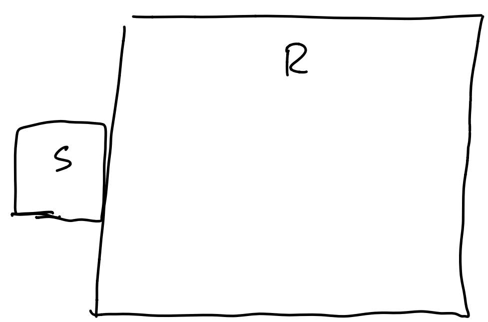
Last Lecture



What is the prob that the energy in the system will be U?

$$P(U) = \frac{e^{-\beta U}}{Z} \; ; \quad \beta = \frac{1}{kT}$$

$$Z = \sum_i e^{-\beta E_i}$$

The sum is over microstates

Example: QM Harmonic oscillator

(Like the Einstein Solid but only one)

In thermal contact with res @ temp T

Possible energies:

$$E_n = \left(n + \tfrac{1}{2}\right)\hbar\omega$$

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega}$$

$$Z = e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}$$

An aside: solving a geometric series

$$s = \sum a r^n = a + ar + ar^2 + \ldots ar^n$$

$$a = e^{-\frac{1}{2}\beta\hbar\omega}, \quad r = e^{-\beta\hbar\omega}$$

$$S = a + ar + ar^2 + \dots ar^n$$

mult by r

$$rS = ar + ar^2 + ar^3 + \dots ar^{n+1}$$

$$S - rS$$

$$S = a + \cancel{ar} + \cancel{ar^2} + \dots ar^n$$

mult by r

$$rS = \cancel{ar} + \cancel{ar^2} + ar^3 + \dots ar^{n+1}$$

$$S - rS = a - ar^{n+1}$$

$$S(1-r) = a(1-r^{n+1})$$

$$S = a\left(\frac{1-r^{n+1}}{1-r}\right) \quad ; \quad r \neq 1$$

if $n \to \infty$ AND $|r| < 1$, then $r^{n+1} \longrightarrow 0$

$$S = \frac{a}{1-r} \quad ; \quad |r| < 1$$

$$S = \frac{a}{1-r}$$

$$a = e^{-\frac{1}{2}\beta\hbar\omega}, \quad r = e^{-\beta\hbar\omega}$$

$$Z = S = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

mult top & bot by $e^{\frac{1}{2}\beta\hbar\omega}$

$$= \frac{1}{e^{\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}}$$

$$Z = \frac{1}{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)}$$

$$P(n) = \frac{e^{-(n+\frac{1}{2})\beta\hbar\omega}}{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)}$$

I previous exampe Σ over microstates $=$ Σ over energy levels

To see the difference, consider a system of 3 oscillators

$$Z = \sum_{\vec{s}} e^{-E(\vec{s})/kT}$$

$\vec{s}$ is a vector specifying the microstate of the entire system

$$\vec{s} = \langle s_1, s_2, s_3 \rangle$$

s_i specifies the state of each object in the system

Ex: $\vec{s} = \langle \frac{3}{2}\hbar\omega, \frac{1}{2}\hbar\omega, \frac{5}{2}\hbar\omega \rangle$

$\sum_{\vec{s}}$ sums over all possible combinations of $\langle s_1, s_2, s_3 \rangle$

$\vec{S}_1 = \langle \frac{1}{2}\hbar\omega, \frac{1}{2}\hbar\omega, \frac{1}{2}\hbar\omega \rangle$

$\vec{S}_2 = \langle \frac{3}{2}\hbar\omega, \frac{1}{2}\hbar\omega, \frac{1}{2}\hbar\omega \rangle$

$\vec{S}_3 = \langle \frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{1}{2}\hbar\omega \rangle$

$\vec{S}_4 = \langle \frac{1}{2}\hbar\omega, \frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega \rangle$

$\vec{S}_5 = \langle \frac{3}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{1}{2}\hbar\omega \rangle$

$\vec{S}_6 = \langle \frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{3}{2}\hbar\omega \rangle$

$\vdots$

This is just an Einstein solid where each oscillator has energy $U_i = \frac{1}{2}\hbar\omega + q\hbar\omega$

$\vec{S} = \langle q_1, q_2, q_3 \rangle$

$\vec{S}$	q_1	q_2	q_3	$E(\vec{S})$
1	0	0	0	$\frac{3}{2}\hbar\omega$
2	1	0	0	$\frac{5}{2}\hbar\omega$
3	0	1	0	$\frac{5}{2}\hbar\omega$
4	0	0	1	$\frac{5}{2}\hbar\omega$
5	1	1	0	$\frac{7}{2}\hbar\omega$
6	0	1	1	$\frac{7}{2}\hbar\omega$
7	1	0	1	$\frac{7}{2}\hbar\omega$
8	2	0	0	$\frac{7}{2}\hbar\omega$
9	0	2	0	$\frac{7}{2}\hbar\omega$

$E(\vec{S}) = (q_1 + q_2 + q_3)\hbar\omega + \frac{3}{2}\hbar\omega$

10 0 0 2 $\frac{7}{2}\hbar\omega$

$$Z = \sum_{\vec{s}} e^{-\frac{E(\vec{s})}{kT}}$$

$$= e^{-\frac{3}{2}\frac{\hbar\omega}{kT}} + e^{-\frac{5}{2}\frac{\hbar\omega}{kT}} + e^{-\frac{5}{2}\frac{\hbar\omega}{kT}} + e^{-\frac{5}{2}\frac{\hbar\omega}{kT}} + \ldots$$

$$= e^{-\frac{3}{2}\frac{\hbar\omega}{kT}} + 3e^{-\frac{5}{2}\frac{\hbar\omega}{kT}} + 6e^{-\frac{7}{2}\frac{\hbar\omega}{kT}} + \ldots$$

$$= \frac{(0+3-1)!}{0!\,(3-1)!} e^{-\frac{3}{2}\frac{\hbar\omega}{kT}} + \frac{(1+3-1)!}{1!\,(3-1)!} e^{-\frac{5}{2}\frac{\hbar\omega}{kT}} + \frac{(2+3-1)!}{2!\,(3-1)!} e^{-\frac{7}{2}\frac{\hbar\omega}{kT}} + \ldots$$

$$Z_N = \sum_{q=0}^{\infty} \frac{(q+N-1)!}{q!\,(N-1)!} e^{-\left(\frac{1}{2}+q\right)\frac{\hbar\omega}{kT}}$$

$$= ?$$

Come back to this in a minute ...

OK, so we know the probability distribution, big deal

Why is this useful?

We can use the probability distribution to obtain macroscopic (average) quantities

Ex: Say I have 5 atoms

Energies (above min) can be: 0, 4, 7 eV

Upon measurement

2 atoms have 0 eV

2 have 4 eV

1 has 7 eV

What is the average energy of all the atoms?

$$\bar{E} = \frac{(0\,eV)\cdot 2 + (4\,eV)\cdot 2 + (7\,eV)\cdot 1}{5}$$

$$\bar{E} = 3\,eV$$

Can write like this:

$$\bar{E} = (0\,eV)\cdot\frac{2}{5} + (4\,eV)\cdot\frac{2}{5} + (7\,eV)\frac{1}{5} = 3\,eV$$

$$\bar{E} = (E_{state\,1})(P_{state\,1}) + (E_{state\,2})(P_{state\,2}) + (E_{state\,3})(P_{s3})$$

Prob(E) is the probability distribution

If we know the probability dist in advance, we can calculate the expected value

Example: I put 10 dollar bills (of different values) in a bag. 2 are 20's, 3 are 10's, 1 is a 5, 4 are 1's

Here's the game: you can randomly select 1 of the bills from the bag (no peaking!) but I charge you \$6.

Do you play?

How much should you expect to win if you play?

Expected winnings $= \langle m \rangle$

$$\langle m \rangle = \$20 \cdot P(\$20) + \$10\,P(\$10) + \ldots$$

$$\langle m \rangle = 20(0.2) + 10(0.3) + 5(0.1) + 1(0.4)$$

$$\langle m \rangle = \$7.90$$

it cost \$6 to play, but you should expect to win \$7.90

so you come out ahead, by \$1.90

- This is on average! If you played the game 1000 times, sometimes you draw \$20, sometimes \$1 (never \$7.90) but the average amount will be \$7.90

$$\text{Expected outcome} = \sum_{\text{all outcomes}} (\text{outcome}_i)(P_{\text{outcome}\ i})$$

$$\langle y \rangle = \sum_i y_i \cdot P(y_i)$$

$$\langle E \rangle = \sum_i E_i \cdot P(E_i)$$

$$= \sum_i E_i \frac{e^{-\beta E_i}}{Z}$$

$$\langle E \rangle = \frac{1}{Z} \sum_i E_i e^{-\beta E_i}$$

H.O.

$$Z = e^{-\frac{3}{2}\frac{\hbar\omega}{kT}} + e^{-\frac{5}{2}\frac{\hbar\omega}{kT}} + e^{-\frac{5}{2}\frac{\hbar\omega}{kT}} + e^{-\frac{5}{2}\frac{\hbar\omega}{kT}} + \dots$$

$$\langle E \rangle = \frac{1}{Z}\left[\left(\frac{3}{2}\hbar\omega\right) e^{-\frac{3}{2}\frac{\hbar\omega}{kT}} + \left(\frac{5}{2}\hbar\omega\right) e^{-\frac{5}{2}\frac{\hbar\omega}{kT}} + \left(\frac{5}{2}\hbar\omega\right) e^{-\frac{5}{2}\frac{\hbar\omega}{kT}} + \dots \right]$$

$$Z_N = \sum_{q=0}^{\infty} \frac{(q+N-1)!}{q!\,(N-1)!} e^{-\left(\frac{1}{2}+q\right)\frac{\hbar\omega}{kT}}$$

$$\langle E \rangle = \frac{1}{Z_N} \sum_{q=0}^{\infty} \left(\tfrac{1}{2}+q\right)\hbar\omega \frac{(q+N-1)!}{q!\,(N-1)!} e^{-\left(\frac{1}{2}+q\right)\frac{\hbar\omega}{kT}}$$

A better way of dealing with multiparticle systems

Scenario: my system consists of N identical objects (harmonic oscillators, spin 1/2 electrons, etc)

Let's assume that the N objects are <u>non-interacting</u> (the state of one object does not affect the state of any other)

Think of s as a vector specifying the state of the entire system

Ex: for a 2-state paramagnet

$$s = \langle \uparrow, \uparrow, \downarrow, \ldots, \uparrow \downarrow \rangle$$

For a collection of QM oscillators

$$s = \langle q_1, q_2, q_3 \ldots, q_N \rangle = \left(\frac{3}{2}\hbar\omega, \frac{1}{2}\hbar\omega, \ldots \right)$$

so

$\sum_s$ is over all possible values of s

$$\langle \uparrow \downarrow \downarrow, \ldots \downarrow \downarrow \rangle$$
$$\langle \downarrow \downarrow \downarrow, \ldots \downarrow, \downarrow \rangle$$
$$\langle \uparrow \uparrow \downarrow \downarrow, \ldots \rangle$$

Microstate of the system is the vector of states of the composite systems

In general, $S = \langle S_1, S_2, S_3, \ldots, S_N \rangle$

S_i could also be a vector i.e. $S_i = \langle x_i, p_{xi} \rangle$

$$Z_N = \sum_{\vec{S}} e^{-\frac{E(\vec{s})}{kT}}$$

$$E(\vec{s}) = E(\langle s_1, s_2, s_3, \ldots, s_N \rangle)$$

IF particles are non-interacting

Then $E(\vec{s}) = E_1(s_1) + E_2(s_2) + \ldots + E_N(s_N)$

$$Z_N = \sum_{s_1, s_2, \ldots s_N} e^{-\frac{1}{kT}\left[E_1(s_1) + E_2(s_2) + \ldots E_N(s_N)\right]}$$

$$E_1(\uparrow_1) + E_2(\downarrow) + \ldots$$

$$Z_N = \sum_{s_1, s_2, \ldots s_N} e^{-\frac{1}{kT}E_1(s_1)} e^{-\frac{1}{kT}E_2(s_2)} \ldots e^{-\frac{1}{kT}E_N(s_N)}$$

if particles are <u>distinguishable</u>

(more on this in a moment)

$$Z_N = \sum_{s_1} e^{-\frac{1}{kT}E_1(s_1)} \sum_{s_2} e^{-\frac{1}{kT}E_2(s_2)} \ldots \sum_{s_N} e^{-\frac{1}{kT}E_N(s_N)}$$

$$Z_N = Z_1 Z_1 Z_1 \cdots Z_1$$

$$Z_N = Z_1^N$$

Assumptions: oscillators are

- non interacting

(the state of each oscillator is independent of the other oscillators)

- distinguishable

(I can tell each oscillator apart)

What do we mean by distinguishable?

Forget oscillators for a second,

think of 3 spin 1/2 electrons

- How do I label their microstates?

1st e- is blue
2nd is green
3rd is red

$\uparrow \; \uparrow \; \uparrow$] $N_\uparrow = 3$

$\uparrow \; \uparrow \; \downarrow$
$\uparrow \; \downarrow \; \uparrow$
$\downarrow \; \uparrow \; \uparrow$] $N_\uparrow = 2$ $\quad 2!$

$\uparrow \; \downarrow \; \downarrow$
$\downarrow \; \downarrow \; \uparrow$
$\downarrow \; \uparrow \; \downarrow$] $N_\uparrow = 1$ $\quad 2!$

$\downarrow \; \downarrow \; \downarrow$] $N_\uparrow = 0$

these states only differ if I can tell one electron from another

---

if all electrons are blue, then

$\uparrow \; \uparrow \; \downarrow$ &

$\uparrow \; \downarrow \; \uparrow$

are the same state

In this case, we have overcounted

- We will deal with this overcounting in a rigorous way next chapter
- Assume we're off by N!

- For now, $Z_N = \frac{1}{N!} z^N$

Z_N for a system of N many non-interacting particles

$$Z_N = Z_1^N \text{ ; distinguishable}$$

$$Z_N = \frac{1}{N!} Z^N \text{ ; indistinguishable}$$

Example : the 2 state paramagnet (N-many)

In general

$$Z_N = \sum_s e^{-U(s)/kT}$$

system states specified by $N\uparrow$

$$U(s) = U(N\uparrow) = \mu B (N - 2N\uparrow)$$

There are $\frac{N!}{N\uparrow!(N-N\uparrow)!}$ many states for each $N\uparrow$

$$Z_N = \sum_{N\uparrow=0}^{N} \frac{N!}{N\uparrow!\,(N-N\uparrow)!}\, e^{-\frac{\mu B}{kT}(N-2N\uparrow)}$$

?

Instead: $Z_N = Z_1^N$

$$Z_1 = \sum_{\mu=\pm 1} e^{-\frac{\mu B}{kT}} = e^{-\frac{\mu B}{kT}} + e^{\frac{\mu B}{kT}}$$

$$= 2\cosh\left(\frac{\mu B}{kT}\right)$$

so: $Z_N = \left(2\cosh\left(\frac{\mu B}{kT}\right)\right)^N$

What is $\langle E \rangle$?

$$\langle E \rangle = \frac{1}{Z_N} \sum_{\vec{s}} E(\vec{s})\, e^{-\frac{1}{kT} E(\vec{s})}$$

Non-interacting:

$$\langle E \rangle = \frac{1}{Z_N} \sum_{s_1, s_2, \ldots s_N} \Big(E_1(s_1) + E_2(s_2) + \ldots E_N(s_N) \Big) e^{-\frac{1}{kT}\left(E_1(s_1) + E_2(s_2) + \ldots E_N(s_N) \right)}$$

$$= \frac{1}{Z_N} \sum_{s_1 \ldots s_N} \Big(E_1(s_1) + E_2(s_2) + \ldots E_N(s_N) \Big) e^{-\frac{1}{kT} E_1(s_1)}\, e^{-\frac{1}{kT} E_2(s_2)} \cdots$$

$$= \frac{1}{Z_N} \sum_{s_1 \ldots s_N} E_1(s_1) e^{-\frac{1}{kT} E_1(s_1)}\, e^{-\frac{1}{kT} E_2(s_2)} \cdots + E_2(s_2) e^{-\frac{1}{kT} E_1(s_1)}\, e^{-\frac{1}{kT} E_2}$$

$$= \frac{1}{Z_N} \Bigg[\sum_{s_1} E_1(s_1) e^{-\frac{1}{kT} E_1(s_1)} \sum_{s_2 \ldots s_N} e^{-\frac{1}{kT} E_2(s_2)}\, e^{-\frac{1}{kT} E_3(s_3)} \cdots$$

$$+ \sum_{s_2} E_2(s_2) e^{-\frac{1}{kT} E_2(s_2)} \sum_{s_1, s_3 \ldots s_N} e^{-\frac{1}{kT} E_1(s_1)}\, e^{-\frac{1}{kT} E_3(s_3)} \cdots$$

$$+ \ldots$$

$$+ \sum_{s_N} E_N(s_N) e^{-\frac{1}{kT} E_N(s_N)} \sum_{s_1 \ldots s_{N-1}} e^{-\frac{1}{kT} E_1(s_1)}\, e^{-\frac{1}{kT} E_2(s_2)} \cdots e^{-\frac{1}{kT} E_{N-1}} \Bigg]$$

$$= \frac{1}{Z_N}\Big[Z_1 \langle E_1 \rangle Z_{N-1} \quad +$$

$$Z_1 \langle E_1 \rangle Z_{N-1} \quad + \quad \ldots \Big]$$

$$= \frac{1}{Z_N} N \langle E_1 \rangle Z_N$$

$$= N \langle E_1 \rangle$$

$$\langle E \rangle = U = N \langle E_1 \rangle$$

Ex: Two state paramagnet

$$Z_1 = 2\cosh(\beta \mu B)$$

$$\langle E_1 \rangle = \frac{1}{2\cosh(\beta\mu B)}\Big[\mu B e^{-\beta\mu B} + (-\mu B) e^{\beta\mu B} \Big]$$

$$= \frac{\mu B}{2\cosh(\beta\mu B)}\left(-2\sinh(\beta\mu B)\right)$$

$$\langle E_1 \rangle = -\mu B \tanh(\beta\mu B)$$

$$U = N\langle E_1\rangle = -\mu B N \tanh\left(\frac{\mu B}{kT}\right)$$

$$\langle \mu \rangle = \mu \frac{e^{\beta\mu B}}{Z} + (-\mu)\frac{e^{-\beta\mu B}}{Z}$$

$$= \frac{\mu}{Z}\left(e^{\beta\mu B} - e^{-\beta\mu B}\right)$$

$$= \frac{2\mu \sinh(\beta\mu B)}{2\cosh(\beta\mu B)} = \mu \tanh(\beta\mu B)$$

$$\boxed{M = N\mu \tanh(\beta\mu B)}$$

$$\langle E \rangle = \frac{1}{Z}\sum_{\vec{s}} E(\vec{s})e^{-\beta E(\vec{s})}$$

$$E(\vec{s})e^{-\beta E(\vec{s})} = -\frac{\partial}{\partial\beta} e^{-\beta E(\vec{s})}$$

$$\langle E \rangle = \frac{-1}{Z} \sum_{\vec{s}} \frac{\partial}{\partial \beta} e^{-\beta E(\vec{s})}$$

$$= -\frac{1}{Z} \frac{\partial}{\partial \beta} \left(\sum_{\vec{s}} e^{-\beta E(\vec{s})} \right)$$

$$= -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$\boxed{\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln(Z)}$$

$$Z = 2 \cosh(\beta \mu B)$$

$$\frac{\partial Z}{\partial \beta} = 2 \mu B \sinh(\beta \mu B)$$

$$\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{1}{2 \cosh(\beta \mu B)} (2 \mu B \sinh(\beta \mu B))$$

$$\langle E \rangle = -\mu B \tanh(\beta \mu B) \checkmark$$

N distinguishable oscillators

$$Z_1 = \frac{1}{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)}$$

$$Z_N = Z^N$$

$$-\frac{1}{Z}\frac{\partial Z}{\partial\beta} = \frac{-1}{Z_1^N}\frac{\partial}{\partial\beta}\left(Z_1^N\right) = \frac{-1}{Z_1^N} N Z_1^{N-1}\frac{\partial}{\partial\beta} Z_1$$

$$= -\frac{N}{Z_1}\frac{\partial}{\partial\beta} Z_1 = -\frac{N}{Z_1}\frac{1}{2}\frac{\partial}{\partial\beta}\sinh^{-1}\left(\frac{1}{2}\beta\hbar\omega\right)$$

$$= -\frac{N}{Z_1}\frac{1}{2}\left(-1\sinh^{-2}\left(\frac{1}{2}\beta\hbar\omega\right)\cosh\left(\frac{1}{2}\beta\hbar\omega\right)\frac{1}{2}\hbar\omega\right)$$

$$= \frac{1}{4}\frac{N}{Z_1}\hbar\omega\frac{\cosh\left(\frac{1}{2}\beta\hbar\omega\right)}{\sinh^2\left(\frac{1}{2}\beta\hbar\omega\right)}$$

$$Z_1 = \frac{1}{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)}$$

$$= \frac{1}{2}N\hbar\omega \frac{\cosh\left(\frac{1}{2}\beta\hbar\omega\right)}{\sinh\left(\frac{1}{2}\beta\hbar\omega\right)}$$

$$\coth\left(\frac{1}{2}\beta\hbar\omega\right)$$

if $KT \gg \hbar\omega$, $\beta\hbar\omega \ll 1$

$$\coth\left(\frac{1}{2}\beta\hbar\omega\right) \approx \frac{2}{\beta\hbar\omega}$$

$$\frac{1}{2}N\hbar\omega \frac{\cosh\left(\frac{1}{2}\beta\hbar\omega\right)}{\sinh\left(\frac{1}{2}\beta\hbar\omega\right)} \approx \frac{N\hbar\omega}{2}\frac{2}{\beta\hbar\omega}$$

$$\approx NKT$$