3.11 Problem Set #8 Solutions

RUBBER ELASTICITY PROBLEMS
(Only three problems because of the Holiday Monday and Tuesday)

1. Explain why a freely jointed chain left to itself tries to coil itself. What is it trying to maximize or minimize by doing that?

A freely jointed chain tends to coil itself because it is trying to maximize entropy. The entropy of a macromolecular chain is dependent upon the number of different conformations that the chain can have in space (configurational entropy: $S(r) = k_b*\ln(\Omega)$). If the chain were totally stretched out, it would only have one possible conformation. By coiling itself, it increases the number of conformations it can have, and therefore, its entropy.

Answer: A freely-jointed chain tends to coil itself because it is trying to maximize entropy. The entropy of a macromolecular chain is dependent upon the number of different conformations that the chain can have in space (configurational entropy: $S(r)=k_B*\ln(\Omega)$. If the chain were totally stretched out, it would only have one possible conformation. By coiling itself, it increases the number of conformations it can have, and therefore, its entropy.

2. In class, while deriving the expression for the Helmholtz free energy of a single Gaussian chain, an approximation was made. Show what that approximation was by deriving the expression for Helmholtz free energy starting with A(r) = -T*k_b*lnP(r). P(r) is the probability that the end of the chain is located at a distance, r, from the origin of the chain.

Answer:

$$A(r) = -k_B T * \ln(P(r))$$

$$P(r) = \frac{4b^3 r^2}{\sqrt{\pi}} \exp(-b^2 r^2)$$

$$\Rightarrow A(r) = -k_B T * \ln\left(\frac{4b^3 r^2}{\sqrt{\pi}} \exp(-b^2 r^2)\right)$$

$$A(r) = -k_B T * \left[\ln\left(\frac{4b^3 r^2}{\sqrt{\pi}}\right) + \ln(\exp(-b^2 r^2))\right]$$

$$= -k_B T * \left[\ln\left(\frac{4b^3 r^2}{\sqrt{\pi}}\right) - b^2 r^2\right]$$

$$= k_B T * b^2 r^2 - k_B T * \ln\left(\frac{4b^3 r^2}{\sqrt{\pi}}\right)$$

$$b = \sqrt{\frac{3}{2 * n * a^2}}$$

$$\Rightarrow A(r) = k_B T * \left(\sqrt{\frac{3}{2 * n * a^2}}\right)^2 r^2 - k_B T * \ln\left(\frac{4b^3 r^2}{\sqrt{\pi}}\right)$$

$$A(r) = \boxed{\left[\frac{3 k_B T}{2 * n * a^2}\right] r^2} - k_B T * \ln\left(\frac{4b^3 r^2}{\sqrt{\pi}}\right) \rightarrow \text{negligible}$$

The first term in the expression above is the expression that was derived for A(r). Thus, the **second term was deemed negligible**. That is the approximation that was made.

3. (a) A polymer chain with a statistical segment length of 5nm and containing 10,000 segments is stretched with a force of $0.25*10^{-12}$ N at room temperature (25ºC). What is the end-to-end distance of the chain?
(b) If the temperature is raised to 100ºC, what does the end-to-end distance become if you assume the polymer does not degrade? What if the statistical segment length is 2nm instead of 5nm, but the contour length remains the same at room temperature? (Careful with your conversions)

a)

$$f_{rest}(r) = -0.25*10^{-12}N = -\frac{3k_BT}{n*a^2}r = -\frac{3*1.38*10^{-23}\,J/K * 298K}{10{,}000*(5*10^{-9}m)^2}r$$

$$\Rightarrow r = f_{rest}(r)\left(-\frac{n*a^2}{3k_BT}\right) = -0.25*10^{-12}N\left(-\frac{10{,}000*(5*10^{-9}m)^2}{3*1.38*10^{-23}\,J/K * 298K}\right)$$

$r = 5.1*10^{-6}m =$ **5.1 µm**

b)
With T = 100°C = 373 K, all else remaining equal,

$$\frac{r_{373K}}{r_{298K}} = \frac{298}{373}$$

$\Updownarrow$

$$r_{373K} = r_{298K}*\frac{298}{373} = 5.1\mu m*\frac{298}{373} = \mathbf{4.1\ \mu m}$$

With the change in statistical segment length (a = 2nm), the contour length of the chain, L_c, does not change. Since all else (but n) remains equal,

$$\frac{r_{a=2nm}}{r_{a=5nm}} = \frac{(n*a^2)_{a=2nm}}{(n*a^2)_{a=5nm}} = \frac{L_C*2nm}{L_C*5nm} = \frac{2}{5}$$

$\Updownarrow$

$$r_{a=2nm} = r_{a=5nm}\frac{2}{5} = \frac{2}{5}5.1\mu m = \mathbf{2.0\ \mu m}$$