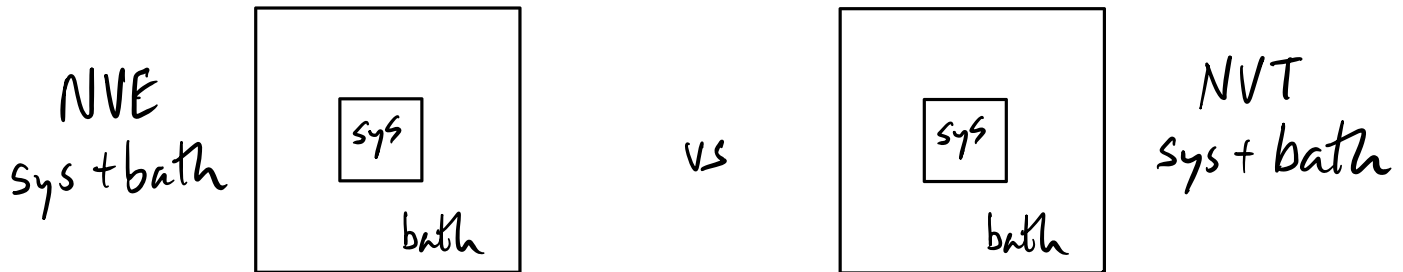


Lecture 9

Whether the system can exchange with the bath clearly matters (energy vs. Helmholtz vs. Gibbs), but how do I know my system+bath was really microcanonical (NVE)?

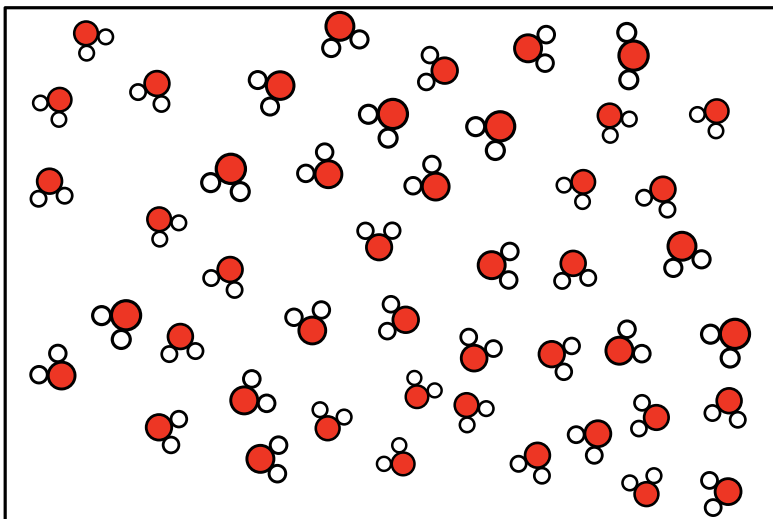


For large systems and baths, the details of how the bath is realized cannot really matter.

It should be possible to arrive at the same result via NVE or NVT!

This idea gets a fancy name: Ensemble Equivalence

We start with NVE:



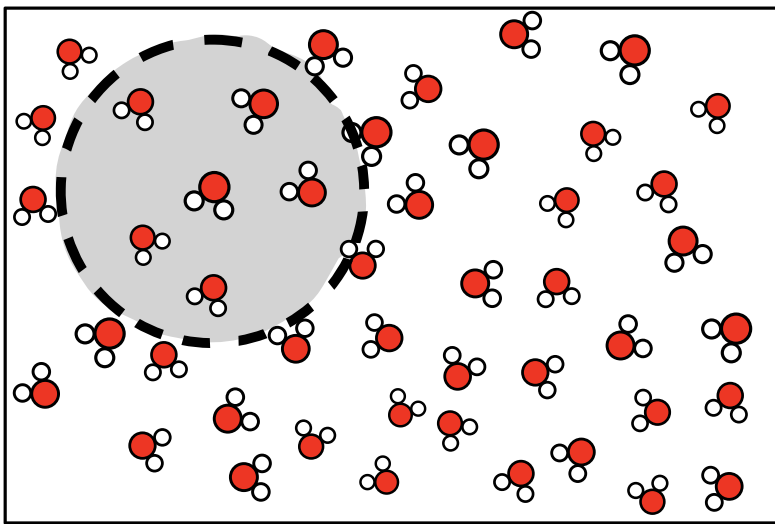
A box of H_2O molecules simulated with Newton's laws (fixed E)

What is the temperature?

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

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

We could also split the problem up into multiple regions



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 distribution:

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

↑ Positions of H_2O coordinates } momenta

Notice that $H(\vec{r}, \vec{p}) = K(\vec{p}) + U(\vec{r})$

Kinetic energy Potential energy

$$\Rightarrow P(\vec{r}, \vec{p}) \propto e^{-\beta(K(\vec{p}) + U(\vec{r}))}$$

$$= e^{-\beta K(\vec{p})} e^{-\beta U(\vec{r})} \quad \text{Factorizes!}$$

$$P(\vec{p}) = \int d\vec{r} P(\vec{r}, \vec{p}) \propto \int d\vec{r} e^{-\beta K(\vec{p})} e^{-\beta U(\vec{r})}$$

$$\propto e^{-\beta K(\vec{p})} \int d\vec{r} e^{-\beta U(\vec{r})}$$

$$\propto e^{-\beta K(\vec{p})} \quad (\text{Regardless of } \vec{r}!)$$

Equilibrium statistics of configurations and momenta are independent!
 (When observed at the same moment in time)

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

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

$$= \prod_j \phi(\vec{p}_j)$$

Maxwell-Boltzmann distribution

$$\Phi(\vec{p}) = \Phi(p_x, p_y, p_z) \propto e^{-\beta \left(\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \right)}$$

Another factorization

$$\rho(p_x) \propto e^{-\beta \frac{p_x^2}{2m}} = e^{-p_x^2 / 2 \left(\frac{m}{\beta} \right)}$$

an unnormalized Gaussian with mean 0 and variance m/β .

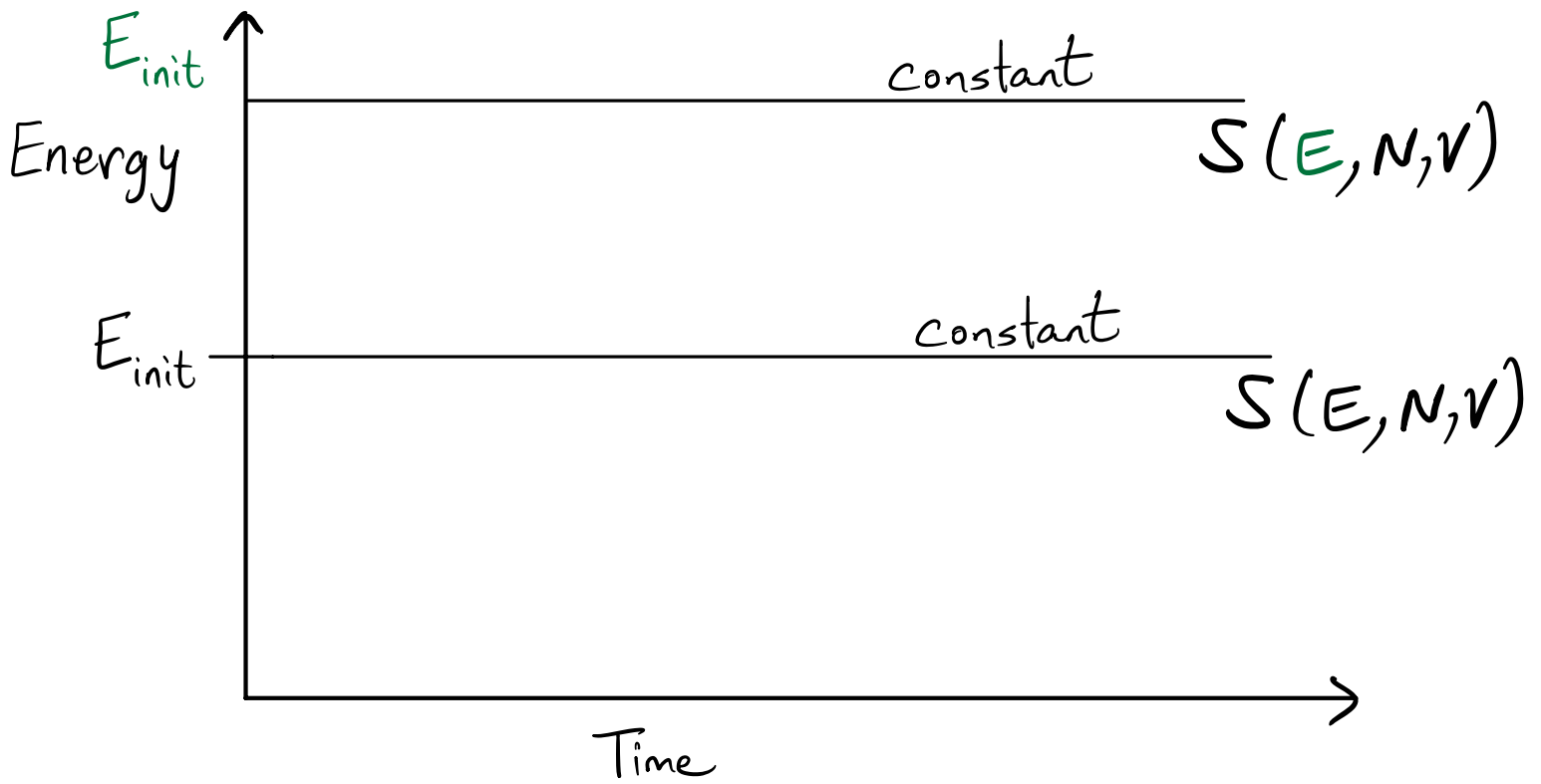
Thanks for helping us get so comfortable with Gaussians, Todd.
- said no one ever

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

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

↑
Root-mean square

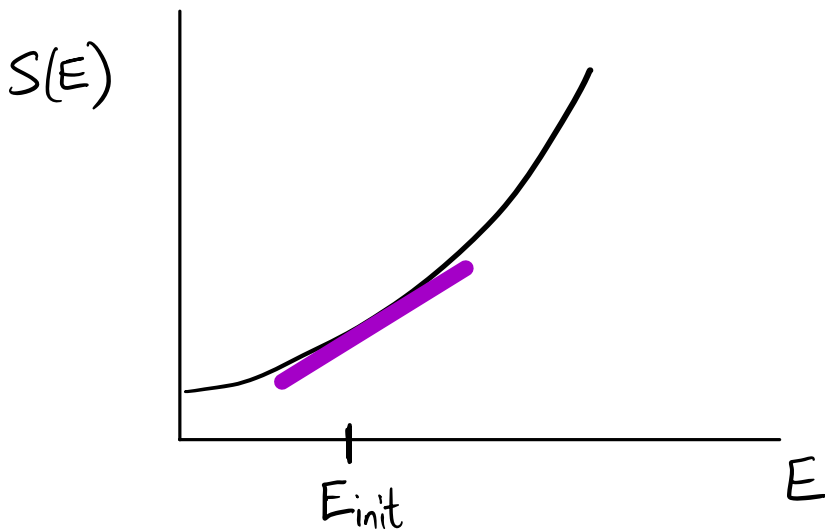
One route to computing temperature is to perform the **microcanonical** simulation/calculation then look at the momentum fluctuations for a single particle.



Every fixed E you start with will have a different

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

The temperature you compute is a function of the fixed E .



Alternatively, one can do an N, V, T simulation of H_2O .

How? "Thermostatted" dynamics

- Nosé-Hoover
 - Langevin
- (Not Newton's law)

For each simulated value of T , you compute $\langle E \rangle$
(Remember, now E fluctuates) to get

$\langle E \rangle (T)$



Average E is a function
of the fixed T .



$T(E)$ and $\langle E \rangle (T)$ must
be inverses of each other

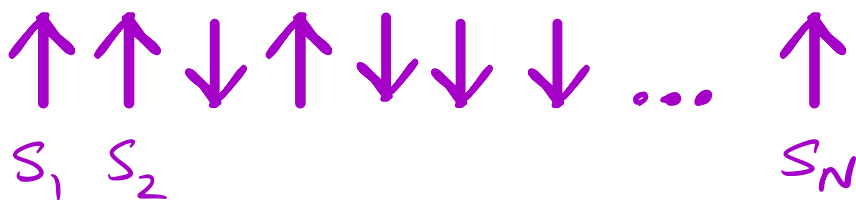
\Rightarrow You can get the same information
from either ensemble.

So why mess with anything other than the microcanonical ensemble if it has all the information?

Convenience!

Let's work through a calculation both ways.

Non-interacting spins in an external field.

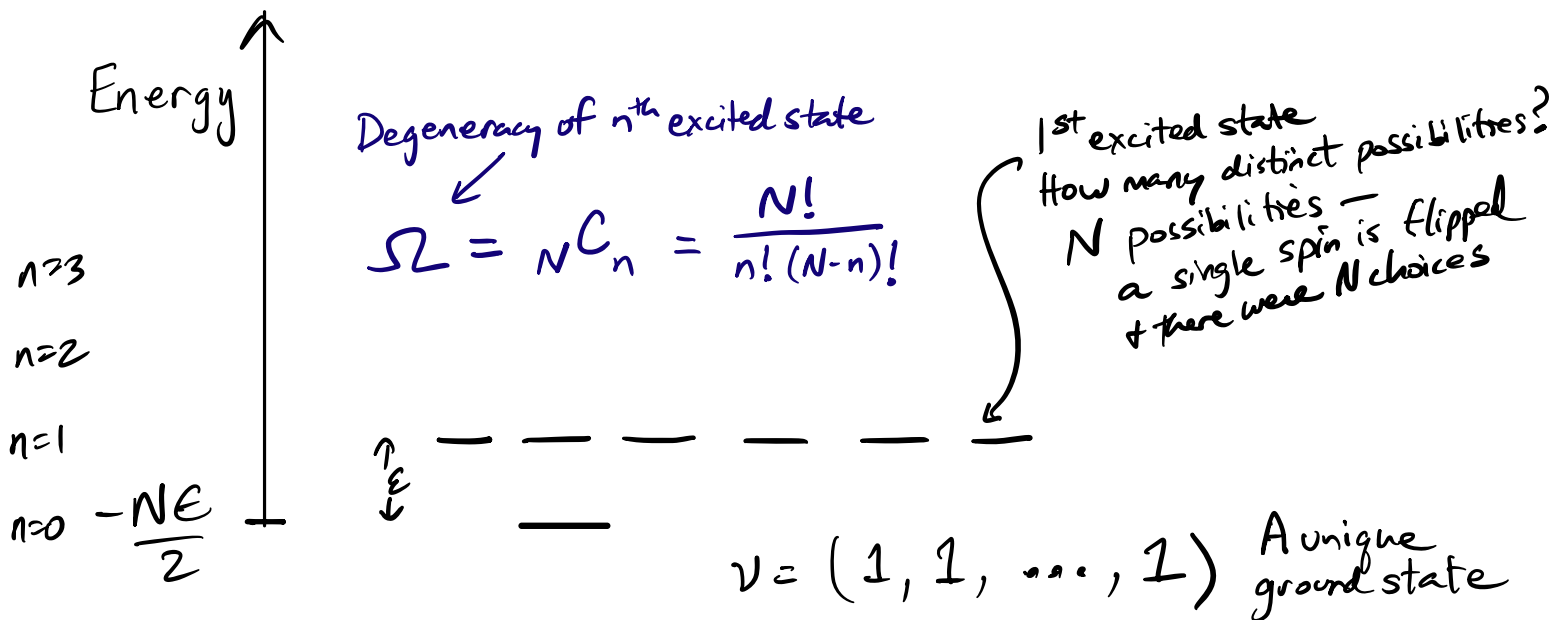


$$S_i = \begin{cases} +1, & \text{aligned with the field} \\ -1, & \text{anti-aligned} \end{cases}$$

$$\nu = \{S_1, S_2, \dots, S_N\} \quad E(\nu) = -\frac{\epsilon}{2} \sum_i S_i$$

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

Route 1: Microcanonical



$$\Rightarrow S = k_B \ln \Omega = k_B \ln \left(\frac{N!}{n!(N-n)!} \right)$$

Stirling

$$\approx k_B [N \ln N - n \ln n - (N-n) \ln (N-n)]$$

$$= -N k_B \left[\ln \frac{N-n}{N} - \frac{n}{N} \ln \frac{N-n}{n} \right]$$

$$= -N k_B \left[\ln (1-f) - f \ln \frac{1-f}{f} \right]$$

$$f = \frac{n}{N}$$

Fraction of excited spins.

$$= -N k_B \left[(1-f) \ln (1-f) + f \ln f \right]$$

"Entropy of mixing"

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_N = \left(\frac{\partial S}{\partial f} \right)_N \left(\frac{\partial f}{\partial E} \right)$$

$$= -Nk_B [\ln f + 1 - \ln(1-f) - 1] \left(\frac{\partial f}{\partial E} \right)$$

$$= -Nk_B [\ln f - \ln(1-f)] \frac{1}{Ne}$$

$$= -\frac{k_B}{e} \ln \frac{f}{1-f} = \frac{k_B}{e} \ln \frac{1-f}{f}$$

⇒ Microcanonical calculation yields:

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

Route 2: Canonical

$$E(v) = -\frac{E}{2} \sum_i S_i$$

$$P(S_1, S_2, \dots, S_N) \propto e^{-\beta E(S_1, S_2, \dots, S_N)}$$

It factorizes! $\Rightarrow = e^{\beta \frac{E}{2} \sum_i S_i}$

$$= e^{\beta \frac{E}{2} S_1} e^{\beta \frac{E}{2} S_2} \dots e^{\beta \frac{E}{2} S_N}$$

$$= p(S_1) p(S_2) \dots p(S_N) \leftarrow \begin{array}{l} \text{Spins are} \\ \text{statistically} \\ \text{independent} \\ \\ \text{(b/c they are} \\ \text{non-interacting)} \end{array}$$

$$p(s) \propto e^{-\beta E(s)}$$

$$p(s=1) \propto e^{+\beta E/2}$$

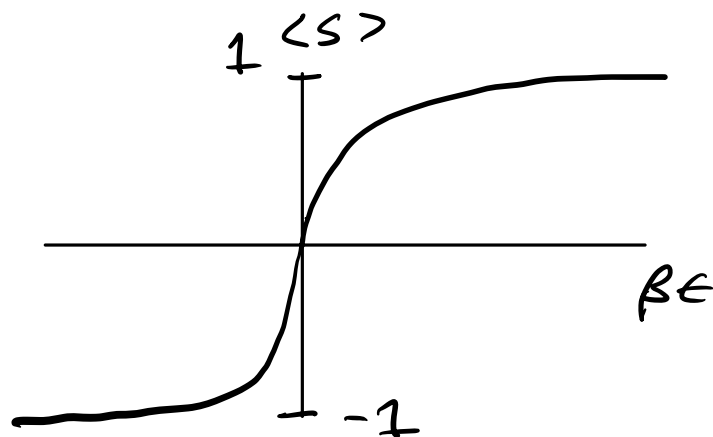
$$p(s=-1) \propto e^{-\beta E/2}$$

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

$$\therefore \langle s \rangle = p(s=1) * 1 + p(s=-1) * (-1)$$

$$= \frac{e^{\beta E/2} - e^{-\beta E/2}}{e^{\beta E/2} + e^{-\beta E/2}} = \tanh\left(\frac{\beta E}{2}\right)$$

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



To compare w/ the microcanonical result,

$$\langle s \rangle = \underset{\substack{\uparrow \\ \text{fraction of} \\ \text{excited spins}}}{f}(-1) + (1-f) \underset{\substack{\uparrow \\ \text{fraction of} \\ \text{unexcited spins}}}{1} = 1 - 2f$$

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

$$\Rightarrow \cancel{e^{\beta E}} + 1 - 2f e^{\beta E} - 2f = \cancel{e^{\beta E}} - 1$$

$$\Rightarrow -2f e^{\beta E} = 2f - 2$$

$$\Rightarrow e^{\beta E} = \frac{1-f}{f}$$

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

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

We were after a relationship between T and the fraction of excited spins (an excited spin has $S_i = -1$). NVE and NVT give the same answer!