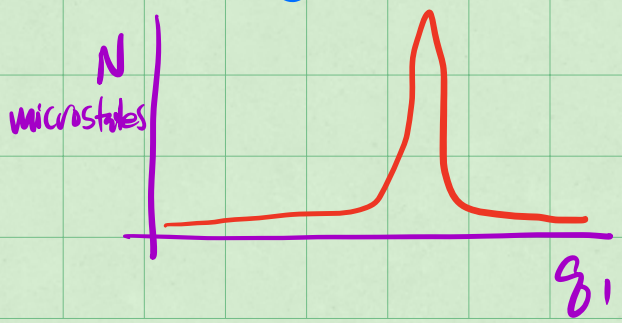
We found that most of what we do in thermodynamics is finding the mean value of some quantity,

$$\langle x \rangle = \sum_s x_s P(E_s)$$

We noticed that the set of States, s, can be very large. so that,

$$\sum_s x_s P(E_s)$$ is a prohibitively large sum

But our counting game showed that probability of given macrostate can vary wildly with some contributing lots and others very little. e.g. the QHO

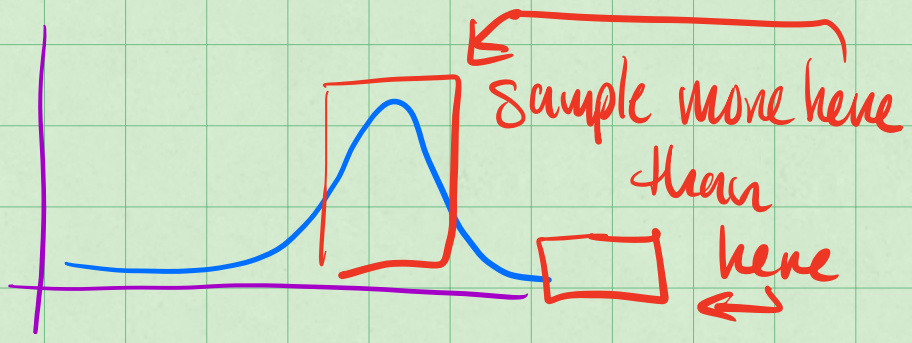


Approximate Solutions,

With $\langle x \rangle = \sum_S x_S P(E_S)$ being prohibitively cumbersome, we can selectively sample states, Let's sample N states. Then,

$$\langle x \rangle \approx \sum_{k=1}^{N} x_k P(E_k) \quad \left(\begin{matrix} \text{with} \\ N \ll S \end{matrix} \right)$$

But we want to sample carefully so that N can be small and the sum be representative.



Q: But how much more?

We use $P(E_i)$ as the probability of inclusion. The details work out by using the mathematics of weighted averages,

$$\langle g \rangle_w = \frac{\sum_i w_i g_i}{\sum w_i}$$ where w_i is a weight

This results in an estimate for $\langle x \rangle$ of,

$$\langle x \rangle \simeq \frac{1}{N} \underbrace{\sum_{k=1}^{N} \frac{x_k P(E_k)}{w_k}}_{\text{our N sampled values}} \underbrace{\sum_i w_i}_{\text{all states}}$$

Choose $P(E_i) = w_i$ thus $\sum P(E_i) = 1$

and $w_k = P(E_k)$

$$\left[\langle x \rangle \simeq \frac{1}{N} \sum_{k=1}^{N} x_k \right]$$ N samples chosen with $P(E_i)$

Markov Chain

$$P(E_i) = \frac{e^{-E_i/kT}}{Z}$$

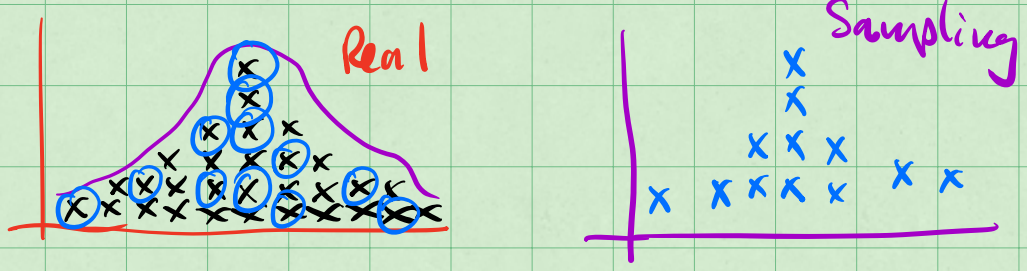
$$Z = \sum_i e^{-E_i/kT}$$

We need this ↔ to evaluate our sampling but we don't have this

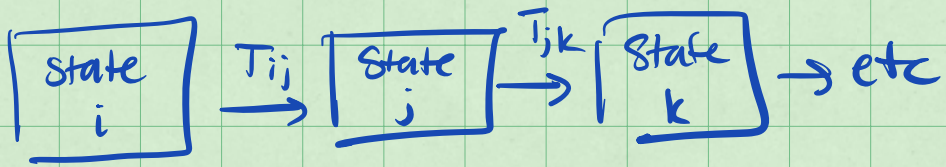
B/c if we did we'd be done already LOL

So how do we choose states with probability $P(E_i)$?

Canonical Sampling



Markov Chain



the states are iteratively constructed so that they (after many iterations) follow the Boltzmann Distribution.

that is the aim is to generate a chain of states that represent the system and then just add up x_k for those N states,

$$\sum_{k=1}^{N} x_k \approx \langle x \rangle$$

Transition Probabilities

The first thing to do is to understand how the chain is formed.

+ Consider some phase space where each state is uniquely known.
+ We are attempting to find a path through that space where adding x_k up gives $\langle x \rangle$ approx.

+ There are many such paths

Consider a state i and j.

The probability of going from i to j is,

T_{ij} transition prob $i \to j$

T_{ji} note: $j \to i$

We can choose T_{ij} so that our scheme will work.

$$\sum T_{ij} = 1$$

probability of all moves is 1 (including $i \to i$!)

Markov Choice,

$$\frac{T_{ij}}{T_{ji}} = \frac{P(E_j)}{P(E_i)} = \frac{e^{-E_j/kT}/Z}{e^{-E_i/kT}/Z} = e^{-(E_j - E_i)/kT}$$

Z cancels out and energy of states is often known!

Critical: We better get a Boltzmann distro at the end of this,

$$P(E_i) = e^{-E_i/kT}/Z$$

If we start knowing $P(E_i)$ does the next step give $P(E_j)$?

Transition to j?

$$\sum_i T_{ij} P(E_i) = \sum_i T_{ji} P(E_j)$$

$$= P(E_j) \underbrace{\sum_i T_{ji}}_{1} = P(E_j)$$

✓ so we start with Boltzmann we get it back!

~~✗~~ Turns out waiting a long time gives Boltzmann so even better

we can actually select starting state @ random!

Metropolis Algorithm

1. choose random starting state
2. choose a random move from the allowed move set (change state of one atom)
3. Calculate probability of the move having occurred.

$$E_i \leftarrow \text{calc}$$

$$E_j \leftarrow \text{calc}$$

$$P_a = e^{-(E_j - E_i)/kT}$$

4. Keep the move with P_a; otherwise dismiss it.
5. Measure X of the state (Accepted or rejected) and add to total
6. Repeat step 2