LAST TIME:

MICROSTATES
MACROSTATES

ANALOGY

4 COINS FLIPPED

H H H H

	H	H	H	T
EQUALLY	H	H	T	H
LIKELY	H	T	H	H
	T	H	H	H

MACROSTATE w/ 1 TAIL ~~DOWN~~

IN ISOLATED SYSTEM IN THERMAL EQUILIBRIUM, ALL ACCESSIBLE MICROSTATES ARE EQUALLY PROBABLE

$q = 6 \qquad N = 4$

1	2	3	4	
6	0	0	0	EQUALLY PROBABLY
1	1	2	2	

(10)

REAL SYSTEMS

30g OF ALUMINUM 26.98 g/mol

$\frac{30g}{26.98g}$ mol ~ 1 mol

6.022×10^{23} ATOMS

~~SO~~ DEALING W/ THESE NUMBERS LOOKS VERY DIFFERENT

~~SMALL NUMBERS~~

FOR EXAMPLE,

$10^{23} + 23 = 10^{23}$

SO $10^{10^{23}} \times 10^{23} = 10^{23 + 10^{23}} = 10^{10^{23}}$ STRANGE

TO KEEP TRACK JUST TAKE LOG

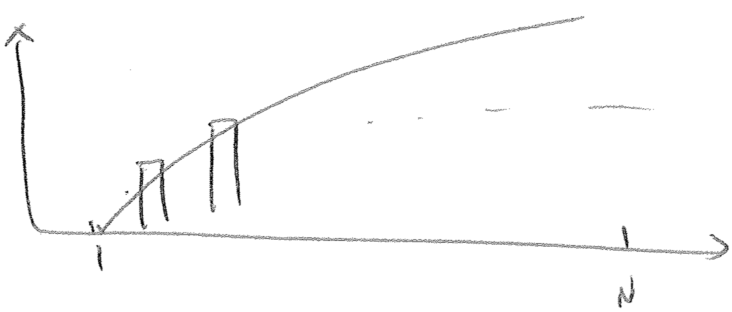
11

STIRLING'S APPROXIMATION

$$N! = N^N e^{-N} \sqrt{2\pi N} \qquad N \gg 1$$

$$\boxed{\ln N! \simeq N \ln N - N} \qquad N \gg 1$$

$$\ln N! = \ln 1 + \ln 2 + \ln 3 \cdots + \ln N$$



$$= \int_1^N \ln x \, dx = \left[x \ln x - x \right]_1^N$$

$$= N \ln N - N + 1$$

$$\sim N \ln N - N \qquad N \gg 1$$

(12)

MULTIPLICITY OF LARGE EINSTEIN SOLID AT HIGH TEMPERATURE

$N \gg 1, \quad q \gg N$

$$\Omega = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!\,(N-1)!} \approx \frac{(q+N)!}{q!\,N!}$$

$$\ln \Omega = \ln\left(\frac{(q+N)!}{q!\,N!}\right)$$

$$= \ln (q+N)! - \ln q! - \ln N!$$

$$= (q+N)\ln(q+N) - (q+N) - q\ln q + q - N\ln N + N$$

$$= (q+N)\ln(q+N) - q\ln q - N\ln N$$

$$= (q+N)\ln q\left(1+\frac{N}{q}\right) - q\ln q - N\ln N$$

~~CONSIDER $q \gg N$ HIGH TEMP LIMIT~~

$$= (q+N)\left[\ln q + \ln\left(1+\frac{N}{q}\right)\right] - q\ln q - N\ln N$$

$$= (q+N)\ln q + (q+N)\ln\left(1+\frac{N}{q}\right) - q\ln q - N\ln N$$

$$= (q+N)\ln q + (q+N)\left(\frac{N}{q}\right) - q\ln q - N\ln N$$

(13)

$$\ln \Omega = N \ln \frac{q}{N} + N + \frac{N^2}{q}$$

$N >> 1 \quad q >> N$

$$\ln \Omega = N \ln \frac{q}{N} + N$$

$$\Omega = e^{N \ln \frac{q}{N} + N} = \cancel{e^{N \ln (q/N)}} \cdot e^{N}$$

$$= \left(e^{\ln \frac{q}{N} + 1}\right)^N$$

$$\boxed{\Omega = \left(\frac{q}{N} e\right)^N}$$

14

SHARPNESS OF MULTIPLICITY

A $\quad q_A \quad , N$

B $\quad q_B \quad , N$

$$\Omega_{TOTAL} = \left(\frac{e\,q_A}{N}\right)^N \left(\frac{e\,q_B}{N}\right)^N$$

$$q_A + q_B = q$$

$$\Omega_{MAX} = \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N}$$

$$q_A = \frac{q}{2} + x \qquad q_B = \frac{q}{2} - x$$

$$\Omega = \left(\frac{e}{N}\right)^{2N} \left[\left(\frac{q}{2}\right)^2 - x^2\right]^N$$

15

$$\ln\left[\left(\frac{q}{2}\right)^2 - x^2\right]^N = N \ln\left[\left(\frac{q}{2}\right)^2 - x^2\right]$$

$$= N \ln\left[\left(\frac{q}{2}\right)^2\left[1 - \left(\frac{2x}{q}\right)^2\right)\right.$$

$$= N\left[\ln\left(\frac{q}{2}\right)^2 + \ln\left(1 - \left(\frac{2x}{q}\right)^2\right)\right]$$

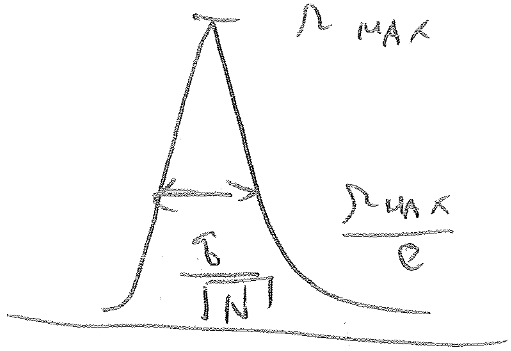
$$\cong N\left[\ln\left(\frac{q}{2}\right)^2 - \left(\frac{2x}{q}\right)^2\right]$$

$$\Omega = \left(\frac{e}{N}\right)^{2N} e^{N \ln(q/2)^2} \cdot e^{-N\left(\frac{2x}{q}\right)^2}$$

$$= \Omega_{MAX}\, e^{-N(2x/q)^2}$$

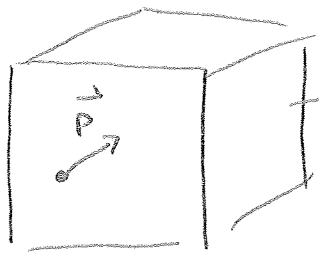
GAUSSIAN

(16)



IF $\frac{8}{\sqrt{N}} \ll 1$ THEN THERMODYNAMIC LIMIT

IDEAL GAS : SEEMS IT WOULD BE COMPLICATED



MULTIPLICITY

HOW MANY WAYS CAN YOU HAVE PLACED A GAS MOLECULES IN 3D SPACE WITH GIVEN ENERGY?

<u>MOMENTUM SPACE (OR P-SPACE)</u>

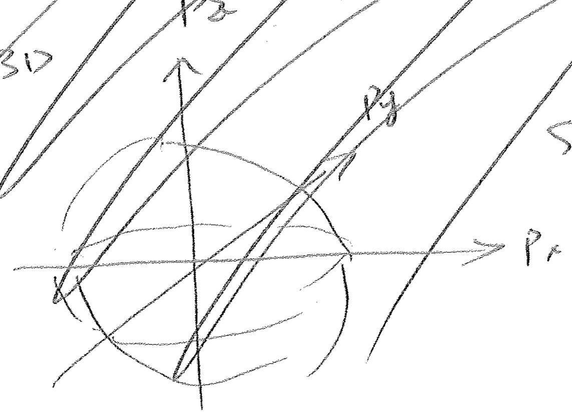
1D EXAMPLE

IF $E = \frac{p^2}{2m}$ $|p| = \sqrt{2mE}$

~~SAY YOU HAVE~~ E_{MAX}

~~THEN $p < \sqrt{2mE_{MAX}}$~~

~~3D~~

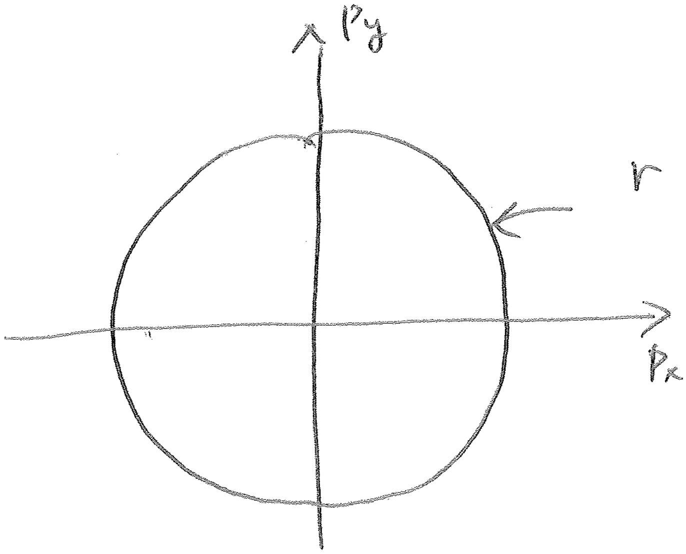


SPHERE.

2D

$$\frac{p_x^2}{2m} + \frac{p_y^2}{2m} = E$$

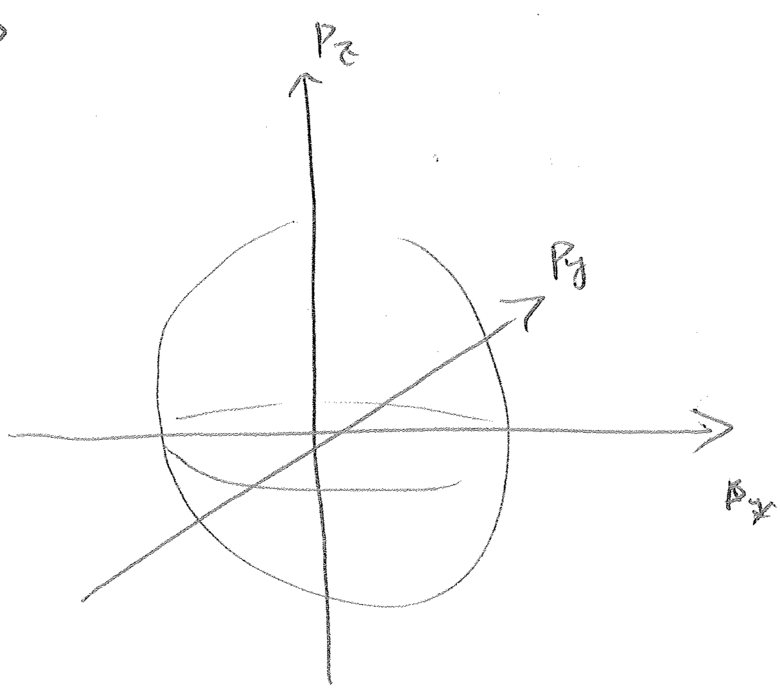
$$p_x^2 + p_y^2 = 2mE$$



$r = \sqrt{2mE}$

CIRCUMFERENCE

3D



SHELL

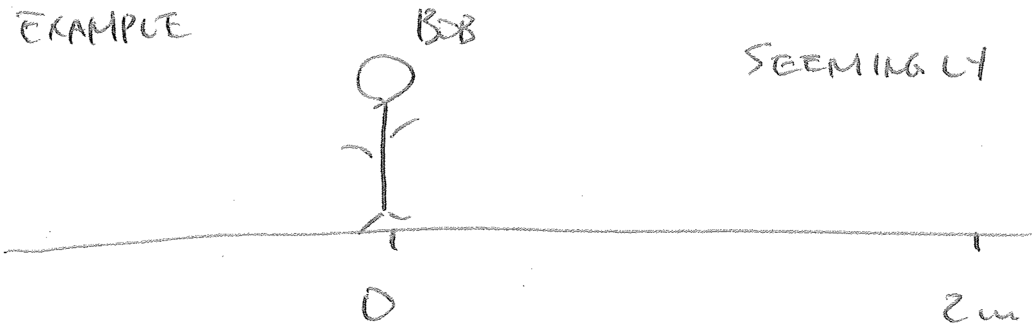
AREA = $4\pi r^2$

VOLUME = $\frac{4\pi r^3}{3}$

$$\frac{d\,\text{VOLUME}}{dr} = 4\pi r^2 = \text{AREA}$$

OK. BUT HOW DO WE COUNT POSSIBILITIES OF CONTINUOUS THINGS

EXAMPLE



SEEMINGLY INFINITE?

~~$\Delta x \, \Delta p_x$~~ ~~Δy~~

$$\Delta x \, \Delta p_x \approx h$$

$$\Delta y \, \Delta p_y \sim h$$

$$\Delta z \, \Delta p_z \sim h$$

$$\Delta V \, \Delta V_p = h^3$$

$$\text{AREA} = \frac{2\pi^{d/2} \, r^{d-1}}{\left(\frac{d}{2}-1\right)!}$$

$$\Omega_1 = \frac{V \, A_p \cdot dp}{h^3}$$

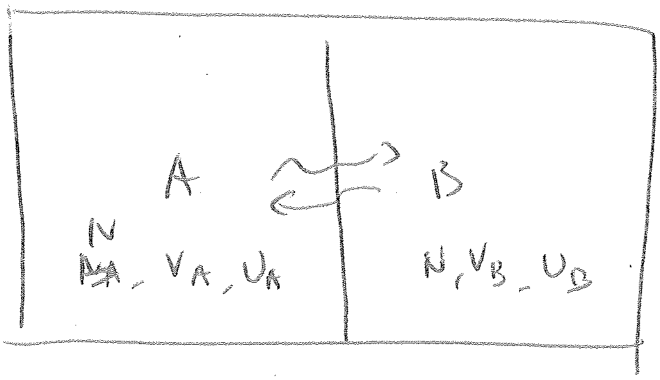
$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} \left(\sqrt{2mU}\right)^{3N-1}$$

$$= f(N) \, V^N \, U^{3N/2}$$

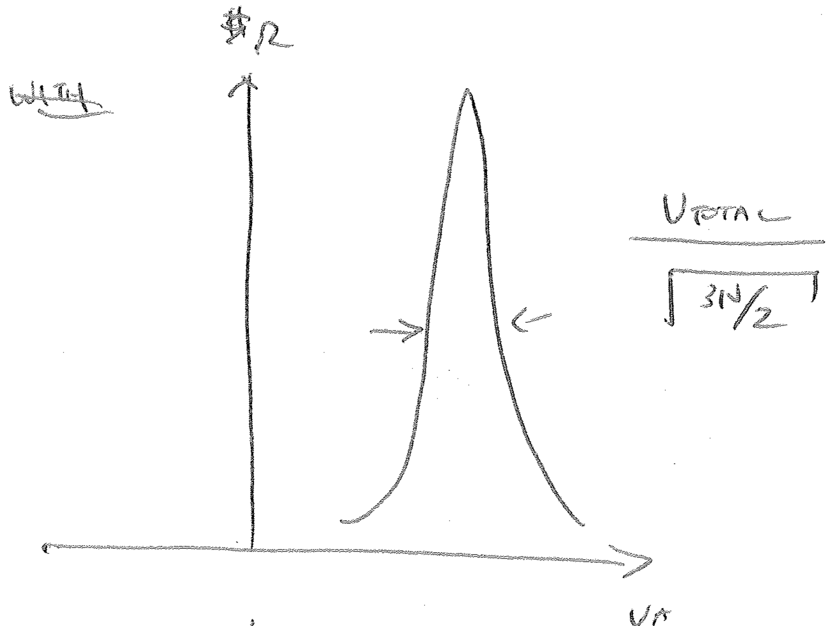
$3N-1 \approx 3N$

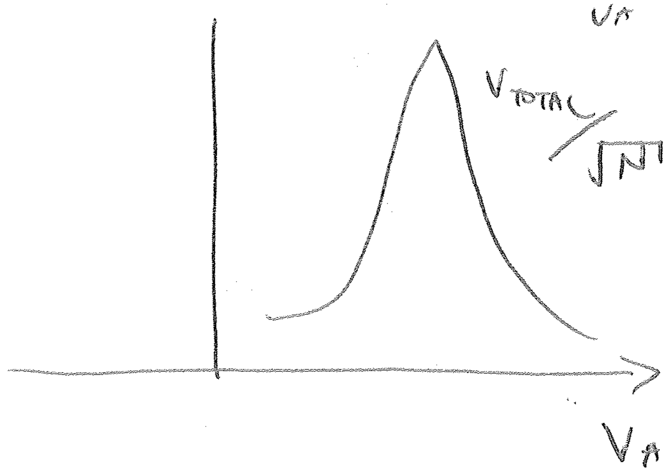
$\left(\frac{3N}{2}-1\right)! \approx \frac{3N}{2}$

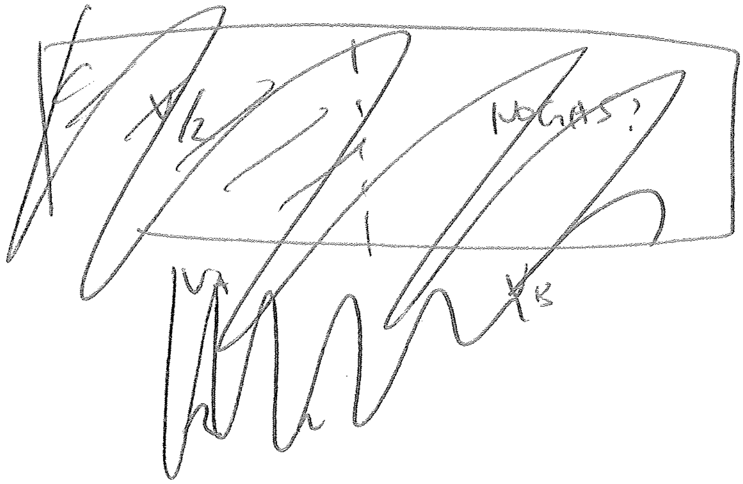
INTERACTING GASES

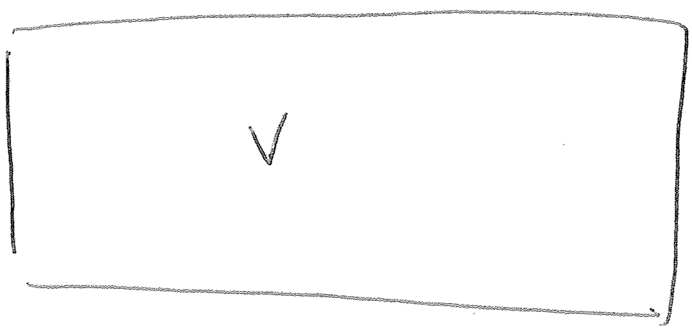


$$\Omega_{TOTAL} = [f(N)]^2 \, (V_A V_B)^N \, (U_A U_B)^{3N/2}$$

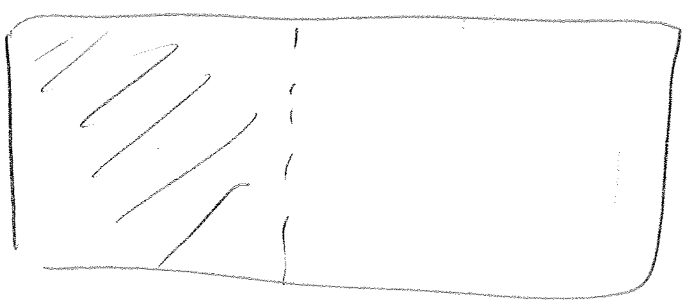








$$\Omega(U, V, N) = f(N)\, V^N\, U^{3N/2}$$



$$\Omega\left(U, \frac{V}{2}, N\right) = f(N)\left(\frac{V}{2}\right)^N U^{3N/2} = \frac{\Omega(U, V, N)}{2^N}$$

NOT LIKELY

ENTROPY

ANY SYSTEM IN THERMAL EQUILIBRIUM

↳ IN MACROSTATE W/ LARGEST MULTIPLICITY

i.e. MULTIPLICITY TENDS TO INCREASE

ENTROPY

$$S = k \ln \Omega$$

$$S \ (J/K)$$

EINSTEIN SOLID

$$\Omega = \left(\frac{eq}{N}\right)^N$$

$$S = k \ln \Omega = k \ln \left(\frac{eq}{N}\right)^N = Nk \{ \ln \frac{eq}{N}$$

$$\cancel{Nk \left(\ln\left(\frac{q}{N}\right)+1\right)}$$

$N = 10^{22}$ $\quad q = 10^{24}$

$$S = Nk \ln \frac{2.73 \cdot 10^{24}}{10^{22}} = 10^{22} k \ln 273$$

$$= 0.77\, J/K$$

EXAMPLE

ICE → WATER

↑

MORE MULTIPLICITY

LATTICE w/ A DEFECT

MORE MULTIPLICITY

MORE DISORDER

~~UNSORTED → SOR~~

SORTED → UNSORTE

PPT

SECOND LAW

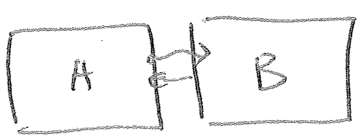
ANY LARGE SYSTEM IN THERMAL EQUILIBRIUM IS IN THE MACROSTATE W/ THE GREATEST ENTROPY

ENTROPY TENDS TO INCREASE

Ex

ADDITIVE QUALITY OF ENTROPY

Ex:



$$\Omega_{TOTAL} = \Omega_A \Omega_B$$

$$S_{TOTAL} = k \ln \Omega_T = k \ln \Omega_A \Omega_B$$

$$= k \ln \Omega_A + k \ln \Omega_B$$

$$= S_A + S_B$$