- 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:

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

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

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

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

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

$$+ \ldots$$

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

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

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

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

$$= N \langle E_1 \rangle$$

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

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

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

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

$$\approx NKT$$

The macroscopic connection

We have seen how to obtain U from Z.

What about S, T, P, V, etc?

- First, let's consider how we got them previously

In previous chapters

- our system was isolated

U, V, N were constant

Our fundamental principle was

the second law (entropy/multiplicity will increase)

$$\Omega(U,V,N) = \sum_{\vec{s} \text{ w/ constant } U,V,N}$$

- Since all microstates are equally likely, states w/ higher Ω are more likely

$$S = k \ln(\Omega)$$

$$T = \frac{\partial S}{\partial U}, \quad \frac{P}{T} = \frac{\partial S}{\partial V}, \quad \frac{\mu}{T} = -\frac{\partial S}{\partial N}$$

Now, U is no longer constant

We want something like Ω

We could try this:

$$W(T,V,N) \stackrel{?}{=} \sum_{\vec{s} \text{ w/ } T,V,N \text{ const}} = \sum_i \Omega(E_i,V,N)$$

W is the multiplicity of a state with $T, V, \& N$

- <u>But</u> Can no longer say that $W \propto$ prob, like we could with Ω

- Even if a macrostate T, V, N has more microstates, Some of those microstates are high-energy & thus less likely to occur

- The system prefers microstates w/ lower energy

instead we use Z

$$Z = \sum_{\vec{s} \text{ w/ const } V,N} e^{-\frac{E(\vec{s})}{kT}} = \sum_i \Omega(E_i,V,N) e^{-\frac{E_i}{kT}}$$

Thus, $Z = \langle \Omega \rangle$ | Partition function is the (weighted) avg multiplicity

So it is $\langle \Omega \rangle$ that will tend to increase

$e^{-\frac{E}{kT}}$ weights the average toward lower energies

- The system wants to minimize its energy

- Cannot minimize energy too much w/o violating entropy: $\Omega(E_i, V, N)$ increases w/ energy + represents the entropy

Z balances the system's tendency to minimize energy while also increasing $S_{tot} = S + S_R$

$$Z = \langle \Omega \rangle = \max \implies \text{equilibrium}$$

This reminds us of chapter 5

In chapter 5, we considered a system which can exchange energy w/ its environment at const temp

Starting from the 2^{nd} Law

$$\Delta S_{tot} = \Delta S + \Delta S_R \geq 0$$

We showed that $\Delta S_{tot} = -\frac{1}{T}\Delta F$

$$S_{tot} = -\frac{1}{T} F$$

F tends to decrease

$$F = U - TS$$

$$\Delta F = \Delta U - T\Delta S$$

Process happens spontaneously if
$\Delta F < 0$ $\quad (\Delta U < T\Delta S)$

F balances the system's tendency to minimize Energy w/ the second law

This suggests a connection between F + Z

$Z \sim -F$

- In an isolated system:

  $S = k \ln \Omega$ tends to <u>increase</u>

- Exchange energy @ const T, V, N

  S <u>can</u> decrease

  F tends to <u>decrease</u>

  $Z = \langle \Omega \rangle$ tends to increase

Guess: $F \sim -\ln Z$?

$[F] = \text{Eng}$

$[\ln Z] = -$

Try:

$$F = -kT \ln Z$$

$$S = k \ln \Omega \longrightarrow F = -kT \ln Z$$

Proof:

$$F \equiv U - TS$$

$$dF = dU - TdS - SdT$$

$$= TdS - PdV + \mu dN - TdS - SdT$$

$$dF = -SdT - PdV + \mu dN$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$$

$$\frac{F-U}{T} = -S$$

$$\boxed{\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{F-U}{T}}$$

Show that this holds when

$$F = -kT \ln Z$$

$$\frac{\partial F}{\partial T} = \frac{\partial}{\partial T}\left(-kT \ln Z\right) = -k \ln Z - kT \frac{\partial}{\partial T} \ln Z$$

$$\frac{\partial}{\partial T} \ln Z = ?$$

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

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta}$$

$$\frac{\partial}{\partial T} \ln Z = \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \ln Z$$

$$= -\frac{\partial}{\partial T}\left(\frac{1}{kT}\right) U$$

$$\frac{\partial}{\partial T} \ln Z = \frac{U}{kT^2}$$

so:

$$\frac{\partial F}{\partial T} = -k \ln Z - kT \frac{\partial}{\partial T} \ln Z$$

$$= -k \ln Z - kT\left(\frac{U}{kT^2}\right)$$

$$\frac{\partial}{\partial T}\left(-kT \ln Z\right) = -k \ln Z - \frac{U}{T}$$

$$= \frac{-kT \ln Z - U}{T}$$

$$\frac{\partial F}{\partial T} = \frac{F - U}{T} \qquad \text{so: } F = -kT \ln Z$$