

7.3

(a) $E = \sum (\sigma_1 + \sigma_2) + J \sigma_1 \sigma_2$

N O_2 molecules

Ω lattice sites

$$Z = \binom{\Omega}{N} e^{-\beta N \epsilon_{sol}} + 2 \binom{\Omega}{N-1} e^{-\beta (N-1) \epsilon_{sol}} e^{-\beta \epsilon} + \binom{\Omega}{N-2} e^{-\beta (N-2) \epsilon_{sol}} e^{-2\beta \epsilon - \beta J}$$

$$\langle N \rangle = \frac{\partial \ln Z}{\partial (-\beta \epsilon)}$$

$$= \frac{2 \binom{\Omega}{N-1} e^{-\beta (N-1) \epsilon_{sol}} e^{-\beta \epsilon} + 2 \binom{\Omega}{N-2} e^{-\beta (N-2) \epsilon_{sol}} e^{-2\beta \epsilon - \beta J}}{\binom{\Omega}{N} e^{-\beta N \epsilon_{sol}} + 2 \binom{\Omega}{N-1} e^{-\beta (N-1) \epsilon_{sol}} e^{-\beta \epsilon} + \binom{\Omega}{N-2} e^{-\beta (N-2) \epsilon_{sol}} e^{-2\beta \epsilon - \beta J}}$$

$$= \frac{2 \cdot \frac{\Omega^{N-1}}{(N-1)!} e^{-\beta (N-1) \epsilon_{sol}} e^{-\beta \epsilon} + 2 \frac{\Omega^{N-2}}{(N-2)!} e^{-\beta (N-2) \epsilon_{sol}} e^{-2\beta \epsilon - \beta J}}{\frac{\Omega^N}{N!} e^{-\beta N \epsilon_{sol}} + 2 \cdot \frac{\Omega^{N-1}}{(N-1)!} e^{-\beta (N-1) \epsilon_{sol}} e^{-\beta \epsilon} + \frac{\Omega^{N-2}}{(N-2)!} e^{-\beta (N-2) \epsilon_{sol}} e^{-2\beta \epsilon - \beta J}}$$

$$= \frac{2 \cdot \frac{N}{\Omega} e^{-\beta (\epsilon - \epsilon_{sol})} + 2 \frac{N(N-1)}{\Omega^2} e^{-\beta (2\epsilon + J - 2\epsilon_{sol})}}{1 + 2 \frac{N}{\Omega} e^{-\beta (\epsilon - \epsilon_{sol})} + \frac{N(N-1)}{\Omega^2} e^{-\beta (2\epsilon + J - 2\epsilon_{sol})}}$$

$$= \frac{2 \frac{c}{c_0} e^{-\beta (\epsilon - \epsilon_{sol})} + 2 \frac{c^2}{c_0^2} e^{-\beta (2\epsilon + J - 2\epsilon_{sol})}}{1 + 2 \frac{c}{c_0} e^{-\beta (\epsilon - \epsilon_{sol})} + \frac{c^2}{c_0^2} e^{-\beta (2\epsilon + J - 2\epsilon_{sol})}}$$

$$\mu = \mu_0 + kT \ln \frac{c}{c_0} \quad \rightarrow \text{then} \quad \langle N \rangle \approx \frac{2 e^{-\beta (\epsilon - \mu)} + 2 e^{-\beta (2\epsilon + J - 2\mu)}}{1 + 2 e^{-\beta (\epsilon - \mu)} + e^{-\beta (2\epsilon + J - 2\mu)}}$$

$$\frac{\mu - \mu_0}{kT} = \ln \frac{c}{c_0}$$

$$\frac{c}{c_0} = e^{\beta (\mu - \mu_0)}$$

Set $\mu_0 = \epsilon_{sol}$

(b)

$$\begin{aligned}
 P_0 &= \frac{1}{Z} \left[\binom{\Omega}{N} e^{-\beta N \epsilon_{sol}} \right], & Z &= \binom{\Omega}{N} e^{-\beta N \epsilon_{sol}} + 2 \binom{\Omega}{N-1} e^{-\beta(N-1)\epsilon_{sol}} e^{-\beta \epsilon} \\
 & & & + \binom{\Omega}{N-2} e^{-\beta(N-2)\epsilon_{sol}} e^{-2\beta \epsilon - \beta J} \\
 P_1 &= \frac{1}{Z} \left[2 \binom{\Omega}{N-1} e^{-\beta(N-1)\epsilon_{sol}} e^{-\beta \epsilon} \right] \\
 P_2 &= \frac{1}{Z} \left[\binom{\Omega}{N-2} e^{-\beta(N-2)\epsilon_{sol}} e^{-2\beta \epsilon - \beta J} \right]
 \end{aligned}$$

$$\therefore P_0 \approx \frac{1}{1 + 2 \frac{N}{\Omega} e^{-\beta(\epsilon - \epsilon_{sol})} + \left(\frac{N}{\Omega}\right)^2 e^{-\beta(2\epsilon + J - 2\epsilon_{sol})}}$$

$$P_1 = \frac{2 \left(\frac{N}{\Omega}\right) e^{-\beta(\epsilon - \epsilon_{sol})}}{1 + 2 \left(\frac{N}{\Omega}\right) e^{-\beta(\epsilon - \epsilon_{sol})} + \left(\frac{N}{\Omega}\right)^2 e^{-\beta(2\epsilon + J - 2\epsilon_{sol})}}$$

$$P_2 = \frac{\left(\frac{N}{\Omega}\right)^2 e^{-\beta(2\epsilon + J - 2\epsilon_{sol})}}{1 + 2 \left(\frac{N}{\Omega}\right) e^{-\beta(\epsilon - \epsilon_{sol})} + \left(\frac{N}{\Omega}\right)^2 e^{-\beta(2\epsilon + J - 2\epsilon_{sol})}}$$

$$\left(\frac{N}{\Omega}\right) e^{-\beta(\epsilon - \epsilon_{sol})} = \left(\frac{c}{c_0}\right) e^{-\beta(\epsilon - \epsilon_{sol})}$$

Replace $\left(\frac{c}{c_0}\right) \equiv e^{\beta(\mu - \epsilon_{sol})}$ then

$$\therefore P_2 = \frac{e^{-\beta(2\epsilon - 2\mu + J)}}{1 + 2 e^{-\beta(\epsilon - \mu)} + e^{-\beta(2\epsilon - 2\mu + J)}}$$

P_0, P_1 can be expressed in a similar way

8.1

$$P(R; N) = \frac{N!}{\left(\frac{N}{2} + \frac{R}{2a}\right)! \left(\frac{N}{2} - \frac{R}{2a}\right)!} \frac{1}{2^N}$$

$$\begin{aligned} \ln P(R; N) &\cong N \ln N - N + \ln \sqrt{2\pi N} \\ &- \left[\left(\frac{N}{2} + \frac{R}{2a}\right) \ln \left(\frac{N}{2} + \frac{R}{2a}\right) - \left(\frac{N}{2} + \frac{R}{2a}\right) + \frac{1}{2} \ln 2\pi \left(\frac{N}{2} + \frac{R}{2a}\right) \right] \\ &- \left[\left(\frac{N}{2} - \frac{R}{2a}\right) \ln \left(\frac{N}{2} - \frac{R}{2a}\right) - \left(\frac{N}{2} - \frac{R}{2a}\right) + \frac{1}{2} \ln 2\pi \left(\frac{N}{2} - \frac{R}{2a}\right) \right] \\ &- N \ln 2 \end{aligned}$$

$$\therefore \left(\frac{N}{2} + \frac{R}{2a}\right) \ln \frac{N}{2} \left(1 + \frac{R}{Na}\right) + \left(\frac{N}{2} - \frac{R}{2a}\right) \ln \frac{N}{2} \left(1 - \frac{R}{Na}\right)$$

$$= \left(\frac{N}{2} + \frac{R}{2a}\right) \ln \frac{N}{2} + \left(\frac{N}{2} - \frac{R}{2a}\right) \ln \frac{N}{2}$$

$$+ \left(\frac{N}{2} + \frac{R}{2a}\right) \left(\frac{R}{Na} - \frac{1}{2} \left(\frac{R}{Na}\right)^2\right) + \left(\frac{N}{2} - \frac{R}{2a}\right) \left(-\frac{R}{Na} - \frac{1}{2} \left(\frac{R}{Na}\right)^2\right)$$

$$= N \ln(N/2) - \frac{R^2}{4Na^2} \times 2 + \frac{R^2}{2Na^2} \times 2$$

$$= N \ln(N/2) + \frac{R^2}{2Na^2}$$

$$\begin{aligned} &\therefore \frac{1}{2} \ln 2\pi \frac{N}{2} + \frac{1}{2} \left(\frac{R}{Na} - \frac{1}{2} \left(\frac{R}{Na}\right)^2\right) + \frac{1}{2} \ln 2\pi \frac{N}{2} - \frac{1}{2} \left(\frac{R}{Na} + \frac{1}{2} \left(\frac{R}{Na}\right)^2\right) \\ &= \ln \pi N - \left(\frac{R}{Na}\right)^3 \end{aligned}$$

$$\therefore \ln P(R; N) = \cancel{N \ln N} + \ln \sqrt{2\pi N} - \left(\cancel{N \ln N} - \cancel{N \ln 2} + \frac{R^2}{2Na^2} \right) - \left(\ln \pi N - \left(\frac{R}{Na}\right)^3 \right)$$

$$= \ln \frac{\sqrt{2\pi N}}{\pi N} - \frac{R^2}{2Na^2} - \cancel{N \ln 2} \quad \text{small}$$

$$= \ln \frac{2}{\sqrt{2\pi N}} - \frac{R^2}{2Na^2} = \ln 2 - \frac{1}{2} \ln 2\pi N - \frac{R^2}{2Na^2}$$

(b) One dimensional random walk.

$$P(R; N) = \frac{1}{\sqrt{2\pi Na^2}} e^{-\frac{R^2}{2Na^2}}$$

$$\langle R \rangle = \int_{-\infty}^{\infty} dR R \underbrace{\frac{1}{\sqrt{2\pi Na^2}} e^{-\frac{R^2}{2Na^2}}}_{\text{even}} = 0$$

odd

$$\langle R^2 \rangle = \langle R^2 \rangle - \underbrace{\langle R \rangle^2}_0 = \int_{-\infty}^{\infty} dR R^2 \frac{1}{\sqrt{2\pi Na^2}} e^{-\frac{R^2}{2Na^2}}$$

$$= \frac{1}{\sqrt{2\pi Na^2}} \frac{2}{2(-\alpha)} \int_{-\infty}^{\infty} dR e^{-\alpha R^2}$$

$$= \frac{1}{\sqrt{2\pi Na^2}} \frac{1}{2\alpha} \sqrt{\frac{\pi}{\alpha}} \quad \alpha = \frac{1}{2Na^2}$$

$$\therefore \langle R^2 \rangle = Na^2$$

8.2.

$$\sqrt{\langle R_G^2 \rangle} = \sqrt{\frac{L l_p}{3}}$$

$$\begin{aligned} \text{pf)} \quad \langle R_G^2 \rangle &= \frac{1}{N} \sum_{i=1}^N (R_i - R_{cm})^2 = \frac{1}{N} \sum_{i=1}^N \left(R_i - \frac{1}{N} \sum_j R_j \right)^2 \\ &= \frac{1}{N} \left(\sum_i R_i^2 - 2 \left(\frac{1}{N} \sum_i R_i \right) \left(\frac{1}{N} \sum_j R_j \right) + \left(\frac{1}{N} \sum_i R_i \right) \left(\frac{1}{N} \sum_j R_j \right) \right) \\ &= \frac{1}{N} \left(\sum_i R_i^2 - \frac{1}{N} \sum_i R_i \sum_j R_j \right) \\ &= \frac{1}{2N^2} \left(\sum_i \sum_j R_i^2 - 2 \sum_i R_i \sum_j R_j + \sum_j \sum_j R_j^2 \right) \\ &= \frac{1}{2N^2} \left\langle \sum_i \sum_j (R_i - R_j)^2 \right\rangle = \frac{1}{2N^2} \sum_{i,j} (i-j) a^2 = \frac{1}{2N^2} 2 \sum_{i=1}^N \sum_{j=i+1}^N (j-i) a^2 \\ &= \frac{1}{6} Na^2 = \frac{1}{6} \langle R^2 \rangle \end{aligned}$$

for semiflexible chain

$$\begin{aligned}\langle R^2 \rangle &= \int_0^L ds \int_0^L du e^{-|s-u|/l_p} \\ &= 2Ll_p \left[1 + \frac{l_p}{L} (e^{-L/l_p} - 1) \right]\end{aligned}$$

when $L \gg l_p$

$$\langle R^2 \rangle = 2Ll_p$$

$$\therefore \langle R_G^2 \rangle = \frac{1}{6} (2Ll_p) = \frac{1}{3} Ll_p$$

$$\therefore \sqrt{\langle R_G^2 \rangle} = \sqrt{\frac{Ll_p}{3}}$$