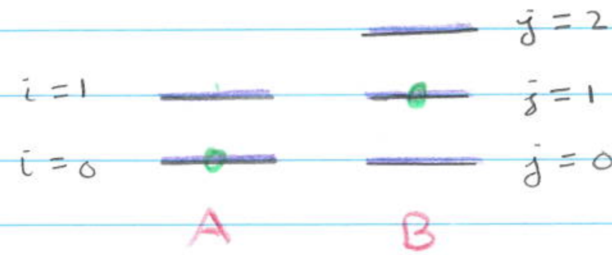
Factorization of Partition Fcns

- Suppose we have a system consisting of two distinguishable atoms, A & B. (We will talk about the indistinguishable case later.) Let the energy be a sum, energy of A plus energy of B

$$E_{i,j} = \mathcal{E}_i^A + \mathcal{E}_j^B$$



The states are labelled by i and j. For example, in the figure we have drawn the state with $i=0$ and $j=1$. In this example there are six states in total; $i=0,1$ and $j=0,1,2$, e.g. $0,0$; $0,1$; $1,0$; ...

- Then

$$Z = \sum_i \sum_j e^{-\beta E_{i,j}} = \sum_{i,j} e^{-\beta(\mathcal{E}_i^A + \mathcal{E}_j^B)}$$

$$= \sum_i e^{-\beta \mathcal{E}_i^A} \sum_j e^{-\beta \mathcal{E}_j^B}$$

$$= Z^A Z^B$$

☆ So the partition function factorizes into a partition fcn of A times a partition fcn of B

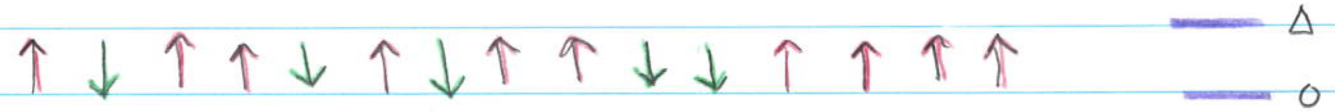
- The free energy and entropy are sums

$$F = -kT \ln Z = (-kT \ln Z^A) + (-kT \ln Z^B)$$

$$= F^A + F^B$$

Ex:

The two state paramagnet. The spins can be spin up or spin down



The energy of spin up is 0, and the energy of spin down is Δ as discussed in HW

$$Z = Z_1^N \qquad Z_1 = 1 + e^{-\beta \Delta}$$

Then

$$F = -kT \ln Z = -NkT \ln(1 + e^{-\Delta/kT}) = NF_1$$

grows linearly with system size

Now from F you can find the entropy:

$$dU = T\,dS$$

$$dF = -S\,dT$$

use by parts $T\,dS = d(TS) - S\,dT$ and recall $F = U - TS$

So

$$S = -\frac{\partial F}{\partial T} = -N\frac{\partial F_1}{\partial T} = NS_1$$

$$S = N\left[k\ln\left(1+e^{-\Delta/kT}\right) + \frac{\Delta}{T}\frac{e^{-\Delta/kT}}{1+e^{-\Delta/kT}}\right]$$

This is what we found for S_1 previously.

See slide again

The point to take away is that because of factorization, $Z_N = Z_1^N$. Then the free energy is a logarithm, $F = -kT\ln Z_N$, which grows linearly with N, i.e. the free energy is extensive. The entropy is a derivative of F and thus also is extensive, $S = NS_1$, growing linearly with the number of sites.

Entropy of Two State System