Lecture 5 -
Canonical Ensemble
Other thermodynamic ensembles

Idea: Our hypothesis before was that if we could enumerate all the states of a system and the likelihood of seeing them, then we could predict any observables:

\[ \langle A \rangle = \sum_{\text{states}} P(n) A(n) \]

For closed isolated system, const N, V, E we expect all states to have the same weight, \( \mathcal{N}(N,V,E) \) states

\[ \langle A \rangle = \frac{\int d\phi \, \delta(S(H(\phi)) - E) A(\phi) \, / \, \int d\phi \, \delta(S(H(\phi)) - E)}{} \]

But we don't live in an isolated closed system ➔
Chemistry usually happens at constant $T \& V$ or $T \& P$

So we have to see how likely a configuration is under these conditions.

First, how is this dealt with in classical thermo?

In microcanonical ensemble we had $S(N, V, E)$ &

$$dS = \frac{1}{T} dE + \frac{1}{P} dV + \frac{1}{N} dN$$

Let's rewrite in terms of $E$, b/c that may be easier to think about.

$$dE = T dS - P dV + m dN$$
This means \( T = \frac{\partial E}{\partial S}(p, p) \), \( P = -\left( \frac{\partial E}{\partial V} \right)_S, m = \left( \frac{\partial E}{\partial N} \right)_V \).

And \( E(N, V, S) \) is a state function.

If we want a thermodynamic state function that depends on a conjugate variable instead of a current variable, we have a trick called a Legendre transform.

\[
\begin{align*}
 & y = f(x), \quad f' = \frac{df}{dx}, \\
 & x = f^{-1}(y), \quad \text{slope intercept} \quad : y = x f'(a) + y(a) \\
 & f(a) = \frac{f'(a) a + y(a)}{1}, \\
 & f(b) = \frac{f'(b) b + y(b)}{1}, \\
 & \text{in general} \quad f(x) = u(x)x + y(x). \\
\end{align*}
\]

E.g. New funce \( A(N, V, T) = E(N, V, S) - S\left( \frac{\partial E}{\partial S} \right)_N, A(N, V, S) - TS \).

\( A \) is the "Helmholz free energy"
Chain rule for $A(N, u, T)$ gives

$$dA = \left( \frac{\partial A}{\partial T} \right)_{N, u} dT + \left( \frac{\partial A}{\partial u} \right)_{T, N} du + \left( \frac{\partial A}{\partial N} \right)_{T, u} dN$$

but $A = E - TS \Rightarrow dA = dE - T ds - S dT$

$$= (dE - pdv + d\mu N) - S dT - pdT - pdv + d\mu N$$

$$= -S dT - pdv + d\mu N$$

$$\Rightarrow \left( \frac{\partial A}{\partial T} \right)_{N, u} = -S \quad \left( \frac{\partial A}{\partial u} \right)_{N, T} = -p \quad \left( \frac{\partial A}{\partial N} \right)_{T, u} = \mu$$

$A$ is like an energy

This is all classical thermo. To derive things based on a particle basis, we need to figure out how likely a state is, i.e. the inside of the partition function

The system can be described as a subsystem interacting with a bath.

$$\text{Total} = H(p, g) = H_1(p_1, g_1) + H_2(p_2, g_2)$$
Integrate over coordinates $(p', q')$; this is a type of what we call "course-graining", reduce complexity of system. May cover this more later.

What is $f(p', q')$ prob of state in subsystem.

$$f(p', q') = \frac{\int dp'' dq'' \delta (H(p'', q'') - H_1(p', q') - H_2(p''))}{\int \mathcal{D} (N_1, N_2) \exp \text{const}}$$

Since System I is small, expand function around $H_1(p', q') = 0$, commence to expand $h(f)$

Remember $f(x) = f(a) + (x-a)f'(a) + \frac{(x-a)^2 f''(a)}{2} + \ldots$

$$= \sum_{n=0}^{\infty} \frac{f^{(n)}(a) (x-a)^n}{n!} \text{ for a series}$$

$$\log f(p', q') = \log \int dp'' dq'' \delta (H(p'', q'') - H_1(p', q'') - H_2(p'')) - \text{const}$$

$$\approx \log \int dp'' dq'' \delta (H(p'', q'') - H_2(p', q'))$$

First order

$$+ \left( \frac{\partial}{\partial H_1} \log \int dp'' dq'' \delta (H(p'', q'') - H_1(p', q') - H_2(p'')) \right) H_1 \bigg|_{H_0}$$

large system

$$+ \ldots$$
Let’s sharpen $\theta(p|q) = \theta$ and use property of delta func:

$$\nabla \delta (H_1 + H_2 - E) = -\frac{\partial}{\partial E} \delta (H_1 + H_2 - E)$$

So

$$\log f = \log \int dp \, dp' \, \delta (H_2(p', q') - E)$$

and

$$\frac{\partial}{\partial E} \log \int dp \, dp' \, \delta (H_1(p, q) + H_2(p', q') - E) = \frac{\partial}{\partial E} \log \int dp \, dp' \, \delta (H_1(p, q) + H_2(p', q') - E)$$

$$= \log \int dp \, dp' \, \delta (H_2(p', q') - E) = \mathcal{S}_2 (\mathcal{N}_2, \mathcal{V}_2, \mathcal{E}_2)$$

$$= \mathcal{S}_2$$

$$\log f \approx \frac{\mathcal{S}_2}{k} - \mathcal{H}_1(p|q) \frac{\partial}{\partial E} \frac{\mathcal{S}_2 (\mathcal{N}_2, \mathcal{V}_2, \mathcal{E}_2)}{k}$$

$$\log f \approx \frac{\mathcal{S}_2}{k} - \mathcal{H}_1(p|q') / k T_2 \text{ constant}$$

so $f \propto \exp \left( -\mathcal{H}_1(p|q') / k T \right)$

The normalized prob of seeing a state is:

$$f(p|q) = \frac{C}{\mathcal{S}_2} \int dp \, dp' \, e^{-\mathcal{H}(p|q') / k T}$$

we often call denominator $Z$
and this is true even for systems where we're not thinking about particle systems, so

\[ Z = \int d^3 x \ e^{-\beta H(x)} \quad \text{where} \quad \beta = \frac{1}{k_B T} \]

or for discrete systems \( Z = \sum e^{-\beta E_n} \)

for systems of indistinguishable particles, usually write

\[ Q(N, V, T) = \frac{1}{N! \hbar^3 N} \int d^3 p \ e^{-\beta H(p)} \]

\[ f(q, p) = \frac{1}{N! \hbar^3} e^{-\beta H(q, p)} \quad \text{(} \frac{1}{N! \hbar^3} \text{ cancel out to give some pref func.)} \]

What is the connection between \( Q \) & \( S(N, V, E) \)?
\[ Q(N, \nu, T) = \frac{1}{\mathcal{Z}} \int \mathcal{D}\mathcal{E} e^{-\beta \mathcal{E}} \mathcal{Z}(N, \nu, \mathcal{E}) \]

so the canonical partition function is averaging the number of states at each energy if they have weight \( e^{-\beta \mathcal{E}} \)

Discrete, \[ Q(N, \nu, T) = \sum_{\mathcal{E}} \mathcal{Z}(N, \nu, \mathcal{E}) e^{-\mathcal{E} / k_B T} \]