Reminder: goal of stat mech is to compute average observables

\[ \langle O \rangle_{\text{ensemble}} = \int dx \, O(x) \, P(x) \]

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

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

First: finish canonical ensemble

\[ A = -k_B T \ln \Xi \]
\[ P = \frac{-e^A}{\Xi} \text{ etc} \]
Also known \( E = -\frac{\Xi}{e^A} \)
First finish ideal gas:

\[ Q = \frac{1}{N!} \left( \frac{V}{N^3} \right)^N = \frac{1}{N!} v^n (2\pi m k_B T)^{3/2} \]

\[ = \beta^{-3/2} N. \text{ stop} \]

\[ E = -\frac{\partial \ln Q}{\partial \beta} = \frac{3}{2} N \frac{\partial \ln \beta}{\partial \beta} = \frac{3}{2} N k_B T \quad \checkmark \]

One more thermo quantity of importance!

\[ C = \frac{\partial E}{\partial T} \quad C_v = \left( \frac{\partial E}{\partial T} \right)_V \quad C_p = \left( \frac{\partial E}{\partial T} \right)_p \]

Ideal gas: \( C_v = \frac{3}{2} N k_B \)

In general, \( C = \frac{\partial E}{\partial T} = \frac{\partial E}{\partial \beta} \frac{\partial \beta}{\partial T} = \]

\[ = -\frac{1}{k_B T^2} \frac{\partial E}{\partial \beta} = -k_B \beta^2 \frac{\partial E}{\partial \beta} \]
Now, for NVT

\[ C_V = -k_B \beta^2 \frac{\partial E}{\partial \beta} \quad \text{but} \quad E = -\frac{\beta}{\partial \beta} \]

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

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

\[ = k_B \beta^2 \left[ \langle E^2 \rangle - \langle E \rangle^2 \right] \]

\[ = k_B \beta^2 \text{Var}(E) \]

\[ \tau = \int dx e^{-\beta H(x)} \frac{\partial^2}{\partial \beta^2} \]

\[ \frac{\partial E}{\partial T} = \frac{1}{k_B \tau^2} \text{Var}(E) \]
Example of fluctuation dissipation theorem: fluctuations @ $E_g$

prop to how quantity necessary $E_g$

(Onsager regression)

What does $\text{Var}(E)$ mean physically?

\[ E(\tau) \]

Energy goes in & out of bath

How big is fluct relative to $\delta E$?

\[ \frac{\delta E}{E} = \sqrt{\text{Var}(E)} \times \frac{1}{N} \approx \frac{1}{\sqrt{2N}} \]
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 \( f \)?

Consider the problem of computing

\[
\langle 0 \rangle = \int dx \, O(x) \, P(x)
\]

First, let's consider that most observables may only depend on position

\[
\langle 0 \rangle = \int dx \, \int p^n \, O(x) \, e^{-\beta x^2 / m + U(x)}
\]

and \( H = \sum p_i^2 / 2m + U(x) \).
Then \( \langle 0 \rangle = \frac{\text{const}}{2} \int dx e^{-\beta u(x)} O(x) \)

Can define another pos. \( \tilde{z} = \int dx e^{-\beta u(x)} \)

\[ \langle 0 \rangle = \int dx \, O(\tilde{x}) e^{-\beta u(\tilde{x})} \frac{1}{\tilde{z}} \]

Now consider 1d problem

\[ \text{Can compute } \langle 0 \rangle \text{ numerically} \]

"by quadrature" \( \text{i.e.} \)

\[ \langle 0 \rangle \approx \frac{k}{2} \sum_{j=1}^{N} O(x_j) P(x_j) \Delta x \]
Seems great, what's the problem.

For each dimension:

\# points = \( \frac{1}{\Delta x} \)

So for \( d \) dimensions

\[ \# = \left( \frac{1}{\Delta x} \right)^d = e^{d \ln \left( \frac{1}{\Delta x} \right)} \]

Exponentially large \((d=3N \text{ gets big fast})\)

Idea of sampling:

Generate representative configs

\( X_t \propto P(X_t) \) somehow

Thus \( \langle O \rangle \approx \frac{1}{T} \sum_{t=0}^{T} O(X_t) \)

One way to do this is "Molecular Dynamics", mimic Newtonian temp.
First discuss Monte Carlo
genrate a "Markov Chain"
$X_t \to X_{t+1}$ depends only on
\textit{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 \textit{converges} s.t. $X \sim P(x)$