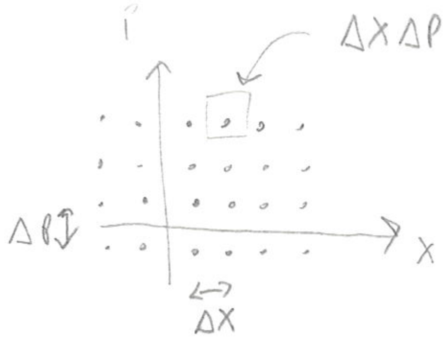
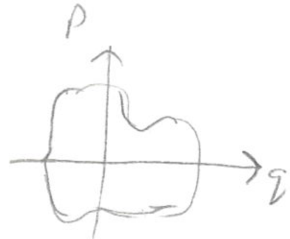
4.1



(1) Ω = # of states for macrostate

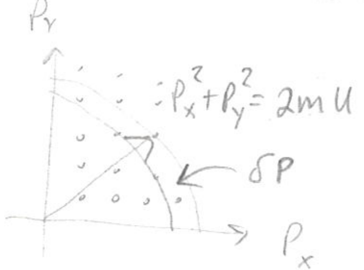
$E = H(p, q)$

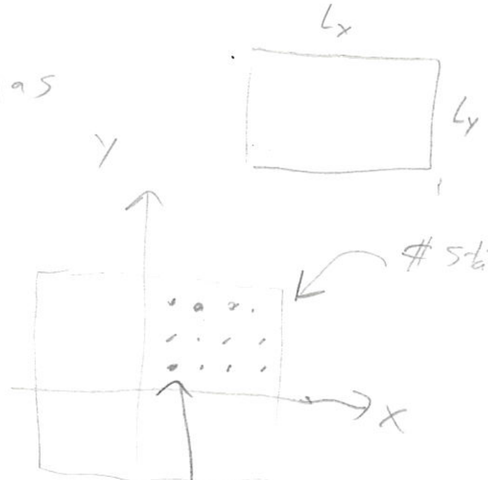


p & q continuous

$\Omega = \infty$!

(3) Consider monatomic gas





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

for each of these there's a whole set of these

Shell δU thick:

uncertainty in U due to p

$$\delta p = \delta\left(\sqrt{2mU}\right) = \sqrt{\frac{m}{2U}}\, \delta U$$

thickness

$$\frac{\delta p \cdot 2\pi \sqrt{2mU}}{\Delta p_x\, \Delta p_y} \cdot \frac{L_x L_y}{\Delta x\, \Delta y}$$

circumference

"Volume" and "area"

$$\frac{V_p}{\Delta p_x \Delta p_y} \cdot \frac{V}{\Delta x \Delta y} = \frac{V_p \cdot V}{h^2}$$

4.2

area of $P_x^2 + P_y^2 + P_z^2 = 2mU$

3D $\quad \Omega = \dfrac{V_p \cdot V}{h^3} = \dfrac{\delta P \cdot 4\pi (\sqrt{2mU})^2 \cdot V}{h^3}$

3D, N particles

"area" of $P_{1x}^2 + P_{1y}^2 + P_{1z}^2 + P_{2x}^2 + \ldots P_{Nz}^2 = 2mU$

$$\Omega_N = \frac{1}{N!} \frac{\delta P A_p \cdot V^N}{h^{3N}} \qquad V = L_x L_y L_z$$

☆ area of hypersphere $= \dfrac{2\pi^{d/2}}{\left(\frac{d}{2}-1\right)!} r^{d-1} \qquad n! = \Gamma(n+1)$

$\frac{1}{2}! = \sqrt{\pi}/2$

$\uparrow_1 \nwarrow_2$ & $\uparrow_2 \nwarrow_1$ are same state, but counted twice ab

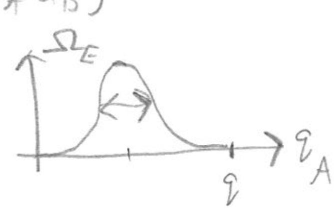
$\rightarrow \times \frac{1}{2}$ to count once $\rightarrow \frac{1}{N!}$

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

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

two **interacting**: $\Omega_{tot} = f(N)^2 (V_A V_B)^2 (U_A U_B)^{3N/2}$

c.f. $\Omega_E = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N \quad$ width $\approx q/\sqrt{N}$



so Ω_N has width V_A: $V_{tot}/\sqrt{N}$

width U_A: $U_{tot}/\sqrt{3N/2}$

4.3

instead of Ω, use its log

for historical reasons, mult. by k

$\rightarrow$ $$S = k \ln \Omega$$ entropy

entropy add: $\Omega_{tot} = \Omega_1 \cdot \Omega_2$ $\quad S_{tot} = S_1 + S_2$

2nd Law of thermodynamics: At equilibrium system will be in the macrostate with the largest Ω $\rightarrow$ largest S.

~~And~~ S (Ω) tends to increase

Sometimes S described as disorder (e.g. molecules on one side of box)

But this is subjective.

more particles
more energy $\Rightarrow$ higher S
bigger volume

4.4

Entropy

Any large system will be found in macrostate w/ largest Ω

Ω tends to increase

Ω large $\rightarrow$ entropy $S \equiv k \ln \Omega$

convention

Einstein solid $\Omega = (eq/N)^N$

$$S = k \ln \left(\frac{eq}{N}\right)^N = Nk\left[\ln \frac{q}{N} + 1\right]$$

$$q >> N$$

$$10^{24} >> 10^{22}$$

$$\rightarrow S = 0.77 \text{ J/K}$$

More particles $\rightarrow$ larger S

" Energy $\rightarrow$ larger S

4.5

irreversible — process that increases entropy

reversible — doesnt increase entropy

stir salt into soup: Na & Cl ions can be anywhere in soup ⇒ more μstates

scramble egg: mix molecules from yolk & white
also denature (unfold) protein molecules

humpty dumpty: more ways to be broken than whole

Wave destroying Sand castle: more ways for sand to be scattered than to be in a castle

Cut down tree: different angles for fallen tree, many configs of sawdust

burn gas: small number of long molecules
→ larger number of exhaust molecules.

thermal Energy released, more ways for exhaust molecules to move

4.6

1 mole He @ STP, $V = 0.025\,m^3$ $\quad \frac{3}{2}nRT = 3700\,J = U$

$$\rightarrow S = Nk\left[\ln 330{,}000 + 5/2\right] \approx 126\ J/K$$

in SI units, typical $S \approx O(1) - O(100)$

<u>NOT</u> Avogadro's # or $\frac{1}{A.\#}$

$$S = k\left\{\ln f(N) + \ln V^N + \ln U^{3N/2}\right\}$$

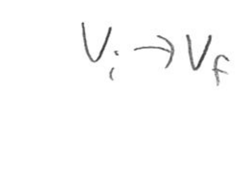
<u>Note</u> $\quad S = Nk \ln V + f(N, U, h)$

So $V_i \rightarrow V_f$: $\Delta S = Nk \ln \frac{V_f}{V_i} + \cancel{f(N,U,h) - f(N,U,h)}$

But increasing N (add particles) V (expand) or U (add heat)

<u>all</u> increase S

<u>free expansion</u> $\quad$ no work, no heat, $\Delta U = 0$



V changes (increase) so S increases

Spontaneously changes towards larger S

4.7

$$\frac{S}{K} = \ln\left[\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{3N/2}}{(3N/2)!}(2mU)^{3N/2}\right]$$

$$= \ln\left[\frac{1}{N!}\frac{V^N}{\boxed{(3N/2)!}}\left(\frac{2mU\pi}{h^2}\right)^{3N/2}\right]$$

$$\simeq \ln\left(\frac{2\pi m U}{h^2}\right)^{\frac{3N}{2}} + N\ln V - \left(N\ln N + N\right) - \boxed{\left(\frac{3N}{2}\right)\ln \frac{3N}{2} + \frac{3N}{2}}$$

$$\simeq N\left[\ln\left(\frac{2\pi m U}{h^2}\right)^{\frac{3}{2}} + \ln\frac{V}{N} + 1 + \boxed{-\frac{3}{2}\ln\frac{3N}{2} + \frac{3}{2}}\right]$$

$$\simeq N\left[\ln\left(\frac{2\pi m U}{h^2}\right)^{\frac{3}{2}} + \ln\frac{V}{N} + \frac{5}{2} - \ln\left(\frac{3N}{2}\right)^{3/2}\right]$$

$$\simeq N\left[\ln\left(\frac{2\pi m U}{h^2}\frac{2}{3N}\right)^{3/2} + \ln\frac{V}{N} + \frac{5}{2}\right]$$

$$\frac{S}{K} \simeq N\left[\ln \frac{V}{N}\underbrace{\left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{3/2}}_{[\ ] = V^{-1}} + \frac{5}{2}\right]$$

Sakur-Tetrode equation

$\frac{V}{N}$: volume per particle, unchanged by partition

$\frac{U}{N}$: energy " " " " "

4.8 1 mole Argon at room temp & 1 atm

(Schroeder 2.33)

$$\frac{V}{N} = \frac{kT}{P} = \frac{(1.38\times10^{-23}\ J/K)(300K)}{10^5\ N/m^2} = 4.14\times10^{-26}\ m^3$$

$$\frac{U}{N} = \frac{3}{2}kT = \frac{3}{2}(1.38\times10^{-23}\ J/K)(300\ K) = 6.21\times10^{-21}\ J$$

Argon mass is 40 u or 6.64×10^{-26} Kg so

$$\frac{V}{N}\left(\frac{4\pi m U}{3h^2 N}\right)^{3/2} = (4.14\times10^{-16}\ m^3)\left(\frac{4\pi\times6.64\times10^{-26}\ Kg\times6.21\times10^{-21}\ J}{3(6.63\times10^{-34}\ J/s)}\right)^{\frac{3}{2}}$$

$$= 1.02\times10^7$$

$$S = Nk\left[\ln(1.02\times10^7) + \frac{5}{2}\right]$$

$$= Nk\left[16.14 + \frac{5}{2}\right] =$$

$$= (6.022\times10^{23}\times1.38\times10^{-23}\ J/K)\left[16.14 + \frac{5}{2}\right]$$

$$= 155\ J/K$$

4.9 explain

$S \propto N_\gamma$ first

relate to $S \propto N$ generally

$T_{sun} \approx 6000K$

$E_\gamma = \hbar\omega_{sun}$

E

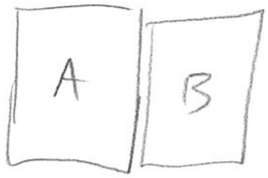
$T_E \approx 300K$

$E_\gamma = \hbar\omega_E = \frac{1}{20}\hbar\omega_{sun}$

$S_\gamma \propto N$

$\rightarrow$ for each 1 unit of S delivered by sunlight, 20 units produced by Earth

4.10 Entropy of Mixing



2 different gases

remove partition

$$\Delta S_A = NK \ln \frac{V_f}{V_i} = NK \ln 2$$

$V_f = 2V_i$

Same for B: $\Delta S_B = NK \ln 2 \rightarrow \Delta S_{tot} = 2NK \ln 2$ Entropy of Mixing

But if you had the same gas on both sides ... you could reversibly remove & replace the partition which does not affect distribution over accessible states

$\rightarrow \Delta S = 0$

<u>Partitioned</u>

$$S = K \frac{N}{2}\left[\ln\left[\frac{V/2}{N/2}\left(\frac{4\pi m U/2}{3h^2 N/2}\right)^{3/2}\right] + 5/2\right]$$

+ same

So partitioning gives $\Delta S = 0$

as long as this is here

Came from $1/N!$
w/o that, partition would DECREASE S
Gibb's paradox

4.11

Interacting gases – just enough to exchange energy

N particles in each (same particles)

$$\Omega_{tot} = \Omega_A \, \Omega_B$$

$$= f(N)^2 \, (V_A V_B)^N \, (U_A U_B)^{\frac{3N}{2}}$$

use $U_B = U - U_A$ $\qquad e^{\frac{3N}{2}\ln U_A (U - U_A)}$

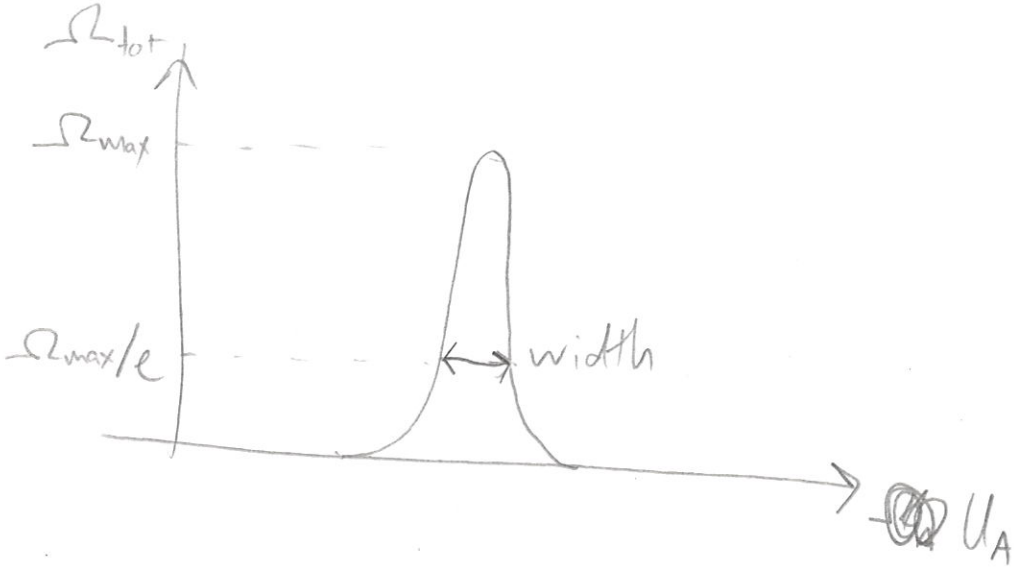
Same method as Einstein solid $\quad e^{\ln \Omega_{tot}(U_A)}$

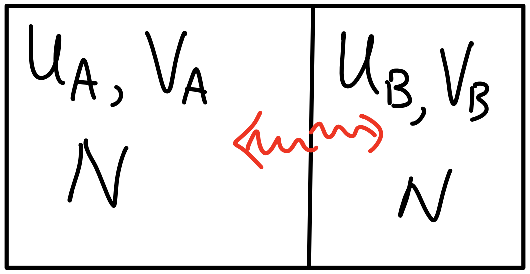
c.f. $\Omega \propto (q - q_A)^N q_A^N \to \Omega \propto \exp\left(-N\left(\frac{2x}{q}\right)^2\right)$

$\to$ gaussian w/ width $= \dfrac{U_{tot}}{\sqrt{3N/2}}$

5/12 $\to$

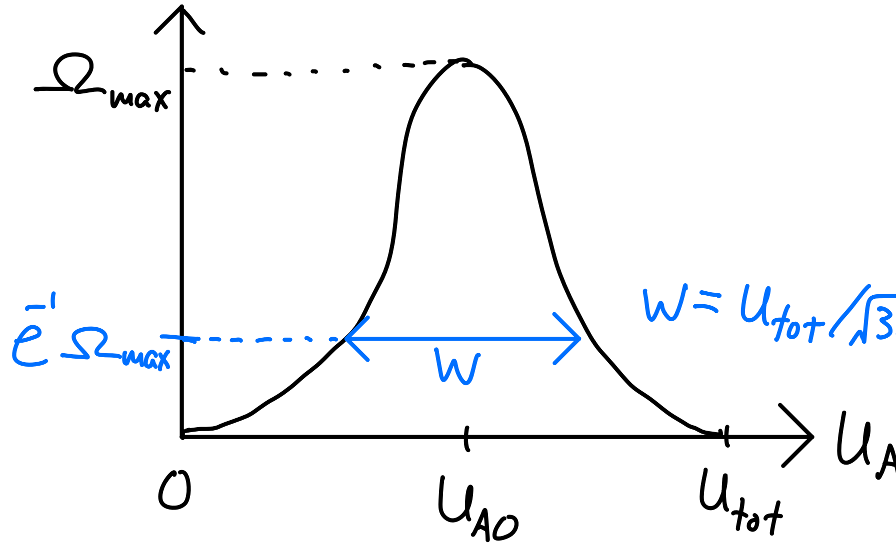
w/ $V = V_A + V_B \to$ (i.e. exchange volume via piston.) $\qquad$ width $= \dfrac{V_{tot}}{\sqrt{N}}$





$$\Omega_{tot} = \Omega_A \cdot \Omega_B$$
$$= f(N)^2 (V_A V_B)^N (U_A U_B)^{\frac{3N}{2}}$$

$$\Omega_{tot} = \Omega_{max} \exp\left(-(U_A - U_{A0})^2 / w^2\right)$$



$U_A - U_{A0}$	Ω_{tot}
0	Ω_{max}
$1 \cdot W$	$e^{-1}\,\Omega_{max}$
$2 \cdot W$	$e^{-4}\,\Omega_{max}$
$\vdots$	
$10 \cdot W$	$e^{-100}\,\Omega_{max}$

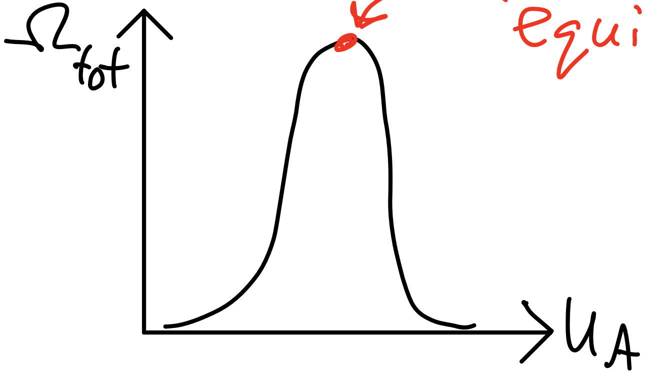
if $N = 6 \times 10^{23}$

$$\frac{1}{\sqrt{3N/2}} \simeq 10^{-12}$$

so $U_A = U_{A0} + 10W$

$$= U_{A0}(1 + 10^{-11})$$

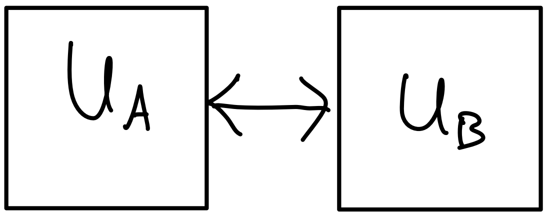
VERY close to U_{A0}



equilibrium : $\dfrac{d\Omega_{tot}}{dU_A} = 0 \rightarrow \dfrac{dS_{tot}}{dU_A} = 0$

$$\frac{d}{dU_A}\left(S_A + S_B\right) = 0$$

$$\frac{dS_A}{dU_A} + \frac{dS_B}{dU_A} = 0$$



exchange energy ONLY

$dU_B = -dU_A$

$$\frac{dS_A}{dU_A} = \frac{dS_B}{dU_B}$$

since only energy exchanged, other variables fixed

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$$

equilibrium obtained when this is the same on both sides, & it has units of temperature^{-1} so

$$\boxed{\frac{1}{T} = \frac{\partial S}{\partial U}}$$

example: Einstein solid with $q >> N$

$$S = k \ln \left(eq/N\right)^N = Nk \ln\left(\frac{q}{N} + \cancel{1}\right) \cong Nk \ln\left(\frac{U/\epsilon}{N}\right)$$

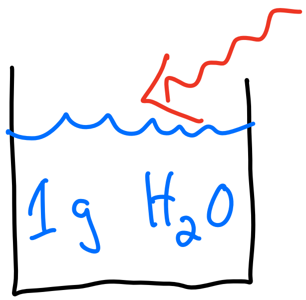
small

ϵ = energy per quantum

$$S = Nk\left[\ln U - \ln N\epsilon\right]$$

$$\frac{1}{T} = \partial_U S = \partial_U Nk \ln U = Nk/U \longrightarrow U = NkT$$

Same as equipartition!



$đQ$ of heat

with no work, $dU = đQ \rightarrow dS = \frac{đQ}{T}$

heat capacity of 1 g H_2O $\quad C_V = 1\ cal/^oC = 4.184\ J/K$

$$dS = \frac{C_V\, dT}{T}$$

$$\Delta S = \int_{T=300K}^{301K} dS = \int_{T=300K}^{301K} C_V \frac{dT}{T} = 4.184 \frac{J}{K} \ln \frac{301}{300}$$

$$= 1.39 \times 10^{-2}\ J/K$$

Huge change in multiplicity

$$\Delta S = S_f - S_i = K \ln \Omega_f - K \ln \Omega_i$$

$$e^{\Delta S/K} = \Omega_f / \Omega_i$$

$$\Omega_f = \Omega_i \exp\left(1.39 \times 10^{-2}\, J/K \,/\, 1.38 \times 10^{-23}\, J/K\right)$$

$$= \Omega_i \exp\left(10^{21}\right) \simeq 10^{0.43 \times 10^{21}}$$

so adding just 1 cal of heat increases the multiplicity by a factor of $\simeq 3 \times 10^{21}$