Chem. 2440 - HW #3

1. problem 3-18 from Chandler

N distinguishable non interacting spins in a magnetic field H. Each spin has a magnetic moment μ and can point parallel or antiparallel to the field.

The energy of a state is then $\sum_i^N -n_i\mu H$, $n_i = \pm 1$ where $n_i\mu_i$ is the magnetic moment in the direction of the field.

$$Q = \sum_{n_1,\ldots,n_N} e^{-\beta E_{n_1,\ldots,n_N}} = \sum_{n_1,\ldots,n_N} e^{-\beta \sum_{i=1}^N(-n_i\mu H)}$$

$$= \sum_{n_1,\ldots,n_N} \prod_{i=1}^N e^{\beta n_i \mu H} = \prod_{i=1}^N \sum_{n=\pm 1} e^{\beta\mu H n}$$

$$= \left(e^{\beta\mu H} + e^{-\beta\mu H}\right)^N = \left[2 \cdot \cosh(\beta\mu H)\right]^N$$

$$\langle E\rangle = -\frac{\partial \ln Q}{\partial\beta} = N\mu H \frac{\left(-e^{\beta\mu H} + e^{-\beta\mu H}\right)}{e^{\beta\mu H} + e^{-\beta\mu H}} = N\mu H \tanh(\beta\mu H)$$

$$S = \frac{\langle E\rangle - \langle A\rangle}{T} = Nk\ln\left(e^{\beta\mu H} + e^{-\beta\mu H}\right) - \frac{N\mu H}{T}\tanh(\beta\mu H)$$

How do $\langle E\rangle$ and S behave as $T \to 0$

$$\langle E\rangle \xrightarrow[T\to 0]{} -N\mu H$$

$$S \xrightarrow[T\to 0]{} Nk\ln e^{\beta\mu H} - \frac{N\mu H}{T} = \frac{N\mu H}{T} - \frac{N\mu H}{T} = 0$$

2. 3.19 from Chandler

Calculate $\langle m \rangle = \langle \sum_{i=1}^{N} \mu n_i \rangle$

There is an easy way of doing this

$$\left\langle \sum_{i=1}^{N} \mu n_i \right\rangle = \frac{1}{H} \left\langle \sum_{i=1}^{N} \mu n_i H \right\rangle = \frac{\langle E \rangle}{H} = N\mu \tanh(\beta \mu H)$$

Thus $\langle m \rangle \xrightarrow[T \to 0]{} N\mu$ (all spins alligned)

Now calculate the fluctuations in m.

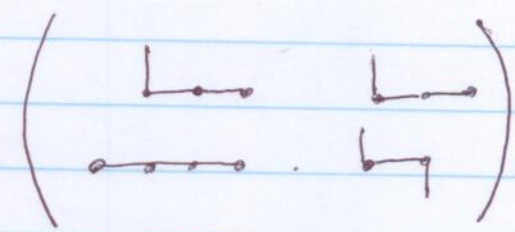
$$\langle m^2 \rangle = \frac{1}{Q} \frac{\partial^2 Q}{(\partial \beta H)^2}$$

$$\langle m^2 \rangle - \langle m \rangle^2 = N\mu^2 \left[1 - \tanh^2(\beta \mu H)\right] \to 0 \text{ as } T \to 0$$

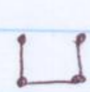
In the $T \to 0$ limit, all spins become alligned, and thus there are no fluctuations in that limit

3. 4 unit polymer on a 2D lattice

all have energy 0



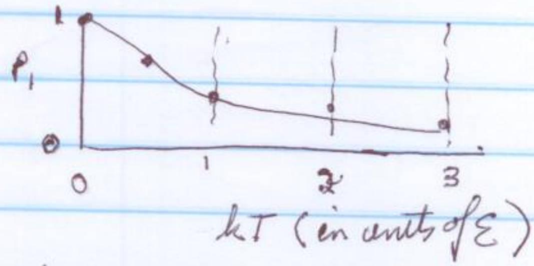
energy $-\epsilon$



redefine the zero of energy so that the most stable arrangement has ϕ energy. The four degenerate configurations then have energy ϵ

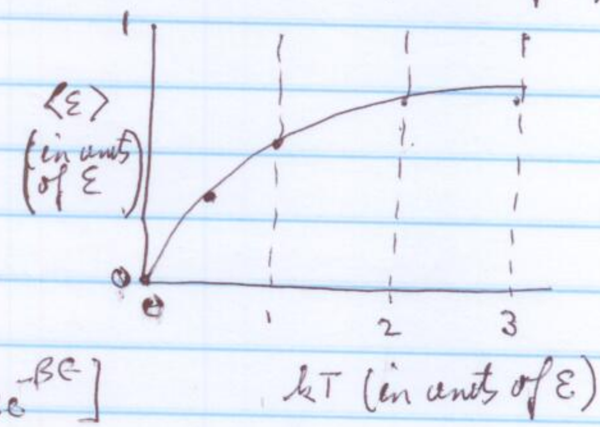
$$Q = 1 + 4e^{-\beta \varepsilon}$$

$$P_1 = \frac{1}{1+4e^{-\beta\varepsilon}} \qquad P_2 = \frac{4e^{-\beta\varepsilon}}{1+4e^{-\beta\varepsilon}}$$



$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta}$$

$$= \frac{4\beta}{1+4e^{-\beta\varepsilon}}$$



$$S = \frac{E-A}{T}$$

$$= \frac{4\varepsilon}{T}\frac{e^{-\beta\varepsilon}}{(1+4e^{-\beta\varepsilon})} + k\ln\left[1+4e^{-\beta\varepsilon}\right]$$

$\rightarrow 0$ as $T \rightarrow 0$

$\rightarrow k\ln 5$ as $T \rightarrow \infty$