# Chapter 2

## Some combinatorics

coin flips → 5 coins

H H T T H ← microstate

T H H H H ← microstate

3 heads ← macrostates

4 heads ← macrostates

how many microstates are in a macrostate?

↳ Depends on the macrostate

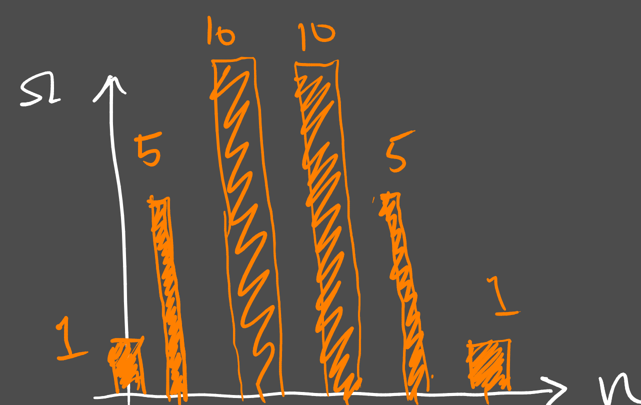
multiplicity $\Omega(n) = \dfrac{5!}{n!(5-n)!}$ ← combinations for 5 coins

$n$ ↑ macrostate # of heads

$0! = 1$ $\quad n! = n(n-1)\cdots 1$

$1! = 1$

$2! = 2$



↳ generalize to N coins

$$\Omega(N,n) = \frac{N!}{n!(N-n)!} \qquad \binom{N}{n}$$

$N$: # of coins

$n$: # of heads

<u>10 atoms</u> → each atom can have 0 or 1 $\underbrace{\text{energy unit}}_{\text{quanta}}$

So how many possible arrangements of 4 quanta (10 quanta)

○ ● ● ○ ○ ● ○ ● ○ ○ ← microstate

4 energies vs. 10 energies ← macrostate

What if atoms can have more than 1 energy unit at a time

○ ● ● ○ ○ ○ ○ ● ○ ○ ← microstate

1 2 1

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

$N$: # of atoms

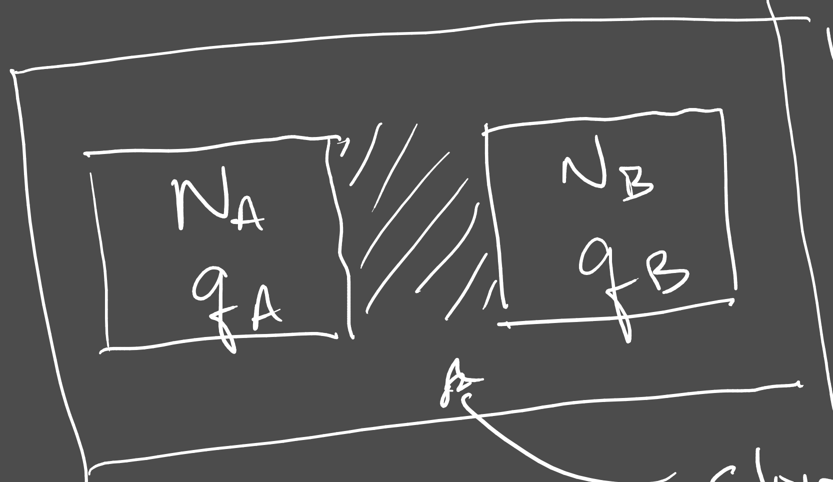
$q$: packets of energy $\}$ macrostate

This model → Einstein Solid

# 1,5

Two Solids that can exchange energy

isolated from surroundings

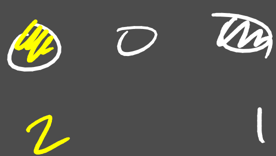



slow energy transfer

A


macrostate

$q = 3$




$q = 1$

$\Omega_A(1) = 3$

B

← microstate

$q = 3$



$q = 5$

$\Omega_B(5) = 21$

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

$\Omega_{total} = 63$

Total number of microstates possible → 462

$\Omega(6,6) = 462$

All microstates are equally likely

→ Fundamental assumption of statistical mechanics.
(axiom)

→ But all macrostates are not equally likely.

$$\text{Probability of solid A having } q \text{ energy} = \frac{\Omega_{total}(q_A)}{\sum_{q_A} \Omega_{total}(q_A)}$$

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Large Numbers, $10^{23}$

Addition of small numbers is not important

$$10^{23} + 50 \approx 10^{23}$$

Very Large Numbers $\rightarrow$ Multiplication of Large numbers is not important

$$10^{10^{23}}, \quad 10^{10^{100}}$$

$$10^{10^{23}} \cdot 10^{23} = 10^{10^{23}+23} \approx 10^{10^{23}}$$

Stirling's Approximation

$$N! \approx N^N e^{-N} \sqrt{2\pi N}$$

$$\approx \frac{N^N}{e^N} \underbrace{\sqrt{2\pi N}}_{\text{not all that important}}$$

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

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

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

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

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

↳ high temperature → $q >> N$

$$\boxed{\begin{array}{c}\ln(1+x) \approx x \\ \text{for small } x\end{array}}$$

$\ln(q+N)$

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

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

$$\ln\Omega = N\ln\frac{q}{N} + N + \underbrace{\frac{N^2}{q}}_{\text{small}}$$

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

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

$\Omega(N,q)$

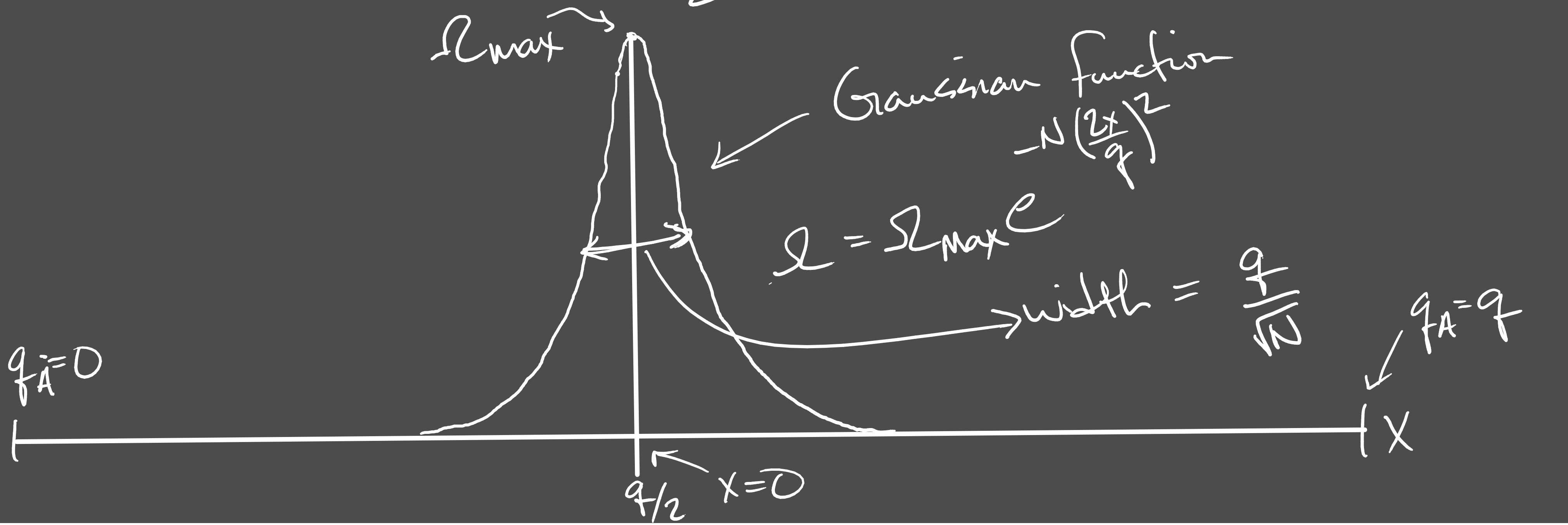
Now go back and use this w/ Einstein solid.

same # particles

$$\Omega_{total} = \left(\frac{e q_A}{N_A}\right)^{N_A} \left(\frac{e q_B}{N_B}\right)^{N_B} = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N$$

$$N_A = N_B$$

$$\Omega_{max} \rightarrow q_A = q_B = \frac{q}{2} \qquad \Omega_{max} = \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N}$$




Gaussian function

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

width $= \frac{q}{\sqrt{N}}$

$$\frac{\text{width}}{\text{full range}} = \frac{q/\sqrt{N}}{q} = \frac{1}{\sqrt{N}} \longrightarrow N = 10^{20} \qquad \frac{1}{\sqrt{10^{20}}} = \frac{1}{10^{10}}$$

HW: 9, 10, 13, 18, 22

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The multiplicity of an ideal gas.

→ macrostate → volume, total energy, number

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

$$\Omega_1 \propto V \cdot V_p$$

$V$: physical volume

$V_p$: volume of momentum space (surface area of momentum space)

Heisenburg Uncertainty Principle

$$\Delta x \cdot \Delta p_x \simeq h$$

$h \rightarrow$ Planck Constant

$\dfrac{L_x}{\Delta x} \rightsquigarrow$ # of distinct places to put particle in x-direction

$\dfrac{L_{p_x}}{\Delta p_x} \rightsquigarrow$ # of distinct momentum states

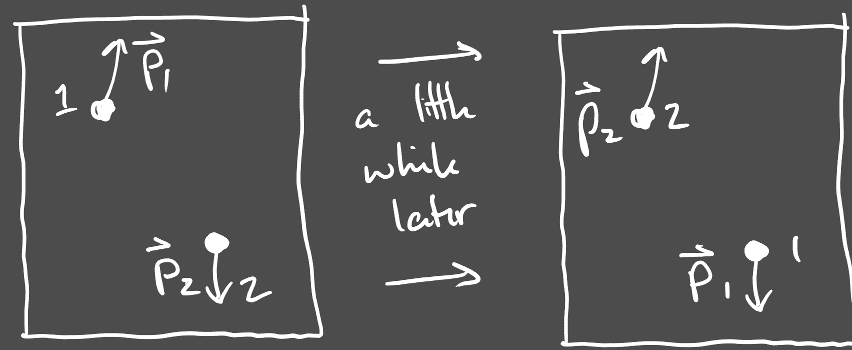
$$\Omega_1 = \overbrace{\frac{L_x}{\Delta x} \cdot \frac{L_y}{\Delta y} \cdot \frac{L_z}{\Delta z}}^{V} \cdot \overbrace{\frac{L_{p_x}}{\Delta p_x} \cdot \frac{L_{p_y}}{\Delta p_y} \cdot \frac{L_{p_z}}{\Delta p_z}}^{V_p}$$

$h \qquad h \qquad h$

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

What about two particles?

$$\Omega_2 = \Omega_A \Omega_B = \underbrace{\frac{V^2}{(h^3)^2} \cdot V_p^{*}}_{\text{double counts}} \cdot \frac{1}{2}$$




what about N particles?

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

go back to one particle has energy $U$

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

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

$$p_x^2 + p_y^2 + p_z^2 = \left(\sqrt{2mU}\right)^2$$

$$x^2 + y^2 + z^2 = r^2 \rightsquigarrow 4\pi r^2 \rightsquigarrow 4\pi\left(\sqrt{2mU}\right)^2$$

$$8\pi m U$$

2 particles ?

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

6 dimensional sphere → hypersphere

surface area
for an any
dimensional sphere

3N dimensional hypersphere

1D area → $0$

2D area → $2\pi r$

3D area → $4\pi r^2$

D area → $\dfrac{(2\pi)^{d/2}}{\left(\frac{d}{2}-1\right)!} r^{d-1}$

$$\Gamma(n-1) = n!$$

gamma function

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

↓

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

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

2 ideal gasses interacting

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

$$S = k_B \ln \Omega$$

entropy

$q = 2N$

$$\Omega(N,q) \simeq \frac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{2\pi q(q+N)/N}}$$

$$\Omega_{total} = \Omega_A \Omega_B = (\Omega)^2 =$$

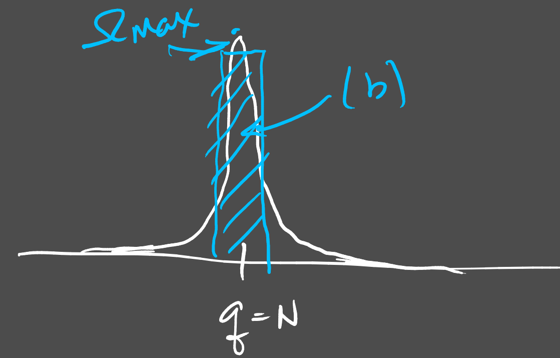
$$\Omega_{total,max} =$$

26, 28, 29, 30

2.22 (a) $q = 2N$

$N_A = N_B = N$

total macrostates $= 2N+1$




(b) $$\Omega = \frac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\left(2\pi q(q+N)/N\right)^{1/2}} \qquad \begin{cases} N = 2N \\ q = 2N \end{cases}$$

$\vdots$ a few step

$$= \frac{2^{4N}}{(8\pi N)^{1/2}}$$

(c) $$\Omega_{max} \doteq \underbrace{\Omega_A(N=N,\, q=N)}\,\underbrace{\Omega_B(N=N,\, q=N)}$$

$\vdots$

$$= \frac{2^{4N}}{4\pi N}$$

(d) $A = \text{width} \cdot \text{height}$

$$\text{width} = \frac{A}{\text{height}} = \frac{(b)}{(c)} = \ldots \quad \sqrt{2\pi N} \longrightarrow \frac{\sqrt{2\pi N}}{2N+1} \underset{N=10^{23}}{=} \ldots\ldots = 2.5 \cdot 10^{-12}$$

total macrostates $= 2N+1$

Any large system in equilibrium will be found in the macrostate, with the greatest multiplicity.

(entropy)

2nd Law of thermodynamics

Multiplicity tends to increase

(entropy)

spontaneous process

$$S = k_B \ln \Omega$$

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Entropy of an ideal gas

$$S = k_B \ln \Omega \qquad \Omega_N = \frac{1}{N!}\frac{V^N}{h^{3N}} \cdot \frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!}(2mU)^{\frac{3N}{2}}$$

$$N! = N\ln N - N$$

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

Sackur-Tetrode

What is the entropy of 1 mol of $N_2$ at room temp + atm pressure?

$U = \frac{5}{2} N k_B T$

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$$\Delta S = S(V_f) - S(V_i) = k_B \ln\left(\frac{\Omega_f}{\Omega_i}\right)$$

$$\underbrace{\Delta S = k_B \cdot N \ln\left(\frac{V_f}{V_i}\right)}_{\text{isothermal expansion}}$$

constant $N, U$

$\Delta U = 0$

$Q = -W$

causing the change in entropy

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