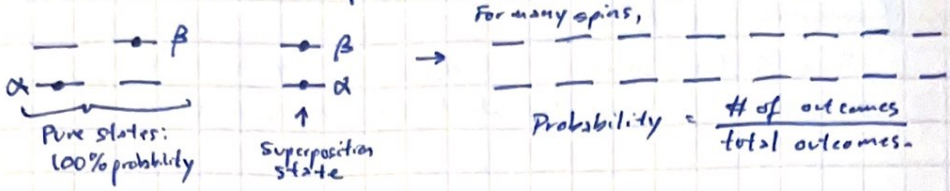
Statistical Thermodynamics

So far we have observed microscopic properties of a single molecule or a single atom. For these systems, we observed the system using quantum mechanics. For a macroscopic system of many atoms, we must use statistical mechanics.

- Statistical mechanics is a probabilistic system, but different in probability as understood in Q.M.



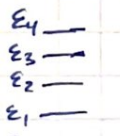
$E = -B_0\mu_z = -\gamma\hbar B_0 \begin{Bmatrix} 1/2 \\ -1/2 \end{Bmatrix} \xrightarrow[\text{many spins}]{\text{For}} -\sum B_0\mu_0 = E = -B_0 M_0$, where M_0 = total magnetization of all spins.

$M_z = \gamma\hbar(1/2)(+-++--+\dots) \rightarrow$ In general, $M_z = \gamma\hbar 1/2\,(M_\alpha - M_\beta)$

Consider a system of n non-interacting particles, in a closed system. Energy can be exchanged, but particles cannot be exchanged. Assuming the value of energy is E_i $\quad E = \sum_{\text{particles}} E_k$ ↳ Energy of each particle.

The problem with the statement $E = \sum_{\text{particles}} E_k$ is that it requires us to know the state of each particle. However, we can simplify this problem:

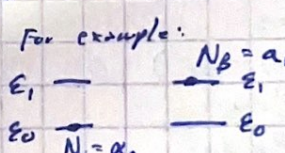
→ We do not care about ~~how many~~ per what state each particle is in. Instead, we care about how many particles are in one state compared to another.



Occupation number $= a_i$

$\sum a_i = N$ ↳ total number of particles

For example:



$\sum a_i \varepsilon_i = E$

Configuration: $\{a_0, a_1, a_2 \dots\}$

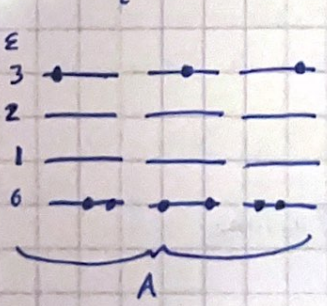
$P_i = \dfrac{\#\text{ particles in state}}{\text{Total \# of particles}} = \boxed{\dfrac{a_i}{N}}$ ← Fractional Population

For a purely statistical description,

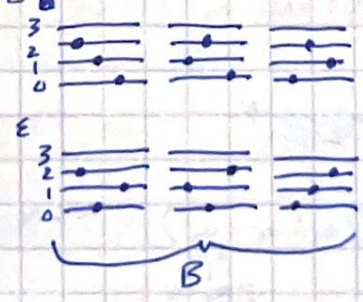
$$\sum P_i = \frac{\sum a_i}{N} = 1$$

If we suppose $N = 3$, $\varepsilon = \{0, 1, 2, 3\} \rightarrow \{a_0, a_1, a_2, a_3\}$ then

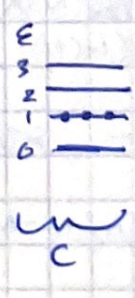
$E = \sum_i a_i \times \varepsilon_i = a_0\times 0 + a_1\times 1 + a_2\times 2 + a_3\times 3$. Considering the possible configurations:



Possible micro states: $\{2, 0, 0, 1\}$



Possible microstates: $\{1, 1, 1, 0\}$



Possible microstates: $\{0, 3, 0, 0\}$

Each microstate is equally probable. Therefore, the one with the most possible microstates than the others is the preferred state.

We can describe the system by a weighted configuration of microstates:

A: $W = 3$

B: $W = 6$ ← Dominant state

C: $W = 1$

This approach works when $N = 3$, but what happens in a realistic system, when $N = 100$, or $N = 1000$? The number of permutations is $N!$:

$0! = 1$
$1! = 1$
$2! = 2 \cdot 1$
$3! = 3 \cdot 2 \cdot 1 = 6$

Since A has degeneracy as well as C, we overcount by a permutation of 2 particles which are in the same state.

General rule: $W = N!$ if each state is non-degenerate.

$W = \frac{N!}{a_0! a_1! a_2! \dots}$ if states have degeneracy.

A: $W = \frac{3!}{2!\,0!\,0!\,1!} = 3$

C: $W = \frac{3!}{0!\,3!\,0!\,0!} = 1$

To find the maximum configuration, we find the maximum W:

$$W = \frac{N!}{a_0! a_1! a_2! \dots a_n!}, \quad dW = \sum_i \frac{\partial W}{\partial a_i} da_i = 0$$

If we assume all a_i's are independent of each other, then $\sum_i \frac{\partial W}{\partial a_i} = 0$. BUT, this is not the case. a's are dependent on each other:

$\sum a_i = N$, $\sum a_i \varepsilon_i = E$ both must be obeyed: to solve, we used undetermined Lagrange Multipliers:

$$d(W + \alpha N - \beta E) = 0$$
$$dN = \sum da_i$$
$$dE = \sum \varepsilon_i da_i$$

But, there is one problem: $W = \frac{N!}{a_0! a_1! a_2! \dots}$ is not a function. How can we differentiate this?

We can use the Sterling Approximation to estimate $N!$:

$N! \approx \sqrt{2\pi}\, N^{(N+1/2)} e^{-N} = \sqrt{2\pi N}\left(\frac{N}{e}\right)^N$, and $\ln(N!) \approx N\ln(N) - N$, if we assume $N >>> 1$, and the max of N $\approx$ Max of $N!$ (N is very large)

Then $\ln(N!) = \ln(2\pi) + (N+1/2)\ln(N) - N$, when $N >>> 1$,

~~$\ln(2\pi)$~~ + ~~N~~$(N+1/2)\ln(N) - N$

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

If we take $\ln W$, then ~~$\ln\left(\frac{N!}{a_0! a_1! \dots}\right)$~~

$$\ln W = (N\ln N - N) - \sum(a_i \ln a_i - a_i) = N\ln N - \sum a_i \ln a_i$$

($\sum a_i = N$)

The most predominant configuration is when $a_i = \frac{e^{-\varepsilon_i\beta}}{\sum e^{-\varepsilon_i\beta}} N$, where $\beta = \frac{1}{k_B T}$

$P_i = \frac{e^{-\varepsilon_i\beta}}{\sum e^{-\varepsilon_i\beta}}$ The distribution most preferred is simply related to the boltzmann, an exponential function.

↳ Normalization coefficient, the partition function: $q = \sum e^{-\varepsilon_i\beta}$

$\boxed{E = \sum a_i\varepsilon_i}$, substitute a_i with $a_i = \frac{e^{-\varepsilon_i\beta}}{\sum e^{-\varepsilon_i\beta}} N$, then $E = \frac{N}{q}\sum e^{-\varepsilon_i\beta}\varepsilon_i$

$E = -\frac{N}{q}\frac{d}{d\beta}\sum e^{-\varepsilon_i\beta} = -\frac{N}{q}\frac{d}{d\beta}q = -N\frac{d}{d\beta}\ln q$ → $\underline{d\beta = -\frac{1}{k_B}\frac{1}{T^2}dT}$ $\frac{d}{d\beta}e^{-\varepsilon_i\beta} = e^{-\varepsilon_i\beta}\cdot\varepsilon_i$

$\frac{d}{d\beta}\ln q = \frac{1}{q}\frac{d}{d\beta}q$

Once the partition function is known, the energy can immediately be determined.

Recall that $M = -\gamma\hbar\tfrac{1}{2}(N_\alpha - N_\beta)$ ($\alpha_{1/2}$, $\alpha_{-1/2}$) We subtract the energy of the lowest level to make the consideration simpler.

$\alpha_{1/2} = \frac{1}{1+e^{-\Delta E/k_BT}}$, $\alpha_{-1/2} = \frac{e^{-\Delta E/k_BT}}{1+e^{-\Delta E/k_BT}}$ → $\frac{\alpha_{-1/2}}{\alpha_{1/2}} = e^{\frac{-\Delta E}{kT}} = e^{-10^{-4}}$

Recall that $e^x \approx 1+x$, $1-10^{-4} \approx 0.9999$

$M = -\gamma\hbar\tfrac{1}{2}N\left(\frac{1-e^{-\frac{\Delta E}{k_BT}}}{1+e^{-\frac{\Delta E}{k_BT}}}\right) \approx -\gamma\hbar\tfrac{1}{2}N\left(\frac{1-(1-\frac{\Delta E}{k_BT})}{1+(1-\frac{\Delta E}{k_BT})}\right) = -\gamma\hbar\tfrac{1}{2}\left(\frac{N}{2}\right)\left(\frac{\Delta E}{k_BT}\right)$

Substituting $\Delta E = \gamma\hbar B_0$, $-\gamma\hbar\tfrac{1}{2}\left(\frac{N}{2}\right)\left(\frac{\gamma\hbar B_0}{k_BT}\right) = -\frac{(\gamma\hbar)^2 B_0 N}{4k_BT}$ ↳ Proportional to magnetic field.

$a_i = N\frac{e^{-\varepsilon_i\beta}}{q}$, where $\beta = \frac{1}{k_BT}$, where $q = \sum e^{-\varepsilon_i\beta}$.

↳ Counts through all the possible states, including the degenerate states: overcounts!

$P_i = \frac{e^{-\varepsilon_i\beta}}{q}$

ε_2, ε_1, ε_0 → $\underbrace{\varepsilon_i - \varepsilon_0}_{=\varepsilon_i'} + \varepsilon_0 = \varepsilon_i' + \varepsilon_0$ $q = \sum_i e^{-\varepsilon_i'\beta}\cdot e^{-\varepsilon_0\beta} = e^{-\varepsilon_0\beta}\underbrace{\sum e^{-\varepsilon_i'\beta}}_{=q'} = q'\cdot e^{-\varepsilon_0\beta}$

We can modify P_i for the difference in energy: $P_i = \frac{e^{-\varepsilon_i'\beta}\cdot e^{\varepsilon_0\beta}}{q' e^{-\varepsilon_0\beta}}$ → $P_i = \frac{e^{-\varepsilon_i\beta}}{q'}$, accounts for 0 point energy

If $E = \sum\varepsilon_i a_i$, then $E = \underbrace{\sum\varepsilon_i' a_i}_{E'} + \sum\varepsilon_0 a_i \to N\cdot\varepsilon_0$

To account for overcounting in $q = \sum e^{-\varepsilon_i\beta}$, we must consider the degenerate states:

for a particle in a sphere, $E = \frac{\hbar^2}{2I}l(l+1)$

$m_l = \pm 1$, $m_l = 0$; $l = 1$, $l = 0$; ε

$q = e^0 + e^{-\varepsilon\beta} + e^{-\varepsilon\beta} + e^{-\varepsilon\beta}$

$m_l = -1$ $m_l = 0$ $m_l = 1$

$\boxed{q = \sum_{\text{states}} e^{-\varepsilon_i\beta} \cdots (g_i)}$

↓ Degenerate states

$\boxed{P_i = \frac{g_i e^{-\varepsilon_i\beta}}{q}}$

Discussing q in the context of temperature:

$q = \sum_{\text{states}} e^{-\varepsilon_i\beta} = \sum_{\text{states}} e^{-\varepsilon_i\frac{1}{k_BT}}$, For a higher temperature, $q\uparrow$. For a lower temperature, $q\downarrow$.

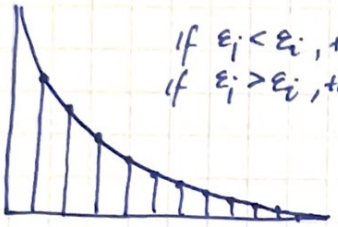
Consider two states: i and j:

$$p_i = \frac{e^{-\varepsilon_i \beta}}{q}, \quad p_j = \frac{e^{-\varepsilon_j \beta}}{q} \rightarrow \frac{p_i}{p_j} = e^{-(\varepsilon_i - \varepsilon_j)\beta}, \text{ then } \ln\left(\frac{p_i}{p_j}\right) = -(\varepsilon_i - \varepsilon_j)\beta$$

Rearranging the expression for T, $T = \frac{1}{k_B}\left[\frac{\varepsilon_i - \varepsilon_j}{\ln\left(\frac{p_i}{p_j}\right)}\right]$: Note that this assumes each level is not degenerate

Accounting for degenerate states, $T = \frac{1}{k_B}\left[\frac{(\varepsilon_i - \varepsilon_j)}{\ln\left(\frac{p_i}{p_j}\frac{g_j}{g_i}\right)}\right]$

$$p_i = \frac{e^{-\varepsilon_i \beta}}{q}$$



If $\varepsilon_j < \varepsilon_i$, then $p_j > p_i$
If $\varepsilon_j > \varepsilon_i$, then $p_j < p_i$

Considering if temperature $\rightarrow \infty$:
When $T \rightarrow \infty$, $p_i \approx p_j$, $\ln\left(\frac{p_i}{p_j}\right) \approx 0$: Therefore, the equation:

$$T = \frac{1}{k_B}\frac{\varepsilon_i - \varepsilon_j}{\ln\left(\frac{p_i}{p_j}\right)}$$ cannot be solved unless $\varepsilon_i - \varepsilon_j = 0$.

→ The high levels of energy are more populated than the lower levels, results in negative temperatures.

Recall that $E = -N\frac{\partial}{\partial \beta}\ln q$. When we know q, we know the energy.

- Can the partition be infinitely high? Can it be 0? $q = \sum e^{-\varepsilon_i \beta} = e^{-\varepsilon_0 \beta} + e^{-\varepsilon_1 \beta} + e^{-\varepsilon_2 \beta} + \ldots$

Consider a system of 2 states:

ε ——
0 ——

→ If $T \rightarrow 0$ and $\beta \rightarrow \infty$,
then $q = e^0 + e^{-\varepsilon\beta} = 1 + e^{-\varepsilon\beta}$

Fractional population of ε: $p_\varepsilon = \frac{e^{-\varepsilon\beta}}{1+e^{-\varepsilon\beta}} = 0$ (Since $e^{-\varepsilon(\infty)} \rightarrow 0$)

Fractional population of 0: $p_0 = \frac{1}{1+e^{-\varepsilon\beta}} = 1$

→ If instead $\beta \rightarrow 0$ and $T \rightarrow \infty$, then

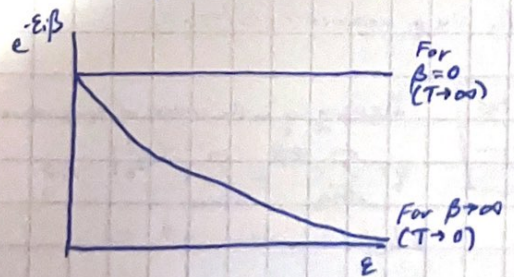
$e^{-\varepsilon\beta} \rightarrow 1$

Fractional population of ε: $p_\varepsilon = \frac{e^{-\varepsilon\beta}}{1+e^{-\varepsilon\beta}} = \frac{1}{2}$
Fractional population of 0: $p_0 = \frac{1}{1+e^{-\varepsilon\beta}} = \frac{1}{2}$
} Both states are equally populated.

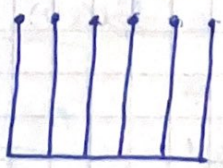
	q	# populated states
$T \rightarrow 0$	1	1
$T \rightarrow \infty$	2	2

The partition function corresponds to the number of thermally populated states.

If we graph $e^{-\varepsilon_i \beta}$ as a function of ε, the relationship becomes much clearer:

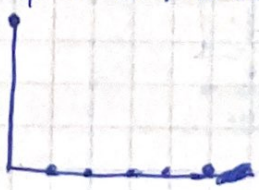


If $T \rightarrow \infty$, p becomes infinitely large:



$\rightarrow \infty$

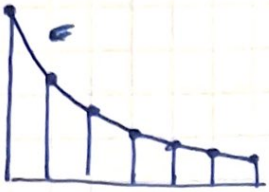
If $T \rightarrow 0$, p is only represented by the ground state:



$= 1$

(In degenerate systems, there may be another lowest level for p)

Considering a system in which $0<\beta<\infty$ and $0<T<\infty$, then



$e^{-\frac{\varepsilon}{k_B T}}$, if

$\varepsilon = k_B T$, $e^{-1} = 0.37$

$\varepsilon = 2k_B T$, $e^{-2} = 0.13$

...

Consider a degenerate system:

g	ε	
4	5ε	With no other possible energy levels
1	3ε	
2	0	

Then the partition function may be represented as:

$$q = \sum_{\text{states}} e^{-\varepsilon_i \beta} \cdot g_i$$

$$q = 2\cdot e^{0} + 1\cdot e^{-3\varepsilon\beta} + 4e^{-5\varepsilon\beta}$$

- Maximum q, $\beta \to 0$, $T \to \infty$ $= 7$
- Minimum q, $\beta \to \infty$, $T \to 0$ $= 2$

What about for a harmonic oscillator?

$E_{HO}(n) = h\nu(n+\frac{1}{2})$ → No limit on the number of energy levels possible

- For the zero point energy, $\varepsilon_{HO} = h\nu n$, and $q = 1 + e^{-h\nu\beta} + e^{-2h\nu\beta} + \dots$

Let $e^{-h\nu\beta} = b$. Then, $q = 1 + b + b^2 + b^3 + \dots + b^n$ → a taylor approximation!

$q = 1 + b + b^2 + b^3 + \dots + b^n = \frac{1-b^{n+1}}{1-b}$. Since $n \to \infty$, the expression simplifies to $\frac{1}{1-b}$.

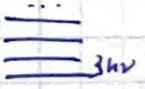
We find the partition function of the harmonic oscillator:

$$\boxed{q_{HO} = \frac{1}{1-e^{-h\nu\beta}}}, \quad q_{T\to 0} = 1.$$ If $h\nu \ll k_B T$, then $e^{-h\nu\beta} \to e^{-x}$, where x is a small number.

Recall that $e^{x} \approx 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$ Then for $q = \frac{1}{1-e^{-x}}$,

$$q_r = \frac{1}{1-e^{-h\nu\beta}} \approx \frac{1}{1-(1-h\nu\beta)} = \frac{1}{h\nu\beta} = \frac{k_B T}{h\nu}$$

Result tells us how many levels fall between the range of 0 to $k_B T$:



A Consideration of Entropy

Recall that for any reversible thermodynamic process, $\oint \frac{\delta q_{rev}}{T} = 0$. Then entropy is defined $\Delta S = \int_{S_1}^{S_2} \frac{\delta q_{rev}}{T}$, and $dS = \frac{\delta q_{rev}}{T}$

Entropy is a measure of disorder. So what is disorder?

→ More than 1 possibility: (1) All states are in one spin = no disorder. (2) All states can be in two different spins = disorder. Therefore, the more possible microstates, the more disorder.

S is an extensive function: $\boxed{S_A}\boxed{S_B}$, $S_{total} = S_A + S_B$. Just as energies add and wave functions multiply, entropies add and the number of microstates, W, multiply.

what function does this? — Logarithm.

Statistical Weight { W_A = number of microstates in A; W_B = number of microstates in B; then $W_A(W_B)$, assuming W_A is independent of W_B. } → $S = f(W) = f(W_A) + f(W_B) = f(W_A \cdot W_B)$