Chemistry C3102-2006: Polymers Section

Practise problems & SOLUTIONS

Instructor's notes: I anticipate that I solve these problems differently than others. Reading over these questions, attempting/providing a solution is a valuable learning exercise. Note that your correct solution to the problem may be a little different (and much shorter) to the one I provide here.

- 1. An isolated chain which is otherwise ideal, adsorbs onto a flat substrate. Each of the N monomers of size a is restricted to the plane of the substrate, but is otherwise mobile within the plane of the substrate.
 - (a) What is the mean size of the chain? The average square end-to-end distance of a 2-D, as well as a 3-D freely jointed, ideal chain, is < R² >∼ Na².
 - (b) What is the change in entropy of the chain upon adsorption? Invoking a discrete or lattice model for the placement of monomers of the chain, where z is the coordination per dimension (so that z × d is the coordination of the lattice in d dimensions), then the number of conformations available to a chain of N monomers in d = 3 dimensions is (3 × z)^N and in d = 2 dimensions is (2 × z)^N. Then by Boltzmann's equation,

$$\Delta S = S_{2d} - S_{3d} = k_B \ln\left(\frac{(2 \times z)^N}{(3 \times z)^N}\right),$$

or $\Delta S = k_B N \times \ln (2/3)$. The argument of the logarithm is less than unity, $\Delta S < 0$, as you would expect: entropy is lost in confining the chain in a lower dimension of space.

Alternatively you can invoke a continuum model. Each monomer link can freely rotate about its other end in 2 or 3 dimensions. In 2-dimensions, the end can be located on a circumference of length $2\pi a$, centered about the other end. In 3dimensions, the one end can be located on a shell of area $4\pi a^2$ about the other end. Thus, linking monomers end-to-end, the number of possible placements of each consecutive link is proportional to $2\pi a$ in two dimensions and $4\pi a^2$ in three dimensions. Then, by Boltzmann's equation:

$$\Delta S = k_B \ln\left(\frac{(2\pi a)^N}{(4\pi a^2)^N}\right),$$

or $\Delta S \sim k_B N \times \ln(1/(2a))$, which again is negative as it should be.

2. What is the change of entropy associated with an ideal chain of N monomers transformed into a molecular ∞ or "crazy-8"?

I chose to solve this as a two-part "reaction: first, I consider gluing the ends of a linear chain, that is, monomers 1 and N together, such that $R_{1,N} = 0$, and let the entropy

change for this first reaction be $\Delta S_1(N)$. Then, as the second-part, I consider gluing together two arbitrary monomers, m and n, located on the ring. The entropy change for this reaction is $\Delta S_2(|m-n|)$, and the sum of these entropies yields the entropy of formation of a "crazy-8" with loop sizes of |m-n| and N-m+n:

$$\Delta S(\mid m-n \mid) = \Delta S_1 + \Delta S_2(\mid m-n \mid)$$

First Reaction: Formation of a ring from a linear chain of N **monomers:** This reaction was solved in the notes under the Example Problem: •• What is the change of entropy associated with an ideal chain of N monomers forming a ring?

The probability distribution of end-to-end vector ${\cal R}$ for a linear chain of N monomers in d dimensions is

$$p_N(R) = \left(\frac{d}{2\pi N a^2}\right)^{d/2} \exp\left(-\frac{dR^2}{2N a^2}\right)$$

Consequently, the probability of observing a ring, or where R = 0 is

$$p_N(R=0) = (\frac{d}{2\pi N a^2})^{d/2}.$$

Now the change in entropy is

$$\Delta S_1 = k_B \ln \left(\frac{\Gamma(R=0)}{\Gamma(-\infty < R < \infty)} \right),$$

where $\Gamma(R=0)$ is the number conformations with R=0, and $\Gamma(-\infty < R < \infty)$ is the number of conformations of any R. As $p_N(R)$ is a normalised probability distribution, this ratio of the number of conformations is $p_N(R=0)$. Therefore, the entropy change upon ring formation of a chain of N statistical monomers, each of size a, is

$$\Delta S_1 = k_B \ln p_N(R=0) = \frac{dk_B}{2} \ln \left(\frac{d}{2\pi N a^2}\right) \\ = \frac{dk_B}{2} [\ln (d) - \ln (2\pi N a^2)].$$

As N is large and d small, $\ln(d) \ll \ln(2\pi Na^2)$, and ΔS is negative, that is, entropy is lost in the process of ring formation.

Second Reaction: Formation of an intersection of a ring chain of N monomers: This reaction was solved in the notes under the Example Problem: ••• What is the distribution of monomer-monomer distances of an ideal chain of N monomers whose first and last monomers are joined to form a ring?

"First, consider a Gaussian ring chain where the monomers are labelled 1 to N. Let R_{mn} be the end-to-end distance between any two arbitrary monomers n and m within the Gaussian ring. Clearly $R_{1,N} \equiv R = 0$. Let $p_N(R_{mn}; R = 0)$ be the distribution of end-to end distances R_{mn} given that the freely jointed chain of N monomers is a ring. We can write an expression from this distribution in terms of the distribution of linear chains:

$$P_N(R_{m,n}; R = 0) = P_{n-m}(R_{mn})P_{N-n+m}(R_{mn})$$

where $P_{n-m}(R_{mn})$ is the distribution of distances for a linear chain of n-mmonomers and $P_{N-n+m}(R_{mn})$ is the distribution associated with a linear chain of N-n+m monomers. This equation results from the fact that the subcomponents of a Gaussian chain remain Gaussian, as long as they contain a large number of monomers.

You can then show, by replacing the RHS of the above equation with Gaussian distributions (remembering that a linear chain of n - m monomers has $\langle R^2 \rangle = (n - m)a^2$ and that a chain of N - n + m monomers has $\langle R^2 \rangle = (N - n + m)a^2$) that

$$P_N(R_{mn}; R=0) = \left(\frac{d}{2\pi\mu^2}\right)^{d/2} \exp\left(-\frac{dR_{mn}^2}{2\mu^2}\right),$$

where

$$\mu^{2} = |m - n| a^{2}(\frac{N - m + n}{N}).$$

That is, for the Gaussian ring, $\langle R_{mn}^2 \rangle = \mu^{2"}$.

Now, $P_N(R_{mn} = 0; R = 0)dR_{mn}$, represents the probability that monomers m and n overlap. Again, as the distribution is normalised, we can express the entropy change of having overlap in a ring chain by

$$\Delta S_2(|m-n|) = k_B \ln P_N(R_{mn} = 0; R = 0 = \frac{dk_B}{2} \ln \left(\frac{d}{2\pi\mu^2}\right)$$
$$= \frac{dk_B}{2} [\ln (d) - \ln (2\pi\mu^2)],$$

Now

$$\Delta S(\mid m-n \mid) = \Delta S_1 + \Delta S_2(\mid m-n \mid)$$

= $\frac{dk_B}{2} \left[\ln \left(\frac{d}{2\pi N a^2} \right) \right] + \frac{dk_B}{2} \left[\ln \left(\frac{d}{2\pi \mu^2} \right) \right]$
= $\frac{dk_B}{2} \times \left(\ln \left(\frac{d}{2\pi N a^2} \right) + \ln \left(\frac{d}{2\pi N a^2} \times \frac{1}{\frac{|m-n|}{N} \frac{N-m+n}{N}} \right) \right)$

Again, as |m-n| and N-m+n represent the monomer lengths in each of the loops of the ∞ , let |m-n|/N be the fraction of contour in one loop, θ and $1-\theta$ the fraction of contour in the other loop. Then, the last expression becomes

$$\Delta S(\mid m-n \mid) = \frac{dk_B}{2} \times \left(2 \times \ln\left(\frac{d}{2\pi N a^2}\right) - \ln\left(1-\theta\right)\theta\right),$$

so that, to first order the entropy reduction of making a molecular crazy-8 is roughly equal to twice the entropy reduction of forming a ring (see first term on RHS of last expression). Actually, from the last term on the RHS, you see that the entropy reduction isn't as large as twice the entropy reduction of forming a ring, as the term $-\ln(1-\theta)\theta$) is a positive number, that is minimal when $\theta = 0.5$.

3. Explain why a rubber band, slowly stretched feels cold while a metal paper clip similarly deformed feels warm.

First, when you deform the rubber band or the metal clip, you are doing work on the system. Usually, if you are performing the work quickly, there is no time available for heat transfer with the surroundings, and the process is said to be adiabatic, $\delta q = 0$. In this case, the work must go into the internal energy of the system.

$$\Delta U = \delta q - \delta W$$

So, if you take an ideal gas and compress it, you do work on the system by applying external forces. As no heat is exchanged with the surroundings, then all of the work is transformed into the internal energy of the gas, and consequently, the gas temperature increases. Likewise, if you stretch a rubber band adiabatically you are applying external forces, and this energy is transformed into internal energy, and there is an attendant increase in the temperature. So both metal clip and rubber band will warm up if stretched adiabatically (usually quickly).

However, now consider the case when you deform the rubber band and metal isothermally, in contact with a heat bath (your lips are a particularly good heat bath that can additionally sense the flow of heat: if your lips sense a "cold" object, heat is being transferred *from* your lips *to* the object; if your lips sense a "hot" object, then heat is being transferred *to* your lips *from* the object.) In general isothermal processes are "slow" and not "quick" as indicated in the problem statement, allowing time for heat transfer such that the system is isothermal. Such slow processes are called "reversible" and require the minimum amount of work. For an isothermal system with no interactions (say an ideal chain or an ideal gas) $\Delta U = 0$ So, for the purely elastic sub-chains, $\delta w_{rev} = \delta q_{rev} = T\Delta S$. As the rubber band's entropy decreases with stretching, heat is extracted from the surroundings to the system. Now, the metallic clip is different, as under isothermal processes $\Delta U \neq 0$ because of the changes in the atomic interactions. Thus, the work of deforming a metallic clip is $\delta q_{rev} = T\Delta S = \delta w_{rev} - \Delta U + T\Delta S$. That is the work goes into breaking crystalline bonds, with the net energy being dumped as heat to the surroundings.

4. In 1997, a paper appeared in Science that demonstrated the stretching of a single protein molecule using AFM. In that paper, the researchers investigated the tension-induced unfolding of domains in titin, a giant protein found in muscles. They found that the force versus extension profile was "sawtooth-like" with a periodicity that was commensurate with the length of the chain in the folded domain. In that work, the stretching force was fitted not to the purely entropic model, f = -kx, but rather a model that incorporated entropic, enthalpic, and finite size of the chain, referred to as the WLC or Worm-like Chain Model, $f = -k(0.25(1 - x/L)^{-2} - 0.25 + x/L)$, where L was the contour length.

Fig. 3. The characteristic sawtooth pattern of unfolding can be explained as stepwise increases in the contour length of a polymer whose elastic properties are described by the wormlike chain model (WLC) (*27, 28*). The figure shows a force extension curve obtained by stretching of a single lg8 titin fragment. The force extension curve shows a characteristic sawtooth pattern with seven peaks. The force extension curve [F(x) versus x] leading up to each peak is well described by the



WLC equation F(x) 5 (kT/b) [0.25(12 x/L)^{2 2} 2 0.25 1 x/L] with a persistence length b 5 0.4 nm and a contour length L that began at 58 nm for the first peak and then increased by 28 to 29 nm to fit consecutive peaks, reaching a maximum of 227 nm for the last peak. k is Boltzmann's constant and 7 is temperature. Thus, the WLC model predicts that the contour length of the polypeptide chain increases by 28 to 29 nm each time an lg domain unfolds. This value is close to the 30 nm predicted by fully extending a polypeptide chain comprising 89 amino acids (minusa folded length of 4 nm). At a force of 150 to 300 pN, the polypeptide chain is not fully extended, hence the peaks are spaced by only; 25 nm. Unfolding of the first domain reduces the force to zero, whereas unfolding of consecutive domains reduces the force to a lesser extent. This effect is also well explained by this simple model: Upon reaching a certain force (peaks), the abrupt unfolding of a domain lengthensthe polypeptide by 28 to 29 nm and reduces the force (troughs) to that of the value predicted by the force extension curve of the enlarged polypeptide.

Taken from Rief, M/ Gautel, M., Oesterhelt, F., Fernandez, J.M., Gaub, H.E., "Reversible Unfolding of Individual Titin Immunoglobulin Domains by AFM", *Science* **276**, 1109-1112, 1997.

Predict the AFM force versus extension profile for a polypeptide chain having 3 folded domains, the length of the unravelled domains are 30, 40, and 60 nm in length. The contour length of the fully-unfolded chain is 300 nm. Assume, that outside of the instantaneous unfolding of domains, the measured force is purely entropic with a k = 2/3 pN/nm and justify any other necessary assumptions. Make sure you label pertinent features of the force profile.

The following assumptions were made:

- The contour length of the unstretched chain is 300 30 40 60 = 170 nm.
- Like the reference, the rate of stretching is small in comparison to the rate at which the domains completely unfold, so that unravelling occurs "instantaneously" on the timescale of the experiment, providing an extra 30, 40, or 60 nm of contour length when a domain unravels.
- The tension is uniform along the chain, irrespective of its contour length. In reality, the tension is greater near the tether points or ends of the chain and consequently, those domains closer to the chain ends will "feel" a large tension and might then unravel first. By assuming uniform tension, we are affectly assuming that the ordering of the domains along the contour length does not affect the order by which they are unravelled.
- The energy of unfolding of all 3 domains are equivalent to within kBT so that there is no preference as to which domain unfolds first. Under this assumption, and the assumption of uniform chain tension, the order of domain unfolding is random. An alternative, reasonable assumption is that the energy of unfolding of a domain increases with the domain size so that the domains unfold from smallest to largest.
- Two plots are given. The first assume k is independent of contour length. The second assumes that $k \sim 1/N$ according to the class notes so that the slope of the force profile decreases upon consecutive domain unfoldings.



Figure 1: Prediction of the AFM force profile of an ideal chain with folded domains of 30, 40, and 60 nm. The contour length of the chain is 300nm. Predictions are made for a chain that unfolds domains randomly or non-selectively. This particular AFM trace depicts domains unfolding in the order of 40, 60, and 30 nm, before detaching from the AFM tip or substrate at full contour length of 300 nm. The red line is the prediction for a chain with constant value of $k = 2/3 \text{ pN}/\mu\text{m}$. The blue dotted line accounts for the N^{-1} dependence on the chains's spring constant. I've assumed that $k = 2/3 \text{ pN}/\mu\text{m}$ describes the spring constant for the contour length of 300nm and that k decreases to 2/3 as the contour length is increased from 170, to 210, and to 270nm.