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Last time:

$$Z = \sum_r e^{-\beta E_r}$$

$\beta = 1/kT$ canonical partition function.

We found:

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

$$\overline{\Delta E^2} = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

Work:

If the system is characterized by external parameters $\{x_\alpha\}$ such as $x = V$, for example, under a quasi-static change from x to $x + dx$ for a system in a microstate r we'll have that

$$\Delta_x E_r = \frac{\partial E_r}{\partial x} dx$$

Then we saw that

$$đW = \sum_{\alpha=1}^{m} \bar{X}_\alpha \, dx_\alpha = - \sum_{\alpha=1}^{m} \overline{\left(\frac{\partial E_r}{\partial x_\alpha}\right)} dx_\alpha \qquad (1)$$

we found that
$$\bar{X}_\alpha = \overline{\left(-\frac{\partial E_r}{\partial x_\alpha}\right)}$$

Assume $n=1$.

$$dW = -\overline{\left(\frac{\partial \epsilon_r}{\partial x}\right)}dx = \frac{\sum_r e^{-\beta \epsilon_r}\left(-\frac{\partial \epsilon_r}{\partial x}\right)}{\sum_r e^{-\beta \epsilon_r}} \quad (2)$$

$$\left\langle \frac{\partial \epsilon_r}{\partial x}\right\rangle \neq \frac{\partial \langle \epsilon_r\rangle}{\partial x}$$

But $\displaystyle \sum_r e^{-\beta \epsilon_r}\frac{\partial \epsilon_r}{\partial x} = -\frac{1}{\beta}\frac{\partial}{\partial x}\underbrace{\left(\sum_r e^{-\beta \epsilon_r}\right)}_{Z}$.

$$= -\frac{1}{\beta}\frac{\partial Z}{\partial x} \quad (3)$$

Using (3) in (2) we obtain that

$$dW = \frac{1}{\beta Z}\frac{\partial Z}{\partial x}dx = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}dx = \bar{X}\,dx \quad (4)$$

From (9)

$$\bar{X} = \beta^{-1}\frac{\partial \ln Z}{\partial x}$$

or if $\alpha : 1, \ldots n$

$$\bar{X}_\alpha = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x_\alpha}$$

If $x = V \Rightarrow \bar{X} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} = \bar{p}$

Then

$$\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}$$

is going to provide the equation of state for the system.

In general $Z = Z(\beta, x_\alpha)$

If $n=1$ $x = V$ then $Z = Z(T, V)$

Connecting Z to thermodynamics

We saw that all thermodynamic properties are obtained from $\ln \Omega$ then we also should be able to obtain them from Z.

We know $P \propto \Omega$

We also know that

$$Z = \sum_r e^{-\beta E_r}$$ Here $Z = Z(\beta, x)$ since $E_r = E_r(x)$.

Then

$$d(\ln Z) = \frac{\partial \ln Z}{\partial x} dx + \frac{\partial \ln Z}{\partial \beta} d\beta \qquad (5)$$

Consider a quasistatic change in x and β:

$$\frac{\partial \ln Z}{\partial x} = \beta \bar{X} \qquad \text{and} \qquad \frac{\partial \ln Z}{\partial \beta} = -\bar{E} \qquad (6)$$

Plugging ⑥ in ⑤ we obtain;

$$d(\ln Z) = \beta \underbrace{\bar{X}\, dx}_{đW} - \bar{E}\, d\beta = \beta\, đW - \bar{E}\, d\beta$$

but

$$d(\bar{E}\beta) = \beta\, d\bar{E} + \bar{E}\, d\beta \quad \therefore \quad -\bar{E}\, d\beta = \beta\, d\bar{E} - d(\bar{E}\beta)$$

Then

$$d(\ln Z) = \beta\, đW + \beta\, d\bar{E} - d(\bar{E}\beta) = \beta(\underbrace{đW + d\bar{E}}_{đQ \text{ (first law)}}) - d(\bar{E}\beta)$$

Then:

$$d(\ln Z + \bar{E}\beta) = \beta\, đQ = \frac{\boxed{đQ}}{kT}^{dS} = \frac{dS}{k}$$

Then

$$\ln Z + \bar{E}\beta = \frac{S}{k}$$

or

$$\boxed{S = k(\ln Z + \bar{E}\beta)}$$

but we also know that

$$S = k \ln \Omega(\bar{E}).$$

Since

$$Z = \sum_r e^{-\beta E_r} = \sum_E \Omega(E)\, e^{-\beta E} \simeq \Omega(\bar{E})\, e^{-\beta \bar{E}} \frac{\Delta^* E}{\delta E}$$

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Taking ln of (?):

very small compared to the other terms

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

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

Then

$$\ln Z + \beta \bar{E} = \ln \Omega(\bar{E}) \equiv \frac{S}{k}$$

Then $\ln Z + \beta \bar{E} = \frac{S}{k}$ as we found before.

Now

$$\ln Z = \frac{S}{k} - \beta \bar{E} \Rightarrow k \ln Z = S - \frac{\bar{E}}{T}$$

$$kT \ln Z = TS - \bar{E} = -F$$

Helmholz free energy

Then we see that

$$\boxed{F = -kT \ln Z}$$

Since F allows to obtain all the thermodynamical properties of a system, we see that Z contains the same information.

Notice that for $T \to 0$ ($\beta \to \infty$):

$Z \to \Omega_0 e^{-\beta E_0}$ then $S \to k \ln \Omega_0$

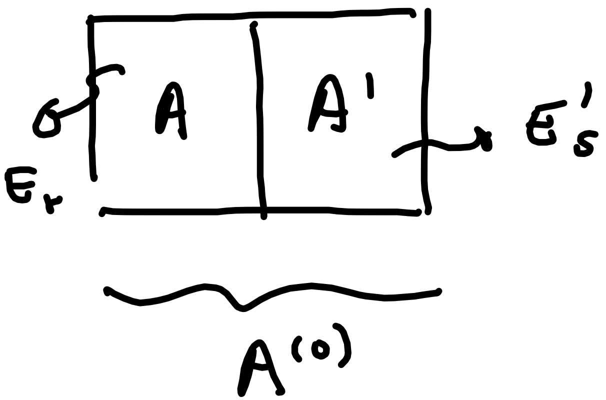
E_0: ground state

$k(\ln Z + \beta \bar{E})$

$k(\ln \Omega_0 \cancel{- \beta \bar{E}_0} \cancel{+ \beta E_0}) =$

We reobtain the 3rd law.

Z for weakly interacting system:



Now the states of $A^{(0)}$ are labeled by r and s.

$$E^{(0)}_{rs} = E_r + E'_s$$ (energies are added).

Then

$$Z^{(0)} = \sum_{r,s} e^{-\beta E^{(0)}_{r,s}} = \sum_{r,s} e^{-\beta (E_r + E'_s)} =$$

$$= \sum_{r,s} e^{-\beta E_r} e^{-\beta E'_s} = \sum_r e^{-\beta E_r} \sum_s e^{-\beta E'_s} =$$

$= Z \cdot Z'$

Then $\ln Z^{(0)} = \ln Z + \ln Z'$

This is true for N weakly interacting systems so

$Z^{(0)} = \prod_{i=1}^{N} Z_i$ or $\ln Z^{(0)} = \sum_{i=1}^{N} \ln Z_i$

Notice that $\bar{E}^{(0)} = \bar{E} + \bar{E}'$ or $\bar{E} = \sum_{i=1}^{N} \bar{E}_i$

and $S^{(0)} = S + S'$ or $S = \sum_{i=1}^{N} S_i$

Example:

Consider a system of N spins 1/2 weakly interacting in a field H.

μH

$-\mu H$

per particle.

We can find z for one single spin:

$$z = e^{\beta\mu H} + e^{-\beta\mu H} = 2\cosh\beta\mu H$$

For the system of N spins

$$Z = z^N = 2^N(\cosh\beta\mu H)^N.$$

Instead of having to deal with the 2^N possible states.

Probability and Entropy

We found that for a system with average energy $\bar{E}$

(1) $P_r = \dfrac{e^{-\beta E_r}}{Z}$ canonical probability distribution.

Then

$$e^{-\beta E_r} = Z P_r$$

and

$$-\beta E_r = \ln(Z P_r) \quad \text{or} \quad \boxed{E_r = -\frac{\ln(Z P_r)}{\beta}} \quad (2)$$

and $\bar{E} = \sum_r P_r E_r$ (3)

In a quasistatic process we have that (from ⓢ)

$$d\bar{E} = \sum_r (E_r \, dP_r + P_r \, dE_r) = đQ - đW$$

We know that

$$đW = \frac{\sum_r e^{-\beta E_r} \overbrace{\left(-\frac{\partial E_r}{\partial x} dx\right)}^{dE_r}}{\sum_r e^{-\beta E_r}} = -\sum_r P_r \, dE_r$$

Then

$$\sum_r E_r \, dP_r = đQ \, .$$

Notice that:

$$S = k(\ln Z + \beta \bar{E}) = k(\ln Z + \beta \underbrace{\sum_r P_r E_r}_{\bar{E}}) \overset{(2)}{=}$$

$$= k\left(\ln Z - \cancel{\beta} \sum_r P_r \frac{\ln(ZP_r)}{\cancel{\beta}}\right) =$$

$$= k\left(\ln Z - \sum_r P_r \left[\ln(Z) + \ln P_r\right]\right) =$$

$$= k\left[\ln Z - \underbrace{\sum_r \ln Z\, P_r}_{\ln Z \underbrace{\sum_r P_r}_{1}} - \sum_r P_r \ln P_r\right] =$$

$$= \boxed{-k \sum_r P_r \ln P_r} = -k \langle \ln P_r \rangle$$

Earlier (H-theorem for equilibrium) we defined

$$H = \sum_r P_r \ln P_r$$

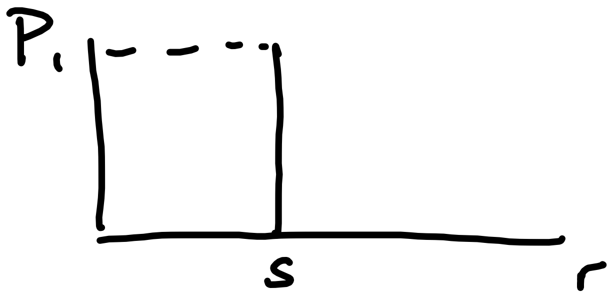
Then $S = -kH$

For equilibrium we needed a minimum for H which corresponds to a maximum in S.

Then

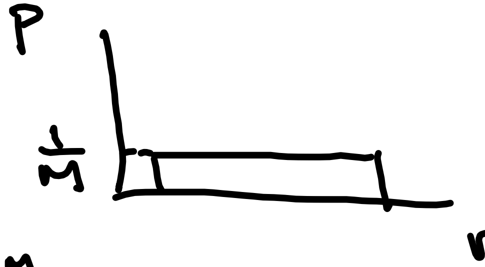
$$S = -k \langle \ln P_r \rangle$$

Notice that if $P_r = \delta_{r,s}$ for M possible outcomes



$$S = -k \sum_{r=1}^{M} \ln P_r \, \delta_{r,s} = -k \ln 1 = 0$$

If $P_r = \frac{1}{M}$ for all r



$$S = -k \sum_{r=1}^{M} \frac{\ln P_r}{M} = -k \sum_{r=1}^{M} \frac{\ln 1/M}{M} = -k \sum_{r=1}^{M} \frac{-\ln M}{M}$$

$$= k \ln M$$

$S = k \ln M$ (uniform distribution) gives, as we will see, the maximum entropy.

So S measures the "dispersity" or disorder of the probability distribution.

Unbiased estimates.

- If all outcomes M are equally likely we get the maximum possible value of S:

Assume that we only know that

$\sum_r P_r = 1$. (1)

Then to make the unbiased estimation we calculate $S = -k \sum_r P_r \ln P_r$ and we include (1) (a constraint) using a Lagrange multiplier and we request that

$$\frac{\partial S(\alpha, \{p_r\})}{\partial p_r} = 0$$

$$S = -k \sum_r p_r \ln p_r - \alpha\left(\sum_r p_r - 1\right)$$

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

$$\ln p_r = -\frac{\alpha}{k} - 1$$

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

Since $\sum_r p_r = 1 = \sum_r e^{-\frac{\alpha}{k} - 1} = M e^{-\frac{\alpha}{k} - 1}$

$$\boxed{e^{-\frac{\alpha}{k} - 1} = \frac{1}{M}}$$

microcanonical.

then

$$p_r \overset{(1)}{=} \frac{1}{M} \quad \forall r$$

uniform distribution