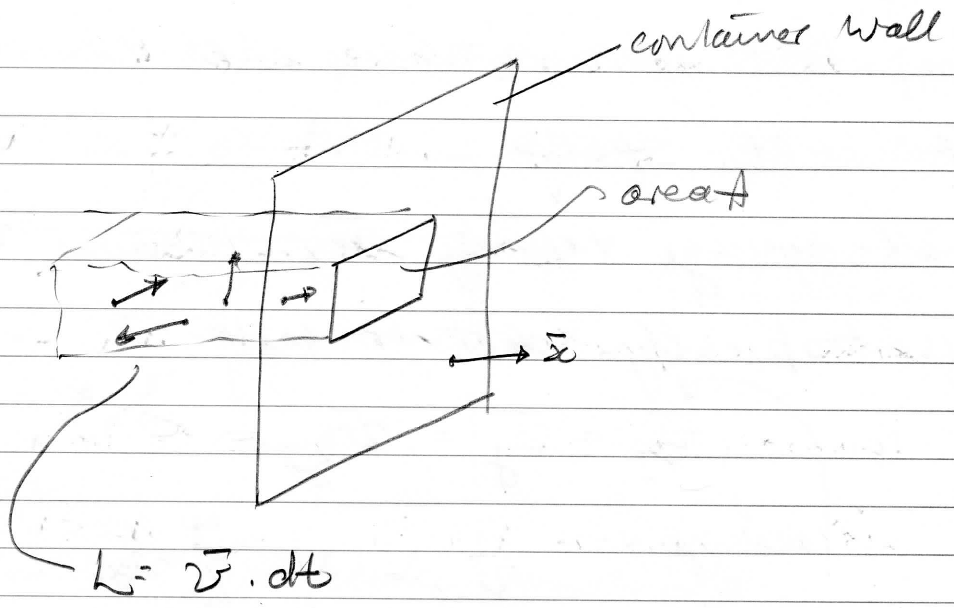
$$\bar{v}_x = \frac{1}{N}\sum_{i=1}^{N} v_{x_i}$$

because as many move left as right we can expect $\bar{v}_x = 0$, also $\bar{v}_y$, $\bar{v}_z$

$\overline{v_x^2}$ need not vanish, and we assume that it does not

$$\overline{v_x^2} = \frac{1}{N}\sum_{i=1}^{N} v_{x_i}^2$$

$\sqrt{\overline{v_x^2}} = \bar{v}$ is our definition of $\bar{v}$



In box LA volume there are

$\underset{\substack{\uparrow \\ \text{density}}}{\frac{N}{V}} \cdot \underbrace{L \cdot A}_{\text{volume}}$ molecules

expect that $\frac{1}{2}$ of molecules have velocity pointing in $\bar{x}$ direction

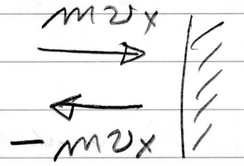
$L = \bar{v}\, dt$, in time dt all of the molecules inside the box will hit the wall

So, in time dt there will be

$$\frac{1}{2}\,\frac{N}{V}\cdot L\cdot A = \frac{1}{2}\,\frac{N}{V}\,\bar{v}\,dt\,A \quad (1)$$

collisions with the wall

when a particle with x- momentum mv_x bounces off the wall, the change in its momentum is $-2mv_x$



$$|\delta p| = |mv_x - (-mv_x)|$$
$$= 2mv_x$$

but it is in the $-ve$ x direction

$$\therefore \quad \delta p = -2mv_x \quad ③$$

this is how molecules exert pressure on the wall

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Ignore the fact that some molecules will have $v_y, v_z \neq 0$ and may not hit A

From ① and ③ we have that the total change in momentum of the wall of area A

= # collisions in time dt × change in momentum of A for each collision

$$\left(\frac{1}{2}\frac{N}{V}\,\bar{v}\,dt\,A\right)\times\left(2m\bar{v}\right) \qquad (3')$$

Change in momentum of A is, by Newton's Second Law = force on the wall

$$\frac{dp_x}{dt} = F_x \qquad ④$$

$$(3') \rightarrow \text{force}\,.\,dt = dp_x = \frac{1}{2}\frac{N}{V}\,2m\bar{v}^2 A\,.\,dt$$

$$④ \quad \text{force} = \frac{dp_x}{dt} = \frac{N}{V}\,m\bar{v}^2 \cancel{A}$$

↳ force on A, perpendicular to it.

Pressure is "force per unit area"

$$\frac{\text{force}}{\text{Area}} = \frac{N}{V} m \bar{v}^2 A \Big/ A$$

pressure $P = \frac{N}{V} m \bar{v}^2$ ⑤

Remember ideal gas law.

$$pV = N kT$$

$$pV = N m \bar{v}^2$$

$\hookrightarrow$ actually v_x^2

So, we conclude that

$$kT = m v_x^2$$

But we chose the x-direction arbitrarily

so by isotropy $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$

So $\overline{v_x^2} = \frac{1}{3}(\bar{v}^2) = \frac{1}{3}\left(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}\right)$

More generally. $\overline{v^2} = \frac{1}{N}\sum_{i=1}^{N} \overline{v_i^2}$

so we have that

$$kT = m\overline{v_x^2} = \frac{1}{3} m \overline{v^2}$$

$$kT = \frac{1}{3}\underbrace{m\overline{v^2}}$$

kinetic energy $= \frac{1}{2} m v^2$

$$kT = \frac{2}{3}\,\frac{m\overline{v^2}}{2}$$

$$\boxed{\frac{m\overline{v^2}}{2} = \frac{3}{2} kT}$$

In thermodynamic equilibrium the average kinetic energy per particle is $\frac{3}{2} kT$ in an IDEAL GAS

$$T \propto \frac{1}{2} m\overline{v}^2$$

So now we have a more "scientific" definition of TEMPERATURE

TEMP → is a measure of the average kinetic energy of the particles in the gas this is a nice example of:

microscopic ⟷ macroscopic

↓ ↓

Kinetic energy per particle ⟷ Temperature of gas

↳ under the assumption of a uniform, random in direction velocity distribution

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Numerical stuff is always important and interesting

what is $\sqrt{\langle \vec{v}^{\,2} \rangle}$ Root Mean Square

$$v_{RMS} = \sqrt{\frac{3kT}{m}}$$

$$= \left(\frac{3 \times \overset{k}{1{\cdot}381 \times 10^{-23} \frac{\text{joules}}{\text{Kelvin}}} \times \overset{T}{300 \text{ Kelvin}}}{\underbrace{2 \times 14}_{\text{atomic mass of } N_2} \times \underbrace{1{\cdot}6605 \times 10^{-27}}_{\text{atomic mass} \to \text{kilo}}} \right)$$

$= 517$ m/s

Let's just check dimensions

Newton = Force that would give 1kg an acceleration of $1\, m\, s^{-2}$

$$F = ma$$

$$[\text{newton}] = [kg]\frac{[m]}{[s^2]}$$

Joule = work done by one Newton over 1 m

$$[\text{Joule}] = [\text{Newton}] \times [m]$$

$$\therefore [\text{Joule}] = \frac{[kg] \times [m] \times [m]}{[s^2]}$$

So
$$\frac{[\text{Joule}]}{[kg]} = \frac{[m^2]}{[s^2]}$$

$$\left(\frac{[\text{Joule}]}{[kg]}\right)^{\frac{1}{2}} = \frac{m}{s} \quad \checkmark$$

SUMMARY

- thermodynamic Equilibrium means uniform, isotropic, no MACROSCOPIC flows

- All dilute and hot gases obey

$$PV = NkT$$

→ this is a universal law, it does not depend on the detailed composition of the gas [as long as it is IDEAL]

- $\frac{m\langle \vec{v}^2 \rangle}{2}$ = average translational kinetic energy

$$= \frac{3}{2} kT$$

so kT = energy

UNITS & DIMENSIONS

$$\underset{\frac{N}{m^2}}{p}\,\underset{m^3}{V} = \underset{\#\text{ of moles}}{n}\,\underset{\text{gas constant}}{R}\,T - k$$

$$R = \frac{\overbrace{N \cdot m}^{\text{Joules}}}{n \quad T \leftarrow k}$$

$$pV = [N][m] = [\text{mole}][k][R]$$

$$\text{so } [R] = \frac{[N \cdot m] \leftarrow J}{[\text{mole}][k]}$$

Above [N] is Newtons

Can use N for number of particles

$$n[\text{moles}] = \frac{N}{N_A} \leftarrow \text{AVOGADRO}$$

So can write

$$pV = \frac{N}{N_A} \cdot R \cdot T$$

$$PV = \frac{N}{N_A} \cdot R \cdot T$$

Boltzmann

Also have $PV = N k T$

$$k = \frac{R}{N_A} = \frac{[J]}{[\text{mole}]} \cdot \frac{1}{[K]} \cdot [\text{mole}]$$

units

$$k = \frac{[J]}{[K]} \qquad \frac{[\text{Joules}]}{[\text{Kelvin}]}$$

$$R = 8.31 \frac{J}{\text{mole} \cdot K}$$

$$k = \frac{8.31}{N_A} \frac{J}{\text{mole}\, K} = 1.38 \times 10^{-23}$$

Extra points from Schöder

average translational kinetic energy

$= \bar{K}_{trans} = \frac{3}{2}kT$

Nice interpretation of k. It has just the right units to convert between temperature and energy

$$[k] = \left[\frac{J}{K}\right]$$

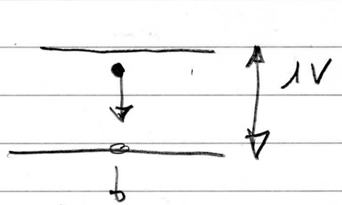
at Room temperature of 300K

$$kT = 1.38\times10^{-23}\frac{J}{K}\cdot 300K$$

$$= 4.14\times10^{-21}\,J$$

this is TINY, but since molecules are tiny – that's just what we expect.

As a particle physicist, I like to use ELECTRON VOLTS



electron emerges with kinetic energy of 1 volt.

$1\,\text{ev} = 1.6 \times 10^{-19}\,\text{J}$

in these units $k = 8.62 \times 10^{-5}\,\text{eV/K}$

so, at room temperature

$$kT = 8.62 \times 10^{-5}\,\frac{\text{eV}}{\text{K}} \cdot 300\,\text{K} = 0.026\,\text{eV}$$

Even in electron volts molecular energies are pretty small numbers

$$v_{RMS} \sim \bar{v}$$

Derivation breaks down if molecules exert forces on each other, or if collisions with walls are inelastic

↳ gas becomes so dense that space occupied by molecules is a substantial fraction of the volume of the container

↳ then approximation of molecules flying in straight lines breaks down

$\bar{K}_{\text{trans.}} = \frac{3}{2} kT$ remains true even for liquids & solids