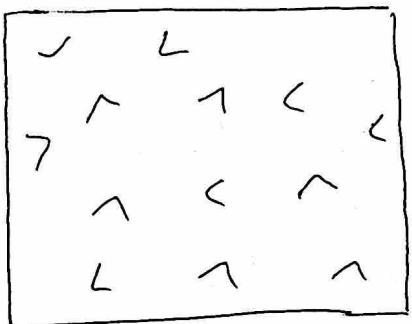


Recap:

Lots of different ensembles for different scenarios - fluctuating E vs. fixed E , fluctuating V vs. fixed V , etc.

For large systems you can perform different calculations using the different ensembles to get the same answer - Ensemble Equivalence



A box of H_2O molecules simulated with Newton's laws - NVE

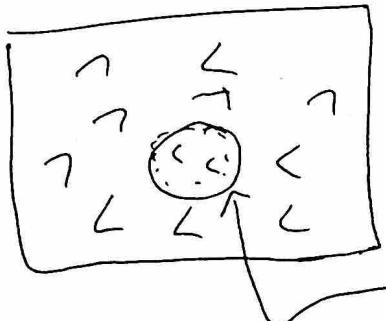
$\overbrace{\quad}^{\text{fixed } E}$

What is the temperature?

Does this make sense to ask given that E is held fixed?

We're really asking about $\left(\frac{\partial E}{\partial S}\right)_{N,V}$

We could also split the problem up into multiple regions



Now the E in this region does fluctuate and the outside bath effectively holds it at temperature T

Or in the extreme, take the system to be a single H_2O molecule. Dynamics of that molecule will sample from the Boltzmann dist.

$$P(\vec{r}, \vec{p}) \propto e^{-\beta H(\vec{r}, \vec{p})}$$

⌈ momenta
 ⌈ positions of H_2O coordinates

Notice that $P(\vec{r}, \vec{p}) = \underbrace{K(\vec{p})}_{\text{kinetic energy}} + \underbrace{U(\vec{r})}_{\text{potential energy}}$

$$\Rightarrow P(\vec{r}, \vec{p}) \propto e^{-\beta K(\vec{p})} e^{-\beta U(\vec{r})} \leftarrow \text{Factorizes!}$$

$$\Rightarrow P(\vec{p}) = \int d\vec{r} P(\vec{r}, \vec{p}) \propto e^{-\beta K(\vec{p})} \text{ regardless of } \vec{r}!$$

Equilibrium statistics of configurations & momenta are independent!
(when observed at the same time.)

And kinetic energy is simple! $K = \sum_j \frac{|\vec{p}_j|^2}{2m}$

$$P(\vec{p}) = e^{-\beta \left(\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \dots \right)} \leftarrow \text{Factorizes!}$$

$$= \prod_j \phi(\vec{p}_j) \leftarrow \text{Maxwell-Boltzmann distribution}$$

$$\phi(\vec{p}) = \phi(p_x, p_y, p_z) \propto e^{-\beta(p_x^2 + p_y^2 + p_z^2)/2m} \leftarrow \text{Factorizes!}$$

$$\Rightarrow \text{prob}(p_x) \propto e^{-\beta p_x^2/2m} = e^{-\frac{p_x^2}{2(\frac{m}{\beta})}} \leftarrow \text{A Gaussian w/ variance } \frac{m}{\beta}$$

$$\Rightarrow \langle p_x^2 \rangle = \frac{m}{\beta} = m k_B T.$$

$$\Rightarrow \text{typical momentum } p_{\text{typ}} \sim \sqrt{\langle p_x^2 \rangle} = \sqrt{m k_B T}$$

\uparrow
root mean square

One route to computing the temperature is to perform the microcanonical simulation/calculation, then look at momentum fluctuations for a single particle.

Every fixed E you start with will have a different

$$\left(\frac{\partial E}{\partial S}\right)_{N,V} \Rightarrow T(E)$$

Temperature you compute is a function of
the fixed E

Another thing you could do is perform an N, V, T simulation of the H_2O

$$\boxed{< \tau < \tau | \tau < \tau | \tau}$$

Now the dynamics
is Langevin.

for each simulated value of T (imposed by
the Langevin dynamics), you compute
 $\langle E \rangle$ (Remember E now fluctuates)

$$\text{to get } \langle E \rangle(T)$$

↑ Avg. energy is a function
of the fixed T .

Ensemble equivalence says that

$T(E) + \langle E \rangle(T)$ are inverses of each other

⇒ you can get the same information from either ensemble.

So why mess w/ anything other than the microcanonical ensemble
if it has all the info?

Convenience! Let's work through a calculation both ways.

Non interacting spins in an external field ~~at fixed E~~

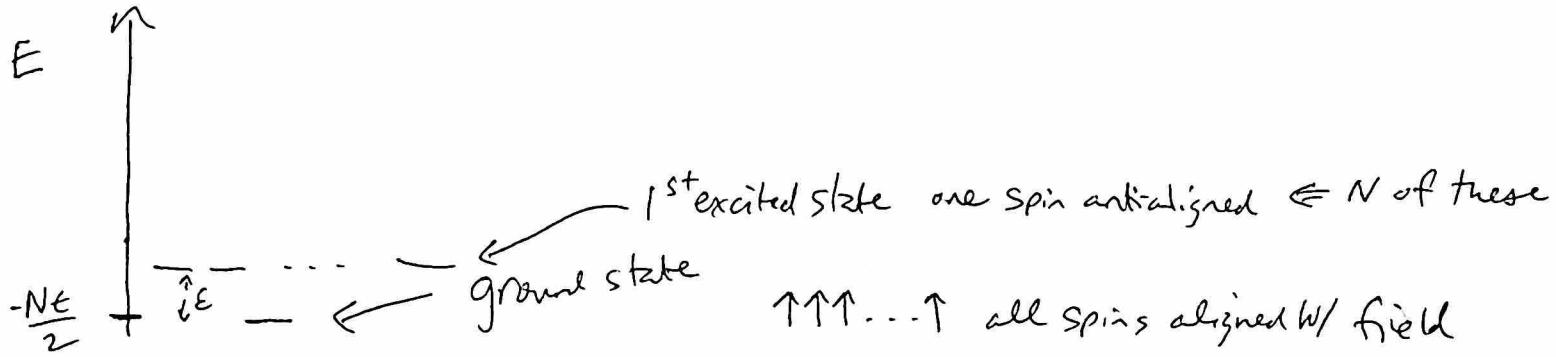
$$\begin{array}{ccccccc} \uparrow & \uparrow & \downarrow & \uparrow & \downarrow & \downarrow & \cdots \\ s_1 & s_2 & & & & & s_N \end{array}$$

$$s_i = \begin{cases} +1, & \text{aligned w/ field} \\ -1, & \text{anti-aligned} \end{cases}$$

$$\nu = \{s_1, s_2, \dots, s_N\} \quad E(\nu) = -\frac{\epsilon}{2} \sum s_i$$

We are after a relationship between T and the fraction of excited spins ($s_i = -1$).

Route 1 : Microcanonical



The degeneracy of the n^{th} excited state is $\Omega = N C_n = \frac{N!}{n!(N-n)!}$

$$\begin{aligned} \Rightarrow S &= k_B \ln \Omega = k_B \ln \left(\frac{N!}{n!(N-n)!} \right) \quad \xrightarrow{\text{Stirling}} \\ &\approx k_B [N \ln N - n \ln n - (N-n) \ln (N-n)] \\ &= -N k_B \left[\ln \frac{N-n}{N} - \frac{n}{N} \ln \frac{N-n}{n} \right] \quad \xrightarrow{f = \frac{n}{N}} \\ &= -N k_B \left[\ln(1-f) - f \ln \frac{1-f}{f} \right] \\ &= -N k_B [(1-f) \ln(1-f) + f \ln f] \end{aligned}$$

↑ "entropy of mixing"

$$\begin{aligned} \frac{1}{T} &= \left(\frac{\partial S}{\partial E} \right)_N = \left(\frac{\partial S}{\partial f} \right)_N \left(\frac{\partial f}{\partial E} \right) = -N k_B [\ln f + 1 - \ln(1-f) - 1] \left(\frac{\partial f}{\partial E} \right) \\ &= -N k_B [\ln f - \ln(1-f)] \frac{1}{Ne} = -\frac{k_B}{e} \ln \frac{f}{1-f} = \underline{k_B} \cdot \underline{f \cdot \frac{1-f}{n}} \end{aligned}$$

So the microcanonical calculation gives

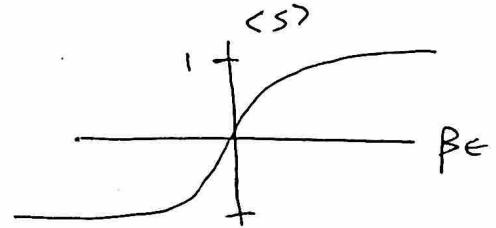
$$\boxed{\frac{E}{k_B T} = \ln \frac{1-f}{f}}$$

Route 2 : Canonical

$$\begin{aligned} P(s_1, \dots, s_N) &\propto \cancel{e^{-\beta E(s_1, s_2, \dots, s_N)}} e^{-\beta E(s_1, s_2, \dots, s_N)} \\ &= e^{\beta \frac{E}{2} s_1} e^{\beta \frac{E}{2} s_2} \dots e^{\beta \frac{E}{2} s_N} \leftarrow \text{factors!} \\ &= p(s_1) p(s_2) \dots p(s_N) \leftarrow \text{spins are statistically independent.} \end{aligned}$$

$$p(s) = \frac{e^{\beta \frac{E}{2} s}}{e^{\beta \frac{E}{2}} + e^{-\beta \frac{E}{2}}} \quad \cancel{+ \langle s \rangle} = p(+1) + p(-1) (-1)$$

$$\Rightarrow \langle s \rangle = \frac{e^{\beta E/2} - e^{-\beta E/2}}{e^{\beta E/2} + e^{-\beta E/2}} = \tanh(\beta E/2)$$



$$\Rightarrow \langle s \rangle = \frac{e^{\beta E} - 1}{e^{\beta E} + 1} \quad (*)$$

To compare with the microcanonical result.

$$\langle s \rangle = f(-1) + (1-f)(1) = 1 - 2f$$

$$\text{So } (*) \text{ becomes } (1-2f)e^{\beta E} + (1-2f) = e^{\beta E} - 1 \Rightarrow e^{\beta E} = \frac{1-f}{f}$$

$$\Rightarrow \boxed{\frac{E}{k_B T} = \ln \left(\frac{1-f}{f} \right)} \quad \text{Same Answer!}$$

Macroscopically, it doesn't matter if we constrain E or instead fix its average $\langle E \rangle$ through T .