Chapter 2 - 2^{nd} Law of Thermodynamics

↳ heat spontaneously flows from high temp to low temp

Einstein Solid → $\boxed{\text{Entropy}}$ ← Ideal Gas

→ $\boxed{\text{Anaconda}}$ python language

install

Monty Python

Combinatorics

one coin

$$P(\text{heads}) = \frac{1}{2}$$

multiple coins

$$P(n) = \frac{n}{N}$$

$$P(3 \text{ heads}) = \frac{\Omega(3)}{\Omega(\text{all})} = \frac{\Omega(3)}{\sum_{n=0}^{n} \Omega(n)}$$

← microstate in the macrostate of 3

← all of the microstates

5 coins

$$\text{microstates}\left\{\begin{array}{l} H\,H\,T\,T\,H \;-\; 3H \\ T\,H\,H\,H\,H \;-\; 4H \end{array}\right\}\text{macrostates}$$

how many microstates are in a macrostate?

↳ multiplicity

$$\Omega(n) = \frac{5!}{n!(5-n)!}$$

number of heads

$\Omega(0) = 1$
$\Omega(1) = 5$
$\Omega(2) = 10$
$\Omega(3) = 10$
$\Omega(4) = 5$
$\Omega(5) = 1$

$$\Omega(1) = \frac{5!}{1!(5-1)!} = \frac{5!}{1!4!}$$

$$= \frac{5\cdot\cancel{4}\cdot\cancel{3}\cdot\cancel{2}\cdot\cancel{1}}{1\cdot\cancel{4}\cdot\cancel{3}\cdot\cancel{2}\cdot\cancel{1}}$$

$$= 5$$

$$\Omega(2) = \frac{5!}{2!3!} = 10$$

$$\Omega(N, n) = \frac{N!}{n!(N-n)!} \leftarrow \text{Notation: } \binom{N}{n}$$

# of coins

10 atoms each w/ 0 or 1 packets of energy (energy unit)

How many possible ways are there to distribute 4 energy units

← microstate

$$\Omega(10, 4) = \frac{10!}{4!\,6!} = 210$$

4 energy packets ← macrostate

What if an atom can have more than one energy packet at a time?

} microstates

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

# of atoms

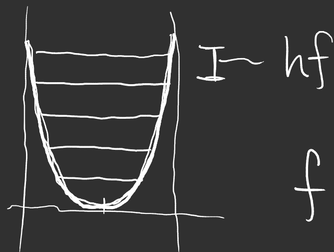
# of energy packets

q = macrostate

4 energy packets ← macrostate

This model of a collection of atoms w/ equal size energy quanta distributed among them is the <u>Einstein Solid</u>.

↳ <u>Debye Model</u>



$$\underline{\underline{\tfrac{1}{2}kx^2}}$$

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

- <u>Large Number</u> → addition of small numbers is not important

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

- <u>Very Large Number</u>

$$10^{10^{23}} \times 10^{23} = 10^{10^{23}+23} \simeq 10^{10^{23}}$$

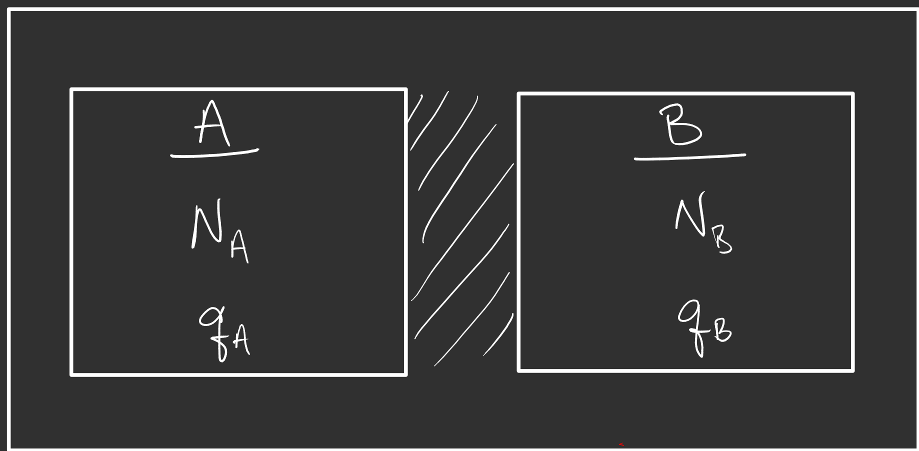
Stirling's Approximation

$$N! \approx N^N e^{-N}\sqrt{2\pi N} = \frac{N^N}{e^N}\underbrace{\sqrt{2\pi N}}_{\substack{\text{very large numbers} \\ \text{we leave this off}}}$$

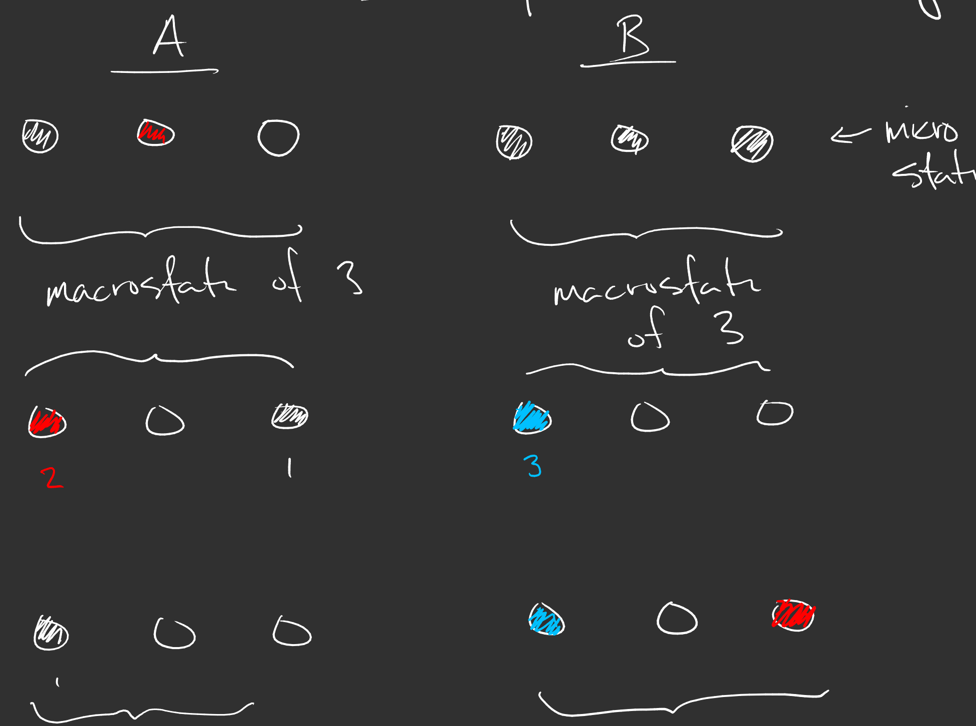
$$\downarrow$$

$$\ln N! \approx N\ln N - N$$

Two Systems



Ex. Each system has 3 particles and 6 total quanta of energy



macrostate of 1

$\Omega(3,1) = 3$

macrostate of 5

$\Omega(3,5) = \frac{7!}{5!\,2!} = 21$

q_A	mult_A	q_B	mult_B	mult_total
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
~~3~~	~~10~~	~~3~~	~~10~~	~~100~~
~~4~~	~~15~~	~~2~~	~~6~~	~~90~~
5	21	1	3	63
6	28	0	1	28

macrostate w/ the most microstates

462

total number of microstates

Fundamental Assumption of Stat Mech:

all microstates are possible and equally probable

But that does not mean that every microstate will occur.

Not all macrostates are equally probable.

$$P_A(q) = \frac{\Omega_{total}(q_A)}{\sum_{q_A} \Omega_{total}(q_A)}$$

We could find the total # of microstates:

$$\underset{\substack{\uparrow \\ N}}{\Omega(6}, \underset{\substack{\uparrow \\ q}}{6)} = \frac{(6+6-1)}{6!\,(6-1)!} = \underline{\underline{462}}$$

So lets apply Stirling's Approx to Multiplicity $[\ln N! = N\ln N - N]$

$$\Omega(N,q) = \frac{(q+N-1)!}{q!\,(N-1)!} \approx \underbrace{\frac{(q+N)!}{q!\,N!}}_{\text{very large number}}$$

$$\ln\Omega = \underbrace{\ln(q+N)!} - \ln q! - \ln N!$$

$$\ln N! \rightarrow N\ln N - N$$

$$\ln q! \rightarrow q\ln q - q$$

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

$$\ln\Omega = (q+N)\ln(q+N) \cancel{-q} \cancel{-N} - q\ln q \cancel{+q} - N\ln N \cancel{+N}$$

$$\rightarrow \boxed{\ln\Omega = (q+N)\ln(q+N) - q\ln q - N\ln N}$$

high temperature limit $\rightarrow q \gg N$

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

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

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

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

$\ln(1+x) \approx x$ for small x

$$\frac{N}{q}$$

$$= \ln q + \frac{N}{q} \approx \ln(q+N)$$

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

$$= N\ln\left(\frac{q}{N}\right) + N + \underbrace{\frac{N^2}{q}}_{\text{small}}$$

$$\ln\Omega(q \gg N) \approx N\ln\left(\frac{q}{N}\right) + N$$

$$\Omega(q \gg N) = e^{N\ln\left(\frac{q}{N}\right)+N} = e^{N\ln\left(\frac{q}{N}\right)}\cdot e^{N} = \Big(\underbrace{e^{\ln\left(\frac{q}{N}\right)}}\Big)^{N}\cdot e^{N}$$

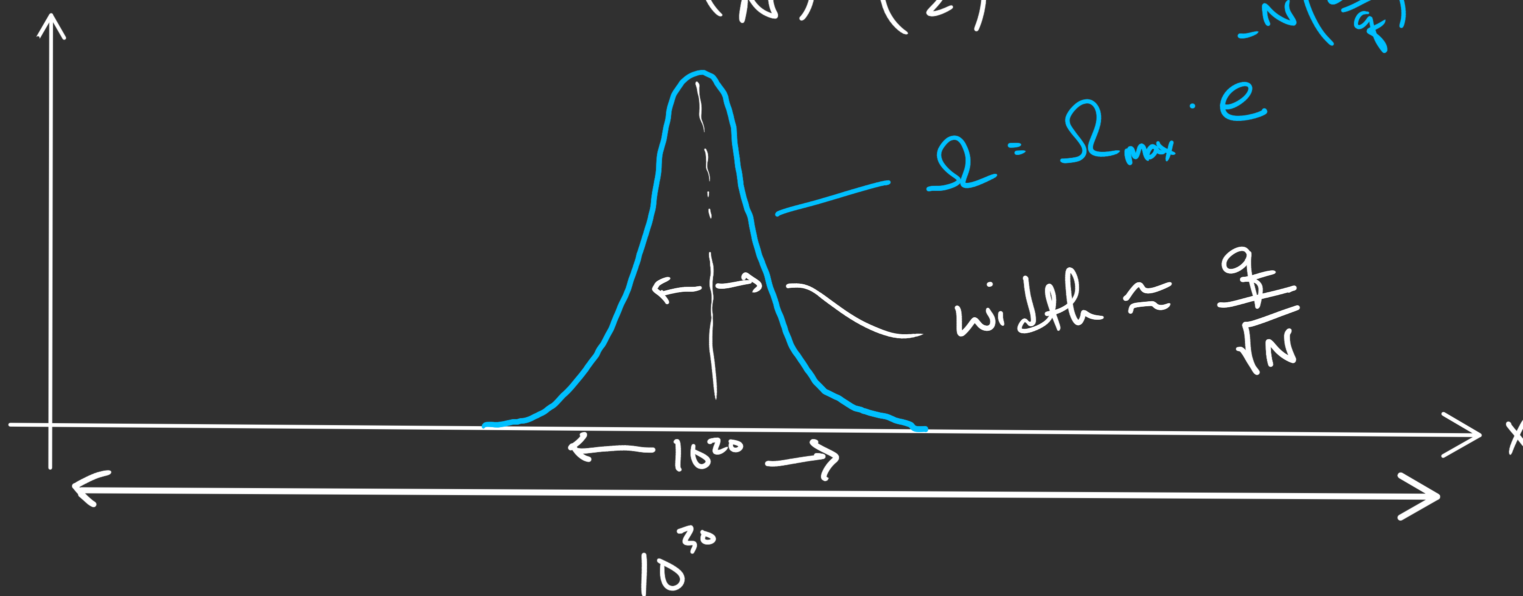
$$\Omega(q \gg N) = \left(\frac{q}{N}\right)^{N} e^{N} = \boxed{\left(\frac{eq}{N}\right)^{N}}$$

- 2 Einstein solids (high temperature limit) $(q >> N)$

$$\Omega_A = \left(\frac{e q_A}{N_A}\right)^{N_A} \qquad \Omega_B = \left(\frac{e q_B}{N_B}\right)^{N_B} \qquad q = q_A + q_B$$

if $N_A = N_B$, multiplicity max will occur $\frac{q}{2} = q_A = q_B$

$$\Omega = \Omega_A \Omega_B = \left(\frac{e}{N}\right)^{2N} \cdot \left(\frac{q}{2}\right)^{2N}$$



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

$$\text{width} \approx \frac{q}{\sqrt{N}}$$

$q = 10^{30}$

$N = 10^{20}$

$\frac{q}{\sqrt{N}} = 10^{20}$

Entropy + the 2nd Law:

Any large system in equilibrium will be found in the macrostate with the greatest ~~multiplicity~~ entropy

$$\underbrace{}$$

2nd Law of Thermodynamics

~~Multiplicity~~ Entropy tends to increase.

Multiplicities are very large! Take the natural log of them.

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

$$\frac{S}{k_B} = \ln \Omega$$

Ex: Entropy of an Einstein solid

homework

$$\Omega = \left(\frac{eq}{N}\right)^N \qquad \underline{q \gg N} \text{ Einstein solid} \qquad \left(\underline{\underline{q \approx N}}\right)$$

$$N = 10^{23} \qquad q = 10^{25}$$

$$S = k_B \ln\left(\left(\frac{eq}{N}\right)^N\right) = N \cdot k_B \ln\left(\frac{eq}{N}\right) = \underset{\substack{\uparrow \\ 10^{23} \cdot 1.38 \cdot 10^{-23}}}{N k_B}\left(1 + \ln\left(\frac{q}{N}\right)\right)$$

$$= 1.38\left(1 + \underbrace{\ln(10^2)}_{4.6}\right)$$

$$S = 7.7 \ J/K$$

Entropy of a composite system

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

$$S = k_B \ln \Omega_A \cdot \Omega_B = k_B \ln \Omega_A + k_B \ln \Omega_B$$

$$S_t = S_A + S_B$$

Chapter 3

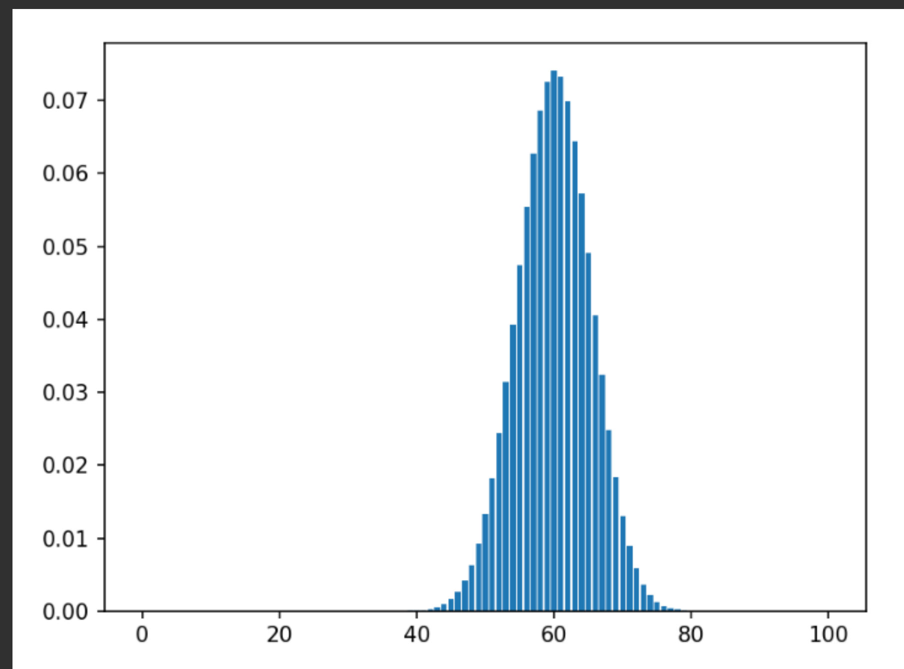
Thermal equilibrium

For the Einstein solid

$$\frac{\partial S_{total}}{\partial q_A} = 0$$

generalize

$$\frac{\partial S_{total}}{\partial U_A} = 0$$



$$\frac{\partial (S_A + S_B)}{\partial U_A} = 0$$

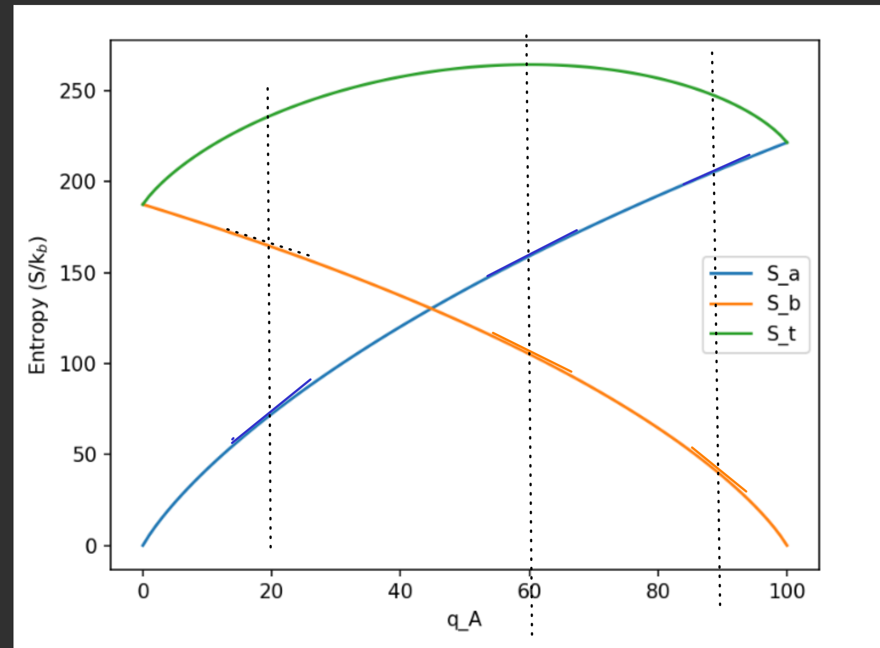
$$\frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0$$

$U_B = U - U_A$

$\{ dU_B = -dU_A$

$$\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B} = 0$$

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



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

$$T = \left(\frac{\partial S}{\partial U}\right)^{-1}_{N,V}$$

Now apply to our Einstein solid $(q \gg N)$

$U = q \cdot \epsilon \Rightarrow q = \frac{U}{\epsilon}$

# of energy packets

energy in one packet

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

$$S = k_B \ln \Omega$$

$$S = k_B \ln\left(\left(\frac{eq}{N}\right)^N\right) = N \cdot k_B \ln\left(\frac{eq}{N}\right) = Nk_B\left(1 + \ln\left(\frac{q}{N}\right)\right)$$

$$S = Nk_B\left(1 + \ln\left(\frac{U}{N\epsilon}\right)\right)$$

$$S = Nk_B + Nk_B \ln U - Nk_B \ln(N\epsilon)$$

$$\underbrace{\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{\partial}{\partial U}\left(Nk_B \ln U\right) = \frac{Nk_B}{U}}$$

$$\underline{U = Nk_B T} \longleftrightarrow U = \frac{f}{2} N k_B T$$

$f = 2$ } Einstein solid

↳ 1D kinetic energy

↳ 1D spring pot. energy

Heat Capacity of Einstein solid:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = Nk_B$$ ← experimentally testable quantity

Review our process so far:

1. Used combinatorics and QM to find Ω in terms of N, V, U etc. } could be impossible!

2. $S = k_B \ln \Omega$ to get entropy

3. $T = \left(\frac{\partial S}{\partial U} \right)^{-1}_{N,V,\text{etc}}$

stat mech give an alternative to arriving at #4

4. Solve step #3 for U as a function of T

5. $C_v = \frac{\partial U}{\partial T}$

<u>But</u>, going backward to measure the entropy is <u>easy</u>

$$dS = \underbrace{\frac{\partial S}{\partial U}} \cdot dU$$

$$dS = \frac{dU}{T}$$

→ use constant volume process (isochoric)

$$\left.\begin{aligned} dV &= 0 \\ đW &= 0 \end{aligned}\right\} \quad dU = đQ + đW$$

$$dU = đQ$$

$$\boxed{dS = \frac{đQ}{T}}$$

→ important! used to be the definition of entropy!

→ T does not change much w/ a small addition of heat!

$$dS = \frac{C_v \cdot dT}{T}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_v}{T}\, dT$$

C_v can be constant, or a function of temperature

$$S(T_f) - S(T_i) = \int_{T_i}^{T_f} \frac{C_v}{T}\, dT$$

$$S(T) - S(0) = \int_0^T \frac{C_v}{T}\, dT$$

but you need to know this function all the way to zero kelvin!

$C_v \to 0$ as $T \to 0$

could be 0 or residual entropy but some constant

3rd Law of Thermodynamics

much experimental data has gone into this for many substances

$$\Omega = \frac{N!}{q!\,(N-q)!}$$

$$\frac{\Omega(1000, 500)}{2^{1000}} \qquad \Omega(1000,500) = \frac{1000!}{(500!)^2} \approx \frac{1000^{1000}\, e^{-1000} \sqrt{2\pi 1000}}{\left(500^{500}\, e^{-500} \sqrt{2\pi 500}\right)^2} = \frac{1000^{1000} \sqrt{2\pi 1000}}{500^{1000} \left(\sqrt{2\pi 500}\right)^2}$$

$$= \left(\frac{1000}{500}\right)^{1000} \frac{\sqrt{2\cancel{\pi} 1000}}{\sqrt{2^2 \pi^{\cancel{2}} 500^2}}$$

$$= 2^{1000} \cdot \sqrt{\frac{2 \cdot 1000}{\underbrace{(2 \cdot 500)^2}_{1000} \pi}}$$

$$= 2^{1000} \cdot \sqrt{\frac{2}{1000\pi}}$$

$$= \frac{2^{1000}}{\sqrt{500\pi}}$$

$$2^{1000} = \sum_{q=1}^{1000} \frac{1000!}{q!\,(1000-q)!} \quad ??$$

?

2.5 Ideal Gas Multiplicity

Multiplicity is the number of microstate in a macrostate.

$\underbrace{\text{total energy, volume}}_{\text{what defines macrostate for ideal gas}}$

$$\Omega = \text{distribution of particles in space} \cdot \text{distribution of energy among particles}$$

For a single particle,

$$\Omega_1 \propto V \cdot \underbrace{\text{combination of momentums that has some energy}}_{\text{volume of momentum space}}$$

$\Omega_1 \propto V \cdot V_p$

Heisenberg Uncertainty Principle

$\Delta x \cdot \Delta p_x \approx h$ ← Plank constant

uncertainty in position

uncertainty in momentum

inversely proportional

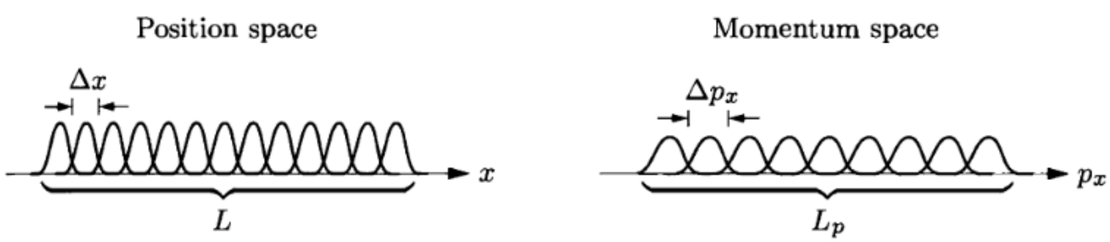


Figure 2.9. A number of "independent" position states and momentum states for a quantum-mechanical particle moving in one dimension. If we make the wavefunctions narrower in position space, they become wider in momentum space, and vice versa.

$$\Omega_1 = \frac{L_x L_y L_z}{\Delta x \, \Delta y \, \Delta z} \cdot \frac{L_{p_x} L_{p_y} L_{p_z}}{\Delta p_x \, \Delta p_y \, \Delta p_z}$$

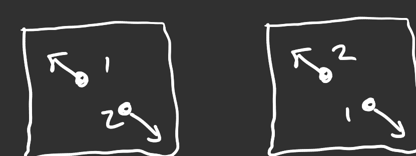
$$\Omega_1 = \frac{V \cdot V_p}{h \cdot h \cdot h} = \frac{V \cdot V_p}{h^3}$$

So what about two particles?

$$\Omega_2 = \Omega_A \cdot \Omega_B$$

cannot distinguish the particles

$$= \frac{V^2 \cdot V_p^2}{(h^3)^2} \cdot \frac{1}{2}$$



$$\Omega_N = \frac{1}{N!} \frac{V^N V_p^N}{(h^3)^N}$$

So lets go back to one particle that has all of the energy of the system, U.

$$U = \frac{1}{2}mv^2 = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right) \cdot \frac{m}{m}$$

$$U = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

$$\underbrace{p_x^2 + p_y^2 + p_z^2 = 2mU = \left(\sqrt{2mU}\right)^2}_{\text{equation of a sphere in momentum space that has a radius, } r = \sqrt{2mU}}$$

So the "volume" of momentum space that represents all of the possible momenta that the particle can have and still have U amount of energy is really the surface area of the sphere in momentum space $\rightarrow \underline{4\pi r^2} \rightarrow \underline{4\pi\left(\sqrt{2mU}\right)^2}$

For two particles constrained to U total energy,

then

$$p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2 = \left(\sqrt{2mU}\right)^2$$

6 dimensional sphere? hypersphere!

"surface area" $= \dfrac{2\pi^{d/2}\, r^{d-1}}{\left(\frac{d}{2}-1\right)!}$

TEST: $d=2$

$$2\pi r \overset{?}{=} \frac{2\pi^{2/2}\, r^{2-1}}{\left(\frac{2}{2}-1\right)!} = 2\pi r \checkmark$$

3N dimensional sphere

"surface area" $= \dfrac{2\pi^{3N/2}\, r^{3N-1}}{\left(\frac{3N}{2}-1\right)!}$

$\sqrt{2mU} = (2mU)^{1/2}$

TEST: $d=3$

$$4\pi r^2 \overset{?}{=} \frac{2\pi^{3/2}\, r^{3-1}}{\left(\frac{3}{2}-1\right)!} = 2\underbrace{\left[\frac{\pi^{3/2}}{(1/2)!}\right]}_{2\pi} r^2$$

$$\frac{1}{\left(\frac{1}{2}\right)!} = \frac{2}{\sqrt{\pi}}$$

$$= 4\pi r^2 \checkmark\checkmark$$

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

so let's throw away what does not matter for large numbers

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

$2! = 2 \cdot 1$

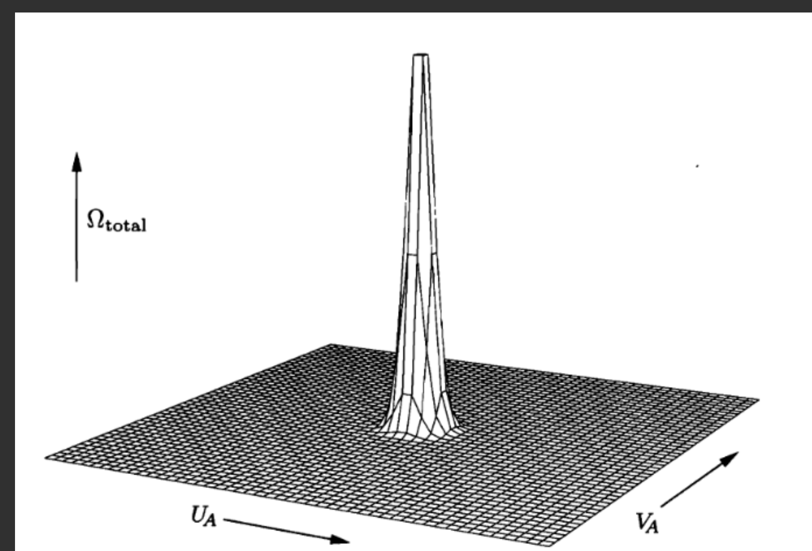
$\frac{1}{2}! = \frac{\sqrt{\pi}}{2} = 0.8862$

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

Put two ideal gasses in thermal contact (barrier exchanges energy + volume)

$$\Omega_{total} = f(N)\, V_A^N\, U_A^{3N/2} \cdot f(N)\, V_B^N\, U_B^{3N/2}$$

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



Entropy of an ideal gas

$$\Omega_N = \frac{1}{N!}\frac{V^N}{h^{3N}} \cdot \frac{(2\pi m U)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}$$

$$S = k_B \ln \Omega = k_B \ln\left[\frac{1}{N!}\frac{V^N}{h^{3N}} \cdot \frac{(2\pi m U)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}\right]$$

$$S = k_B\left[\underbrace{-\ln(N!)}\ \underbrace{-\ln\left(\frac{3N}{2}!\right)} + N\ln V + \frac{3N}{2}\ln(2\pi m U) - \frac{3N}{2}\ln(h^2)\right]$$

$$-\ln(N!) \to -N\ln N + N$$

$$N\ln\frac{1}{N} + N$$

$$-\ln\left(\frac{3N}{2}!\right) \to -\frac{3N}{2}\ln\left(\frac{3N}{2}\right) + \frac{3N}{2}$$

$$\frac{3N}{2}\ln\left(\frac{2}{3N}\right) + \frac{3N}{2}$$

$$S = k_B N\left(\ln\left[\frac{V}{N}\left(\frac{2\pi m U}{h^2}\cdot\frac{2}{3N}\right)^{3/2}\right] + 1 + \frac{3}{2}\right)$$

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

Sackur-Tetrode Equation

$\frac{V}{N} \rightarrow$ volume per particle

$\frac{U}{N} \rightarrow$ energy per particle

apply to one mole of N_2 gas at room temp and atmospheric pressure. Find entropy. $n_m = 1$, or $N = N_A \cdot n_m$

- $U = \frac{5}{2} n_m R T = \frac{5}{2} N k_B T$
- $V = \frac{n_m R T}{P} = \frac{N k_B T}{P}$

$\hookrightarrow V = \frac{RT}{P} = \frac{N_A k_B T}{P}$

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

$$= k_B N_A\left(\ln\left[\frac{\cancel{N_A} k_B T}{\cancel{N_A} \cdot P}\left(\frac{4\pi\,(4.65\cdot 10^{-26}\,kg)\cdot \frac{5}{2}\cancel{N_A}\cdot k_B \cdot 293K}{3\,\cancel{N_A}\,h^2}\right)^{3/2}\right] + \frac{5}{2}\right)$$

$$= 8.31\left(\ln\left[\frac{1.38\cdot 10^{-23}\cdot 293K}{10^5\,Pa}\left(\frac{4\pi\,(4.65\cdot 10^{-26}\,kg)\cdot \frac{5}{2}\cdot 1.38\cdot 10^{-23}\cdot 293}{3\cdot(6.626\cdot 10^{-34})^2}\right)^{3/2}\right] + \frac{5}{2}\right) = 135.5\ J/K$$

$N_2 = 28\,g/mol = 0.028\,\frac{kg}{mol} = \frac{0.028\,kg}{6.022\cdot 10^{23}\text{ atoms}} = 4.65\cdot 10^{-26}\,kg$

HW: Ch 2.26, 32

HW: Ch 3.1, 10, 14 ←

$$\boxed{\Omega(\text{all}) = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} = \cancel{N!}\ 2^N}$$

2.26| $\Omega_1 = \dfrac{A \cdot A_p}{h^2}$

so how do you adapt for 2D gas → $\Omega_N = \dfrac{1}{N!} \dfrac{V^N}{h^{3N}} \times$ (area of the momentum hypersphere)

3.4| Mechanical Equilibrium + Pressure