

1. Here we need to compare the grand canonical ensemble to the canonical ensemble of the Ising model. So the statistical weight with which we will be working is

$$-\beta E_\nu + \beta \mu N_\nu = -\beta E_\nu + \beta \mu_1 N_1 + \beta \mu_2 N_2$$

Plugging in the relevant expressions,

$$\begin{aligned} E - \mu_1 N_1 - \mu_2 N_2 &= - \sum_{ij}' \left[\epsilon_{11} n_i n_j + \epsilon_{22} (1 - n_i)(1 - n_j) + \epsilon_{12} n_i (1 - n_j) + \epsilon_{12} (1 - n_i) n_j \right] \\ &\quad - \mu_1 \sum_i n_i - \mu_2 \sum_i (1 - n_i) \\ &= - \sum_{ij}' \epsilon_{11} n_i n_j - \epsilon_{22} \sum_{ij}' 1 + \epsilon_{22} \sum_{ij}' (n_i + n_j) - \epsilon_{22} \sum_{ij}' n_i n_j \\ &\quad - \epsilon_{12} \sum_{ij}' (n_i + n_j - 2n_i n_j) - \mu_1 \sum_i n_i - \mu_2 \sum_i (1 - n_i) \end{aligned}$$

Combining sums with the same terms and accounting for the number of nearest neighbors z , we have

$$\begin{aligned} &= -(\epsilon_{12} + \epsilon_{22} - 2\epsilon_{12}) \sum_{ij}' n_i n_j + \epsilon_{22} N \frac{z}{2} \\ &\quad - \sum_{ij}' [-2\epsilon_{22} + 2\epsilon_{12}] n_i - \mu_2 N - (\mu_1 - \mu_2) \sum_i n_i \end{aligned}$$

We don't need to consider the constant terms as they just shift the energy scale. Then, eliminating the nearest neighbor sum in the third term,

$$\sim -(\epsilon_{12} + \epsilon_{22} - 2\epsilon_{12}) \sum_{ij}' n_i n_j - \sum_{ij}' [z(\epsilon_{12} - \epsilon_{22}) + (\mu_1 - \mu_2)] n_i$$

This gives us:

$$\begin{aligned} \epsilon_{12} + \epsilon_{22} - 2\epsilon_{12} &= 4J \\ z(\epsilon_{12} - \epsilon_{22}) + (\mu_1 - \mu_2) &= 2(h - Jz). \end{aligned}$$

2. See solutions manual.
3. i Since each length is uncorrelated with the next length: $\Omega = \omega^N$, where ω is the number of ways to arrange one length. In any dimension the vector can point in two ways, so for a system with d dimensions $\omega = 2d$. Therefore

$$\begin{aligned} \Omega &= (2d)^N \\ S &= k_B \ln \Omega \\ S &= k_B N \ln 2d \\ a &= 2d \end{aligned}$$

ii Let's write down the expression for $\langle |\mathbf{R}|^2 \rangle$ and expand it:

$$\begin{aligned}
 \langle |\mathbf{R}|^2 \rangle &= \left\langle \left(l \sum_i^N \hat{b}_i \right) \left(l \sum_j^N \hat{b}_j \right) \right\rangle \\
 &= \left\langle l^2 \sum_i^N \sum_j^N \hat{b}_i \cdot \hat{b}_j \right\rangle \\
 &= \left\langle l^2 \sum_i^N \sum_j^N \delta_{ij} \right\rangle \\
 &= \left\langle l^2 \sum_i^N 1 \right\rangle \\
 &= l^2 N
 \end{aligned}$$

So we find that $R \sim \sqrt{\langle |\mathbf{R}|^2 \rangle} = l\sqrt{N}$. Therefore:

$$\nu = 1/2$$

- iii The experimental ν is larger than ours, suggesting that the polymer is less tightly coiled in a solvent. This could occur for a number of reasons, including solvent-polymer attraction and the fact that the polymer is 'self-avoiding', meaning that it cannot overlap with itself, which was not excluded in our calculations.
4. i Since all the configurations have the same energy, we need to use the microcanonical ensemble. The partition function we are looking for is therefore simply Ω , the number of microstates. Therefore the probability of being in a state with length \mathbf{R} is the number of ways to arrange the system in state \mathbf{R} divided by the total number of ways to arrange the system Ω .

$$p(\mathbf{R}) = \frac{\Omega_{\mathbf{R}}}{\Omega} = \gamma \exp \left[-\frac{dR^2}{2Nl^2} \right]$$

Furthermore, we know that $S = k_B \ln \Omega$, so $\Omega(\mathbf{R}) = e^{S(\mathbf{R})/k_B}$. Plugging this in:

$$\begin{aligned}
 \gamma \exp \left[-\frac{dR^2}{2Nl^2} \right] &= \frac{e^{S(\mathbf{R})/k_B}}{\Omega} \\
 \ln \gamma - \frac{dR^2}{2Nl^2} &= S(\mathbf{R})/k_B - \ln \Omega \\
 \ln \gamma \Omega - \frac{dR^2}{2Nl^2} &= S(\mathbf{R})/k_B \\
 k_B \ln \gamma \Omega - \frac{k_B dR^2}{2Nl^2} &= S(\mathbf{R})
 \end{aligned}$$

Define $S_0 = k_B \ln \gamma \Omega$, which gets us to

$$S(R) = S_0 - \frac{k_B dR^2}{2Nl^2}$$

ii For a mean-field type analysis we assume that

$$N_{v_o} = \frac{v_o}{V} N$$

where N_{v_o} is the number of particles in volume v_o . Tagging one of these particles means there's "one less" particle in the volume (i.e. all the other particles in the volume interact with the tagged particle), allowing us to get:

$$\text{Average energy of a tagged particle} = \epsilon \left(\frac{v_o}{V} N - 1 \right)$$

To get the total average energy of repulsion $E_{\text{rep}}(R)$, we multiple this by $N/2$, so we don't overcount the interactions. Noting that $V = gR^d$, we get

$$E_{\text{rep}}(R) = \epsilon \frac{N}{2} \left(\frac{v_o}{gR^d} N - 1 \right)$$

iii Since $A = E - TS$, we get

$$A(R) = \epsilon \frac{N}{2} \left(\frac{v_o}{gR^d} N - 1 \right) - T \left(S_0 - \frac{k_B d R^2}{2N l^2} \right)$$

iv The most likely R for a chain that is able to exchange energy with a heat bath will minimize the free energy (according to the second law of thermodynamics):

$$\left(\frac{\partial A}{\partial R} \right)_T = 0$$

Let's minimise the free energy!

$$\begin{aligned} \left(\frac{\partial A}{\partial R} \right)_T &= \epsilon \frac{N}{2} \left(\frac{v_o}{g} N (-d) R^{-d-1} \right) + T \frac{k_B d R}{N l^2} = 0 \\ \epsilon \frac{N}{2} \left(\frac{v_o}{g} N d R^{-d-1} \right) &= T \frac{k_B d R}{N l^2} \\ \epsilon \frac{N^3}{2} \left(\frac{v_o}{g} R^{-d-1} \right) &= T \frac{k_B R}{l^2} \\ \epsilon \frac{N^3}{2} \left(\frac{v_o}{g} \right) &= T \frac{k_B R^{d+2}}{l^2} \\ N^3 \left(\frac{l^2 \epsilon v_o}{2g k_B T} \right) &= R^{d+2} \end{aligned}$$

We finally get that

$$R = N^{3/(d+2)} \left(\frac{l^2 \epsilon v_o}{2g k_B T} \right)^{1/(d+2)}$$

The term $(l^2 \epsilon v_o / (2g k_B T))^{1/(d+2)}$ is a constant and

$$\nu = 3/(d+2)$$

The resulting ν shows that the mean-field values agree with the measured values.

- v The representative configurations show that chain is quite uncoiled, which might not hold when the interaction energy is not highly repulsive (for instance, when there are opposite charges on the polymer, it might want to fold in on itself). Thus, the average repulsive energy might not be fully representative for individual monomer-monomer interactions. Additionally, the interaction volume estimate might be incorrect because it smooths out any difference in interaction between different units, which might be important.

5. i For a positive charge q :

$$E = q\phi = q\bar{\phi}(r)$$

$$P(r) \propto e^{-\beta E} = e^{-\beta q\bar{\phi}(r)}$$

$$Q = \int dr e^{-\beta E} = \int dr e^{-\beta q\bar{\phi}(r)} \simeq V \text{ (from the hint in the problem)}$$

Therefore for a positive charge, the probability (density) is

$$p_+(r) = \frac{e^{-\beta q\bar{\phi}(r)}}{V}$$

For the negatively charged ion $-q$ we also get a similar expression.

$$p_-(r) = \frac{e^{\beta q\bar{\phi}(r)}}{V}$$

- ii To estimate the mean field value we can use probability to describe the average. Starting with the positively charged ion q we get

$$\bar{\rho}_+(r) = q \times N \times p_+(r)$$

$$\bar{\rho}_+(r) = q \times C \times e^{-\beta q\bar{\phi}(r)}$$

For the negatively charged ion $-q$ we similarly get

$$\bar{\rho}_-(r) = q \times C \times e^{\beta q\bar{\phi}(r)}$$

- iii Plugging in the expressions from part ii, we get:

$$\begin{aligned} \nabla^2 \bar{\phi}(r) &= -\frac{4\pi}{\epsilon} [\bar{\rho}_0(r) + \bar{\rho}_+(r) + \bar{\rho}_-(r)] \\ &= -\frac{4\pi}{\epsilon} [\bar{\rho}_0(r) + qC e^{-\beta q\bar{\phi}(r)} - qC e^{\beta q\bar{\phi}(r)}] \end{aligned}$$

This is the Poisson-Boltzmann equation, which combines both the Poisson equation and Boltzmann weighting to describe the electrostatic interactions in ionic solutions.

- iv For small x , $e^x \simeq 1 + x + O(x^2)$. We then expand the result from part (iii) to first order:

$$\begin{aligned} \nabla^2 \bar{\phi}(r) &= -\frac{4\pi}{\epsilon} [\bar{\rho}_0(r) + qC e^{-\beta q\bar{\phi}(r)} - qC e^{\beta q\bar{\phi}(r)}] \\ &\simeq -\frac{4\pi}{\epsilon} [\bar{\rho}_0(r) + qC [1 - \beta q\bar{\phi}(r)] - qC [1 + \beta q\bar{\phi}(r)]] \\ &= -\frac{4\pi}{\epsilon} [\bar{\rho}_0(r) - 2q^2 C \beta \bar{\phi}(r)] \\ &= \left(\frac{8\pi}{\epsilon} q^2 C \beta \right) \bar{\phi}(r) - \frac{4\pi}{\epsilon} \bar{\rho}_0(r) \end{aligned}$$

Thus, we see that that

$$\lambda = \left(\frac{8\pi}{\epsilon} q^2 C \beta \right)^{-1/2}$$

v Using dimensional analysis, we can find the units of lambda.

$$\lambda = \left(\frac{8\pi}{\epsilon} q^2 C \beta \right)^{-1/2}$$

$$\text{unit of } \lambda = \left(\frac{1}{C^2/(N \cdot m^2)} \cdot C^2 \cdot 1/m^3 \cdot (N \cdot m) \right)^{-1/2}$$

$$\text{unit of } \lambda = (1/m^2)^{-1/2} = m, \text{ which is length!}$$

This λ is also known as the Debye length.

vi We now have to calculate the mean electric potential $\bar{\phi}(r)$ in the system given $\rho_0(r) = q_0 \delta(\mathbf{r})$.

We just plug in our charge distribution to get:

$$\begin{aligned} \bar{\phi}(r) &= \int dr' G(r - r') \rho_0(r') \\ &= \int dr' G(r - r') q_0 \delta(r') \\ &= q_0 G(r) \\ &= \frac{q_0}{\epsilon r} e^{-r/\lambda} \end{aligned}$$

vii In a solution without any ions, an isolated q generates an electrostatic potential of the form $\phi = \frac{q}{\epsilon r}$. The exponential decay comes screening due to the fact that there are ions in solution. λ determines the length scale of ion-ion interactions in an ionic solution and is a measure of how effective charge screening is. For example, in water at room temp, the length scale is on the order of nm's. From the equation for λ , we see that λ increases with temperature, and decreases with increasing ion concentrations. This is because higher temperature leads to higher fluctuations in ion positions \implies less effective charge screening. Higher ion concentrations means that there are more charges available to shield a given ion \implies more effective screening.