**Canonical Ensemble**

Last time

\[ m \text{ states with energies } \{E_1, E_2, \ldots, E_m\} \]

...in a system

make \( A \) copies of our system

\[ N_1 = \text{num systems in state } 1 \]

\[ N_2 = \text{# in } 2 \text{ et } \]

Prob being in state \( i = P_i = \frac{N_i}{A} \)
\[ p_i = \frac{e^{-\beta E_i}}{\sum_{i=1}^{m} e^{-\beta E_i}} \] 

\[ Q(T) = \frac{1}{Z} \sum_{i=1}^{m} e^{-\beta E_i} \] 

\[ \langle \mathcal{E} \rangle = \frac{1}{Z} \sum_{i=1}^{m} E_i e^{-\beta E_i} \] 

\[ \frac{\partial Q}{\partial \beta} = - \frac{1}{Q} \frac{\partial Q}{\partial \beta} \]

\[ \partial \mu \]
$U = -\partial \ln \Omega \over \partial \beta$

$\beta$ is an unknown constant

$S = -k_B \sum_{i=1}^{n} p_i \ln p_i$

Gibbs Entropy

$S = k_B \beta U + k_B \ln \Omega$

$\partial U = dq + dw = Tds - \partial U$

$U(s,v) \Rightarrow \delta U = \left( \partial U \over \partial s \right)_v ds + \left( \partial U \over \partial v \right)_s \delta v$
\[ T = \frac{1}{k_B \beta} \Rightarrow \beta = \frac{1}{k_B T} \]

Get rid of \( \beta \)'s for now:

\[
U = \frac{-\partial U}{\partial \beta} = -\left( \frac{\partial U}{\partial T} \right) \left( \frac{\partial T}{\partial \beta} \right)
\]

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

\[
U = +k_B T^2 \frac{\partial U}{\partial T}
\]
\[ S = k_B B U + k_B \ln Q \]

\[ = k_B \left[ \frac{U}{k_B T} \right] + k_B \ln Q \]

\[ = \frac{U}{T} + k_B \ln Q \]

Remember: thermodynamic potentials are maximized or minimized at Eq. S\textsuperscript{T} at eq for NUE. Go far m\textsubscript{17}, T.
\[ A = U - TS \]

minimized @ eq

for const \( N, u, T \)

canonical ensemble

\[ A = U - T \left[ \frac{U}{T} + k_B \ln Q \right] \]

\[ A = -k_B T \ln Q \]

similar to

\[ S = k_B \ln W \]
Another important quantity is $C_V$

$$C_V = \left( \frac{\partial u}{\partial T} \right)_V$$

$\text{energy required to increase by } T^2$

$$= \left( \frac{\partial u}{\partial \beta} \right)_V \left( \frac{\partial \beta}{\partial T} \right)_V = -\frac{1}{K_B T^2} \left( \frac{\partial u}{\partial \beta} \right)_V$$

$$u = -\frac{\partial u}{\partial \beta}$$

$$C_V = \frac{1}{K_B T^2} \cdot \left( \frac{\partial^2 u}{\partial \beta^2} \right)_V$$
\[ C_U = -\frac{1}{k_BT^2} \left( \frac{\partial u}{\partial \beta} \right)_V \]

\[ u = -\frac{\partial mQ}{\partial \beta} = -\frac{1}{Q} \frac{\partial Q}{\partial \beta} \]

\[ = \pm 1 \frac{1}{k_BT^2} \frac{C}{\partial \beta} \left[ \frac{1}{Q} \frac{\partial Q}{\partial \beta} \right] \]

\[ \left[ \frac{\partial}{\partial \beta} \frac{\partial Q}{\partial \beta} + \frac{1}{Q} \frac{\partial Q}{\partial \beta} \right] \]
$$C_v = -\frac{1}{k_B T^2} \left[ \frac{\partial (\frac{1}{2})}{\partial \beta} \frac{\partial Q}{\partial T} + \frac{1}{\theta} \frac{\partial}{\partial \beta} \left[ \frac{\partial Q}{\partial \beta} \right] \right]$$

$$\left[ \left( -\frac{1}{2} \frac{\partial Q}{\partial \beta} \right) \left( \frac{\partial Q}{\partial T} \right) + \frac{1}{\theta} \frac{\partial}{\partial \beta} \left[ \frac{\partial Q}{\partial \beta} \right] \right]$$

$$\frac{1}{\theta} \frac{\partial Q}{\partial \beta} = \frac{\partial}{\partial \beta} = \frac{\partial Q}{\partial \beta} = \langle 3 \rangle$$

$$C_v = -\frac{1}{k_B T^2} \left[ -\langle 3 \rangle \langle 3 \rangle + \frac{1}{\theta} \frac{\partial}{\partial \beta} \frac{\partial}{\partial \beta} Q \right]$$
\[ C_V = \frac{1}{k_B T^2} \left[ -\langle E^2 \rangle + \frac{1}{2} \frac{\partial^2 \Omega}{\partial \beta^2} \right] \]

\[ \frac{\partial \Omega}{\partial \beta} = \sum_{i=1}^{n} (E_i - \langle E_i \rangle) e^{-\beta E_i} \]

\[ \frac{1}{Q} \frac{\partial}{\partial \beta} \left[ \frac{\partial \Omega}{\partial \beta} \right] = \sum_{i=1}^{n} \frac{E_i^2}{\langle E_i \rangle} e^{-\beta E_i} \]

\[ C_V = \frac{1}{k_B T^2} \left[ \langle E^2 \rangle - \langle E \rangle^2 \right] = \frac{1}{k_B T^2} \text{Var}(E) \]
\[ C_v = \left( \frac{\partial U}{\partial T} \right)_v = \frac{1}{k_B T^2} \text{Var}(U(T)) \]

**Fundamental Points:**

1) **Linear response**
   - A small change in a control parameter, results in a small response in a conjugate property.
   - Linear response is proportional to equilibrium fluctuations.
2) wide distribution of energies means you have a large heat capacity

a) 2 ways to have a large variance

\[ P(E) \]

\[ \sigma = \sqrt{\text{Var}(E)} \]

two states

\[ \mathcal{E}_1, \mathcal{E}_2 \]
Phase transition 1st order

\[ \langle E \rangle \]

\[ \Rightarrow \]

\[ \text{Efusion} \downarrow \]

\[ \frac{\partial E}{\partial T} \text{ goes to } \infty \]

\[ T_m \]

\[ T = T_m \]

\[ T > T_m \] for small \( N \)

\[ T_n < T_m \]
\[ P(\varepsilon) \mid N \to \infty \]

\[ \text{Var}(\varepsilon) \to \varepsilon \quad \text{as} \quad N \to \infty \quad @ T_m \]
Systems w/ discrete energy levels & continuous energy

Example discrete system

Previously: we discussed energies $E_1, E_2, \ldots, E_n$

Single particles or multiple

\[ E_2 - \frac{B}{A} \quad \text{or} \quad \frac{A}{B} \quad \text{or} \quad \frac{A}{B} \]

\[ E_1 - \frac{A}{B} \]

\[ E_0 = 2E_1 \quad \text{or} \quad E_1 + E_2 \quad \uparrow \quad 2E_2 \]

\[ E_3 \]

\[ E_0 \]

\[ E_n \]
1 particle in a two level system

\[ Q = e^{-\beta E_1} + e^{-\beta E_2} \]

\[ P_1 = \frac{e^{-\beta E_1}}{e^{-\beta E_1} + e^{-\beta E_2}} \quad P_2 = \frac{e^{-\beta E_2}}{e^{-\beta E_1} + e^{-\beta E_2}} \]

\[ = \frac{1}{1 + e^{-\beta (E_2 - E_1)}} = \frac{1}{1 + e^{-\beta \Delta E}} \]

all that matters here is the gap could say \( E_1 = 0 \quad E_2 = \Delta E \)
\[ P_1 = \frac{1}{1 + e^{-\Delta \epsilon/k_B T}} \]
\[ P_2 = e^{-\Delta \epsilon/k_B T} \]
\[ \frac{P_1}{P_2} = \frac{1}{1 + e^{-\Delta \epsilon/k_B T}} \]

For large \( T = \infty \), \( P = \frac{1}{k_B T} = 0 \)

\[ e^0 = 1 \]

\[ P_1 = P_2 = \frac{1}{2} \]

For small \( T = 0 \), \( e^{-\infty} = 0 \)

\[ e^{\infty} = 0 \]
\[ \langle E \rangle = \sum_{i=1}^{m} E_i P_i = \frac{\varepsilon_1}{1 + e^{-\beta \Delta E}} + \frac{\varepsilon_2 e^{-\beta \Delta E}}{1 + e^{-\beta \Delta E}} \]

\[ = \frac{\varepsilon_1 + \varepsilon_2 e^{-\beta \Delta E}}{1 + e^{-\beta \Delta E}} \]

\[ \text{as } T \to \infty \]

\[ \langle E \rangle = \frac{\varepsilon_1 + \varepsilon_2}{2} \]

\[ \text{as } T \to 0 \]

\[ \langle E \rangle = \frac{\varepsilon_1 + 0}{1 + 0} = \varepsilon_1 \]
Next time:

consider $n$ states $\to \infty$

continuous equivalent of

$Q$, for position & velocity states

also multiple particles