Lecture 33 (2-16), Apr 3, 2023

Boltzmann Distribution

- A *microcanonical distribution* is $\dfrac{1}{\Omega(U,V,N)}$
- Consider a system with fixed V and N, with varying E in thermal contact with a thermal reservoir with energy U_R; the system and the reservoir form a closed system with U_{tot} fixed
- The probability of any microstate of the system and the reservoir is the same, $\dfrac{1}{\sum_{E'}\Omega(E)\Omega_R(U_{tot}-E')}$
- Specify a microstate in the system S by s; what is the probability of S being in a particular microstate s with energy E_s?
  - Note we're not trying to find the probability of the system having energy E_s, since there can be many microstates with the same energy; we're looking for the probability of each microstate with this energy
  - If the system is in s, the reservoir can be in any microstate with energy $U_{tot} = E_s$
  - Therefore we have $\dfrac{\Omega_R(U_{tot}-E_s)}{\sum_{E'}\Omega(E')\Omega_R(U_{tot}-E')}$
- $\dfrac{P(E_{\bar{s}_1})}{P(E_{\bar{s}_2})} = \dfrac{\Omega_R(U_{tot}-E_{\bar{s}_1})}{\Omega_R(U_{tot}-E_{\bar{s}_2})} = e^{\frac{1}{k}S_R(U_{tot}-E_{\bar{s}_1})-S_R(U_{tot}-E_{\bar{s}_1})}$ where S_R is the entropy
- Assume the reservoir is big, so $S_R(U_{tot}-E) \approx S_R(U_{tot}) - E\left.\dfrac{\partial S_R}{\partial U}\right|_{U=U_{tot}}$ (i.e. the changes in entropy are small enough that we can use a linear approximation)
  - $\dfrac{P(E_{\bar{s}_1})}{P(E_{\bar{s}_2})} = e^{\frac{1}{k}\left(\left(E_{\bar{s}_2}-E_{\bar{s}_2}\right)\frac{\partial S_R}{\partial U}\big|_{U=U_{tot}}\right)} = e^{\frac{1}{k}\left(\left(E_{\bar{s}_2}-E_{\bar{s}_2}\right)\frac{1}{T}\right)}$
  - Therefore we find $\dfrac{P(E_{\bar{s}_1})}{P(E_{\bar{s}_2})} = e^{-\frac{E_{\bar{s}_1}-E_{\bar{s}_2}}{kT}}$ – the relative probability only depends on the difference in energy and temperature
  - $\dfrac{P(E_{\bar{s}_1})}{e^{-\frac{E_{\bar{s}_1}}{kT}}} = \dfrac{P(E_{\bar{s}_2})}{e^{-\frac{E_{\bar{s}_2}}{kT}}}$ is true for any $\bar{s}_1$ and $\bar{s}_2$, therefore this ratio must not depend on $\bar{s}$, so let it be a constant, $\dfrac{1}{Z}$
- Therefore $P(E_{\bar{s}}) = \dfrac{1}{Z}e^{-\frac{E_{\bar{s}}}{kT}}$, which is known as the *Boltzmann distribution* (or *canonical distribution*)
  - Z is independent of $\bar{s}$ and characterizes the system; it is a normalization, so that $\sum\limits_{\bar{s}} P(E_{\bar{s}}) = 1$
  - $Z = \sum\limits_{\bar{s}} e^{-\frac{E_{\bar{s}}}{kT}}$
  - Z is known as the Boltzmann partition function (function of state)
- We may also compute it by $Z = \sum\limits_{E} e^{-\frac{E}{kT}}\Omega(E) = \sum\limits_{E} e^{-\frac{E}{kT}}e^{\frac{1}{k}S(E)} = \sum\limits_{E} e^{-\frac{E-TS(E)}{kT}}$
  - Instead of summing over all microstates, we instead sum over all possible energies (i.e. the spectrum of $\hat{H}$)
  - The quantity $F = E - TS(E)$ is known as the Helmholtz free energy
- The probability that the system has energy E is just $\dfrac{1}{Z}e^{-\frac{E-TS(E)}{kT}} = \dfrac{1}{Z}e^{-\frac{F}{kT}}$, which is maximized when F is minimized – therefore macroscopically, the system behaves as to minimize the Helmholtz free energy
  - The thermodynamic potential for the system is therefore the Helmholtz free energy