The Canonical Distribution

Canonical reduced to the simplest or clearest schema possible

Closed System:
Microcanonical Ensemble

Likelihood of \( E_n \propto \) Total # of Bath States \( E^{(0)} - E_n \)
since all states of total system are equally likely.

\[
P_n \propto \Omega' (E^{(0)} - E_n) = e^{\frac{S'(E^{(0)} - E_n)}{k_B}}
\]

\[
\sim e^{\frac{S'(E^{(0)})}{k_B} - \frac{E_n(\partial S/\partial E)}{k_B}}
\]

\[
P_n \propto e^{-E_n/k_B T}
\]

Review: Definition of Temperature

Subsystem in Particular State \( E_n \)

Total System Energy \( E^{(0)} \)

Weak Coupling: \( E^{(0)} = E' + E_n \)

Gibbs distribution
Boltzmann distribution
Canonical distribution
\[ P_n = \frac{e^{-E_n/kT}}{\sum_n e^{-E_n/kT}} \]
\[ = \frac{e^{-E_n/kT}}{Z} \]
\[ Z = \text{Partition Function} = \sum_n e^{-E_n/kT} = \sum_n e^{-\beta E_n} \]
\[ \beta = \frac{1}{kT} \text{ useful, "beta" } \]

Calculating Stuff

Internal Energy
\[ U = \langle E \rangle = \sum_n E_n P_n = \frac{\sum_n E_n e^{-\beta E_n}}{Z} \]
\[ = -\frac{\partial^2 U}{\partial \beta^2} = -\frac{\partial \log Z}{\partial \beta} \]

Specific Heat "\( C_v \) per particle"
\[ \frac{\partial U}{\partial T} = \frac{\partial U}{\partial \beta} d\beta + \frac{\partial U}{\partial T} dT = \]
\[ = -\frac{1}{kT^2} \frac{\partial}{\partial \beta} \left( \frac{\sum_n E_n e^{-\beta E_n}}{\sum e^{-\beta E_n}} \right) \]
\[ = -\frac{1}{kT^2} \left[ \frac{\sum_n E_n^2 e^{-\beta E_n}}{Z} + \frac{(\sum_n E_n e^{-\beta E_n})^2}{Z^2} \right] \]
\[ = \frac{1}{kT^2} \left[ \langle E^2 \rangle - \langle E \rangle^2 \right] \]

\[ \sigma_E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2} = \sqrt{N \left[ \frac{1}{(kT)(c_0 T)} \right]} \]

\[ \frac{1}{c_0 T} \sim 10^{-11} \]
- **Fluctuations in Energy**
  \[ \leftrightarrow \text{Specific Heat} \]
  \[ (\text{Susceptibility of Energy}) \]

- **RMS Fluctuations**
  \[ \frac{\sigma E}{E} \times \frac{1}{\sqrt{N}} \sim 10^{-11} \]

  \[ \rightarrow \text{Canonical } \& \text{ Microcanonical} \]

### Entropy

\[ S = -k_B \sum P_n \log P_n \]

\[ = -k_B \sum \frac{e^{-\beta E_n}}{Z} \log \left( \frac{e^{-\beta E_n}}{Z} \right) \]

\[ = +k_B \sum e^{-\beta E_n} \left( \frac{\beta E_n + \log Z}{Z} \right) \]

\[ = k_B \beta \langle E \rangle + k_B \log Z \sum e^{-\beta E_n} \]

\[ = \frac{\langle E \rangle}{T} + k_B \log Z \]

\[ -k_B T \log Z = \langle E \rangle - TS \]

- Connects Back to
  
  Helmholz free energy \( A \)

  (HW 2.9)
Thermo: Everything calculated from derivatives of $A(T, N, V)$

Stat Mech: Everything averaged over states $P_n$

$$U = \langle E \rangle = \frac{\sum E_n e^{-\beta E_n}}{Z} = -\frac{\partial Z/\partial \beta}{Z} = -\frac{\partial \log Z}{\partial \beta}$$

$$A = -k_B T \log Z$$

$$= k_B T^2 \frac{\partial}{\partial T} \left( \frac{-A/k_B T}{k_B T} \right)$$

$$= k_B T^2 \left( \frac{A}{k_B T} - \frac{1}{k_B T} \frac{\partial A}{\partial T} \right)$$

$$= A + T \frac{\partial A}{\partial T}$$

$$A = U + T \frac{\partial A}{\partial T} \quad \text{in} \quad -S?$$

$$dU = TdS - PdV + \mu dN$$

$$dA = dU - d(TS)$$

$$= -SdT - PdV + \mu dN$$

$$\frac{\partial A}{\partial T} = -S \quad \checkmark$$