Lecture 16

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1 Boltzmann Distribution

Here, we assume the system is in thermal contact with a reservoir. E is the energy of the system, U_R is the energy of the reservoir, and the total energy $U_T = E + U_R$ is fixed. Then the probability of any microstate is

$$\begin{aligned}P &= \frac{1}{\Omega_{S+R}(U_T)} \\ &= \frac{1}{\sum_E \Omega(E)\Omega_R(U_T - E)}\end{aligned}$$

Then

$$P(\text{system in a given microstate with } E_S) = P(S{+}R \text{ in any microstate with } U_T)\Omega_R(U_T{-}E_S)$$

and

$$\frac{P(S \text{ in } E_{S_1})}{P(S \text{ in } E_{S_2})} = \frac{\Omega_R(U_T - E_{S_1})}{\Omega_R(U_T - E_{S_2})} = \frac{\exp\left(\frac{1}{k}S_R(U_T - E_{S_1})\right)}{\exp\left(\frac{1}{k}S_R(U_T - E_{S_2})\right)}$$

where S_R is the entropy of the reservoir. Then note that

$$S_R(U_T - E_S) \approx S_R(U_T) - E_S \frac{\partial S}{\partial U}\bigg|_{U=U_T} = S_R(U_T) - \frac{E_S}{T}$$

Using a Taylor Series approximation, this simplifies the ratio to

$$\frac{P(E_{S_1})}{P(E_{S_2})} = \exp\left(-\frac{E_{S_1} - E_{S_2}}{kT}\right) \Rightarrow \frac{P(E_{S_1})}{\exp\left(-\frac{E_{S_1}}{kT}\right)} = \frac{P(E_{S_2})}{\exp\left(-\frac{E_{S_2}}{kT}\right)}$$

This holds for arbitrary S_1, S_2, so we can denote this constant by z. Now

$$P(E_S) = \frac{1}{z} \exp\left(-\frac{E_S}{kT}\right)$$

Since total probability is 1,

$$\sum_S \frac{1}{z} \exp\left(-\frac{E_S}{kT}\right) = 1 \Rightarrow z = \sum_{S'} \exp\left(-\frac{E_{S'}}{kT}\right)$$

we can also sum over energy by plugging in the multiplicity of energies $N(E)$.

$$\begin{aligned} z &= \sum_E \exp\left(-\frac{E}{kT}\right) N(E) \\ &= \sum_E \exp\left(-\frac{E}{kT}\right) \exp\left(\frac{S(E)}{k}\right) \\ &= \sum_E \exp\left(-\frac{1}{kT}(E - TS(E))\right) \end{aligned}$$

where $F = E - TS$ is the Helmholtz free energy.
Substituting,

$$P(E_S) = \frac{\exp\left(-\frac{E_S}{kT}\right)}{\sum_{S'} \exp\left(-\frac{E_{S'}}{kT}\right)}$$