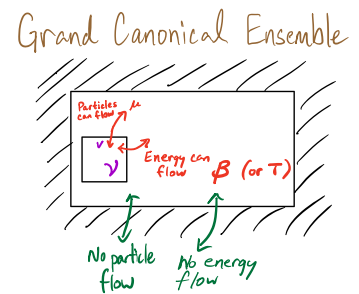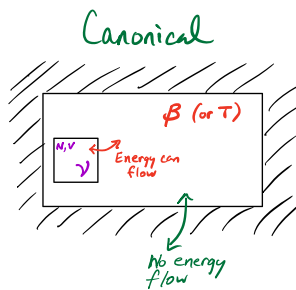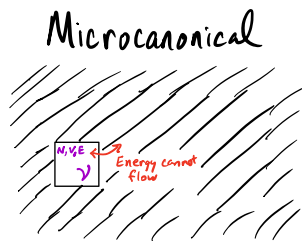# Lecture 9
Recall from last lecture...

Ensembles or how do I replace a rigid constraint by a "softened" exponential bias?

(probability distribution for microstate ν)

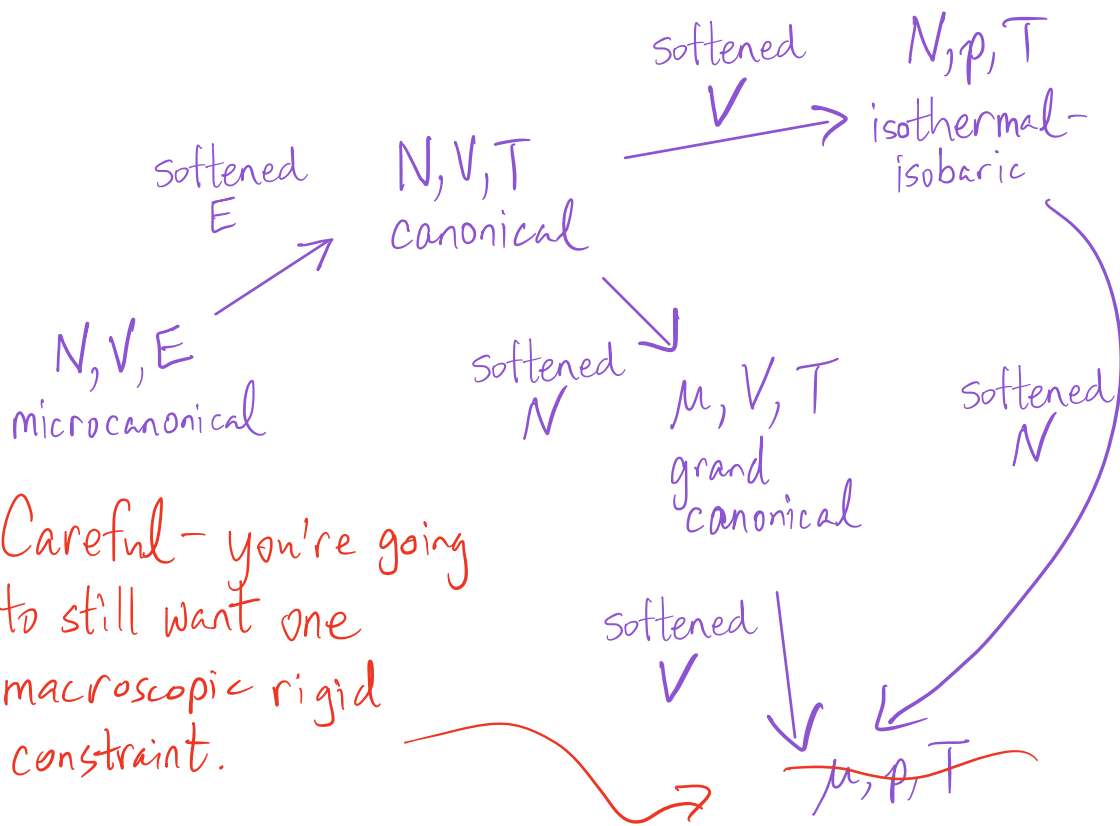|	Microcanonical	Canonical	Grand Canonical Ensemble
What is held fixed?	N, V, E	N, V, T	μ, V, T
$P(\nu)$?	$P(\nu) \propto \begin{cases} 1, & \text{Rigid constraints are met} \\ 0, & \text{Otherwise} \end{cases}$	$P(\nu) \propto \begin{cases} e^{-\beta E(\nu)}, & \text{Rigid constraints are met} \\ 0, & \text{Otherwise} \end{cases}$	$P(\nu) \propto \begin{cases} e^{+\beta\mu N(\nu) - \beta E(\nu)}, & \text{Rigid constraint (only V!) met} \\ 0, & \text{Otherwise} \end{cases}$
Partition Function? (Normalization)	$\Omega(N,V,E) = \sum\limits_{\substack{\nu \text{ meeting} \\ \text{rigid constraints}}} 1$	$Q(N,V,T) = \sum\limits_{\substack{\nu \text{ meeting} \\ \text{rigid constraints}}} e^{-\beta E(\nu)}$	$Z(\mu,V,T) = \sum\limits_{\substack{\nu \text{ meeting} \\ \text{rigid constraints}}} e^{+\beta\mu N(\nu) - \beta E(\nu)}$
Thermodynamic Potential? (Effective Energy)	$S(N,V,E) = k_B \ln \Omega(N,V,E)$ Entropy	$A(N,V,T) = -k_B T \ln Q(N,V,T)$ Helmholtz Free Energy	$\Phi(\mu,V,T) = -k_B T \ln Z(\mu,V,T)$ Grand Potential

Soft constraints vs. hard constraints...

softened
V

N, p, T
isothermal-
isobaric

softened
E

N, V, T
canonical

N, V, E
microcanonical

softened
N

μ, V, T
grand
canonical

softened
N

Careful – you're going
to still want one
macroscopic rigid
constraint.

softened
V

μ, p, T

What is wrong with μ, p, T?

First physical ...   I want ν to be all microstates for
all system sizes?!

Now mathematically ... taking three successive Legendre
transforms of E gives an free energy
for this "μ, p, T ensemble" of
$E - TS + pV - \mu N$

But this expression actually equals zero.

Why?

$$dE = TdS - pdV + \mu dN$$

Double the size $\Rightarrow$ $E \rightarrow 2E$ $S \rightarrow 2S$ $V \rightarrow 2V$ $N \rightarrow 2N$

Let's parameterize everything by a variable c that counts how many copies of a system are glued together

$$\frac{dE}{dc} dc = T \frac{dS}{dc} dc - p \frac{dV}{dc} dc + \mu \frac{dN}{dc} dc$$

$$\Rightarrow \frac{dE}{dc} = T \frac{dS}{dc} - p \frac{dV}{dc} + \mu \frac{dN}{dc}$$

Intensive   (independent of c)

$$\Rightarrow E = TS - pV + \mu N$$

Therefore $E - TS + pV - \mu N$ vanishes.
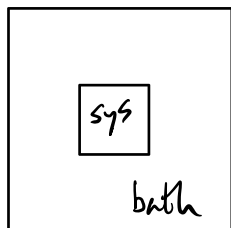
$$0 = d(E - TS - \mu N + pV)$$

$$dE - d(TS) - d(\mu N) + d(pV)$$

$$\cancel{TdS} - \cancel{pdV} + \cancel{\mu dN} - \cancel{TdS} - SdT - \cancel{\mu dN} - Nd\mu$$
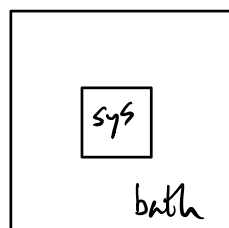$$+ \cancel{pdV} + Vdp$$

$$= -SdT - Nd\mu + Vdp$$

$$(\text{Gibbs - Duhem})$$

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)?
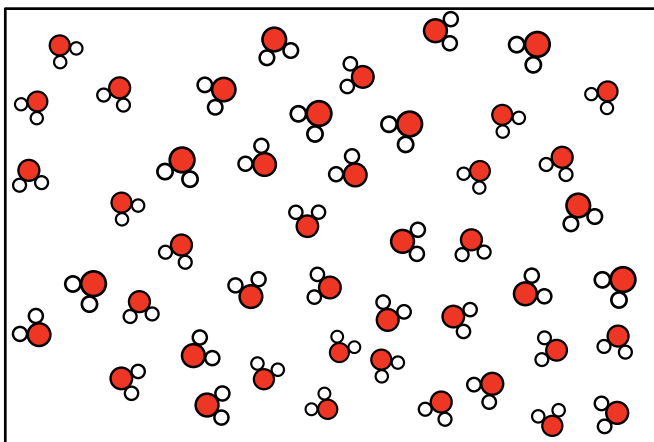
NVE sys + bath   vs   NVT sys + bath

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
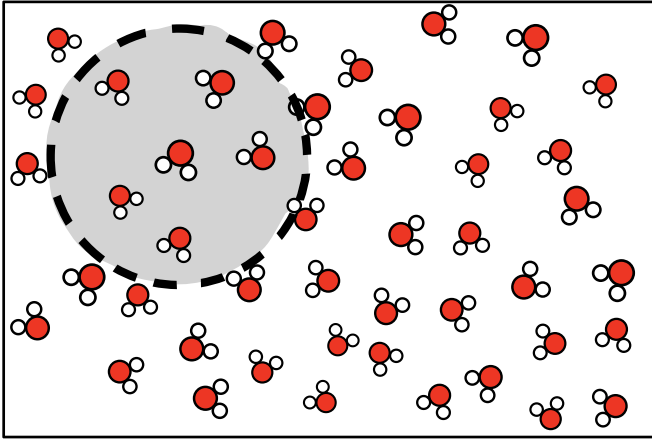
We start with NVE:

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 <u>does</u> 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:

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

Positions of H_2O coordinates   momenta

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

$\textcolor{red}{\text{Kinetic energy}}$ $\textcolor{green}{\text{Potential energy}}$

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

$$= e^{-\beta \textcolor{red}{K(\vec{p})}} e^{-\beta \textcolor{green}{U(\vec{r})}} \qquad \text{Factorizes!}$$

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

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

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

Equilibrium statistics of configurations and momenta are independent!

(When observed at the same moment in time)

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

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

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

$\Uparrow$

Maxwell-Boltzmann distribution

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

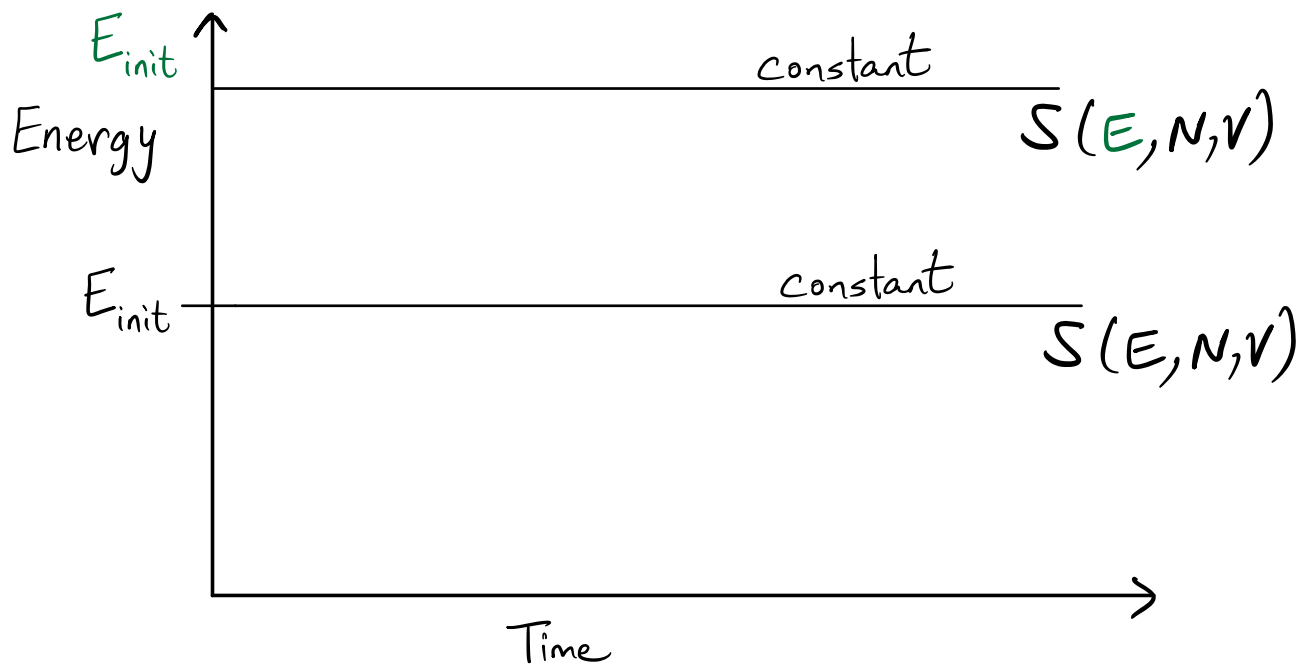$$\rho(p_x) \propto e^{-\beta \frac{p_x^2}{2m}} = e^{-p_x^2/2\left(\frac{m}{\beta}\right)}$$

Thanks for helping us get so comfortable with Gaussians, Todd.

– said no one ever

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

Typical momentum: $p_{typ} \sim \sqrt{\langle p_x^2 \rangle} = \sqrt{mk_BT}$
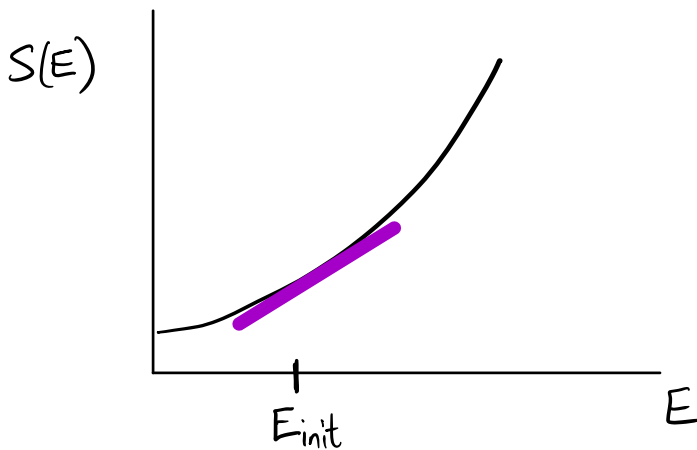
↑
Root-mean square

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

E_{init}

Energy

Constant

$$S(E, N, V)$$

E_{init} ———————————— Constant

$$S(E, N, V)$$

Time

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.

S(E)

E_{init}

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
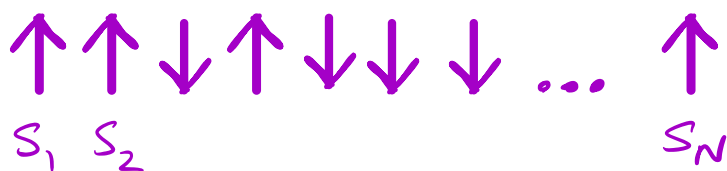
Ensemble Equivalence

$\Rightarrow$ 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.

$$\uparrow \uparrow \downarrow \uparrow \downarrow \downarrow \downarrow \ldots \uparrow$$
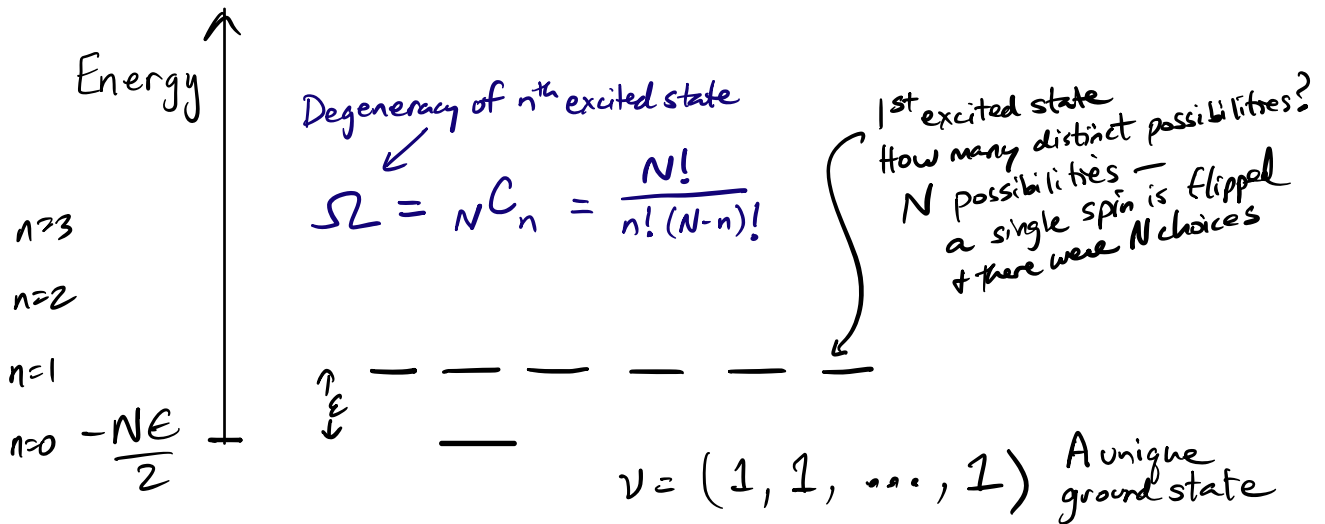$$S_1 \ S_2 \qquad\qquad\qquad\qquad S_N$$

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

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

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

Route 1: Microcanonical

Energy

$n \geq 3$

$n = 2$

$n = 1$

$n = 0$ $\quad -\frac{N\varepsilon}{2}$

Degeneracy of nth excited state

$$\Omega = {}_N C_n = \frac{N!}{n!\,(N-n)!}$$

$\uparrow \varepsilon \downarrow$

1st excited state
How many distinct possibilities?
N possibilities —
a single spin is flipped
+ there were N choices

$\nu = (1, 1, \dots, 1)$ A unique ground state

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

Stirling

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

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

Fraction of excited spins.

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

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

"Entropy of mixing"

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

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

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

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

$\Rightarrow$ Microcanonical calculation yields:

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

Route 2: Canonical

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

$$P(s_1, s_2, \ldots, s_N) \propto e^{-\beta E(s_1, s_2, \ldots s_N)}$$

It factorizes! $\Rightarrow$

$$= e^{\beta\frac{\epsilon}{2}\sum_i s_i}$$

$$= e^{\beta\frac{\epsilon}{2}s_1}\, e^{\beta\frac{\epsilon}{2}s_2} \cdots e^{\beta\frac{\epsilon}{2}s_N}$$

$$= p(s_1)\, p(s_2) \cdots p(s_N) \quad \leftarrow \text{Spins are statistically independent}$$

$$\left(\text{b/c they are non-interacting}\right)$$

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

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

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

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