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Last time:

Unbiased estimations

If we know that $\sum_{r=1}^n p_r = 1$

we construct

$$S = -k \sum_{r=1}^n p_r \ln p_r - \alpha \left(\sum_{r=1}^n p_r - 1 \right)$$

↘ Lagrange multiplier

$$0 = \frac{\partial S}{\partial p_r} = -k \ln p_r - k - \alpha = 0$$

$$\Rightarrow \ln p_r = \frac{-k - \alpha}{k} = -\left(1 + \frac{\alpha}{k}\right)$$

Then

$$p_r = e^{-(1 + \frac{\alpha}{k})}$$

But

$$1 = \sum_{r=1}^M p_r = \sum_{r=1}^M e^{-(1 + \frac{\alpha}{k})} = e^{-(1 + \frac{\alpha}{k})} M \Rightarrow$$

$$e^{-(1 + \frac{\alpha}{k})} = \frac{1}{M}$$

Then

$$\boxed{p_r = \frac{1}{M}}$$

microcanonical case
all p_r 's are equal.

Now consider that we know that

$$\sum_{r=1}^M p_r = 1 \quad \text{and} \quad \langle F(x_r) \rangle = f$$

To find p_r we construct S adding the 2 constraints and we find the p_r that maximizes S :

$$S(p_r, \alpha, \beta) = -k \sum_{r=1}^M p_r \ln p_r - \alpha \left(\sum_{r=1}^M p_r - 1 \right) - \beta \left(\sum_{r=1}^M F(x_r) p_r - f \right)$$

$$0 = \frac{\partial S}{\partial p_r} = -k(p_r + 1) - \alpha - \beta F(x_r) = 0$$

Then

$$p_r = e^{-(1 + \frac{\alpha}{k})} e^{-\frac{\beta}{k} F(x_r)}$$

Use constraint to find α and β :

$$1 = \sum_{r=1}^M p_r = e^{-(1 + \frac{\alpha}{k})} \sum_{r=1}^M e^{-\frac{\beta}{k} F(x_r)} = 1$$

$$e^{-(1 + \frac{\alpha}{k})} = \frac{1}{\sum_{r=1}^M e^{-\frac{\beta}{k} F(x_r)}}$$

Then

$$p_r = \frac{e^{-\frac{\beta}{k} F(x_r)}}{\sum_{r=1}^M e^{-\frac{\beta}{k} F(x_r)}}$$

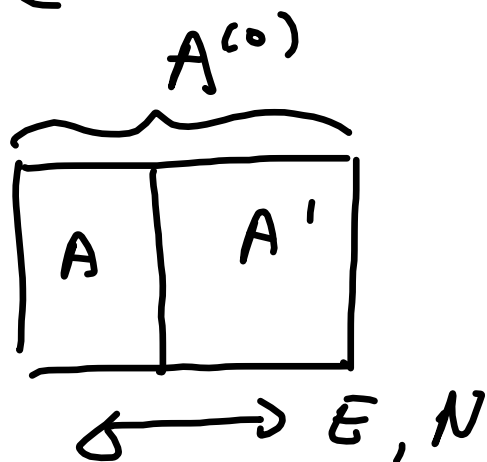
probability for the
canonical distribution
where β is obtained
from $\langle F(x_r) \rangle = f$

For a continuous variable x you can define:

$$S = -k \int dx p(x) \ln p(x) =$$
$$= -k \langle \ln p(x) \rangle .$$

Grand Canonical Ensemble : N is not fixed.

We know $\langle N \rangle$ as an average - As usual $\overline{(\Delta N^*)^2}$ tends to be very small.



energy AND particles
can be exchanged.

$$\bar{E} + \bar{E}' = E^{(0)} \text{ constant}$$

$$N + N' = N^{(0)} \text{ constant}$$

No work done
(partition does not move).

We want to find P_r : the probability that system A will be in a microstate with energy E_r and N_r particles.

$\Omega'(E', N')$ # of states accessible to A'
where A has E_r and N_r

$$\Omega(E_r, N_r) = 1$$

So for $A^{(0)}$ the # of accessible states is

$$\Omega^{(0)}(E^{(0)} - \bar{E}_r, N^{(0)} - N_r) = \Omega'(E', N') \underbrace{\Omega(\bar{E}_r, N_r)}_1$$

$$= \Omega'(E', N')$$

and $P_r(\bar{E}_r, N_r) \propto \Omega'(E^{(0)} - \bar{E}_r, N^{(0)} - N_r)$

Then

Taylor's expansion
about $\bar{E}^{(0)}, N^{(0)}$

$$\ln[\Omega'(E^{(0)} - \bar{E}_r, N^{(0)} - N_r)] \simeq \ln \Omega'(E^{(0)}, N^{(0)})$$

$$- \underbrace{\frac{\partial \ln \Omega'}{\partial \bar{E}'} \Big|_{\bar{E}^{(0)}, N^{(0)}}}_{\beta} \bar{E}_r - \underbrace{\frac{\partial \ln \Omega'}{\partial N'} \Big|_{\bar{E}^{(0)}, N^{(0)}}}_{\alpha} N_r$$

α and β are parameters that characterized A' .

Now

$$\Omega'(E^{(0)} - \bar{E}_r, N^{(0)} - N_r) \approx \Omega'(\bar{E}^{(0)}, N^{(0)}) \cdot e^{-\beta \bar{E}_r - \alpha N_r}$$

then

$$P_r \propto e^{-\beta \bar{E}_r - \alpha N_r}$$

grand-canonical
distribution.

Define $\mu = -\alpha/\beta$ chemical potential

$\therefore \alpha = -\beta\mu$ (In homework you used that $\frac{\partial \Omega}{\partial N} \Big|_{\bar{E}} = -\beta\mu$).

Now

$$\bar{E} = \frac{\sum_r e^{-\beta(E_r - \mu N_r)} E_r}{\sum_r e^{-\beta(E_r - \mu N_r)}}$$

$$\bar{N} = \frac{\sum_r e^{-\beta(E_r - \mu N_r)} N_r}{\sum_r e^{-\beta(E_r - \mu N_r)}}$$

If you know \bar{E} and \bar{N} you can obtain β and μ from these equations.

We define

$$\mathcal{Z} = \sum_r e^{-\beta(\epsilon_r - \mu N_r)}$$

grand-partition
function.

Notice that

$$P_r = \frac{e^{-\beta(\epsilon_r - \mu N_r)}}{\mathcal{Z}}$$

$$\sum_r P_r = 1$$

$$\bar{\epsilon} = - \frac{\partial \ln \mathcal{Z}}{\partial \beta}$$

$$\bar{N} = \frac{\partial \ln \mathcal{Z}}{\partial (\beta \mu)}$$

Connection of Z with thermodynamics:

We know that

$$dE = dQ - dW \quad (\text{first law})$$

$$\textcircled{1} dE = TdS - PdV \quad \left(\text{since } \frac{dQ}{T} = dS \text{ and } \text{if } dW \text{ is due to } dV \right).$$

$$\therefore E = E(S, V)$$

Notice that E, S, V are extensive variables that change with the size of the system.

But T and P are intensive variables.

From ① you see that

$$T = \left. \frac{\partial \bar{E}}{\partial S} \right|_V \quad P = - \left. \frac{\partial \bar{E}}{\partial V} \right|_S$$

But if we change V it is very hard to keep S constant - so other potentials may be more useful to do calculations in actual processes.

$$F = E - TS \quad \text{Helmholtz free energy.}$$

$$dF = dE - TdS - SdT = \cancel{TdS} - PdV + \cancel{TdS} - SdT = -PdV - SdT$$

Now $F = F(V, T)$ and

$$P = -\left.\frac{\partial F}{\partial V}\right|_T \quad S = -\left.\frac{\partial F}{\partial T}\right|_V$$

more useful in a process in which V changes isothermally or T changes isochorically.

Gibbs potential:

$$G = F + PV = E - TS + PV$$

G is a function of all intensive variables (T, P).

$$dG = -SdT + VdP$$

$$G = G(T, P) \Rightarrow \quad S = -\left.\frac{\partial G}{\partial T}\right|_P \quad V = \left.\frac{\partial G}{\partial P}\right|_T$$

Enthalpy:

$$H = E + PV$$

$$dH = TdS + VdP$$

$$H = H(S, P) \quad T = \left. \frac{\partial H}{\partial S} \right|_P \quad V = \left. \frac{\partial H}{\partial P} \right|_S$$

Now we allow N to change then

$$E = E(S, V, N) \quad \text{then} \quad \mu \text{ (define)}$$

$$dE = \left. \frac{\partial E}{\partial S} \right|_{V, N} dS + \left. \frac{\partial E}{\partial V} \right|_{S, N} dV + \left. \frac{\partial E}{\partial N} \right|_{S, V} dN$$

Now

$$d\bar{E} = T dS - P dV + \mu dN$$

Replacing $d\bar{E}$ (above) in the definitions of F , G and H we find the N dependence of these potentials:

$$dF = d(E - TS) = -S dT - P dV + \mu dN$$

$$dG = -S dT + V dP + \mu dN$$

$$dH = T dS + V dP + \mu dN$$

Then

$$\mu = \left. \frac{\partial \bar{E}}{\partial N} \right|_{S, V} = \left. \frac{\partial F}{\partial N} \right|_{T, V} = \left. \frac{\partial G}{\partial N} \right|_{T, P} = \left. \frac{\partial H}{\partial N} \right|_{S, P}$$

Notice that \bar{E} , F , f and H are functions of N - We want to define a thermodynamical potential that is a function of the intrinsic parameter μ which is the conjugate of the extensive property N . This is important because $\tilde{Z} \equiv \tilde{Z}(\mu)$ not $\tilde{Z}(N)$.

Landau potential or grand-potential:

$$\tilde{\Omega} = F - \mu N$$

$$d\tilde{\Omega} = dF - \mu dN - N d\mu = -S dT - P dV - N d\mu$$

Then $\tilde{\Omega} = \tilde{\Omega}(T, V, \mu)$ all intrinsic parameters that appear in $\tilde{\mathcal{Z}}$.

Relationship between $\tilde{\Omega}$ and $\tilde{\mathcal{Z}}$:

$$\tilde{\mathcal{Z}} = \sum_r e^{-\alpha N_r} e^{-\beta \bar{E}_r} =$$

$$= \sum_{E, N} \Omega(E, N) e^{-\beta E} e^{-\alpha N}$$

$\alpha = -\beta \mu$
 this has a sharp maximum at \bar{E}, \bar{N}

$$\approx \Omega(\bar{E}, \bar{N}) e^{-\beta \bar{E}} e^{-\alpha \bar{N}} \frac{\Delta^* E}{\delta E} \frac{\Delta^* N}{\delta N}$$

Then

$$\ln \tilde{Z} = \ln \Omega(\bar{E}, \bar{N}) - \beta \bar{E} - \alpha \bar{N} + \ln \frac{\Delta^* \delta \bar{E} \delta \bar{N}}{\delta \bar{E} \delta \bar{N}}$$

$$\approx \ln \Omega(\bar{E}, \bar{N}) - \beta \bar{E} - \alpha \bar{N}$$

negligibly
compared
to the
other terms

$$\ln \tilde{Z} + \beta \bar{E} + \alpha \bar{N} = \ln \Omega(\bar{E}, \bar{N}) = \frac{S(\bar{E}, \bar{N})}{k}$$

\therefore

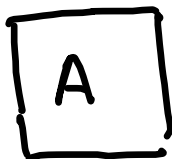
$$k \ln \tilde{Z} + \frac{\bar{E}}{T} - \frac{\mu}{T} \bar{N} = S$$

$$k T \ln \tilde{Z} = \underbrace{T S}_{-F} - \bar{E} + \mu \bar{N} = -F + \mu \bar{N} = -\tilde{\Omega}$$

Then

$$\tilde{\Omega} = -kT \ln \tilde{Z}$$

Canonical Distribution and Maximum Randomness.



a : # of identical systems A .

a_r : # of systems (or ensembles) with
 $E = E_r$

\bar{E} : constant

$$\bar{E} = \frac{1}{a} \sum_r a_r E_r$$

$$\sum_r a_r = a$$

$$\Gamma(a_1, a_2, \dots) = \frac{a!}{a_1! a_2! \dots}$$

of ways in
which we can
select a_i
arranges in
states $i = r$.

$$\ln \Gamma = \ln a! - \sum_r \ln a_r! \quad \sim \text{Stirling's}$$

$$a \ln a - a - \sum_r (a_r \ln a_r - a_r)$$

For what values of a_i is Γ a maximum?

$$\delta(\ln \Gamma) = - \sum_r \left(\frac{a_r}{a_r} \delta a_r + \ln a_r \delta a_r \right) =$$

$$= - \sum_r (1 + \ln a_r) \delta a_r = 0 \quad (1)$$

↳ for max

But $\sum_r a_r = a \Rightarrow \sum_r \delta a_r = 0 \quad (2)$

$$\frac{1}{a} \sum_r a_r \bar{\sigma}_r = \bar{\sigma} \Rightarrow \sum_r \bar{\sigma}_r \delta a_r = 0 \quad (3)$$

\therefore due to (2), (1) becomes $\sum_r \ln a_r \delta a_r = 0 \quad (4)$

Adding the constraints via Lagrange multipliers
we get:

$$\sum_r (\underbrace{\ln a_r}_{(1)} + \underbrace{\alpha}_{(2)} + \underbrace{\beta E_r}_{(3)}) \delta a_r = 0 \quad \rightarrow \text{for } \tilde{a}_r \text{ max.}$$

The maximum occurs for

$$\ln \tilde{a}_r + \alpha + \beta E_r = 0$$

$$\ln \tilde{a}_r = -\beta E_r - \alpha$$

$$\tilde{a}_r = e^{-\alpha - \beta E_r}$$

$$a = \sum_r a_r = \sum_r e^{-\alpha - \beta E_r} = e^{-\alpha} \sum_r e^{-\beta E_r}$$

$$\therefore e^{-\alpha} = \frac{a}{\sum_r e^{-\beta E_r}}$$

β is found from $\frac{1}{\Omega} \sum_r a_r \epsilon_r = \bar{\epsilon}$

then

$$\bar{\epsilon} = \frac{\sum_r e^{-\alpha} e^{-\beta \epsilon_r} \epsilon_r}{e^{-\alpha} \sum_r e^{-\beta \epsilon_r}} = \frac{\sum_r \epsilon_r e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}}$$

$$P_r = \frac{\tilde{a}_r}{\Omega} = \frac{e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}}$$

Canonical distribution
which maximizes
 P_r if we know
 $\langle \epsilon \rangle$