# Homework #3 Solutions.

1. Jackson 3.6

| | Residues | $l$ (Å) | $l_{eff}$ (Å) | z | C |
|---|---|---|---|---|---|
| poly-L-alanine | 100 | 3.8 | 36 | 0.95 | |
| DNA | 1000 | 3.5 | 300 | | |

Rms end-to-end distances.

$$\sqrt{R_N^2} = l_{eff} N^{1/2}$$

Now for poly-L-alanine $\frac{l_{eff}}{l} = 9.5$ residues per $l_{eff}$

$$\sqrt{R_N^2} = \sqrt{\frac{100}{9.5}}\, 36\,\text{Å} = 117\,\text{Å}.$$

For DNA $\frac{l_{eff}}{l} = \frac{300}{3.5} = 86$ residues per $l_{eff}$

$$\sqrt{R_N^2} = \sqrt{\frac{10^3}{86}}\, 300\,\text{Å} = 1023\,\text{Å}.$$

If we try the other lengths:

poly-L at $10^3$ residues $\sqrt{\frac{10^3}{9.5}}\, 36\,\text{Å} = 369\,\text{Å}$

DNA at $10^2$ residues $\sqrt{\frac{10^2}{86}}\, 300\,\text{Å} = 323\,\text{Å}$.

2. Jackson 3.9

Modulin $T_m = 350\,K$ and $\Delta H^\circ = 50$ kcal/mole.
Chemically modified so that the 5 valine residues go from $\underline{3}$ rotational states to $\underline{\underline{1}}$.

Rotational entropy before modification

$$S_{before} = k_B \log 3^5 = 5 k_B \log 3$$

$$S_{after} = k_B \log 1^5 = 0$$

Change in entropy : $-5R\log 3$ per mole.
Change in enthalpy : $0$

$$\Delta G = G_{unfolded} - G_{folded} = \Delta H^\circ - T_m \Delta S^\circ$$

$$\Rightarrow \quad \Delta H^\circ = H^\circ_{unfolded} - H^\circ_{folded} ; \quad \Delta S^\circ = S^\circ_{unfolded} - S^\circ_{folded}$$

with modification

$$\Delta G^* = \Delta H^\circ - T_m^* \Delta S^{\circ *}$$

$$\Delta S^{\circ *} = S^\circ_{unfolded} - \left(S^\circ_{folded} - 5R\log 3\right) = \Delta S^\circ + 5R\log 3.$$

$$\cancel{T_m^* = \frac{\Delta H^\circ}{\Delta S^{\circ *}} = \frac{\Delta H^\circ}{\Delta S^\circ + 5R\log 3}}$$

$$\Delta G^* = \Delta H^\circ - T_m^* (\Delta S^\circ + 5R\log 3) = 0$$

and $\Delta S^\circ = T_m^{-1} \Delta H^\circ$

$$\Delta G^* = \Delta H^\circ - T_m^* \left[\frac{\Delta H^\circ}{T_m} + 5R\log 3\right] = 0$$

$$\Delta H^\circ \left(1 - \frac{T_m^*}{T_m}\right) = + T_m^* \, 5R\log 3$$

$$\Delta H^\circ = T_m^* \left(5R\log 3 + \frac{\Delta H^\circ}{T_m}\right); \quad T_m^* = \frac{\Delta H^\circ}{\frac{\Delta H^\circ}{T_m} + 5R\log 3}$$

Now, we can put in numbers...

(3) $R = 1.99 \times 10^{-3} \frac{\text{kcal}}{\text{mole K}}$ so

$$\frac{\Delta H^\circ}{R T_m} = \frac{50}{350 \cdot 1.99 \times 10^{-3}} = 72$$

so $$\frac{T_m^*}{T_m} = \frac{72}{72 + 5 \log 3} = 0.93 \text{ or } T_m^* = 326\,K.$$

3. Jackson 4.1

Derive $$[P_i] = \frac{[L]^i [P_0]}{K_1 K_2 \cdots K_i}$$

from $$\frac{[P_i]}{[L][P_{i-1}]} = \frac{1}{K_i}$$

for $i=1 \Rightarrow [P_1] = \frac{1}{K_1}[L][P_0]$

Assume $[P_{i-1}] = \frac{[L]^{i-1} [P_0]}{K_1 K_2 \cdots K_{i-1}}$ and show this holds for $i$.

$$[P_i] = \frac{[L][P_{i-1}]}{K_i} = \frac{[L]^i [P_0]}{K_1 \cdots K_{i-1} K_i}$$ ✓

4. Jackson 4.4

$$\Delta G_t^\circ = -RT \log\left(1 \mathring{A}^3/\lambda^3\right) + RT \log ($$

$R \cong 2\times10^{-3}$ Kcal/mole·K $\Rightarrow$ $\dfrac{\Delta H^\circ}{RT_m} \cong 72$

$$\Rightarrow \quad \frac{T_m^*}{T_m} = \frac{72}{72+5\log 3} = 0.93 \Rightarrow T_m^* = 326K$$

3. Jackson 4.1

Derive $[P_i] = [L]^i [P_0] / \prod_{j=1}^{i} K_j$

from $\dfrac{[P_i]}{[L][P_{i-1}]} = 1/K_i$

By induction: for $i=1$ $[P_1] = \dfrac{[L][P_0]}{K_1}$

Assume $[P_{i-1}] = \dfrac{[L]^{i-1}[P_0]}{K_1 K_2 \cdots K_{i-1}}$

Then $[P_i] = \dfrac{[L]^i [P_0]}{(K_1 K_2 \cdots K_{i-1}) K_i}$ ✓

4. Jackson 4.4.

Translational partition function $Z = \frac{1}{N!}(V/\lambda^3)^N$ for $N$ noninteracting particles.

$$\Rightarrow \quad G = -k_B T \log\left(\frac{1}{N!}(V/\lambda^3)^N\right) = k_B T (N\log N - N) +$$

$$- k_B T N \log(V/\lambda^3) = + N k_B T \left(\log[(N/V)\lambda^3] - 1\right)$$

$$G = N k_B T \log\left(\frac{c\lambda^3}{e}\right)$$ for one mole $N \to N_A$ of particles.

$$\Rightarrow \quad G^\circ = RT\log\left(c\,\lambda^3/e\right)$$

~~$\Delta G^\circ_t = RT\log($ 1 Å$^3$~~

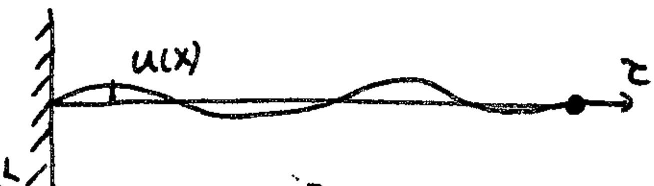
$$\Delta G_t^\circ = RT \log\left(\frac{1}{(1\text{Å})^3}\frac{\lambda^3}{e}\right) - RT\log\left(\frac{N_A}{1L}\frac{\lambda^3}{e}\right)$$

$$\Delta G_t^\circ = \underset{298K}{RT} \log\left(\frac{(10\,cm)^3}{N_A\,(1\text{Å})^3}\right) \Rightarrow \frac{(10^{-1}m)^3}{6\times10^{23}\,(10^{-10}m)^3}$$

$$= \frac{1}{6}\,10^4$$

$$\Delta G_t^\circ = 4.4\ kcal$$

5.




$$H = \int_0^L dx\left\{\frac{1}{2}K(\partial_x^2 u)^2 + \frac{1}{2}\tau(\partial_x u)^2\right\}$$

Fourier Transform: to diagonalize the Hamiltonian

a) Length of the filament:

$$L_0 = \int_0^{L} dx\,\underset{\uparrow\ \text{small undulation}}{\sqrt{1+(\partial_x u)^2}} \cong L + \int_0^{L} \frac{1}{2}(\partial_x u)^2\,dx$$

$$\Rightarrow \quad L_0 - L = \frac{1}{2}\int_0^{L_0} (\partial_x u)^2\,dx$$

b) $u(x) = \sum_q u_q \sin(qx) \qquad q = \frac{n\pi}{L} \quad n = 1, 2, \ldots$

$$H = \frac{L}{2}\sum_{n=1}^{\infty} u_n^2\left[\frac{1}{2}K q_n^4 + \frac{1}{2}\tau q_n^2\right]$$

Use equipartition thm

$$\langle u_n^2 \rangle = \frac{2}{L} \frac{k_B T}{K q_n^4 + \tau q_n^2}$$

$$\Rightarrow \quad \langle L \rangle = L_0 - \frac{1}{2} \times \underset{\uparrow}{2} \sum_n \frac{k_B T}{K q_n^4 + \tau q_n^2} \, q_n^2$$

two polarization states.

$$\Rightarrow \quad \langle L \rangle = L_0 - \sum_{n=1}^{\infty} \frac{k_B T}{K q_n^2 + \tau} = L_0 - \frac{k_B T L^2}{\pi^2 K} \sum_{n=1}^{\infty} \frac{1}{n^2 + \tau/\tau_0}$$

where $\tau_0 = \frac{K \pi^2}{L^2}$

Now Taylor expand for small $\tau/\tau_0$:

$$\langle L \rangle = L_0 - \frac{k_B T L^2}{\pi^2 K} \sum_{n=1}^{\infty} \frac{1}{n^2} + \frac{k_B T L^2}{\pi^2 K} \frac{\tau}{\tau_0} \sum_{n=1}^{\infty} \frac{1}{n^4} + \cdots$$

$$\sum_{n=1}^{\infty} \frac{1}{n^2} = \pi^2/6 \qquad \sum_{n=1}^{\infty} \frac{1}{n^4} = \pi^4/90$$

$$\Rightarrow \quad \langle L \rangle = L_0 - \frac{k_B T L^2}{6K} + \frac{k_B T L^4}{K^2 \, 90} \tau + \cdots$$

d) $\Rightarrow \quad \delta L = \frac{k_B T L^4}{K^2 90} \tau \Rightarrow$

$$\boxed{K_{eff} = \frac{90 K^2}{k_B T \, L^4}}$$

6.

Correlation function

$$\langle s_j \, s_{j+n} \rangle = \frac{1}{Z} \prod_{i=1}^{N} \sum_{s_i = \pm 1} e^{-\beta H[\{s_i\}]} \, s_j \, s_{j+n}$$

Look at the numerator:

$$Z \langle s_j \, s_{j+n} \rangle = \prod_{i=1}^{N} \sum_{s_i=\pm 1} \langle s_1 | T | s_2 \rangle \cdot \cdots \cdot \langle s_{j-1} | T | s_j \rangle \, s_j$$

$$\langle s_j | T | s_{j+1} \rangle \cdot \ \cdots \ \cdot \langle s_{j+n-1} | T | s_{j+n} \rangle \, s_{j+n} \, \langle s_{j+n} | T | s_{j+n+1} \rangle \cdot$$

$$\cdot \ \cdots \ \langle s_N | T | s_1 \rangle$$

Looking at the four terms corresponding to $s_j = \pm$

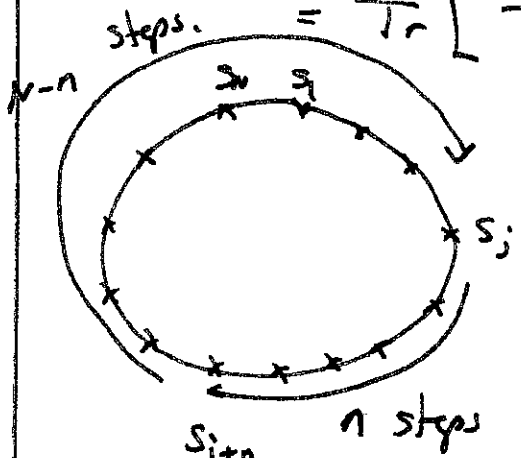
$s_{j+n} = \pm$

we find (as shown in class)

$$Z \langle s_j \, s_{j+n} \rangle = \mathrm{Tr}\left[ T^{j-1} \sigma_z \, T^{n} \sigma_z \, T^{N-(j+n)+1} \right]$$

Pauli Spin matrix $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$$= \mathrm{Tr}\left[ T^{N-n} \sigma_z \, T^{n} \sigma_z \right]$$



Now we diagonalize $T$ (w/ $h=0$) as in class and plug in:

$$Z < s_j s_{j+n} > = \mathrm{Tr}\left[ A \begin{pmatrix} \lambda_1^{N-n} & 0 \\ 0 & \lambda_2^{N-n} \end{pmatrix} A \begin{pmatrix} \lambda_1^{n} & 0 \\ 0 & \lambda_2^{n} \end{pmatrix} \right]$$

where $A = \begin{pmatrix} \Delta & \Delta+\xi \\ -\Delta+\xi & -\Delta \end{pmatrix} \frac{1}{\xi} = \begin{pmatrix} 0 & 1 \\ +1 & 0 \end{pmatrix}$

and $\Delta = 0$ and $\xi = 2e^{-\beta J}$
for $h=0$.

Completing the algebra, you get (see class notes for more details)

$$C(n) = < S_j S_{j+n} > = \left( \frac{e^{\beta J} - e^{-\beta J}}{e^{\beta J} + e^{-\beta J}} \right)^n = \tanh^n(\beta J)$$

exponential decay of correlations.

$$C(n) = \exp\left[ n \log\left( \tanh \beta J \right) \right]$$

$<1$ so $\log(\ ) < 0$

c)

or we have a correlation length of

$$n^* = \frac{1}{\left| \log[\tanh(\beta J)] \right|} \text{ sites.} \qquad e^{-n/n^*} = C(n)$$


Cooperativity parameter.