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 $\dfrac{l_{eff}}{l} = 9.5$ residues per l_{eff}

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

for DNA $\dfrac{l_{eff}}{l} = \dfrac{300}{3.5} = 86$ 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 $\sqrt{\dfrac{10^3}{9.5}} \, 36 \text{Å} = 369 \text{Å}$

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

2. Jackson 3.9

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

②

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

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

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

with modification

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

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

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

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

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...

② $R = 1.99 \times 10^{-3} \dfrac{kcal}{mole\ K}$ so

$$\frac{\Delta H^0}{R T_m} = \frac{50}{350 \cdot 1.99 \times 10^{-3}} = 72$$

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

3. Jackson 4.1

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

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

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

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

i.

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

4. Jackson 4.4

$\Delta G_t^0 = -RT \log \left(1 \mathring{A}^3 / \lambda^3 \right) + RT \log \big($

$$R \cong 2\times10^{-3}\, kcal/mole\cdot K \implies \frac{\Delta H^{\circ}}{RT_m} \cong 72$$

$$\implies \frac{T_m^{*}}{T_m} = \frac{72}{72+r\log 3} = 0.93 \implies T_m^{*} = 326 K$$

3. Jackson 4.1

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

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

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 $Z = \frac{1}{N!}\left(V/\lambda^3\right)^{N}$ for N non interacting particles.

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

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

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

$$\implies G^{\circ} = RT \log\left(c\,\lambda^3/e\right)$$

~~$\Delta G^{\circ} = RT \log\left(\frac{A^3}{e}\right)$~~

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

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

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

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

5.

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

Fourier Transform: to diagonalize the Hamiltonian

a) length of the filament:

$$L_\bullet = \int_0^{L_\bullet} dx \sqrt{1+(\partial_x u)^2} \;\cong\; L_\bullet + \int_0^{L_\bullet} \frac{1}{2}(\partial_x u)^2\,dx$$

$$\uparrow \text{ small undulation}$$

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

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

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

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

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

6.

Correlation functions

$$\langle s_j\, s_{j+n}\rangle = \frac{1}{Z}\prod_{i=1}^{N}\sum_{s_i=\pm1} e^{-\beta H[\{s_i\}]}\, s_j\, s_{j+n}$$

Look at the numerator:

$$Z\langle s_j\, s_{j+n}\rangle = \prod_{i=1}^{N}\sum_{s_i=\pm1}\langle s_i|T|s_2\rangle \cdot \cdots \cdot \langle s_{j-1}|T|s_j\rangle\, s_j$$

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

$$\cdot \cdots \langle s_N|T|s_1\rangle$$
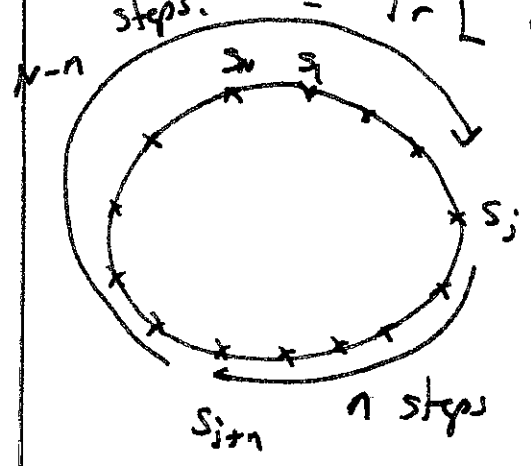
Looking at the four terms corresponding to $s_j = \pm$
$$s_{j+n} = \pm$$

we find (as shown in class)

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

$$\uparrow$$
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:

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

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)

$$C(n) = \langle s_j s_{j+n} \rangle = \left(\frac{e^{\beta J}-e^{-\beta J}}{e^{\beta J}+e^{-\beta J}} \right)^n = \tanh^n(\beta J)$$

exponential decay of correlation.

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

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

c)

or we have a correlation length of

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

$J/k_B T$

Cooperativity parameter.