Canonical Distribution of IDEAL GAS

For a classical system.

$$E_1 = \frac{1}{2m} \vec{p}_1^{\,2} + E_{VIB_1} + E_{ROT_1}$$

Single molecule

Quantize momentum

$$\vec{p}^{\,2} = \left(\frac{\pi \hbar}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right)$$

$\left.\begin{matrix} E_{vib} \\ E_{rot} \end{matrix}\right\}$ depend on their own Quantum numbers

Showed

$$Z_{N\text{-PARTICLES}} = \left(Z_1\right)^N$$

one particle

for indistinguishable particles

$$\rightarrow \frac{1}{N!}$$

$\sum$ μSTATES in Z

μSTATES THAT Differ by permutations of quantum number of any 2 particles describe same μ STATE $\longrightarrow \frac{1}{N!}$

$$Z_{\substack{N\text{-molecule}\\ \text{ideal gas}}} = \frac{1}{N!}\left(Z_1\right)^N$$

partition function of single molecule

↓

advantage of (T, V, N)

Canonical Approach.

Had $Z = \sum_{S} e^{-E/kT}$

$$Z_1 = \left\{ \underbrace{\sum_{n_x n_y n_z}^{\infty} e^{-\frac{1}{2mkT}\left(\frac{\pi\hbar}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)}}_{Z_{1\,TRANS}} \right.$$

$\times Z_{1\,VIB}$ $\times Z_{1\,ROT}$

$$\sum_{n=0}^{\infty} e^{-\hbar\omega_{vib} \cdot n/kT}$$

Harmonic Oscillator

$$\sum_{\ell=0}^{\infty} \frac{\hbar^2 [\ell(\ell+1)]^2}{2IkT}$$

moment of inertia

$$E_{ROT} = \frac{L^2}{2I}$$

ignore Z_{ROT}, Z_{vib} → not active ⇒ $= \underline{1}$

$$kT \ll \left(\hbar\omega_{rot}, \frac{\hbar^2}{I}\right)$$

$$Z_1^{TRANS} = \sum_{n_x=1}^{\infty}\sum_{n_y}^{\infty}\sum_{n_z}^{\infty} \left\{ e^{-\frac{1}{2mkT}\left(\frac{\pi\hbar n_x}{L}\right)^2} \times e^{-\frac{1}{2mkT}\left(\frac{\pi\hbar n_y}{L}\right)^2} \times e^{-\frac{1}{2mkT}\left(\frac{\pi\hbar n_z}{L}\right)^2} \right.$$

single molecule

$$= \left(\sum_{1}^{\infty} e^{-\frac{1}{2mkT}\left(\frac{\pi\hbar n}{L}\right)^2}\right)^3$$

Can do this x, y, z translations indep

Energies additive

$$Z = Z \times Z \times Z$$

So $$Z_{N\text{-gas}} = \frac{1}{N!}\left(\sum_{n=1}^{\infty} e^{-\frac{1}{2mkT}\left(\frac{\pi\hbar n}{L}\right)^2}\right)^{3N}$$

One molecule in one dimension.

$$Z_1^{\text{trans-}x} = \sum_{n=1}^{\infty} e^{-\frac{1}{2mkT}\left(\frac{\pi\hbar n}{L}\right)^2}$$

Can write this as:

$$Z_1^{\text{trans-}x} = \sum_{n=1}^{\infty} \underbrace{\Delta n}_{=1}\, e^{-\frac{1}{2mkT}\left(\frac{\pi\hbar n}{L}\right)^2}$$

put $p_n = \pi\hbar n / L$.

$$p_{n+1} - p_n = \frac{\pi\hbar}{L}\Big[\underbrace{(n+1)-n}_{\Delta n = 1}\Big]$$

so $$\Delta p_n = \frac{\pi\hbar}{L}\Delta n$$

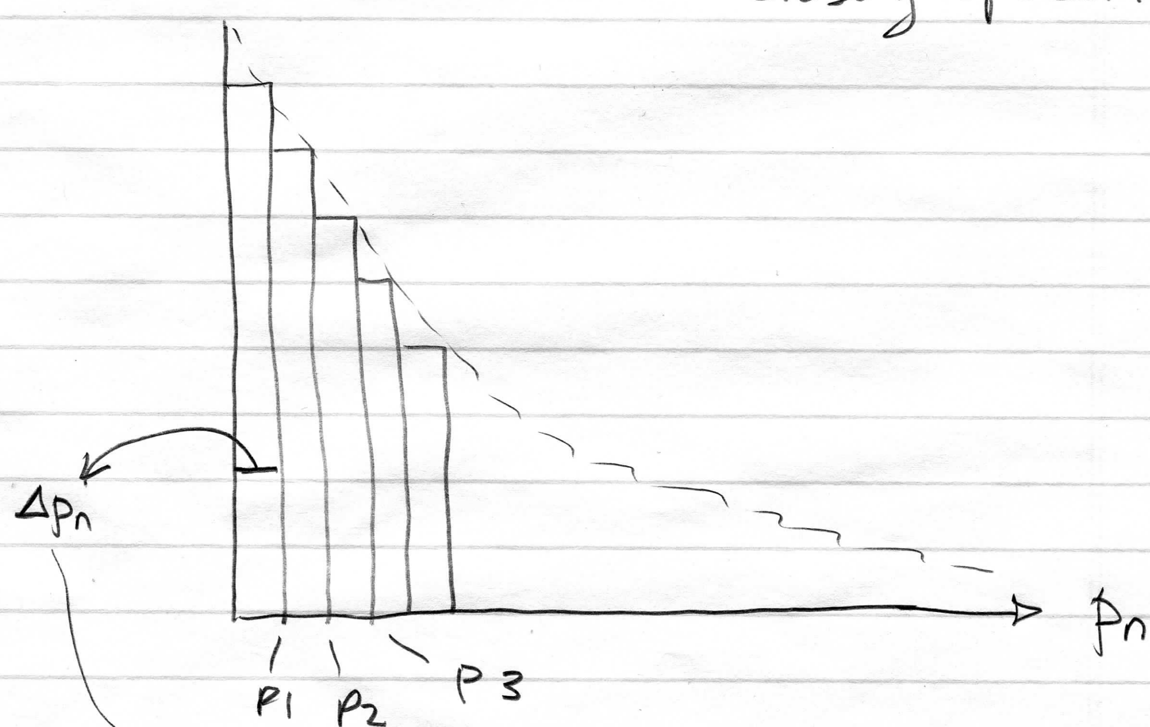
$$\hookrightarrow \Delta n = \frac{L}{\pi\hbar}\cdot\Delta p_n$$

so $\sum$ becomes

$$\sum_{n=1}^{\infty} \underbrace{\frac{L}{\pi\hbar}\,\Delta p_n}_{\Delta n}\, e^{-\frac{1}{2mkT}\cdot p_n^2}$$

$$Z_1^{\text{trans } x} = \frac{L}{\pi\hbar}\sum_{n=1}^{\infty} e^{\frac{-1}{2mkT}\cdot p_n^2}\cdot \Delta p_n$$

$\underbrace{\text{as } L \rightarrow \infty,\ \Delta p_n \rightarrow 0}_{\text{big box} \rightarrow \text{energy levels closely spaced.}}$



$$\Delta p_n = p_1 - p_0 = p_2 - p_1$$

In limit of $L \to \infty$, $\sum \to \int$

$$Z_1^{x\text{-trans}}\Big|_{L\to\infty} = \frac{L}{\pi\hbar}\int_0^{\infty} dp \cdot e^{-p^2/2mkT}$$

can put $L = \int_{-L/2}^{+L/2} dx$

less than ∞!

$$= \frac{L}{2\pi\hbar}\int_{-\infty}^{+\infty} dp_x\, e^{-p_x^2/2mkT}$$

$$= \frac{1}{2\pi\hbar}\int_{-L/2}^{+L/2} dx \int_{-\infty}^{+\infty} dp_x\, e^{-p_x^2/2mkT}$$

$$= \int \frac{dx\,dp_x}{2\pi\hbar}\, e^{-p_x^2/2mkT}$$

See Appendix $\to$ $\displaystyle\int_{-\infty}^{+\infty} e^{-ax^2}\,dx = \sqrt{\frac{\pi}{a}}$

Gaussian Integral

$$Z_1^{x\text{-tran}} = \frac{L}{2\pi\hbar}\sqrt{2\pi m k T}$$

$$= \frac{L}{l_Q} \qquad = \frac{2\pi\hbar}{\sqrt{2\pi m k T}}$$

$$l_Q = \frac{h}{\sqrt{2\pi m k T}} \longrightarrow \text{thermal De Broglie wavelength}$$

So $Z_1^{x\text{-tran}} = \frac{L}{h}(2\pi m k T)^{1/2}$

for N-particles

$$Z_N = \frac{1}{N!}\left(\frac{L}{h}(2\pi m k T)^{1/2}\right)^{3N}$$

$$= \frac{1}{N!}\left[L\left(\frac{2\pi m k T}{h^2}\right)^{1/2}\right]^{3N}$$

$$= \frac{1}{N!}\left[L^3\left(\frac{2\pi m k T}{h^2}\right)^{3/2}\right]^{N}$$

$$= \frac{V^N}{N^N e^{-N}}\left[\left(\frac{2\pi m k T}{h^2}\right)^{3/2}\right]^{N}$$

STIRLING

Helmholtz Free Energy

$$F = -kT \ln Z_N$$

$$F = -kT \ln \left\{ \frac{V}{N} \, e \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right\}^N$$

exponential.

$$= -NkT \left\{ \ln \left[\frac{V}{N} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right] + 1 \right\}$$

$$S = \left(-\frac{\partial F}{\partial T} \right)_{NV}$$

$$-\left(\frac{\partial F}{\partial T} \right)_{NV} = Nk \left\{ \ln \left[\frac{V}{N} \left(\; \right)^{3/2} \right] + 1 \right\} \frac{\partial T}{\partial T}$$

$$+ TNk \frac{\partial}{\partial T} \left\{ \ln \left[\frac{V}{N} \left(\cdots T \right)^{3/2} \right] + 1 \right\}$$

$$= Nk\left\{\ln\left[\frac{V}{N}\left(\quad\right)^{3/2}\right]+1\right\}$$

$$- TNk\frac{1}{\left[\quad\right]}\cdot\left[\quad\right]\frac{3}{2}T^{-1}$$

$$= Nk\left\{\ln\left[\frac{V}{N}\left(\quad\right)^{3/2}\right]+1\right\}+\frac{3}{2}Nk$$

$$S = Nk\left\{\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]+\frac{5}{2}\right\}$$

Sakur - Tetrode in terms of T rather than U

Can derive MACROSCOPIC variables.

$$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T}$$

$\ln Z$ ~

$$-\frac{\partial F}{\partial V} = NkT\left\{\frac{1}{\frac{V}{N}\cancel{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}}}\cdot\frac{1}{N}\cancel{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}}\right\}$$

$$P = \frac{NkT}{V} \rightarrow \underbrace{PV = NkT}_{\text{as we expect.}}$$

Also have: $\langle E\rangle = kT^2\frac{\partial}{\partial T}\ln Z$

as usual $Z = \frac{V^N}{N^N}e^N\left\{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\}$

$$\ln Z = N\ln\left\{\frac{V}{N}e\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\}$$

$$\frac{\partial \ln Z}{\partial T} = N\frac{\partial}{\partial T}\ln\left\{\ \downarrow\ \right\}$$

$$= N\frac{1}{\frac{V}{N}e(\,)^{3/2}}\cdot\frac{V}{N}e(\,)^{3/2}\cdot\frac{3}{2}\cdot T^{+}$$

$$\langle E\rangle = kT^2 N\cdot\frac{3}{2}\frac{1}{T} = \frac{3}{2}NkT$$

again as expected!

Earlier heard

$$Z_N^{\text{trans } x} = \frac{1}{N!}\left(\int \frac{dx\,dp_x}{2\pi\hbar}\, e^{-\frac{p_x^2}{2mkT}}\right)^{3N}$$

$$Z_N = \frac{1}{N!}\left(\int \frac{d^3\vec{r}_i\, d^3\vec{p}_i}{(2\pi\hbar)^3}\, e^{-\vec{p}^2/2mkT}\right)^{N}$$

$$Z_N = \frac{1}{N!}\int \frac{d^3\vec{r}_1 \cdots d^3\vec{r}_N \cdot d^3\vec{p}_1 \cdots d^3\vec{p}_N}{(2\pi\hbar)^{3N}}$$

$$\times\, e^{-\frac{1}{2mkT}\sum_{i=1}^{N}\vec{p}_i^{\,2}}$$

KEEP ON BOARD

Partition function of an N-particle classical ideal gas.

said $E_{gas} = \sum_{i=1}^{N} \frac{\vec{p_i}^2}{2m}$

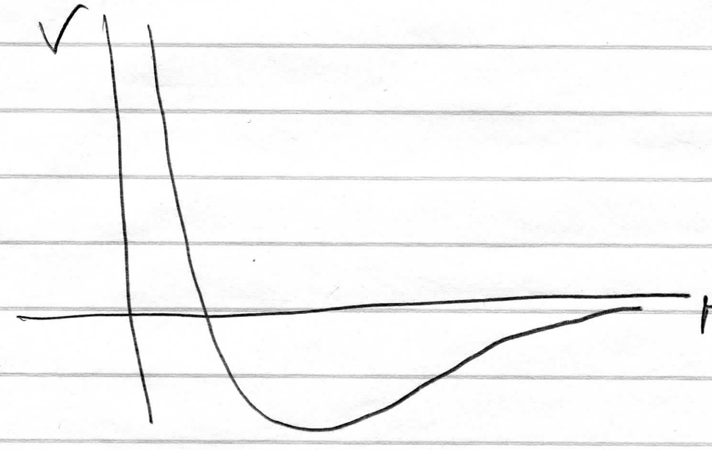
Assumes there is no interaction between particles

Say there is some interaction between particles

↳ described by potential energy $V(\vec{r_i} - \vec{r_j})$

$$E_{gas} = \sum_{i=1}^{N} \frac{\vec{p_i}^2}{2m} + \sum_{i>j}{}' V(\vec{r_i} - \vec{r_j})$$

an example is Van der Waal's force



$\bar{Z}_N$ for gas then becomes.

$$Z_N = \frac{1}{2}\int\left(\text{- - - - - - - -}\right) e^{-\frac{1}{kT}\left(\sum^{N}\frac{\vec{p}_i^{\,2}}{2m} + \sum_{i>j} V(\vec{r}_i - \vec{r}_j)\right)}$$

3N space positions

3N momenta

CLASSICAL Phase Space for N-particle gas.

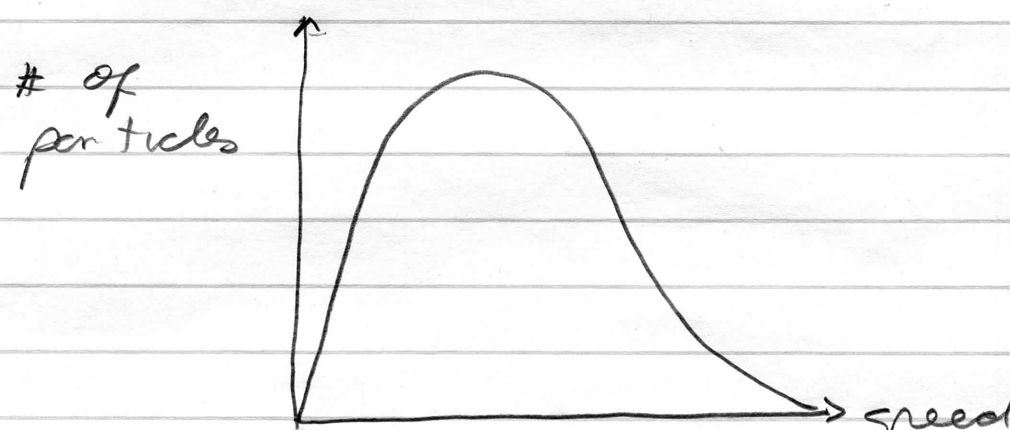
MAXWELL SPEED DISTRIBUTION

Say "speed" velocity is a VECTOR

Usually we have talked about AVERAGES

In a physical gas (even if ideal)

there will be a DISTRIBUTION of speeds



the partition function for the ideal gas is

$$Z_N = \frac{1}{N!}\int \frac{d^3\vec{p}_1 \cdots d^3\vec{p}_N}{(2\pi\hbar)^{3N}}\, e^{-\sum_i^N \vec{p}_i^{\,2}/2mkT}$$

$$P(E) = \frac{e^{-E/kT}}{Z}$$

$$\frac{\overbrace{P(\vec{r}_1 \cdots \vec{r}_N, \vec{p}_1 \cdots \vec{p}_N)}^{\text{Prob density}} \overbrace{d^3r_1 \cdots d^3r_N \, d\vec{p}_1 \cdots d\vec{p}_3}^{\text{volume}}}{(2\pi\hbar)^{3N}}$$

is the PROBABILITY that N particles have positions and momenta in the range

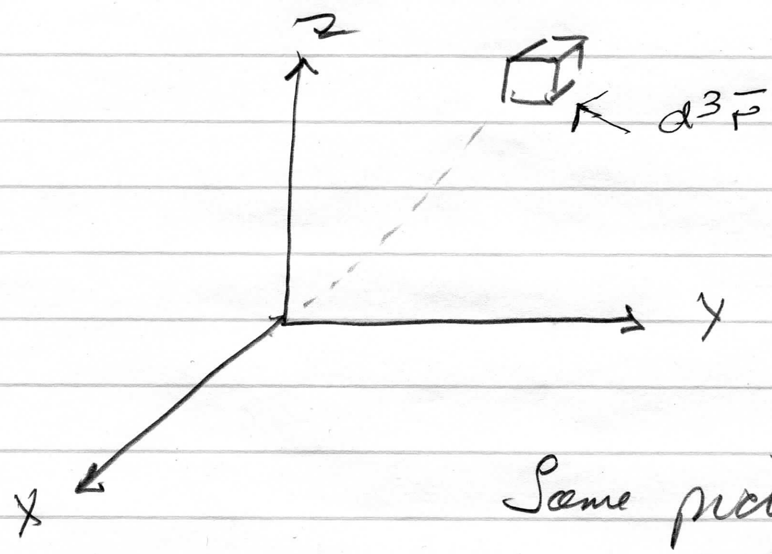
A volume in 6N-dimensional phase space.

$$\left.\begin{array}{l} (\vec{r}_1, \vec{r}_1 + d\vec{r}_1) \\ (\vec{r}_2, \vec{r}_2 + d\vec{r}_2) \\ \vdots \\ (\vec{r}_N, \vec{r}_N + d\vec{r}_N) \\ (\vec{p}_1, \vec{p}_1 + d\vec{p}_1) \\ (\vec{p}_2, \vec{p}_2 + d\vec{p}_2) \\ \vdots \\ (\vec{p}_N, \vec{p}_N + d\vec{p}_N) \end{array}\right\}$$

$$= \frac{1}{N!} \frac{e^{-\sum_{i=1}^{N} \vec{p}_i^{\,2}/2mkT} d^3\vec{r}_1 \cdots d^3\vec{r}_N \, d^3\vec{p}_1 \cdots d^3\vec{p}_N}{(2\pi\hbar)^{3N}}$$

$$\times \frac{1}{Z_N}$$

a small volume in 6N-dim phase space



Same picture for momentum.

$$\int \text{RHS} = \int \text{all PROBABILITY} = 1$$

particle is SOMEWHERE WITH SOME MOMENTUM

① $\int$ over POSITIONS of ALL particles

gives factor $\dfrac{V^N}{(2\pi\hbar)^3}$ ← volume of phase space

smallest quantum box

(2) $\int$ over ALL momenta, except one particle

→ Probability that one particle has momentum in the range.

$$\vec{p}_1 \to \vec{p}_1 + d\vec{p}_1$$

(3) $$Z_N = \frac{1}{N!}\,(Z_1)^N$$

identical particles

partition function for ONE PARTICLE

$$Z_N = \frac{1}{N!}\left(\int d^3p \cdot \frac{V}{(2\pi\hbar)^3} \cdot e^{-\vec{p}/2mkT}\right)^N$$

The $\int$s over $d^3\vec{p}_2 \ldots\ldots d^3\vec{p}_N$

not $\int$ over labels

will cancel $(N-1)$ factors in

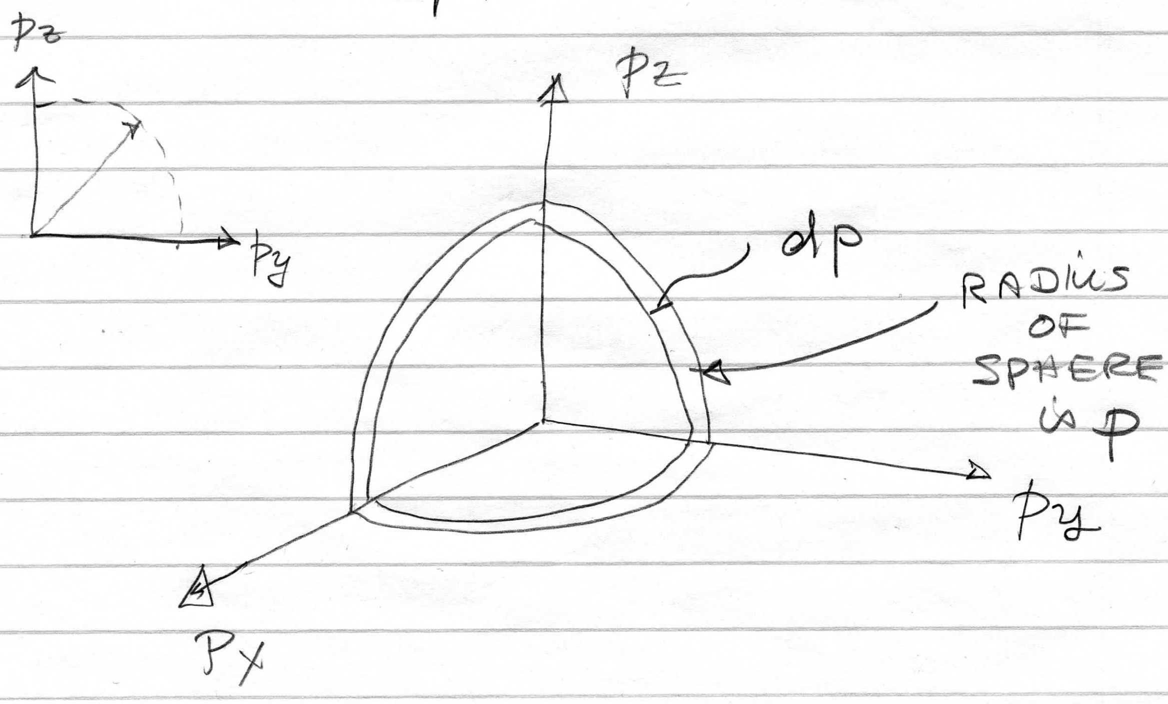
Z denominator

$$\tilde{P}(\vec{p}_1)\, d^3\vec{p}_1 = \frac{d^3 p_1\, e^{-\vec{p}_1^{\,2}/2mkT}}{\int d^3p'\, e^{-p'^2/2mkT}}$$

PROBABILITY that ONE of N particles in gas has momentum $\vec{p}_1$ which is between $\vec{p}_1$ and $\vec{p}_1 + d\vec{p}_1$

→ true for ANY PARTICLE so drop '1' label

Probability distribution is SPHERICALLY SYMMETRICAL



$$\tilde{P}(p)\, 4\pi p^2 dp = \frac{dp\ 4\pi p^2 e^{-p^2/2mkT}}{\int_0^\infty dp'\, 4\pi p'^2 e^{-p'^2/2mkT}}$$

→ Probability that momentum lies between 2 spherical shells

one radius p
second radius $p+dp$

in 3-d (p_x, p_y, p_z) momentum space

the 4π comes from $\int$ over all directions of momentum

So can write:

$$P(p)\,dp = 4\pi p^2 e^{-p^2/2mkT}\,dp \cdot C$$

some normalization ~~Constant~~ ~~that~~ makes

$$\int P(p)\,dp = 1$$

Probability particle has momentum with an ABSOLUTE value $|\vec{p}|$

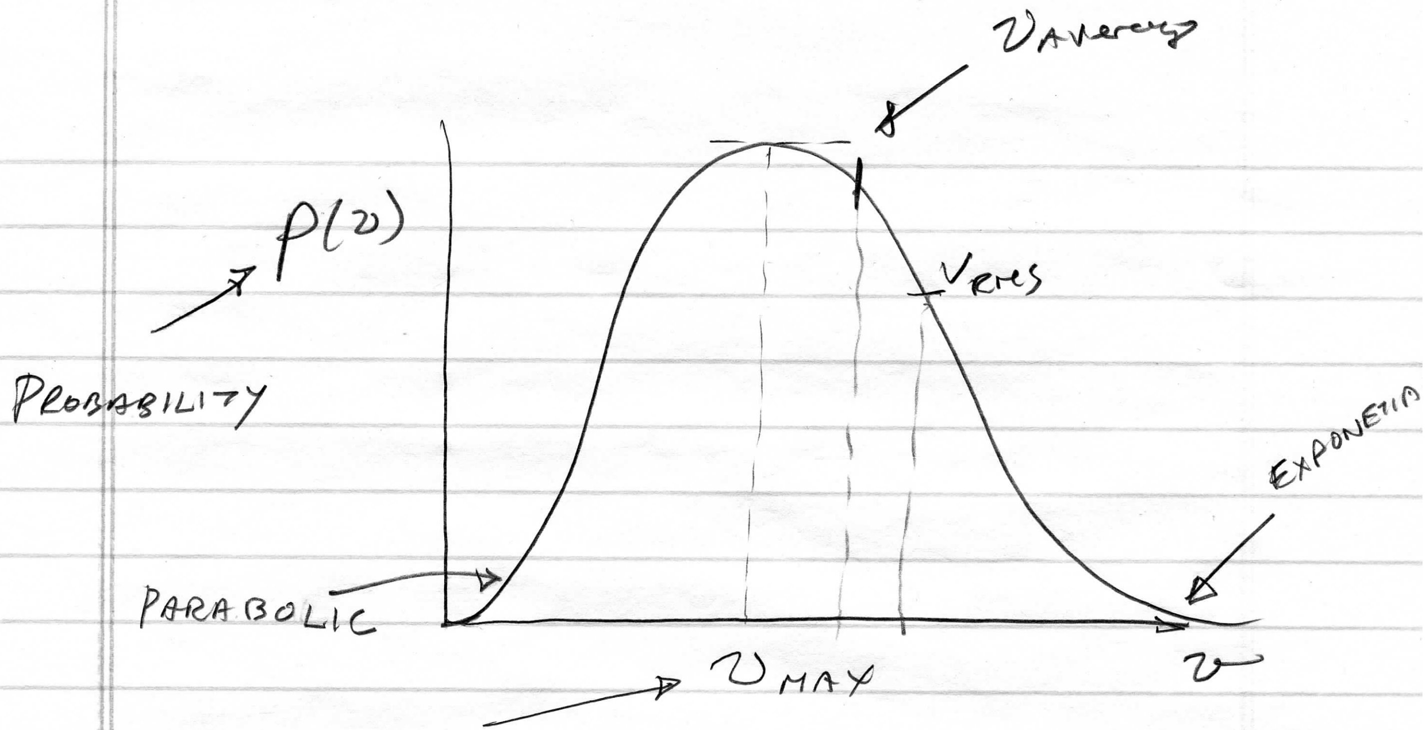
$|\vec{p}| = m|\vec{v}|$ "speed"

so DISTRIBUTION of SPEEDS

$$P(v)\,dv = 4\pi v^2 e^{-mv^2/2kT}\,dv \cdot C'$$

Probability ~~that~~ a particle in a gas in thermoDynamic Equilibrium has speed

$v \rightarrow v \rightarrow v + dv$



MOST LIKELY SPEED

$$P(v) = 4\pi v^2 e^{-\frac{mv^2}{2kT}} \left(\frac{m}{2\pi kT}\right)^{3/2}$$

C' comes from

$$\underbrace{\int_0^\infty P(v)\,dv = 1}_{\text{normalization}}$$

$v \rightarrow$ higher as $T \rightarrow$ higher.

Normalization

$$1 = \int_0^\infty P(v)\,dv$$

$$= 4\pi C \int_0^\infty v^2 e^{-mv^2/2kT}\,dv$$

put $x = v\sqrt{m/2kT}$

then $$1 = 4\pi C\left(\frac{2kT}{m}\right)^{3/2} \underbrace{\int_0^\infty x^2 e^{-x^2}\,dx}_{\sqrt{\pi}/4}$$

Gaussian $\int$

$$1 = \pi C \left(\frac{2kT}{m}\right)^{3/2} \sqrt{\pi}$$

$$C = \left(\frac{m}{2\pi kT}\right)^{3/2}$$

For MOST likely value of speed.

$$\frac{dP(v)}{dv} = 0$$

$$0 = 4\pi v^2 \frac{d}{dv}\left(e^{-\frac{mv^2}{2kT}}\right)$$

$$+ \; e^{-mv^2/2kT} \frac{d}{dv}\left(4\pi v^2\right)$$

$$= 4\pi v^2 \cdot \frac{d}{dv}\left(-\frac{mv^2}{2kT}\right) \cdot e^{-mv^2/2kT}$$

$$+ \; e^{mv^2/2kT} \cdot 8\pi v$$

$$= 8\pi v \, e^{-mv^2/2kT}\left(1 - \frac{4\pi v^2}{8\pi v} \cdot \frac{mv}{kT}\right)$$

$$= 8\pi v \, e^{-mv^2/2kT)} \underbrace{\left(1 - \frac{mv^2}{2kT}\right)}_{0 \text{ for max}}$$

$$v_{max} = \sqrt{\frac{2kT}{m}}$$

$$v^2_{RMS} = \int_0^\infty v^2 P(v)\, dv$$

$$= \int_0^\infty v^2 \cdot 4\pi v^2 e^{-mv^2/2kT} \cdot \left(\frac{m}{2\pi kT}\right)^{3/2}$$

change variable $x = \sqrt{\frac{m}{2kT}} \cdot v$

$$dx = \sqrt{\frac{m}{2kT}}$$

$$V^2_{RMS} = \left(\sqrt{\frac{m}{2\pi kT}}\right)^3 \cdot 4\pi \left(\sqrt{\frac{2kT}{m}}\right)^4 \cdot \sqrt{2kT/m}$$

$$\times \underbrace{\int_0^\infty x^4 e^{-x^2} dx}_{\frac{3}{8}\sqrt{\pi}}$$

$$\hookrightarrow \quad V_{rms} = \sqrt{\frac{3kT}{m}}$$

Maxwell distribution points.

$$P(v)dv = 4\pi v^2 e^{-\frac{mv^2}{2kT}} \left(\frac{m}{2\pi kT}\right)^{3/2}$$

low Temp small v $e^{-\cdots} \rightarrow 1 \rightarrow$ parabola

$$P(v)dv \rightarrow 0 \text{ as } v \rightarrow 0$$

high Temp $P(v)dv$ also $\rightarrow 0$ as $v \rightarrow \infty$

$\hookrightarrow e^{-\cdots} \rightarrow 0.$

Numerically v_{MAX} for N_2 in air

at Room temp $300K \rightarrow 422\ m/s$

QUANTUM GASES

had $Z_n = \frac{1}{N!}\left(Z_1^{3}\right)^N$

$$Z_1^{3} = \left(\frac{L}{l_Q}\right)^3$$

Use STIRLING

$$Z_N \approx \left(\frac{L^3 e}{N l_Q^3}\right)^N$$

$$l_Q = \frac{2\pi\hbar}{\sqrt{2\pi m k T}} = \frac{h}{\sqrt{2\pi m k T}}$$

Notice as l_Q^3 becomes $> \frac{L^3 e}{N}$

because of lns

$$S \sim \ln Z_1 \sim \ln\left(\frac{L^3 e}{N l_Q^3}\right)$$

$$\approx \ln\left(\frac{L^3 e}{N}\right) - \ln\left(l_Q^3\right)$$

we had

$$S = Nk \left\{ \ln\left[\frac{L^3}{N} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right] + \frac{5}{2} \right\}$$

$$= Nk \left\{ \ln\left[\frac{L^3}{N} \left(\frac{1}{l_Q^2} \right)^{3/2} \right] + \frac{5}{2} \right\}$$

$$= Nk \left\{ \ln\left[\frac{L^3/N}{l_Q^3} \right] + \frac{5}{2} \right\}$$

$$S \approx Nk \ln \frac{L^3/N}{l_Q^3} \leftarrow$$ volume per particle

$l_Q > L^3/N \longrightarrow$?!?

"thermal de Broglie wavelength"

$$l_Q \sim \frac{h}{p_{THERMAL}}$$

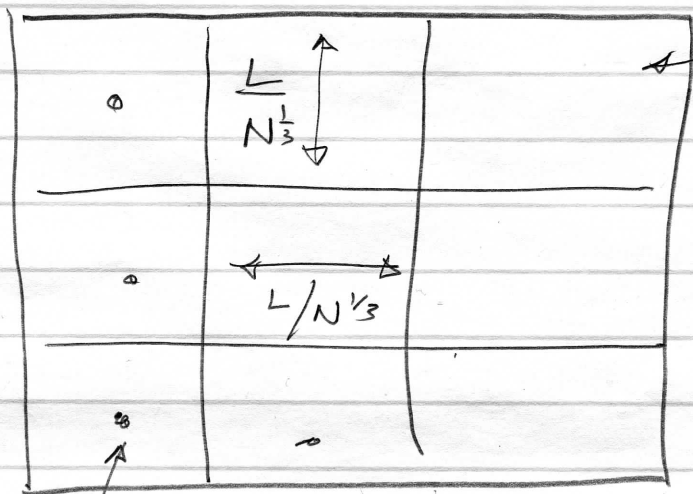
momentum

$$p_{TH} \sim \sqrt{mkT}$$

de Broglie $\lambda \sim h/p$

forget 2π's (Feynman)

$$l_Q \sim \frac{h}{\sqrt{mkT}}$$



size of box containing 1 particle $\sim \frac{L}{N^{1/3}}$

classical particle

$$l_Q \ll \frac{L}{N^{1/3}}$$

quantum size

$m \uparrow \quad l_Q \downarrow$

$T \uparrow \quad l_Q \downarrow$

if T is hi enough l_Q can be made as small as you want as $T \downarrow$ $l_Q \uparrow$

if T is small l_Q becomes bigger than box size

For $l_Q \gtrsim \left(\frac{V}{N}\right)^{1/3} \rightarrow$ quantum gas.

Air molecules are 3×10^{-9} m apart, $l_Q \sim 2 \times 10^{-11}$

Fermions & Bosons.

close together occupy same states