Tutorial #3

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Example #1 - The Two State System

Consider a system of N non-interacting two-state systems. $|i\rangle = \{|\uparrow\rangle, |\downarrow\rangle\}$.

$$E(|\uparrow\rangle) = \epsilon \quad , \quad E(|\downarrow\rangle) = 0$$

1) What is $\langle E \rangle$?

2) What is $\frac{N_\uparrow}{N}$?

3) What is the entropy $S(E)$?

4) What is the heat capacity?

So much to learn in such a simple theory!

(Solution #1)

1) What is $\langle E \rangle$?

We start by considering one system:

$$\langle E_1 \rangle = \sum_{|i\rangle} E(|i\rangle) P(|i\rangle) = \frac{\epsilon e^{-\beta\epsilon}}{Z} + \frac{0 e^{-\beta\epsilon}}{Z}$$

$$\langle E_1 \rangle = \frac{\epsilon e^{-\beta\epsilon}}{Z}$$

Aside, what is Z?

$$Z = \sum_{|i\rangle} e^{-\beta E(|i\rangle)} = e^{-\beta\epsilon} + 1$$

$$\Rightarrow \langle E_1 \rangle = \frac{\epsilon e^{-\beta\epsilon}}{e^{-\beta\epsilon} + 1}$$

$e^{-\beta\epsilon} + 1$

Since the systems are all independent they each supply the same contribution to $\langle E \rangle$

$$\Rightarrow \boxed{\langle E \rangle = N \langle E_i \rangle = \frac{N\epsilon}{1 + e^{+\beta\epsilon}}}$$

$\frac{1}{k_B T}$

Let's consider this briefly, what are the limiting behaviours of $\langle E \rangle$ w.r.t. temperature?

$$\lim_{T \to 0} \langle E \rangle = 0 \qquad \lim_{T \to \infty} \langle E \rangle = \frac{N\epsilon}{2}$$

① ②

① This makes sense, when cold, there is no energy for thermal excitation.

② This one is interesting. Note that the maximum energy in the system is $N\epsilon$. This means a $T \to \infty$ we have half of the maximum energy...

(Solution #2) – Direct solution

This time we'll consider the whole system at once:

$$\langle E \rangle = \sum_{E_i} E_i P(E)$$

what energies are accessible?

$E = k\epsilon$, $k = \{0, 1, 2, \ldots N\}$

$$= \sum_{k=0}^{N} k\epsilon P(E)$$

$$= \sum_{k=0}^{N} k\epsilon \left[\frac{\Omega(k\epsilon) e^{-\beta k\epsilon}}{Z} \right]$$

Q What is $\Omega(E)$? → A How many states of the system have energy $k\epsilon$?

k	0	1	2	3	... k ...
Ω	1	N	$\frac{N(N-1)}{2}$	$\frac{N(N-1)(N-2)}{3!}$	$\frac{N!}{k!(N-k)!}$

$$\Omega(k\epsilon) = \binom{k}{N}$$

$\boxed{Q}$ What is Z?

$\boxed{A}$

$$Z = \sum_{k=0}^{N} \Omega(E) e^{-\beta k\epsilon}$$

$$= \sum_{k=0}^{N} \binom{k}{N} \left(e^{-\beta\epsilon}\right)^{k} (1)^{N-k}$$

$$= \left(e^{-\beta\epsilon} + 1\right)^{N}$$

$$\Rightarrow \langle E \rangle = \frac{1}{(e^{-\beta\epsilon}+1)^N} \sum_{k=0}^{N} k\epsilon \binom{k}{N} e^{-\beta k\epsilon}$$

$$= \frac{1}{(e^{-\beta\epsilon}+1)^N} \frac{d}{d(-\beta)} \underbrace{\sum_{k=0}^{N} \binom{k}{N} e^{-\beta k\epsilon}}_{Z!}$$

$$= \frac{1}{(e^{-\beta\epsilon}+1)^N} \frac{d}{d(-\beta)} \left(e^{-\beta\epsilon}+1\right)^N$$

$$= \frac{N\epsilon\, e^{-\beta\epsilon}}{(e^{-\beta\epsilon}+1)}$$

$$\boxed{\langle E \rangle = \frac{N\epsilon}{1+e^{\beta\epsilon}}}$$

Same as before!

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2) What is $\left\langle \frac{N_1}{N} \right\rangle$?

Let's take the easy road here and look @ one spin again:

$$\langle N_\uparrow^1 \rangle = \sum_i N_\uparrow^1(|i\rangle)\, P(|i\rangle) = \frac{e^{-\beta\epsilon}}{Z_1} = \frac{e^{-\beta\epsilon}}{e^{-\beta\epsilon}+1}$$

$$\langle N_\uparrow^1 \rangle = N \langle N_\uparrow^1 \rangle = \frac{N}{1+e^{\beta\epsilon}}$$

$$\boxed{\frac{\langle N_\uparrow^1 \rangle}{N} = \frac{1}{1+e^{\beta\epsilon}}}$$

Again, let's look @ the limiting cases:

$$\frac{\langle N_\uparrow \rangle}{N} = \frac{1}{1+e^{\frac{\epsilon}{k_B T}}}$$

$$\boxed{\lim_{T\to 0} \frac{\langle N_\uparrow \rangle}{N} = 0 \qquad \lim_{T\to\infty} \frac{\langle N_\uparrow \rangle}{N} = \frac{1}{2}}$$

Again, we find similar contributions as with the energy! $T\to\infty$ leads to half <u>occupation</u>!

hmm....

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3) What is the entropy?

(Solution #1 - À la Boltzmann)

$$S(E) = k_B \log\left(\Omega(E)\right)$$
$$= k_B \log\left(\frac{N!}{K!(N-K!)}\right)$$

we've already seen $\Omega(E) = \binom{K}{N}$

where $K = \frac{E}{\epsilon}$

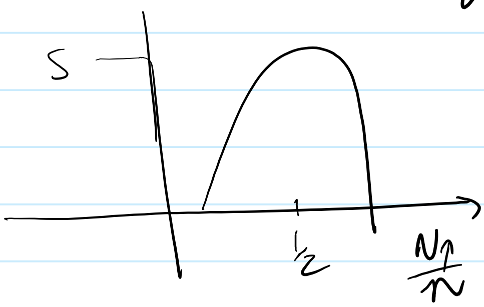
Stirling's Approximation

$$\approx k_B\Big[N\log N - N - [k\log(k) - k] - [(N-k)\log(N-k) - (N-k)]\Big]$$

$$= -k_B\Big[(N-k)\log\Big(\frac{N-k}{N}\Big) + k\log\Big(\frac{k}{N}\Big)\Big]$$

$$\boxed{S(E) = -Nk_B\Big[\Big(1-\frac{E}{N\epsilon}\Big)\log\Big(1-\frac{E}{N\epsilon}\Big) + \frac{E}{N\epsilon}\log\Big(\frac{E}{N\epsilon}\Big)\Big]}$$

form $\quad f(x) = -\big((1-x)\log(1-x) + x\log x\big)$



(Solution #2 - À la Gibbs)

Consider the Gibbs entropy of a single ~~spin~~ spin!

$$S(P(|i\rangle)) = -k_B\sum_{|i\rangle} P(|i\rangle)\log(P(|i\rangle))$$

$$P(|\uparrow\rangle) = \frac{e^{-\beta\epsilon}}{Z} \qquad P(|\downarrow\rangle) = \frac{1}{Z}$$

$$S_1(P) = -k_B\Big[\frac{1}{Z}\log\Big(\frac{1}{Z}\Big) + \frac{e^{-\beta\epsilon}}{Z}\log\Big(\frac{e^{-\beta\epsilon}}{Z}\Big)\Big]$$

Aside

recall $\quad E = \dfrac{N\epsilon e^{-\beta\epsilon}}{Z} \Rightarrow \dfrac{E}{N\epsilon} = \dfrac{e^{-\beta\epsilon}}{Z}$ *

recall $E = \frac{N\epsilon e}{Z} \Rightarrow \frac{E}{N\epsilon} = \frac{e}{Z}$ *

and

$$1 = \frac{1}{Z} + \frac{e^{-\beta\epsilon}}{Z} \Rightarrow \frac{1}{Z} = 1 - \frac{e^{-\beta\epsilon}}{Z}$$

$$\frac{1}{Z} = 1 - \frac{E}{N\epsilon} \quad *$$

$$S_1 = -k_B\left[\left(1-\frac{E}{N\epsilon}\right)\log\left(1-\frac{E}{N\epsilon}\right) + \frac{E}{N\epsilon}\log\left(\frac{E}{N\epsilon}\right)\right]$$

$$\boxed{S_{total} = NS_1 = -k_B N\left[\left(1-\frac{E}{N\epsilon}\right)\log\left(1-\frac{E}{N\epsilon}\right) + \frac{E}{N\epsilon}\log\left(\frac{E}{N\epsilon}\right)\right]}$$

Same as Boltzmann !!

Special Notes

@ $T \to 0$ our system chose the lowest energy state

@ $T \to \infty$ our system chose the highest entropy state

$\boxed{\text{Why?}}$

Recall that for a microscopic state $|i\rangle$ we have

$$P(|i\rangle) \propto e^{-\beta E(|i\rangle)}$$

but for a macroscopic state like $N_\uparrow$ we have:

$$P(N_\uparrow) \propto \Omega(N_\uparrow)\, e^{-\beta E(N_\uparrow)}$$

$$= e^{\ln(\Omega) - \beta E}$$

$$= e^{-\beta F(N_\uparrow)}$$

so $P(N_\uparrow) \propto e^{-\beta F(N_\uparrow)}$

So! the most probable macroscopic state is

@ the minimum of the free energy

$$\boxed{F(N_\uparrow) = E(N_\uparrow) - TS(N_\uparrow)}$$

as $T \to \infty$ the entropy contribution dominates!

as $T \to 0$ the energy contribution dominates!

Problem #4 — Heat Capacity!

$$\boxed{C = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T}\left[\frac{N\epsilon}{1+e^{\beta\epsilon}}\right] = \frac{N\epsilon^2}{k_B T^2}\frac{e^{\beta\epsilon}}{(1+e^{\beta\epsilon})^2}}$$

the Schottky Anomaly

→ usually C_V decreases monotonically with temperature. This is the schottky anomaly shows up in low temperature spin systems!

↳ unless the phonon contributions etc..

Interesting comment:

if we had computed:

$$\boxed{\langle (E - \langle E \rangle)^2 \rangle = k_B T^2 C_V}$$

Fluctuation Dissapation