Lecture 7 - Intro to sampling

Reminder: goal of stat mech is to compute average observables

$$\langle O \rangle_{ensemble} = \int dx \, O(x) \, P(x)$$

If const NVT, $P(x) = e^{-\beta \mathcal{H}(x)} / Z$

Some problems can solve exactly, but most not. Will talk about how to solve numerically

First: finish canonical ensemble

$A = -k_B T \ln Z$

$P = -\partial A / \partial V$ etc

Also knew

$$E = -\frac{\partial \ln Z}{\partial \beta}$$

first finish ideal gas:

$$Q = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N = \frac{1}{N!} V^N (2\pi m \underbrace{k_B T}_{1/\beta})^{3/2 N}$$

$$= \beta^{-3/2 N} \cdot \text{stuff}$$

$$\mathcal{E} = -\frac{\partial \ln Q}{\partial \beta} = \frac{3}{2} N \frac{\partial \ln \beta}{\partial \beta} = \frac{3}{2} N k_B T \checkmark$$

one more thermo quantity of importance!

$$C = \frac{\partial \mathcal{E}}{\partial T} \qquad C_V = \left(\frac{\partial \mathcal{E}}{\partial T}\right)_V \qquad C_P = \left(\frac{\partial \mathcal{E}}{\partial T}\right)_P$$

Ideal gas: $C_V = \frac{3}{2} N k_B$

In general, $C = \frac{\partial \mathcal{E}}{\partial T} = \frac{\partial \mathcal{E}}{\partial \beta}\frac{\partial \beta}{\partial T} =$

$$= -\frac{1}{k_B T^2}\frac{\partial \mathcal{E}}{\partial \beta} = -k_B \beta^2 \frac{\partial \mathcal{E}}{\partial \beta}$$

Now, for NVT

$$C_V = -k_B \beta^2 \frac{\partial \mathcal{E}}{\partial \beta} \quad \text{but} \quad \mathcal{E} = -\frac{\partial \ln Z}{\partial \beta}$$

$$= k_B \beta^2 \frac{\partial}{\partial \beta}\left[\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right]$$

$$= k_B \beta^2 \left[-\frac{1}{Z^2}\frac{\partial Z}{\partial \beta}\frac{\partial Z}{\partial \beta} + \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}\right]$$

$$= k_B \beta^2 \left[\langle \mathcal{E}^2 \rangle - \langle \mathcal{E} \rangle^2\right] \quad \star$$

$$= k_B \beta^2 \, \mathrm{Var}(\mathcal{E})$$

$$Z = \int dx \, e^{-\beta \mathcal{H}(x)}, \quad \frac{\partial^2 Z}{\partial \beta^2} = \int dx \, \mathcal{H}(x)^2 e^{-\beta \mathcal{H}(x)}$$

$$\frac{\partial \mathcal{E}}{\partial T} = \frac{1}{k_B T^2} \mathrm{Var}(\mathcal{E}) \quad \star$$

Example of fluctuation dissipation theorem: fluctuations @ eq prop to how quantity relaxes to eq (Onsager regression)

What does Var(E) mean physically?

Energy goes in & out of bath

How big is fluc relative to E?

$$\sigma_E/E = \sqrt{\sigma_E^2}/E \propto \sqrt{C_v}/E \propto \frac{1}{N}!$$ b/c $C_v \propto N$, $E \propto N$

These energy fluctuations are what allow chemical systems to overcome barriers and undergo reactions. But how do we calculate properties if we can't explicitly get Z?

Consider the problem of computing

$$\langle O \rangle = \int d\vec{x}\, O(\vec{x})\, P(\vec{x})$$

first, lets consider that most observables may only depend on position

$$\langle O \rangle = \int dx^{3N} \int dp^{3N}\, O(\vec{x})\, e^{-\beta \mathcal{H}(\vec{x},\vec{p})} / Z$$

and $\mathcal{H} = \sum p_i^2/2m + U(\vec{x})$

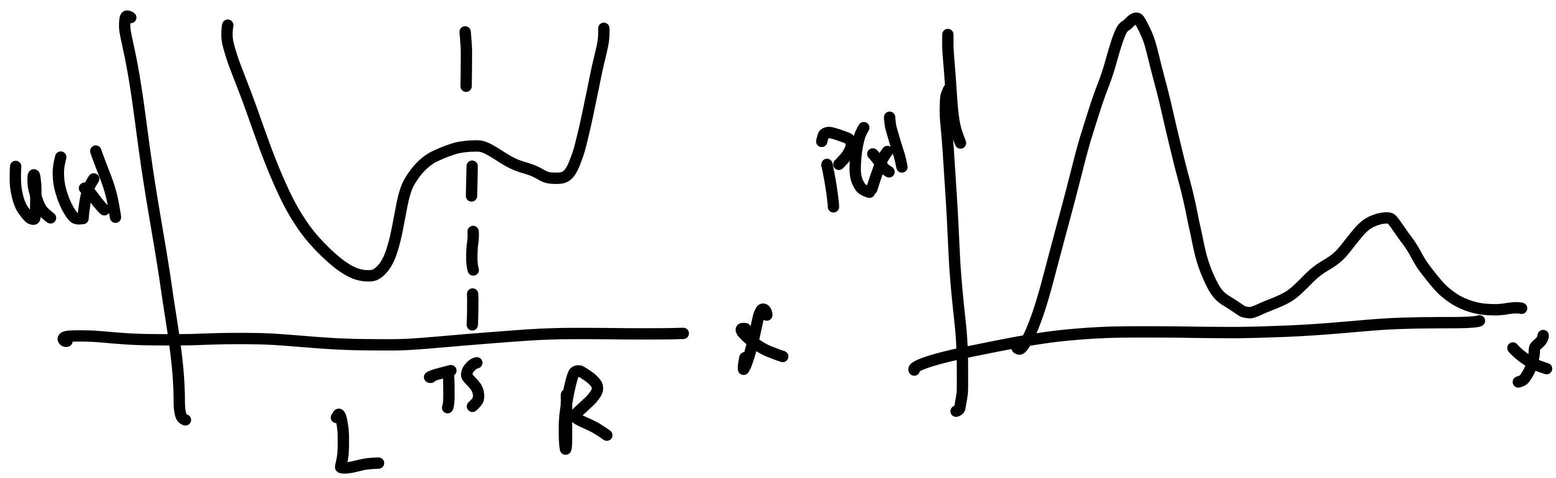
Then $\langle O \rangle = \frac{\text{const}}{Z} \cdot \int d\vec{x}\, e^{-\beta U(\vec{x})}\, O(\vec{x})$

Can define another pos. $\tilde{Z} = \int dx\, e^{-\beta U(x)}$

$Z = \text{const}\ \tilde{Z}$

$\langle O \rangle = \int d\vec{x}\, O(\vec{x}) e^{-\beta U(x)} / \tilde{Z}$

Now consider 1d problem



Can compute $\langle O \rangle$ numerically "by quadrature" ie

$$\langle O \rangle \approx \sum_{j=1}^{k} O(x_j)\, P(x_j)\, \Delta x$$

Seems great, whats the problem

For each dimension:

$\#$ points $= L/\Delta x$

so for d dimensions

$$\# = (L/\Delta x)^d = e^{d \ln(L/\Delta x)}$$

exponentially large ($d = 3N$ gets big fast)

Idea of sampling:

Generate representative cfgs

s.t. $x_t \propto P(x_t)$ somehow

Then $\langle O \rangle \approx \frac{1}{T} \sum_{t=1}^{T} O(x_t)$

One way to do this is "Molecular Dynamics", mimic Newton + temp

First discuss Monte Carlo

generate a "Markov Chain"

$x_t \to x_{t+1}$, depends only on current state

If this satisfies "detailed balance"

$$P(x_t)P(x_t \to x_{t+1}) = P(x_{t+1})P(x_{t+1} \to x_t)$$

then can be proven that chain converges s.t. $x \sim P(x)$