# MULTIPLICITY of STATES OF IDEAL GAS

Monoatomic ideal gas, kinetic energy

$$U = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$$

energy of gas → $\Sigma$ of (momentum)$^2$ of individual atoms.

Count microstates — How many ways can we choose 3N numbers, such that

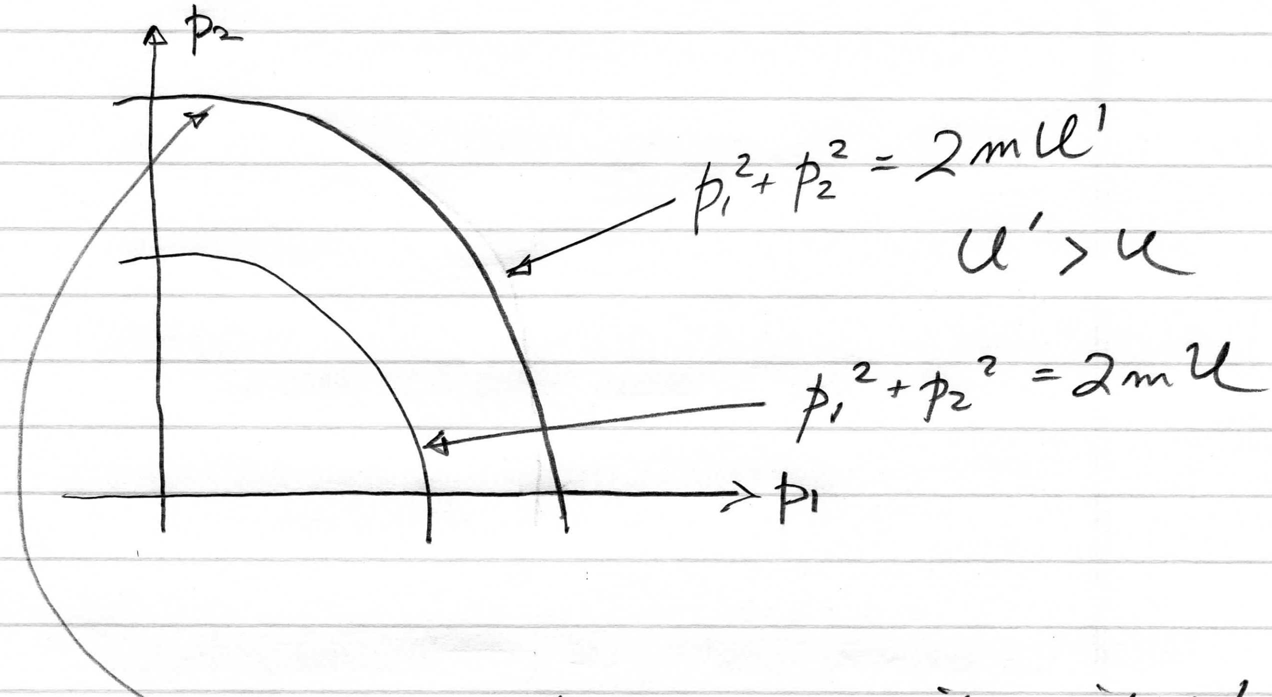
$$\sum_{i=1}^{N} \vec{p}_i^{\,2} = 2mU$$

→ $\Sigma$ of squares fixed.

3 because $\vec{p}_i^{\,2} = \vec{p}_{x_i}^{\,2} + \vec{p}_{y_i}^{\,2} + \vec{p}_{z_i}^{\,2}$

As $U \uparrow$, number of choices $\uparrow$

$x^2 + y^2 \longrightarrow$ a circle!




more $p_1$ and $p_2$ on circle with $U'$

Can guess that

$\Omega(N,U) \sim$ area of 3-N dimensional sphere of $(\text{radius})^2 = 2mU$

From Appendix B in the text

3N dimensional space $x_1 \ldots x_{3N}$ $\mathbb{R}^{3N}$

- $S^{3N-1} \equiv 3N-1$ dimensional sphere

$x_1^2 + \cdots\cdots x_{3N}^2 = R^2$

$\uparrow$ Radius

Drawing is for $3N=2$.

The "surface Area" of $S^{3N-1}$ is

$$A_{3N-1}(R) = \int_{-\infty}^{+\infty} dx_1 \cdots \int_{-\infty}^{+\infty} dx_{3N}\, \delta\left(\sqrt{x_1^2 \cdots x_{3N}^2} - R\right)$$

same as ~~text~~ 3N
↳ Notation

Dirac δ-fn
= 1 when $R = \sqrt{\ }$
= 0 when $R \neq \sqrt{\ }$

Trivial Example is $3N = 2$

$$A_{3N-1}(R) = A_1(R)$$

$S^1$ = circle "area" → circumference
→ length

$$A_1 = \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2\, \delta\left(\sqrt{x_1^2 + x_2^2} - R\right)$$

$$= \int_0^{\infty} r\,dr \int_0^{2\pi} d\phi\, \delta(r - R)$$

$$= 2\pi \int_0^{\infty} r\,dr\, \delta(r - R)$$

$$= 2\pi R$$

"Generalizing"

$$A_{3N-1}(R) = \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!} \cdot R^{3N-1}$$

$$= \frac{2\pi^{3N/2} R^{3N-1}}{\Gamma\left(\frac{3N}{2}\right)}$$

Gamma fn $\longrightarrow \Gamma\left(\frac{3N}{2}\right)$

So, one expects.

$$\Omega(N,U) \sim \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!} \left(\sqrt{2mU}\right)^{3N-1}$$

"goes as"
"prop to"

Radius.

the RHS is NOT A NUMBER

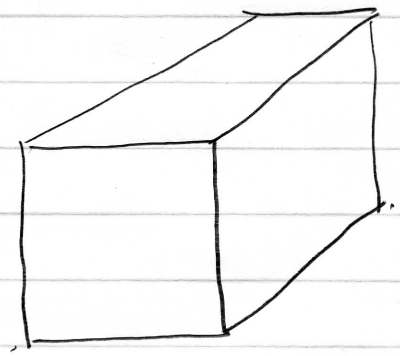
$(2mU) \longrightarrow [\text{momentum}]^2$

COUNTING $\longrightarrow$ need dimensionless number

$p_{x,y,z}$ not continuous

$\hookrightarrow$ Quantized.

Quantization in a box



Volume $V = L^3$

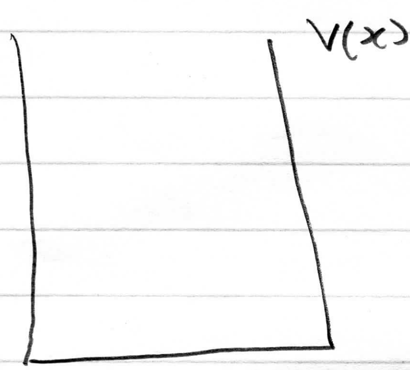
$$\vec{p} = \frac{\pi\hbar}{L}(n_x, n_y, n_z)$$

$n_x = 1, 2, 3 \cdots\cdots$

$\hookrightarrow$ can not be zero!

$\Delta p \Delta x \sim h$

In 1-dimension $\longrightarrow$ Potential Well




$\psi(x=0) = \psi(x=L) \longleftarrow$ PERIODIC WAVE FUNCTION.

$$\psi_n = C_n \sin \frac{\pi n x}{L}$$

NUMERICAL EXAMPLE

$n = 1$ state $\rightarrow$ $v = \frac{p}{m} = \frac{\pi \hbar}{L\,(m)} \sim 10^{-37} \frac{m}{s}$

$n = 2$ has twice – spacing $\sim 10^{-37} \frac{m}{s}$

Hydrogen atom $m \sim 10^{-24} g$

$n = 1$ $10^{-13}$ m/s

$n = 2$ $2 \times 10^{-13}$ m/s

$\rightarrow$ spacing between states is VERY SMALL $\sim 10^{-13}$ m/s

$p_{x,y,z}$ $\rightarrow$ natural discrete minimum values from Quantum Mech

$\rightarrow$ $\frac{n \hbar}{L}$ for box side $L$

So, instead of

$$\Omega(N,u) \sim \frac{2(\pi)^{3N/2}}{\left(\frac{3N}{2}-1\right)!}\left(\sqrt{2mu}\right)^{3N-1}$$

$R \to p$

$p^2 = 2mu$

to get a DIMESIONLESS NUMBER

$$\sqrt{2mu} \to \frac{\sqrt{2mu}}{\frac{\pi\hbar}{L}}$$

CONTINUOUS
$\neq$ QM

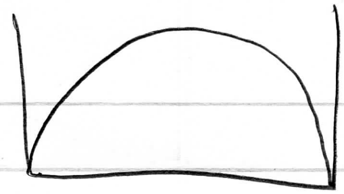
DISCRETE
IN UNITS OF
$\pi\hbar/L$

$$\Omega(N,u) \sim \frac{2(\pi)^{3N/2}}{\left(\frac{3N}{2}-1\right)!}\left[\frac{(2m)^{\frac{1}{2}} L u^{\frac{1}{2}}}{\pi\hbar}\right]^{3N-1}$$

counts number of 3N $p_s$ the
sum of whose squares $= 2mu$

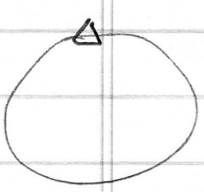
But this is incomplete

$$\vec{p} = \frac{\pi\hbar}{L}(n_x, n_y, n_z)$$

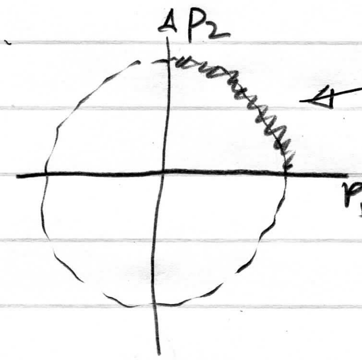


NO quantum number for direction of $\vec{p}$

↳ Area of $S^{3N-1}$ counts +ve & -ve $p_{x_i}$'s



L




want $p > 0$

↓ $\frac{1}{4} \times L$

↓ factor $\frac{1}{2^{3N}}$

$$\Omega(N, U) \sim \frac{1}{2^{3N}} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} \left[\frac{(2m)^{1/2} L U^{1/2}}{\pi\hbar}\right]^{3N-}$$

We are using $|p_x|$ to label the state → not $p_x > 0$ or $< 0$

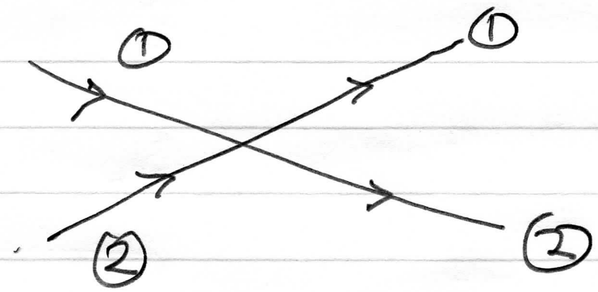
Classically

$$\left.\begin{array}{r} p_x \rightarrow \\ \leftarrow p_x \end{array}\right\} \text{Different states.}$$

N particles ARE IDENTICAL — INDISTINGUISHABLE

CLASSICALly can LABEL particles

↳ follow trajectory

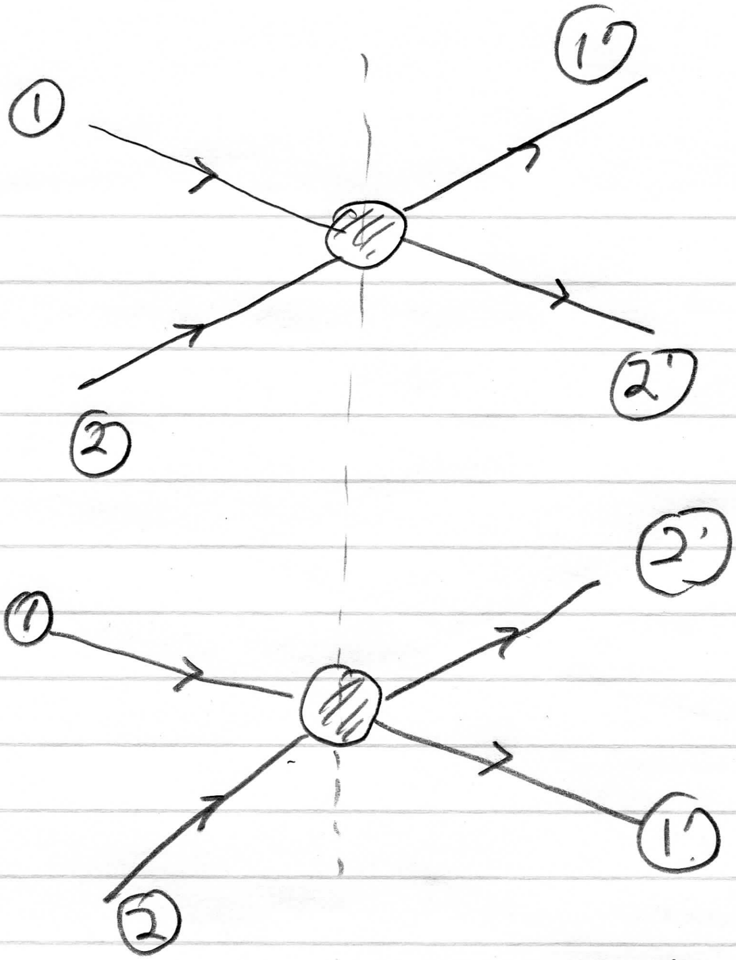



Every moment know which ball is which and what their $\vec{p}$ and $\vec{v}$ are.

In QM → quantum numbers are ONLY labels there are.

↳ nothing else

↳ particles have no well-defined trajectories




THERE ARE NO SUCH Labels to distinguish IDENTICAL PARTICLES

$\downarrow$

CANNOT DISTINGUISH THESE 2 EVENTS

After Collision only $E$ & $\vec{p}$ conserved

Individual "IDENTITY" NOT CONSERVED

$\vec{p}_1 \to (\varepsilon) \to \vec{p}$

$\neq$ NOT TRUE.

For particles in a box interchanging $N$ quantum numbers $\vec{n}_1 - - - - - \vec{n}_N$ does NOT change state

$\Omega$ so far counts number of states

$$\vec{n}_1 \text{-----} \vec{n}_N$$

such that $\vec{n}_1^{\,2} + \vec{n}_2^{\,2} + \text{-----} \vec{n}_N^{\,2} = \left( \frac{2mLU}{\pi\hbar} \right)^2$

Have to divide by number of permutations

of $\underbrace{\vec{n}_1 \text{---------} \vec{n}_N}_{\text{IDENTICAL}} \longrightarrow N!$

$$\Omega(N,U) = \frac{1}{N!} \frac{1}{2^{3N}} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!} \left[ \frac{(2m)^{\frac{1}{2}} L U^{\frac{1}{2}}}{\pi\hbar} \right]^{3N-1}$$

do not erase!

more complex for Quantum mechanics, since Fermi-Dirac and Bose-Einstein statistics are different.

What went into deriving this:-

– $\sum_{i=1}^{N} \vec{p}^{\,2} = 2mU$

– $\vec{p}$ (momentum) quantized in units $\frac{\pi\hbar}{L}$

– $p_{i\,xyz}$ only $> 0$ $\rightarrow$ $\frac{1}{2^{3N}}$

– particles indistinguishable — $\frac{1}{N!}$

↳ no way of knowing which particle goes with which momentum

* All we know about the microworld are the "labels" → quantum numbers

↳ when find new phenomena, need new labels to describe them

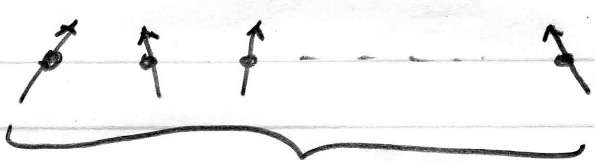
eg spin

" color.

- Gibbs introduced idea of a constant of dimens $[\hbar]$ before QM, also $\frac{1}{N!}$
  - → Gibbs Paradox → later & text book.

- Paramagnet & Einstein solid
  - → did not have $\frac{1}{N!}$
  - → additional quantum number which was IMPLICIT

$$\underbrace{\text{N spins, N oscillators.}}_{\text{DISTINGUISHABLE}}$$



Fixed position on lattice

$$\Omega(N,U) = \frac{1}{N!}\,\frac{1}{2^{3N}}\,\frac{2\pi^{3N/2}}{(3N-1)!}\left[\frac{\sqrt{2mU}\cdot L}{\pi\hbar}\right]^{3N-1}$$

we can try to simplify this

$N \sim 10^{23}$ , $3N-1 \sim 3N$

$L^3 = V$ ; $L = V^{1/3}$

$\left(\frac{3N}{2}\right)! \approx \left(\frac{3N}{2e}\right)^{\frac{3N}{2}}$ ; $\frac{1}{N!} = \left(\frac{e}{N}\right)^N$

$$= \left(\frac{e}{N}\right)^N \left(\frac{1}{8}\right)^N \frac{2\left(\pi^{\frac{3}{2}}\right)^N}{\left(\frac{3N}{2e}\right)^{3N/2}} \left[\frac{V}{(\pi\hbar)^3}\right]^N \left\{\left[2mU\right]^{3/2}\right\}^N$$

drop the 2 → everything else is $(\ )^N$

$$= \left\{ \frac{e^{5/2}}{N}\cdot\frac{1}{8}\cdot\frac{\pi^{3/2}\,2^{3/2}}{3^{3/2}\,N^{3/2}}\,\frac{V}{(\pi\hbar)^3}\,2^{3/2}\,m^{3/2}\,U^{3/2} \right\}^N$$

$e/N \cdot \left(\frac{e}{N}\right)^{3/2}$

$= \frac{e^{5/2}}{N^{5/2}}$ $\quad e^{5/2}/N \cdot \frac{1}{N^{3/2}}$

=

$$\pi^{3/2} \cdot 2^{3/2} \cdot 2^{3/2} \cdot m^{3/2} \cdot u^{3/2}$$

$$= \quad (4\pi \, m \, u)^{3/2}$$

$$\frac{1}{8} \, \frac{1}{3^{3/2}} \cdot \frac{1}{N^{3/2}} \cdot \frac{1}{\pi^3} \, \frac{1}{\hbar^3}$$

$$8 = 2^3 = 2^{3/2 \cdot 2} \, , \quad \pi^3 = \pi^{3/2 \cdot 2} \ldots$$

So

$$\Omega(N, u) = \left\{ \frac{V}{N} \, e^{5/2} \, \underbrace{\frac{(4\pi m u)^{3/2}}{\left[3N(2\pi\hbar)^2\right]^{3/2}}}_{\hbar/2\pi} \right\}^N$$

$$\text{Entropy} = S(N, u, V) = k \ln \Omega(N, u, V)$$

$$S(N, u, V) = Nk \left\{ \ln \left[ \frac{V}{N} \left( \frac{4\pi m u}{3Nh^2} \right)^{3/2} \right] + \underbrace{\frac{5}{2}}_{\ln e^{5/2}} \right\}$$

SAKUR-TETRODE formula for

Entropy of a mono-atomic ideal gas

SAKUR-TETRODE :-

— $S \sim kN$ → double $N, V, U$ such that $\frac{V}{N}$ & $\frac{U}{N}$ cons ~~tant~~

↳ $S$ doubles

↳ EXTENSIVE property of entropy

— $N \sim 10^{23}$ → $S$ is enormous.

— $U\uparrow \rightarrow S\uparrow$ Normal system.