Chapter 2 The Second Law

This chapter will go into basics of statistical mechanics and give indication why the total entropy increases.

Section 2.1 Two state systems

To practice how to statistically treat systems, start with a system with "atoms" that only have 2 states.

Coin H = heads T = tails

1 coin	H, T	2 states
2 coins	HH, HT, TH, TT	4 states
3 coins	HHH, HHT, HTH, THH, HTT, THT, TTH, TTT	8 states

microstate = fully described state for 3 coins THT is a microstate

For N coins there are 2^N microstates

macrostate = state description with only partial information

a macrostate is usually several microstates

for 3 coins, one heads is a macrostate with 3 microstates

multiplicity Ω = number of microstates corresponding to a microstate

↖ Greek Omega

for 3 coins, $\Omega(1 \text{ heads}) = 3$

If each microstate is equally likely, the probability to be in a macrostate is the fraction of states in the macrostate.

Probability(macrostate) = $\Omega(\text{macrostate})/\Omega(\text{all})$

↖ total number of microstates

For coins, N = number of coins and n = number of heads $\Omega(N,n) = \frac{N!}{n!(N-n)!}$

$n! = 1 \cdot 2 \cdot 3 \cdot \ldots (n-1)n$ $0! = 1$

Derive by induction

$\Omega(N,0) = 1 \overset{\checkmark}{=} \frac{N!}{0!\,N!}$

$\Omega(N,1) = N$ because each coin could flip $\overset{\checkmark}{=} \frac{N!}{1!(N-1)!} = \frac{N(N-1)!}{1!(N-1)!} = N$

$\Omega(N,2) = \frac{N(N-1)}{2}$ after flipping 1 coin, $N-1$ could also flip but $\frac{1}{2}$ so don't double count

$\overset{\checkmark}{=} \frac{N!}{2!(N-2)!} = \frac{N(N-1)}{2!}$

etc

This combination occurs many times and is defined $\frac{N!}{m!(N-m)!} \equiv \binom{N}{m}$

For n coins, the probability of n heads $= \frac{\Omega(N,n)}{\Omega(\text{all})} = \frac{1}{2^N}\frac{N!}{n!(N-n)!}$

Prob 2.2 20 coins

a) number of microstates $= 2^{20} = 1{,}048{,}576$

b) probability to get HTHHTTTHTHHHTHHHHTHT $\frac{1}{1048576} \cong 10^{-6}$

c) probability to get 12 heads? $\frac{20!}{12!\,8!}\frac{1}{2^{20}} \cong 0.12$ (12%)

The two state paramagnet has N spin ½ objects. Each object has 2 states ↑ or ↓. $N = N_\uparrow + N_\downarrow$

For N spin ½ with $N_\uparrow$ spin ↑, $\Omega(N, N_\uparrow) = \frac{N!}{N_\uparrow!(N-N_\uparrow)} = \frac{N!}{N_\uparrow!\,N_\downarrow!}$

Section 2.2 The Einstein model of a solid

There are N quantum oscillators with the <u>same</u> frequency $f = \frac{\omega}{2\pi}$

An oscillator j has n_j quanta with energy $E_j = (n_j + \tfrac{1}{2})\hbar\omega = (n_j + \tfrac{1}{2})hf$

The total energy $E_{TOT} = \sum_{j=1}^{N} E_j = \hbar\omega \sum_{j=1}^{N}(n_j + \tfrac{1}{2}) \equiv \hbar\omega(q + \frac{N}{2})$

q = total number of quanta in the system

$\Omega(N,q)$ = the number of microstates of the N oscillator system with q quanta

$\Omega(3,0) = 1$ (0,0,0)

$\Omega(3,1) = 3$ (1,0,0) (0,1,0) (0,0,1)

$\Omega(3,2) = 6$ (2,0,0), (0,2,0), (0,0,2), (1,1,0), (1,0,1), (0,1,1)

$\Omega(3,3) = 10$ (3,0,0) (0,3,0) (0,0,3) (2,1,0) (1,2,0), (2,0,1) (1,0,2) (0,2,1) (0,1,2) (1,1,1)

etc

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!}$$ See book for derivation

Derivation by induction for q quanta

$N=1$ $\Omega(1,q) = 1 = q!/q!\,0!$ ✓

$N=2$ $\Omega(2,q) = q+1$ $[(q,0),(q-1,1),(q-2,2),\dots] = \frac{(q+1)!}{q!\,1!}$ ✓

$N=3$ $\Omega(3,q) = \Omega(2,q) + \Omega(2,q-1) + \Omega(2,q-2) + \dots \Omega(2,0) = (q+1) + (q) + (q-1) + \dots 1$

$= \sum_{j=0}^{q} \frac{(j+2)(j+1)-(j+1)j}{2} = \frac{(q+2)(q+1)}{2} = \frac{(q+2)!}{q!\,2!}$ ✓

$N=4$ $\Omega(4,q) = \Omega(3,q) + \Omega(3,q-1) + \dots \Omega(3,0) = \frac{(q+2)(q+1)}{2} + \frac{(q+1)q}{2} + \dots 1$

$= \sum_{j=0}^{q}[(j+3)(j+2)(j+1) - (j+2)(j+1)j]/(2\cdot 3) = \frac{(q+3)(q+2)(q+1)}{2\cdot 3} = \frac{(q+3)!}{q!\,3!}$ ✓

Prob 2.5 (c) $N=3$ $q=6$ and (d) $N=4$ $q=2$

(6,0,0) (0,6,0) (0,0,6) (5,1,0) (1,5,0) (5,0,1) (1,0,5) (0,5,1) (0,1,5) (4,2,0) (2,4,0) (4,0,2) (2,0,4) (0,4,2) (0,2,4) (4,1,1) (1,4,1) (1,1,4) (3,3,0) (3,0,3) (0,3,3) (3,2,1) (2,3,1) (3,1,2) (2,1,3) (1,3,2) (1,2,3) (2,2,2) 28

$\frac{8!}{6!2!} = 28$ ✓

(2,0,0,0) (0,2,0,0) (0,0,2,0) (0,0,0,2) (1,1,0,0) (1,0,1,0) (1,0,0,1) (0,1,1,0) (0,1,0,1) (0,0,1,1) 10

$\frac{5!}{2!3!} = 10$ ✓

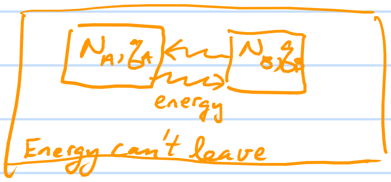
Prob 2.6 $N=30$ $q=30$

$\Omega(30,30) = \frac{59!}{30!29!} = 5.91 \times 10^{16}$

Section 2.3 Interacting systems

Basic idea is to use statistics to understand (for example) how energy is allocated between two systems. Use the Einstein model as an example.

System A has N_A oscillators, System B has N_B oscillators, there are q total quanta [the total system has specific energy $E_{TOT} = \hbar\omega(q + \frac{N_A+N_B}{2})$]



There's a weak mechanism where energy can go from A to B or B to A.

$q = q_A + q_B$

** Assume all possible microstates are equally probable!!! ***

Fundamental assumption of statistical mechanics: In an isolated system in thermal equilibrium, all <u>accessible</u> microstates are equally probable.

accessible = satisfies known constraints

For example above accessible $\Rightarrow$ $q = q_A + q_B$

Case $N_A = 2$ $N_B = 3$ $q = 5 = q_A + q_B$ $\Omega_{TOT} = \Omega(5,5) = \frac{9!}{5!4!} = 126$

$\Omega_{AB} = \Omega_A \Omega_B$ why??

q_A	Ω_A	q_B	Ω_B	Ω_{AB}	prob
0	1	5	21	21	16.7%
1	2	4	15	30	23.8%
2	3	3	10	30	23.8%
3	4	2	6	24	19.0%
4	5	1	3	15	11.9%
5	6	0	1	6	4.8%
				Sum =126	Sum = 100%

Suppose this system had started with $q_A = 5$, $q_B = 0$?? The system likely to evolve toward $q_A = 2, q_B = 3$ or $q_A = 1, q_B = 4$

Thermal equilibrium is a statement about probabilities.

2nd Law of Thermodynamics: The spontaneous flow of energy between two systems stops when the combined system is at, or very near, its most likely macrostate.

See einstein_model

$q_A + q_B = 30 \quad N_A = 5, N_B = 10$

q_A	Ω_A	q_B	Ω_B	Ω_{AB}	P
8	495	22	2.02×10^7	9.98×10^9	0.0868
9	715	21	1.43×10^7	1.02×10^{10}	0.0890
10	1001	20	1.00×10^7	1.00×10^{10}	0.0872
11	1365	19	6.91×10^6	9.43×10^9	0.0820
12	1820	18	4.69×10^6	8.53×10^9	0.0742

$$\sum_{q_A=8}^{12} P(q_A) = 0.42$$

$q_A + q_B = 60 \quad N_A = 10, N_B = 20$

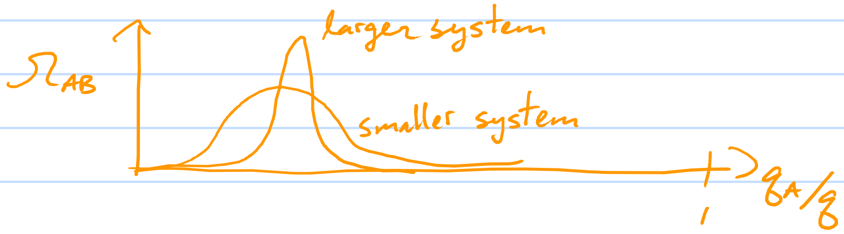
q_A	$\Omega_A(10^6)$	q_B	$\Omega_B(10^{14})$	$\Omega_{AB}(10^{22})$	P
16	2.04	44	61.3	1.25	0.0558
18	4.69	42	29.7	1.39	0.0620 0.0629
20	10.0	40	14.0	1.40	0.0624
22	20.2	38	6.37	1.28	0.0572
24	38.6	36	2.81	1.08	0.0482

$$\sum_{q_A=16}^{24} P(q_A) = 0.52$$

The peak probability is close to where you would expect it

$\max(\mathrm{Prob}(q_A))$ for $q_A \simeq q \cdot N_A/(N_A + N_B) = q/3$

The width of the peak increases when q, N_A, N_B multiplied by 2. The width decreases if plot vs q_A/q



For small systems, the fluctuations of the energy in one subsystem (that is the width of the multiplicity) are observable

For large systems ($\sim 10^{23}$ particles), the fluctuations are not directly observable

Section 2.4 Large systems

This section introduces us to useful approximations for large and very large numbers.

Small numbers: Relatively easily write them 578, 14793, etc
usual math rules apply: addition, subtraction, multiplication, division

Large numbers: are much, much larger than small numbers,
make by exponentiation 10^{23}, e^{5781}, 4.99×10^{50}
Adding a small to a large number hardly changes $105 + 10^{19} \cong 10^{19}$
(Don't use this approx if subsequently subtract the same large number)
$(105 + 10^{19}) - 10^{19} \neq 10^{19} - 10^{19} = 0$

Very large numbers: are much, much larger than large numbers
make by exponentiation of large number $10^{10^{25}}$
Multiply a very large number by a large number hardly changes $10^{19} \times 10^{10^{25}} = 10^{19+10^{25}} = 10^{10^{25}}$
(Don't use this approx. if you're going to divide by the same very large number

$\ln$ (large number) $\sim$ small number
$\ln$ (very large number) $\sim$ large number

Exponentials and logarithms are super useful.
Know $e^a e^b = e^{a+b}$ $(e^a)^b = e^{ab}$ cold

Prob 2.12 Use $e^{\ln x} = x$
b) $\ln(ab) \overset{?}{=} \ln a + \ln b$
$e^{\ln(ab)} = ab \overset{?}{=} e^{(\ln a + \ln b)}$
$= e^{\ln a} e^{\ln b} = ab$ ✓
$\ln(a^b) \overset{?}{=} b \ln a$ $e^{\ln(a^b)} = a^b \overset{?}{=} e^{b \ln a} = (e^{\ln a})^b = a^b$ ✓

c) $\frac{d \ln x}{dx} \overset{?}{=} 1/x$ $\frac{d}{dx} e^{\ln x} = \frac{d}{dx} x = 1 = \frac{d \ln x}{dx} e^{\ln x} = x \frac{d \ln x}{dx} = 1$ ✓

d) $\ln(1+x) \overset{?}{=} x - x^2/2 + x^3/3 + \ldots$ for $|x| < 1$
$F(1+x) = F(1) + x F'(1) + \frac{x^2}{2} F''(1) + \ldots \ldots$
$= \ln(1) + x \frac{1}{1} - \frac{x^2}{2} \frac{1}{1^2} \ldots .$

Stirling's approximation $N! \simeq \sqrt{2\pi N}\, N^N e^{-N}$ for large N

Better $N! \cong \sqrt{2\pi(N+1/6)}\, N^N e^{-N}$ $\quad N^N e^{-N} = (N/e)^N$

See appendix B for derivation

N	$N!$	$\sqrt{2\pi N}\,(N/e)^N$	frac err	$\sqrt{2\pi(N+1/6)}\,(N/e)^N$	frac err
1	1	0.922	7.8×10^{-2}	0.9960	4.0×10^{-3}
5	120	118	1.7×10^{-2}	119.97	2.5×10^{-4}
10	3,628,800	3,598,696	8.3×10^{-3}	3,628,561	6.6×10^{-5}

Usual Stirling's approx is too small by the factor $\sqrt{1+\frac{1}{6N}} \cong 1+\frac{1}{12N}$

See Eqs (B.19) – (B.24) for derivation of usual Stirling's approx

Sidetrack: Gaussian integrals come up a lot. Worth remembering

$$\int_{-\infty}^{\infty} e^{-\alpha x^2}\,dx = \sqrt{\pi/\alpha} \qquad \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2}\,dx = -\frac{d}{d\alpha}\int_{-\infty}^{\infty} e^{-\alpha x^2}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha^3}}$$

See Eqs (B.1) – (B.6) of textbook

Prob 2.18

We can use Stirling's approximation to get a good approximation to the multiplicity of an Einstein solid using simpler functions

N, q are both > ~100 should give better than 1% accuracy

$$\Omega(N,q) = \frac{(q+N-1)!}{q!\,(N-1)!} = \frac{N}{q+N}\,\frac{(q+N)!}{q!\,N!} \simeq \frac{N}{q+N}\,\frac{\sqrt{2\pi(q+N)}\,(q+N)^{(q+N)}\cancel{e^{-(q+N)}}}{\sqrt{2\pi q}\,q^q\,\cancel{e^{-q}}\,\sqrt{2\pi N}\,N^N\cancel{e^{-N}}}$$

$$= \frac{1}{\sqrt{2\pi}}\sqrt{\frac{N}{q(q+N)}}\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N$$

Example $\Omega(15,30) = 1.1496\times10^{11}$ $\quad \Omega_{app}(15,30) = 1.1570\times10^{11}$ $\quad$ 0.64% error

Classical systems have many quanta per oscillator $\Rightarrow q \gg N$

What is the classical limit of the Einstein model? N, q = large

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

$$\left(\frac{q+N}{N}\right)^N = (q/N)^N (1+N/q)^N \cong (q/N)^N e^{N^2/q} = (q/N)^N (e^N)^{N/q}$$

$$\Omega(N,q) \cong \underbrace{\frac{1}{\sqrt{2\pi}}\sqrt{\frac{N}{q(q+N)}}}_{\text{large}}\ \underbrace{(e^N)^{1+N/q}(q/N)^N}_{\text{very large}} \simeq \left(eq/N\right)^N$$

If you write the total energy in the oscillator $U = \hbar\omega\left(q + \frac{3N}{2}\right)$

$q \cong U/\hbar\omega$ for $q \gg N$

$\Omega(N,U) \simeq (e/N)^N (U/\hbar\omega)^N$

Example 1 Two systems N_A, q_A and N_b, q_B with both N, q large and $q \gg N$

$$\Omega_{AB} = \left(\frac{e}{N_a}\right)^{N_a}\left(\frac{e}{N_b}\right)^{N_b} q_A^{N_A}(q-q_A)^{N_B}$$

Where is the max and how wide?

$$q_A^{N_A}(q-q_A)^{N_B} = e^{N_A \ln q_A + N_b \ln(q-q_A)} \equiv e^{F(q_A)}$$

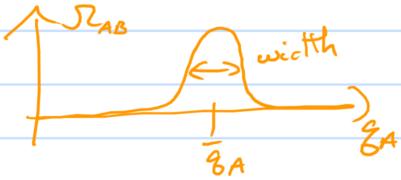
To find max $F'(q_A) = 0 = \frac{N_A}{q_A} - \frac{N_B}{q-q_A} \Rightarrow \boxed{\bar{q}_A = q\,N_A/N}$ $N = N_A + N_B$

To find width

$$F''(\bar{q}_A) = -\frac{N_A}{\bar{q}_A^2} - \frac{N_B}{\bar{q}_B^2} = -\frac{N_A N^2}{q^2 N_A^2} - \frac{N_B N^2}{q^2 N_B^2} = -\frac{N^3}{q^2 N_A N_B}$$

$$\Omega_{AB} = \left(\frac{e\bar{q}_A}{N}\right)^{N_A}\left(\frac{e\bar{q}_B}{N}\right)^{N_B} e^{-(q-\bar{q}_A)^2/q_{wid}^2} \qquad \frac{2}{q_{wid}^2} = -F''(\bar{q}_A) = \frac{N^3}{q^2 N_A N_B}$$

$q_{wid} = \frac{q}{N}\sqrt{\frac{2N_AN_B}{N}}$ Fractional width $q_{wid}/q = \frac{1}{N}\sqrt{\frac{2N_AN_B}{N}} \sim 1/\sqrt{N}$



The book does the case $N_A = N_B \Rightarrow N = 2N_A \Rightarrow q_{wid} = q/2\sqrt{N_A}$ ✓

(Be careful what the book calls N is my N_A)

Example $N_A = N_B = 10^{22}$ $q = 10^{24}$ $\Rightarrow q_{wid} = \frac{10^{24}}{2\,10^{11}} = \frac{1}{2}10^{13}$

Fractional width $\bar{q}_A = \frac{1}{2}q$ $q_{wid}/\bar{q}_A = 10^{-11}$ this is small

At $q_A - \bar{q}_A = \delta q_A = \pm 10\, q_{wid}$ Ω_{AB} decreased by factor $e^{-100} \sim 4 \times 10^{-44}$

$\Rightarrow$ you will always measure $q_A = \bar{q}_A$ to one part in 10^{10}

<u>Thermodynamic limit</u>: when systems are so large that fluctuations away from average values are unmeasurable. $\Rightarrow$ Tiny fraction of macrostates are occupied.

Example 2 System A with N_A, q_A large number $q_A \gg N_A$ and
System B is 1 oscillator $\Omega_B(1,q) = 1$

$$\Omega_{AB} = \left(\frac{e}{N_A}\right)^{N_A}(q-q_B)^{N_A}\,1 = \left(\frac{e}{N_A}\right)^{N_A} q^{N_A}(1-q_B/q)^{N_A} = \left(\frac{eq}{N_A}\right)^{N_A} e^{N_A\ln(1-q_B/q)}$$

$$\simeq \left(\frac{eq}{N_A}\right)^{N_A} e^{-q_B/(q/N_A)}$$ define $q/N_A = \frac{q\hbar\omega}{N_A}\frac{1}{\hbar\omega} = \frac{\bar{E}_1}{\hbar\omega}$ = avg E in 1 oscillator

$$\Omega_{AB} = \text{const}\; e^{-q_B\hbar\omega/\bar{E}_1} = \text{const}\; e^{-(E_B - \hbar\omega/2)/\bar{E}_1} \simeq \text{const}\; e^{-E_B/\bar{E}_1} \qquad q_B \gg 1$$

From Chap 1 Equipartition Thm $\bar{E}_1 = kT$

A single classical oscillator in contact with N thermal oscillators has an energy distribution that decreases exponentially with 1/e factor kT.

Section 2.5 Ideal Gas

See the book for a different derivation.
The multiplicity of an ideal gas can be found from the eigenenergies of a particle in a box. Take the box to be cube of length L since the answer can't depend on shape if there are many quanta.

The energies in 1D $E_n = \frac{\hbar^2\pi^2 n^2}{2mL^2} = \frac{h^2 n^2}{8mL^2}$ $n = 1, 2, \ldots$ $m =$ mass

The energies in 3D $E_{n_x n_y n_z} = \frac{h^2(n_x^2+n_y^2+n_z^2)}{8mL^2}$ n_x, n_y, n_z $n_x = 1, 2, \ldots ; n_y = \ldots$

Unlike harmonic oscillator, transferring 1 quanta between 2 particles does not conserve energy. However for large n there are many states between $E_n = \frac{h^2}{8mL^2} n^2$ and E_{n+1} for many particles.

To get an idea use $\overset{\swarrow \text{momentum}}{P_n} = hn/2L \Rightarrow n = \frac{P\,2L}{h}$
For N_2 at $300\,m/s$ with $L = 1\,m$ $n = 2 \cdot 1m \cdot 300\frac{m}{s}\, 4.7\times10^{-26}\,kg / 6.6\times10^{-34}\,Js$
$\sim 4\times10^{10}$

Changing n by 1, changes it by less than a part in 10^{10}

Multiplicity will be number of states with energies between E_n and E_{n+1}

Example: 1 particle $\Omega_1(n) =$ number of states with $n^2 \leq n_x^2+n_y^2+n_z^2 \leq (n+1)^2$
If $n \gg 1$, this is like finding the volume of 1/8 sphere with radius between n and $n+1$

$$V = \frac{1}{8}\, 4\pi n^2 \Delta n = \boxed{\frac{\pi}{2} n^2 = \Omega_1(n)}$$

$$\Omega_1(n) = \frac{\pi}{2} n^2 = \boxed{\frac{\pi}{2}\frac{8mL^2}{h^2} E_n} = \frac{\pi}{2}\left(\frac{2LP_n}{h}\right)^2$$

Example: 2 particles $E = \frac{h^2}{8mL^2}(n_{1x}^2 + n_{1y}^2 + n_{1z}^2 + n_{2x}^2 + n_{2y}^2 + n_{2z}^2)$
$\Omega_2(n) =$ number of states with $\frac{h^2 n^2}{8mL^2} \leq E \leq \frac{h^2(n+1)^2}{8mL^2}$
To calculate, find the number of states $\beta_2(n)$ with $E \leq \frac{h^2 n^2}{8mL^2}$
$\Omega_2(n) = (\beta_2(n+1) - \beta_2(n)) / [(n+1) - n] = d\beta_2(n)/dn$
This trick works in higher dimensions.

We need formula for $\beta_N(n) = \frac{1}{2^N} V_{3N}(n)$ $\leftarrow$ Volume of 3N dimensional sphere of radius n

$V_1(n) = 2n \qquad V_2(n) = \pi n^2 \qquad V_3(n) = \frac{4\pi}{3} n^3$ how to generalize?

$$V_d(n) = \iint V_{d-2}\left(\sqrt{n^2 - n_x^2 - n_y^2}\right) dn_x\, dn_y \qquad n^2 - n_x^2 - n_y^2 \geq 0$$

$n_x = r\cos\phi \qquad n_y = r\sin\phi$

$$= \int_0^n \int_0^{2\pi} V_{N-2}\left(\sqrt{n^2 - r^2}\right) d\phi\, r\, dr$$

$$= 2\pi \int_0^n V_{N-2}\left(\sqrt{n^2 - r^2}\right) r\, dr$$

$$V_4(n) = 2\pi^2 \int_0^n (n^2 - r^2)\, r\, dr = 2\pi^2\left(\frac{n^4}{2} - \frac{n^4}{4}\right) = \frac{\pi^2}{2} n^4$$

$$V_6(n) = \pi^3 \int_0^n (n^2 - r^2)^2\, r\, dr = \pi^3 \frac{(n^2 - r^2)^3}{-6}\Big|_0^r = \frac{\pi^3}{6} n^6$$

$$V_8(n) = \frac{\pi^4}{3} \int_0^n (n^2 - r^2)^3\, r\, dr = \frac{\pi^4}{3} \frac{(n^2 - r^2)^4}{8}\Big|_0^r = \frac{\pi^4}{24} n^8$$

If d = even $V_d(n) = \frac{\pi^{d/2}}{(d/2)!} n^d$. If d=odd use Γ function. Actually we'll use Stirling approx. for any d and gives accurate result

Back to ideal gas for identical particles $\mathcal{B}_N(n) = \left(\frac{\pi}{4}\right)^{3N/2} \frac{n^{3N}}{(3N/2)!} \underbrace{\frac{1}{N!}}_{\text{identical swaps}}$

$$\Omega_N(n) = \frac{d\mathcal{B}_N(n)}{dn} = 3\left(\frac{\pi}{4}\right)^{3N/2} \frac{n^{3N-1}}{(3N/2)!} \frac{1}{(N-1)!}$$ = number of states $E_n \leq E \leq E_{n+1}$

For monatomic particles $E = U$ = internal/thermal energy of gas

Other types of gases $E = \frac{3}{f} U$

For monatomic $n = \left(\frac{8mL^2}{h^2} U\right)^{1/2} \Rightarrow \Omega_N(U) = 3\left(\frac{\pi}{4}\right)^{3N/2}\left(\frac{4L^2}{h^2}\right)^{\frac{3N-1}{2}} \frac{(2mU)^{\frac{3N-1}{2}}}{(3N/2)!\,(N-1)!}$

Simplify

$$\Omega_N(U) = \frac{3}{2}\frac{h}{L}\frac{V^N \pi^{3N/2}}{h^{3N}} \frac{(2mU)^{\frac{3N-1}{2}}}{\left(\frac{3N}{2}\right)!\,(N-1)!} \approx \frac{N}{N!}\frac{(2m\pi)^{3N/2}}{(3N/2)!\, h^{3N}} V^N U^{3N/2} \equiv \Omega(U,V,N)$$

Example: the nonquantum limit $n \gg N$. Use Stirling

$$\Omega \approx N\left[(2m\pi U)^{3/2} V/h^3\right]^N \Big/ \left(N!\, \tfrac{3N}{2}!\right) \approx N\left[(2m\pi U)^{3/2} V/h^3\right] \frac{1}{\sqrt{2\pi N}} \left(\frac{e}{N}\right)^N \frac{1}{\sqrt{2\pi 3N/2}} \left(\frac{2e}{3N}\right)^{3N/2}$$

$$\approx \left[(2m\pi)^{3/2}\left(\frac{U}{N}\right)^{3/2}\left(\frac{V}{N}\right) e^{5/2} \left(\frac{2}{3}\right)^{3/2}\right]^N$$ why dropped $\frac{1}{2\pi\sqrt{3/2}}$?

The main part of Ω depends on average single particle properties raised to the N^{th} power

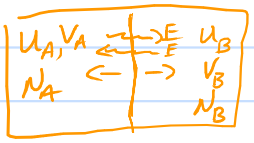
$\bar{E}_1 = U/N$ is the average KE of 1 particle

$\bar{V}_1 = V/N$ " " " volume occupied by 1 particle

$$\Omega \approx \left[\left(\frac{4m\pi}{3}\right)^{3/2} \bar{E}_1^{3/2}\, \bar{V}_1\, e^{5/2}/h^3\right]^N$$

Example: Two interacting ideal gases: partition moves and allows energy through

$V = V_A + V_B$ = fixed $\qquad U = U_A + U_B$ = fixed



$$\Omega_{AB} \approx f(N_A)\, f(N_B)\; V_A^{N_A} (V-V_A)^{N_B}\; U_A^{3N_A/2} (U-U_A)^{3N_B/2}$$

For $G(x) = X^a (X_f - X)^b$ find max and width if a, b large

$$G(x) = e^{a \ln x + b \ln(X_f - x)} = e^{F(x)}$$

$$F'(\bar{x}) = 0 = \frac{a}{\bar{x}} - \frac{b}{X_f - \bar{X}} \qquad \bar{X} = \frac{a}{a+b} X_f$$

$$F''(\bar{X}) = -\frac{a}{\bar{X}^2} - \frac{b}{(X_f - \bar{X})^2} = -\frac{(a+b)^3}{ab X_f^2}$$

$$\Rightarrow \quad G(X) = G(\bar{X})\, e^{-\frac{(X-\bar{X})^2}{\Delta x^2}}$$

$$\frac{2}{\Delta x^2} = \frac{(a+b)^3}{ab X_f^2} \qquad \Delta X = \sqrt{\frac{2ab}{(a+b)^3}} X_f$$

Ω_{AB} has max when $V_A = \frac{N_A}{N} V \qquad U_A = \frac{N_A}{N} U$ makes sense?

spread in values $\Delta V_A = \frac{V}{N} \sqrt{\frac{2N_A N_B}{N}} \qquad \Delta U_A = \frac{U}{N} \sqrt{\frac{4N_A N_B}{3N}}$

Prob 2.27 There are N particles. What is probability for finding <u>all</u> in the leftmost fraction, f, of box

$P = (fV)^N / V^N = f^N$

Suppose $f = 0.99$ $\quad N = 100 \quad$ Prob = 0.37

$N = 1000 \quad$ Prob $= 4.3 \times 10^{-5}$

$N = 10000 \quad$ Prob $= 2 \times 10^{-44}$

Example N_A, V_A fixed $\quad N_B = 1, V_B$ = fixed what is probability for finding particle in B with energy $U_B = P_B^2/2m$?

$\Omega_A = f(N_A)\, V^{N_A} (U - U_B)^{3N_A/2} \qquad \Omega_B = \Omega_1(1) = \frac{\pi}{2} \left(\frac{2L}{h}\right)^2 P_B^2$

$$\Omega_{AB} = \left[f(N_A) V^{N_A} U^{3N_A/2} \frac{\pi}{2} \left(\frac{2L}{h}\right)^2\right] \left(1 - \frac{U_B}{U}\right)^{3N_A/2} P_B^2 = [\,]\, e^{\frac{3N_A}{2} \ln\left(1 - \frac{U_B}{U}\right)} P_B^2$$

$$\approx [\,]\, e^{-\frac{P_B^2}{2m} / (U/3N_A/2)} P_B^2$$

From Equipartition Thm $U/(3N_A/2) = kT$

A single free moving monatomic particle has probability of P_B^2 times exponential decrease with energy.

Repeat 1D $\quad \Omega_A = f(N_A, L)(U - U_B)^{N_A/2} \qquad \Omega_B = g(N_B, L)$

$$\Omega_{AB} = [\,]\,(U - U_B)^{N_A/2} \approx [\,]\, U^{N_A/2}\, e^{-P_B^2/2m/(U/N_A/2)}$$

From Equipartition Thm $U/(N_A/2) = k_B T$

see max_boltz_vs_number.ipynb

Section 2.6 Entropy

2^{nd} Law of Thermodynamics: At thermal equilibrium, any large system will be found in a macrostate with maximum multiplicity (aside from unmeasurably small fluctuations).

$\Rightarrow$ Multiplicity increases (aside from fluctuations). If you start in a macrostate with $\Omega < \Omega_{max}$, the system evolves until $\Omega \to \Omega_{max}$.

Entropy $S = k \ln(\Omega)$ multiplicity increase $\Rightarrow$ entropy increase

Example: find entropy of Einstein model $\Omega(N,q) = \frac{1}{\sqrt{2\pi(q+N)q/N}} \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N$

Define $\bar{q}_1 = q/N$ = average number of quanta in 1 oscillator = small number

$$\Omega(N,q) = \frac{1}{\sqrt{2\pi N \bar{q}_1(\bar{q}+1)}} \left(\frac{\bar{q}_1+1}{\bar{q}_1}\right)^{\bar{q}_1 N} (\bar{q}_1+1)^N = \frac{1}{\sqrt{2\pi N \bar{q}_1(\bar{q}+)}} \left[\frac{(\bar{q}_1+1)^{\bar{q}+1}}{\bar{q}_1^{\bar{q}_1}}\right]^N$$

$$S = k\Big[\underbrace{N \ln\left((\bar{q}+1)\left(1+\frac{1}{\bar{q}_1}\right)^{\bar{q}_1}\right)}_{\text{large}} + \underbrace{\frac{1}{2}\ln\left(2\pi N \bar{q}_1(\bar{q}_1+1)\right)}_{\text{regular = can drop}}\Big]$$

If $\bar{q}_1 >> 1$ $\quad \bar{q}+1 \cong 1 \quad \left(1+\frac{1}{\bar{q}_1}\right)^{\bar{q}_1} \cong e$

$S = Nk[\ln(\bar{q}_1) + 1]$ $\quad$ $\bar{q}_1$ increases with temperature

$\Rightarrow S$ " " " (but not quickly)

In the thermodynamic limit $\lim_{N\to\infty} \frac{S}{N} \to$ const

Repeat for small $\bar{q}_1$ $\quad \frac{S}{N} = k\left[\ln(1+\bar{q}_1) + \bar{q}_1 \ln\left(1+\frac{1}{\bar{q}_1}\right)\right] \cong k[\bar{q}_1 - \bar{q}_1 \ln \bar{q}_1]$

$= k\bar{q}_1 \ln(e/\bar{q}_1)$

Example N = Avogadro # $= N_A$ $\quad \bar{q}_1 = 100$

$S = 6\times10^{23} \; 1.38\times10^{-23}$ J/K $[\ln(100)+1] = 46$ J/K

$\bar{q}_1 = 0.01 \quad S = 6\times10^{23} \; 1.38\times10^{-23} \; 0.01(1 - \ln 0.01) = 0.46$ J/K

Example: Composite system made up of A and B

$\Omega_{TOT} \cong \Omega_{AB} = \Omega(A)\Omega(B)$

$\Rightarrow S_{TOT} = k_B \ln \Omega_{TOT} \cong k_B \ln \Omega(A) + k_B \ln \Omega(B) = S_A + S_B$

Why is this an approximation?

Example: Careful look at Einstein model $N = N_A + N_B$ $\bar{q}_1 = \frac{q}{N} = \frac{q_A}{N_A} = \frac{q_B}{N_B}$

$$S = k_B\{N \ln[\bar{q}_1(1+\tfrac{1}{\bar{q}_1})^{\bar{q}_1}] + \tfrac{1}{2}\ln[2\pi\bar{q}_1(\bar{q}_1+1)N]\}$$

$$S - S_A - S_B = k_B \tfrac{1}{2} \ln\left[\frac{N}{2\pi\bar{q}_1(\bar{q}_1+1)N_A N_B}\right] \quad \Rightarrow \quad S \neq S_A + S_B$$

How large is the difference? $N = 6\times10^{23}$ $\bar{q}_1 = 100 \rightarrow S = 46\,J/K$

Take $N_A = N_B = 3\times10^{23}$ $\bar{q}_1 = 100$ $S - S_A - S_B = -32k_B = -4.4\times10^{-22}\,J/K$

The difference is due to $\Omega_{TOT} \neq \Omega(A)\,\Omega(B)$; need to sum over all combinations of $q_A + q_B = q$, not just take most likely

These differences give fractional errors $\rightarrow 0$ as $N \rightarrow \infty$

The entropy of a monatonic ideal gas $\Omega = \left[\left(\frac{4m\pi}{3}\right)^{3/2} \frac{\bar{E}_1^{3/2}\,\bar{V}_1\,e^{5/2}}{h^3}\right]^N$

$\bar{E}_1 = U/N$ $\bar{V}_1 = V/N$

$$S = Nk\{\ln[(\tfrac{4m\pi}{3})^{3/2}\bar{E}_1^{3/2}\bar{V}_1/h^3] + 5/2\}$$ Sackur-Tetrode eq.

Example: Compute S for 1 mole of He at 300 K and 1 atmosphere

$\bar{E}_1 = \frac{3}{2}kT = 6.21\times10^{-21}\,J$

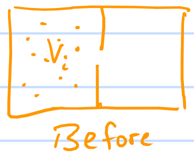
$m \simeq 4 \cdot 1.67\times10^{-27}\,kg \simeq 6.68\times10^{-27}\,kg$

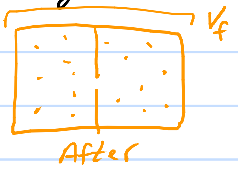
$\bar{V}_1 = kT/p = 4.10\times10^{-26}$

$$S = 6.02\times10^{23}\; 1.38\times10^{-23}\,\frac{J}{K}\left\{\ln\left[\left(\frac{4\cdot6.68\times10^{-27}\pi}{3}\,6.21\times10^{-21}\right)^{3/2}\frac{4.1\times10^{-26}}{(6.63\times10^{-34})^3}\right] + 5/2\right\}$$

$$= 8.31\,J/K\,[\ln(3.22\times10^5) + 5/2] = 8.31\,J/K\,\{12.7 + 2.5\} = \underline{126\,J/K}$$

The entropy changes even if only the volume changes





$S(N,U,V_f) - S(N,U,V_i) =$

$Nk_B\{\ln(\cancel{const}) + \ln(V_f) - \cancel{\ln(const)} - \ln(V_i)\}$

$= Nk_B \ln(V_f/V_i)$

Can the reverse happen

The derivative of S with respect to U or V or N holding the others constant leads to macroscopic properties: P, T, etc.

Example Take derivative of S w.r.t. U keeping V and N constant

$S = Nk\{\frac{3}{2}\ln U + \text{const}\}$

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{3/2\, Nk}{U} = \frac{k}{U/(\frac{3}{2}N)}$$

The combination $U/\frac{3}{2}N$ appeared in the momentum distribution function

For a monatomic gas $\frac{U}{3/2\,N} = kT$ $\Rightarrow \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$ for monatomic gas.

IS $\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T}$ in general?? Chap 3!!

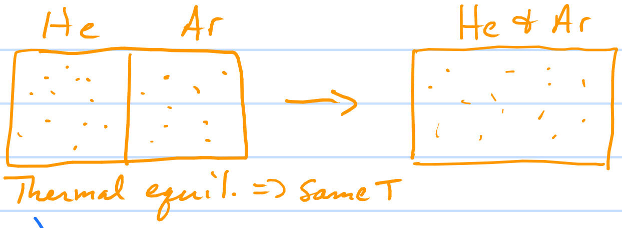
Example Take derivative of S w.r.t. V keeping U and N constant.

$S = Nk\{\ln V + \text{const}\}$

$\left(\frac{\partial S}{\partial V}\right)_{U,N} = Nk/V$ Ideal gas $PV = NkT$ $\Rightarrow \left(\frac{\partial S}{\partial V}\right)_{U,N} = P/T$

Is $\left(\frac{\partial S}{\partial V}\right)_{U,N} = P/T$ in general?? Chap 3!!!

There's an increase of entropy when gases mix



$$\Delta S = N_{He}k\ln\left(\frac{V}{V_i(He)}\right) + N_{Ar}k\ln\left(\frac{V}{V_i(Ar)}\right)$$

If $V_i(He) = V_i(Ar) = V/2$ $\Delta S = (N_{He} + N_{Ar})k\ln(2)$

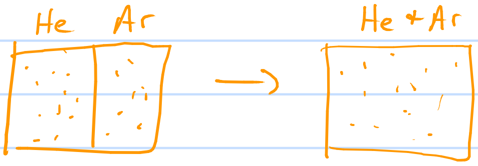
When the original derivation was made for ideal gas the $1/N!$ was not included in the derivation because every atom/molecule was thought to be distinguishable. Gibbs noticed this problem (Gibbs paradox) and showed how to fix it

$\Delta S = 0$ because entropy only depends on V/N

Before $S = 2 * \frac{N}{2}k\ln\left[\left(\frac{4m\pi}{3}\right)^{3/2}\frac{\bar{E}_1^{3/2}\bar{V}_1}{h^3}\right] + 5/2\,]$

After $S = N\ k\ln[\quad \text{same} \quad]$

Prob 2.37 He + Ar start at same T & P



Entropy of mixing when $N_{Ar} = xN$ $\quad V_i(Ar) = xV$

$N_{He} = (1-x)N$ $\quad V_i(He) = (1-x)V$

$$\Delta S = N_{He}\, k \ln\left(\frac{V}{V_i(He)}\right) + N_{Ar}\, k \ln\left(\frac{V}{V_i(Ar)}\right)$$

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

Reversible/irreversible If you do a process where $\Delta S > 0$, you can not exactly undo the process because that would give $\Delta S < 0$ when you reversed.

You can only reverse the process if $\Delta S = 0$

In the real world, no process exactly has $\Delta S = 0$.

Example: Heat flow Heat flows from hot objects to cold objects, increasing their joint multiplicity.

Heat flow "always" gives $\Delta S > 0 \Rightarrow$ not reversible

ΔS_{TOT} of everything is always increasing. Why did the universe start with small S?