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Final Examination **18 March, 2020**

Part A. Short Calculations (40 points total):

0.170

Problem A.1) Assume a protein is composed of N=50 monomeric units.. A dichroism measurement indicates that for a solution of this polypeptide f_H=170. Assuming s=.80 and σ=0.01, calculate the values of f_H according to the: (a) non-cooperative, (b) fully-cooperative, (c) zipper, and (d) Bragg-Zimm models. Which model best describes the helix-coil transition in this polypeptide solution? If you use an approximation for f_H, justify its use. Assume q_0=1.

a) noncooperative

$$f_H = \frac{s}{1+s} = \frac{0.80}{1.80} = \boxed{0.444}$$

b) cooperative

$$f_H = \frac{s^N}{1+s^N} = \frac{0.80^{50}}{0.80^{50}+1} = \boxed{1.43 \cdot 10^{-5}}$$

c) zipper ~~+~~ $N \gg 1$, $s<1$, $\sigma<1$

$$f_H = \sigma s \frac{(N+2)s - N}{N(s-1)^3} = 0.01 \cdot 0.80 \cdot \frac{(52 \cdot 0.80) - 50}{50(0.8-1)^3} = \boxed{0.168}$$

Zipper Model is closest

d) Bragg-Zimm

$$\lambda_+ = \frac{s+1 + \sqrt{(s-1)^2 + 4\sigma s}}{2} = \frac{0.8 + 1 + \sqrt{(0.8-1)^2 + 4(0.01)(0.8)}}{2}$$

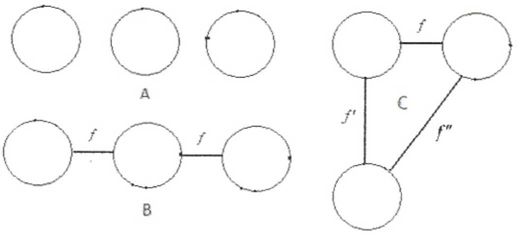
$$\lambda_+ = 1.03$$

$$\frac{d\lambda_+}{ds} = \frac{1}{2}\left(1 + \frac{s-1+2\sigma}{\sqrt{(s-1)^2+4\sigma s}}\right)$$

$$= \frac{1}{2}\left(1 + \frac{0.8-1+0.02}{\sqrt{(0.8-1)^2+4\sigma s}}\right) = 0.165$$

$$f_H = \frac{s}{\lambda_+}\frac{d\lambda_+}{ds} = \frac{0.80}{\cancel{0.165}\ 1.03} \cdot 0.165 = \boxed{0.128}$$

Problem A.2) Assume ligand L binds cooperatively to three binding sites $f > f' > f''$. At [L]=0.001 and k=10^3, optical measurements indicate the fraction of sites bound is $f_B = 0.80$. For each model schematized below calculate the fraction of sites bound, and state which model best fits the observed data. Assume: $f = 3.00$, $f' = 2.50$, and $f'' = 2.00$.

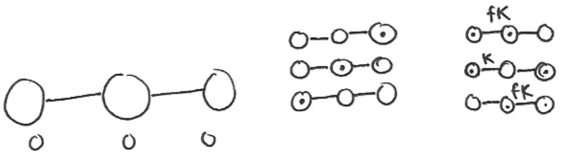


Model A: Unconnected

$$f_B = \frac{K[L]}{1+K[L]} = \frac{10^3(10^{-3})}{1+(1)} = \frac{1}{2} = \boxed{0.5 = f_B}$$

$$\frac{q_B}{[P]} = 1 + 2K[L] + (K[L])^2 + \cancel{K[L]}$$

Model B. Linear



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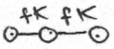


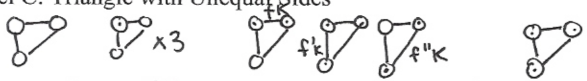
$\rightarrow K[L] = 1$

$$\frac{q_b}{[P]} = 1 + 3K[L] + 2f(K[L])^2 + 1(K[L])^2 + 1f^2(K[L])^3 =$$

$$f_B = \frac{[L]}{Nq_B}\frac{\partial q_B}{\partial L} = \frac{0 + 3K[L] + 4f(K[L])^2 + 2(K[L])^2 + 3f^2(\cancel{\ }K[L])^3}{1 + 3K[L] + (2f+1)(K[L])^2 + \cancel{8f}\, f^2(K[L])^3}$$

$$f_B = \frac{(10^{-3})}{3} \cdot \frac{3 + 4(\overset{3}{\cancel{\ \ }})(1)^2 + 2(1)^2 + 3(3)^2(1)^2}{1 + 3 + 7(3)(1)^2 + 9(1)^3} = \frac{(10^{-3})(44)}{3 \cdot 34} = \boxed{4.31 \cdot 10^{-4}} = f_B$$

Model C: Triangle with Unequal Sides



$$\frac{q_B}{[P]} = 1 + 3K[L] + (f' + f'' + f)(K[L])^2 + ff'f''(K[L])^3$$

$$f_B = \frac{[L]}{Nq_B} \cdot \frac{\partial q_B}{\partial [L]} = \frac{0 + 3K[L] + 2(f' + f'' + f)(K[L])^2 + 3ff'f''(K[L])^3}{3 \cdot (3 + (3+2.5+2) + (3 \cdot 2.5 \cdot 2))} = \frac{3 + 2(3+2.5+2) + 3(3 \cdot 2.5 \cdot 2)}{76.5} = \frac{63}{76.5}$$

$\boxed{f_B = 0.82}$

This model is closest

Problem A.3). The binding of hydrogen atoms to metal surfaces has been studied extensively as a model system for catalytic converters. Assume H atoms adsorb onto a metal surface from the gas phase: $H(g) \rightleftharpoons H(bound)$ Calculate the equilibrium constant for hydrogen atoms adsorbed onto a metal surface from the gas phase at T=300K and P=1.00 bars.. Assume at P=1.00 bars gaseous hydrogen atoms behave ideally. Assume for gaseous and adsorbed hydrogen atoms g_1=2, and the binding energy for monatomic hydrogen to a metal surface is w=-50.0kJ/mol.

→ find K

→ $PV = nRT$

monoatomic: $q = q_{trans} q_{elec}$

$\swarrow \frac{V}{\Lambda^3}$ $\quad \downarrow g_i e^{-\varepsilon/RT}$

$$K = \frac{N\Lambda^3}{V} \cdot e^{-w/RT} = \frac{6.02 \cdot 10^{23}/\text{mol}\ (1.01 \cdot 10^{-10}\,\text{m})^3}{0.0249\ \text{m}^3/\text{mol}} \cdot e^{\frac{+50\,000\ \text{J/mol}}{8.314\ \text{J/molK} \cdot 300\text{K}}}$$

(eq. sheet)

$= 2.49 \cdot 10^{-5} \cdot 5.08 \cdot 10^{8}$

$\boxed{K = 1.26 \cdot 10^{4}}$

$$\Lambda = \frac{h}{\sqrt{2\pi \frac{1\text{g}}{\text{mol}} \cdot \frac{1\text{kg}}{1000\text{g}} \cdot \frac{1\text{mol}}{N_A} \cdot 1.38 \cdot 10^{-23} \cdot 300\text{K}}} = \frac{6.62 \cdot 10^{-34}}{\sqrt{4.32 \cdot 10^{-47}}}\ \text{m} = 1.01 \cdot 10^{-10}\ \text{m}$$

$$V = \frac{nRT}{P} = \left(1.00\ \text{bar} \cdot \frac{10^5\,\text{Pa}}{1\ \text{bar}}\right)^{-1} \left(8.314 \frac{\text{J}}{\text{Kmol}}\right)(300\text{K}) = 0.0249\ \text{m}^3/\text{mol}$$

$C_{v,vib}$ ↑ θ_{vib}

Problem A.4) The bond vibration frequency for I_2 is 6.42×10^{12} s^{-1} . Calculate vibrational temperature and the contribution of vibrational motions to the molar internal energy and the molar heat capacity. How close are the internal energy and heat capacity to the values predicted by the equipartition principle? Assume T=1000K.

→ U_{vib}

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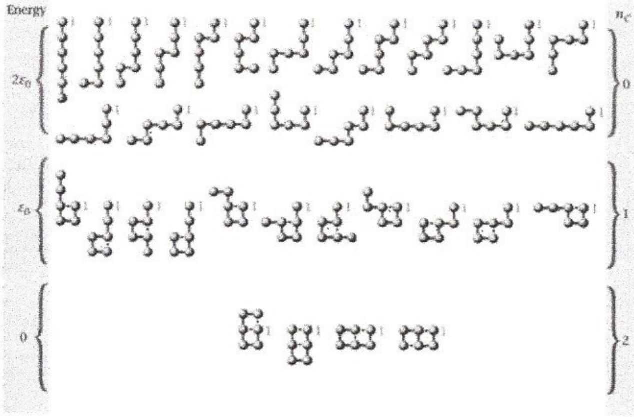
$$\nu = 6.42 \cdot 10^{12} s^{-1} \rightarrow \theta_{vib} = \frac{h\nu}{K_B} = \frac{(6.62 \cdot 10^{-34} Js)(6.42 \cdot 10^{12} s^{-1})}{(1.38 \cdot 10^{-23} J/K)} = \boxed{308K = \theta_{vib}}$$

$$q = \frac{e^{-\theta/2T}}{1-e^{-\theta/T}} \ \& \ \frac{U}{N} = \frac{K_B T^2}{q} \frac{\partial q}{\partial T} \rightarrow U_{vib} = Nh\nu\left(\frac{1}{2} + \frac{e^{-\theta/T}}{1-e^{-\theta/T}}\right) = R\theta_{vib}\left(\frac{1}{2} + 2.77\right) = \boxed{8380 \frac{J}{Mol} = U_{vib}}$$

$$C_{v,vib} = R\left(\frac{\theta}{T}\right)^2 \frac{e^{-\theta/T}}{(1-e^{-\theta/T})^2} = 8.314 \frac{J}{MolK} (0.308)^2 \frac{e^{-0.308}}{(1-e^{-0.308})^2} = \boxed{8.25 J/MolK = C_{v,vib}}$$

$$\boxed{\begin{aligned}\text{Equiparition: } U_{vib} &= RT = 8314 J/Mol \\ C_{v,vib} &= R = 8.31 J/KMol\end{aligned}}$$

calculated values are close to predicted values



Part B: Polymer Chain Statistics (30 points)

We model a polymer as a string of beads held together by "bonds". Structured polymers are chains of beads that wrap back on themselves causing non-bonded beads to be adjacent or "in-contact". The more 'contacts" that are formed the more the polymer is structured and the lower is the polymer's energy. Consider the structures of polymers composed of six beads. See Figure to the right. Highly structured polymers have two contacts (n_C=2) and have energy ε=0. Polymers with single contacts (n_C=1) have energy $\varepsilon = \varepsilon_0$. Unstructured polymers have no contacts (n_C=0) and their energy is $\varepsilon = 2\varepsilon_0$.

a) The figure above shows all the microstates for six-bead polymers with 0, 1, and 2 contacts. Write out the form of the partition function for this polymer system and evaluate the partition function for ε_0=5.00 x10^{-21} J and T=300K.

$$q = 4 \times 1 + 11e^{-\varepsilon_0/K_BT} + 21e^{-2\varepsilon_0/K_BT} = 4 + 11e^{-1.21} + 21e^{-2(1.21)} = [illegible]$$

7?

$$\boxed{9.16 = q}$$

$$-\varepsilon_0/K_BT = \frac{-5 \cdot 10^{-21} J}{1.38 \cdot 10^{-23} J/K \cdot 300K} = -1.21$$

$\varepsilon=2\varepsilon_0,\ \varepsilon=\varepsilon_0,$ or $\varepsilon=0$

b) Calculate the probabilities that a polymer has ε~~Vx~~=2ε0, ε ~~Vx~~=ε0~~1~~, or ε ~~nc~~=0. Assume the same conditions as in part a. Note: In your calculation you have to include the number of microstates in each energy. Based on your calculation, what is the most probable or stable state of the system? Why

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$$P_0=\frac{4}{9.16}=\boxed{0.437=P_{0=\varepsilon}}$$

$$P_{\varepsilon_0}=\frac{11e^{-\varepsilon_0/K_BT}}{9.16}=\frac{11e^{-1.21}}{9.16}=\boxed{0.358=P_{\varepsilon=\varepsilon_0}}$$

$$P_{\varepsilon=2\varepsilon_0}=1-0.437-0.358=\boxed{0.206=P_{\varepsilon=2\varepsilon_0}}$$

most probable State is when $\varepsilon=0$ b/c $P_{\varepsilon=0}$ is greater than the probabilities of other two states

c) Using your results from parts a and b, calculate the average number of contacts $\langle n_C\rangle$, the molar internal energy and the molar entropy. Assume the polymers are distinguishable particles.

$$\frac{U}{N}=\sum p\varepsilon=\langle\varepsilon\rangle=(0.358)(\varepsilon_0)+(0.206)(2\varepsilon_0)=\overset{5E-21J}{\cancel{\varepsilon_0}}(0.358+2(0.206))=3.85\cdot10^{-21}J$$

if $\varepsilon_0=5\cdot10^{-21}J=1$ contact & $\varepsilon=0=$ 2 contacts

the # contacts $=\left(2E20\frac{\text{contact}}{J}\right)(\varepsilon)^{+2}\rightarrow$ $\boxed{\langle n_c\rangle=1.23}$

$$U=N(3.85\cdot10^{-21}J)=\cancel{2.32(KJ/Mol)}\ \boxed{2.32\frac{KJ}{Mol}=U}$$

$$S=\frac{U}{T}+NK_B\ln q=\frac{2320\,J/Mol}{300K}+\left(8.314\frac{J}{MolK}\right)\ln 9.16=\boxed{26.1\,J/KMol=S}$$

d) Suppose the temperature is lowered to T=50K such that the probability p0 of being in the ground state (i.e. the state where nc=2) is $p_0=1$. Calculate $\langle n_C\rangle$, the molar internal energy and the molar entropy at T=50K. Calculate also Δnc, ΔU and ΔS for going from T=300K to T=50K.

$P_0=1\ \therefore\ P_{\varepsilon_0}=0$ & $P_{\varepsilon_0\cdot2}=0$ $\boxed{\langle n_c\rangle=2}$ $\cancel{\frac{U}{N}}$ $U=N(1\cdot0)=\boxed{0\frac{J}{Mol}=U}$

$$S=\overset{0}{\cancel{\frac{U}{T}}}+R\ln q=\boxed{18.4J/Mol\cdot K}$$

$$\Delta n_c=2-1.23=\boxed{0.77=\Delta\langle n_c\rangle}$$

$$\Delta U=0J/Mol-2.32\frac{KJ}{Mol}=\boxed{-2.32\frac{KJ}{Mol}=\Delta U}$$

$$\Delta S=(18.4-26.1)\,J/KMol=\boxed{-7.7J/Kmol}$$

Part C. Structural Study of a Hydrated Protein (30points) DNA ligase is an enzyme that catalyzes the formation of phosphodiester bonds in double-stranded DNA. DNA ligase has a molecular weight of $M_2=74.0kg\bullet mol^{-1}$ and a gram specific volume of $\overline{V}_2=0.703mL\bullet g^{-1}$. A sedimentation experiment was performed on DNA ligase at T=293K, in a buffered solution with density $\rho_1 = 1.01 g \bullet mL^{-1}$, rotating at ν=56050 rpm. After t=8000s the sedimentation front advanced from $r(t_0) = 5.93cm$ to $r(t) = 6.55cm$.

$$\omega = 2\pi\nu = 2\pi\left(\frac{56050}{min}\cdot\frac{1min}{60s}\right)$$
$$= 5870 s^{-1}$$

a) Calculate the sedimentation constant s and give your answer in Svedbergs (S)

~~Equation to use is $\ln\left(\frac{r(t)}{r(t_0)}\right) = s\omega^2(t-t_0)$~~

$$\ln\left(\frac{r(t)}{r(t_0)}\right) = s\omega^2(t-t_0) \therefore \frac{\ln\left(\frac{r(t)}{r(t_0)}\right)}{\omega^2(t-t_0)} = s$$

$$s = \frac{\ln\left(\frac{6.55cm}{5.93cm}\right)}{(5870s^{-1})^2(8000s)} = 3.61\cdot10^{-13}s \cdot \frac{1S}{10^{-13}s} = \boxed{3.61 \text{ Svedbergs} = s}$$

b) Assuming DNA ligase is a globular in solution, calculate the radius of the protein. Assume the solution viscosity $\eta = 0.001 Pa \cdot s$

$$\frac{74.0kg}{mol}\cdot\frac{1mol}{N_A} = 1.23\cdot10^{-22}kg$$

$$s = \frac{m}{f}(1-\bar{V}_2\rho_1) \therefore f = \frac{m}{s}(1-\bar{V}_2\rho_1) = 6\pi\eta R \therefore \frac{m(1-\bar{V}_2\rho_1)}{6s\pi\eta} = R$$

$$\left(1-0.703\frac{mL}{g}\cdot1.01\frac{g}{mL}\right) = 0.28997$$

$$R = \frac{(1.23\cdot10^{-22}kg)(0.28997)}{6(3.61\cdot10^{-13}s)(\pi)(0.001 Pa\cdot s)} = \frac{3.56\cdot10^{-23}}{6.81\cdot10^{-15}} m = \boxed{5.24\cdot10^{-9}m = R}$$

c) Calculate the diffusion coefficient of DNA ligase at T=293K.

$$D = \frac{K_BT}{f} = \frac{(1.38\cdot10^{-23} J/K)(293K)}{9.88\cdot10^{-11}kg/s} = \boxed{4.09\cdot10^{-11} m^2/s = D}$$

$$f = \frac{m}{s}(1-\bar{V}_2\rho_1) = \frac{1.23\cdot10^{-22}kg\cdot0.28997}{3.61\cdot10^{-13}s} = 9.88\cdot10^{-11}kg/s$$

$$\frac{Js}{kg} = \frac{kg\,m^2}{s^2}\cdot s$$

d) Calculate the number of water molecules that hydrate a molecule of DNA ligase.

calculated from soln
$5.24\cdot10^{-9} m = R$

calc for protein only: $\frac{M}{N_A}\cdot\bar{V}_2 = 1.23\cdot10^{-22}kg\cdot\frac{1000g}{1kg}\cdot\frac{0.703mL}{g} = \underline{8.647\cdot10^{-20} cm^3}$

hydrated volume: $\frac{4}{3}\pi(5.24\cdot10^{-7}cm)^3 = 6.03\cdot10^{-19}cm^3$

$$\frac{\text{hydrated}}{\text{dehydrated}}\ \frac{6.02\cdot10^{-19}cm^3}{8.67\cdot10^{-20}cm^3} = \frac{\bar{V}_2 + \delta\bar{V}_1}{\bar{V}_2} \therefore \frac{6.97\left(0.703\frac{mL}{g}\right) - 0.703mL/g}{1.01\,g/mL} = \frac{4.15g\,H_2O}{g\,protein}$$

$\delta\bar{V}_1 \rightarrow$ additional vol.

$$\frac{4.15g\,H_2O}{g\,protein}\cdot\frac{1\,mol\,H_2O}{18g\,H_2O}\cdot\frac{74000g\,prot}{1\,mol\,prot} = \boxed{17082 \text{ molecules } H_2O/\text{molecule protein}}$$