Lecture 7

Recap: $S = k_B \ln \Omega(\underbrace{N,V,E})$

three rigid constraints

How will energy change if I change volume?

To answer questions like this we inverted

$$S(N,V,E) \longrightarrow E(N,V,\underset{\sim}{S})$$

This is now an "entropy knob"

Entropy knobs were very awkward so we swapped a rigid constraint (the only possible ν have exactly this fixed value of E) for a statistical bias that fixed the propensity to gain/lose energy:

$$\beta = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} = \frac{1}{k_B T}$$

Then we could characterize a system by N, V, and T rather than N, V, and E.

$$P(\nu) = \begin{cases} \dfrac{e^{-E(\nu)/k_B T}}{Q(N,V,T)}, & \underline{V_\nu = V,\ N_\nu = N} \\ 0, & \text{otherwise} \end{cases}$$

Now there are only two rigid constraints!

$$E(N,V,S) \xrightarrow{\text{Legendre Transform}} A(\underbrace{N,V,T})$$

The exact same natural variables as Q. Must be some connection b/w A & Q akin to the Ω & S connection.

Let's start with Q.

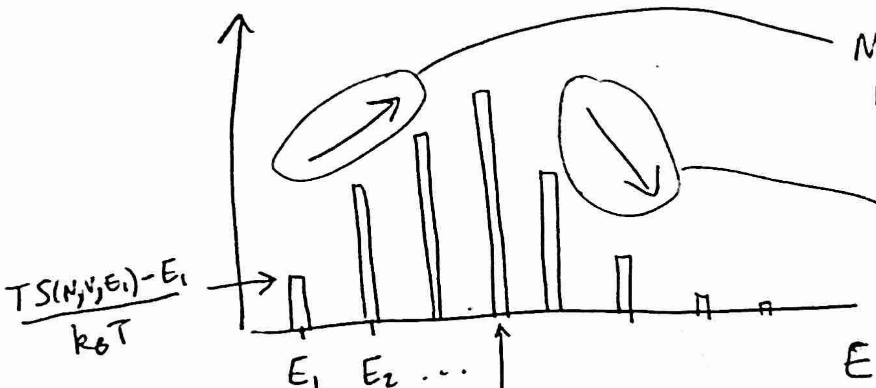
$$1 = \sum_\nu P(\nu) = \frac{\sum_\nu e^{-E(\nu)/k_BT}}{Q(N,V,T)} \Rightarrow \underbrace{Q(N,V,T) = \sum_\nu e^{-E(\nu)/k_BT}}_{\text{A normalization constant}}$$

$$= \sum_E \Omega(N,V,E)\, e^{-E/k_BT}$$

$$= \sum_E e^{S(N,V,E)/k_B}\, e^{-E/k_BT}$$

$$= \sum_E e^{\overbrace{(TS(N,V,E) - E)}^{\text{Extensive or Intensive?}}/\overbrace{k_BT}^{\text{Extensive or Intensive?}}}$$

Is this a sum? an integral? Remember, by $\sum_E$ I mean whichever is appropriate.



More states as E increases – $S(N,V,E)$ monotonically increases w/ E

fewer Boltzmann states as E increases

E^*: the value of E that has the biggest peak.

$$= e^{(TS(N,V,E^*)-E^*)/k_BT} \sum_E e^{\overbrace{[(TS(N,V,E)-E)-(TS(N,V,E^*)-E^*)]}^{\text{positive or negative? extensive or intensive}}/k_BT}$$

$$= e^{(TS(N,V,E^*)-E^*)/k_BT}\left(1 + e^{-(\text{Big \#})/k_BT} + e^{-(\text{Big \#})/k_BT} + \dots\right)$$

when $E=E^*$

This procedure is known as a "saddle point integral" "Laplace's method" "Stationary phase method" "WKB theory"

$$\approx e^{(TS(N,V,E^*)-E^*)/k_BT}$$

large system (thermodynamic limit)

Hence

$$-k_BT \ln Q(N,V,T) \approx E^* - TS(N,V,E^*) = \min_E \left(E - TS(N,V,E)\right)$$

thermo. limit

Notice that E^* was the energy with the biggest $P(E)$ term, so in the thermodynamic limit, $\langle E \rangle = E^* \equiv E$, which is why we would often write

$$-k_BT \ln Q(N,V,T) = \underbrace{E - TS}_{} = A(N,V,T)$$

This manipulation of thermodynamics really means $\min_E \left(E - TS(N,V,E)\right)$.

Take Away:

Fixed Energy	Fluctuating Energy / Fixed T
Microcanonical	Canonical
Partition Function: $\Omega(N,V,E)$	$Q(N,V,T)$
Thermodynamic Potential $S(N,V,E) = k_B \ln \Omega$	$A(N,V,T) = -k_BT \ln Q$