

## Soft Matter Problem set 3 – Polymers Answers

### Problem 9

a)

$$\xi = \frac{1}{\sqrt{\sigma}}$$

b)

$$\xi^2 = b^2 g \quad g = \frac{\xi^2}{b^2} = \frac{1}{b^2 \sigma}$$

c)

$$h_0 = \xi \left( \frac{N}{g} \right) = N b^2 \sigma^{1/2}$$

d)

$$F_{\text{str}} = k_B T \left( \frac{N}{g} \right) = k_B T N b^2 \sigma$$

e)

$$\Pi \text{ (N m}^{-2}\text{)} = \frac{F_{\text{str}} \text{ (N m)}}{V_{\text{chain}} \text{ (m}^3\text{)}} = \frac{k_B T N b^2 \sigma}{h/\sigma} = \frac{k_B T N \sigma}{hg} = \frac{k_B T}{\xi^3} = k_B T \sigma^{3/2}$$

f)

$$\Pi = k_B T \sigma^{3/2} = 2.1 \cdot 10^7 \text{ N m}^{-2} = 210 \text{ bar}$$

g)

$$\begin{aligned} \xi^2 &= b^2 g^{6/5} \\ g &= \left( \frac{\xi}{b} \right)^{5/3} = b^{-5/3} \sigma^{-5/6} \\ h_0 &= N b^{5/3} \sigma^{1/3} \\ F_{\text{str}} &= k_B T N b^{5/3} \sigma^{5/6} \\ \Pi &= \frac{k_B T}{\xi^3} = k_B T \sigma^{3/2} \end{aligned}$$

## Problem 10

a)

$$k_{\text{spring}} = \frac{3k_{\text{B}}T}{Nb^2} = 0.012\text{mN/m}$$

- b) A polymer is an entropic spring, the stretching force originates from a reduction in number of possible conformations. A long polymer has more possible conformations and the relative reduction for a similar absolute extension is smaller.
- c) The spring constant increases with increasing temperature. Therefore, the weight will be lifted up when the rubber band is heated (until it starts to burn of course).

## Problem 11

a)

$$\begin{aligned}h &= R_p \\r &= a + R_p \\V_{\text{cap}} &= \frac{\pi h^2}{3}(3r - h) = \frac{\pi R_p^2}{3}(3(a + R_p) - R_p) = \pi a R_p^2 + \frac{2}{3}\pi R_p^3\end{aligned}$$

The total overlap volume is 2x this cap volume.

- b)  $V_{\text{dep}} = 0$  for  $r = 2(a + R_p)$ . For sketch: see lecture notes.
- c)

$$\begin{aligned}c &= 2 \text{ g/L} = 2 \text{ kg/m}^3 \hat{=} \frac{2 \text{ kg/m}^3}{135 \text{ kg/mol}} = 0.015 \text{ mol/m}^3 \\ \Pi &= nk_{\text{B}}T = cRT = 0.015 \cdot 8.3145 \cdot 298 = 37.2 \text{ N/m}^2 \\ V_{\text{dep}} &= 2\pi a R_p^2 + \frac{4}{3}\pi R_p^3 = 5.77 \cdot 10^{-21} \text{ m}^3\end{aligned}$$

(for 20 g/L,  $V_{\text{dep}}$  is the same,  $\Pi$  is 10 times larger.)

d)

$$F_{\text{dep}} = -\Pi V_{\text{dep}} = -2.14 \cdot 10^{-19} \text{ J} = -54 k_{\text{B}}T$$

- e) The osmotic pressure increases with increasing temperature, so  $F_{\text{dep}}$  decreases with increasing temperature. The attraction becomes stronger, because the entropic gain of the polymers due to overlap of the depletion zones becomes more important at higher temperature.
- f) The colloids are stabilized by charges; counterion osmotic pressure keeps them apart. At 0.1 M salt the screening length is smaller than the depletion zone thickness, and colloids can approach each other to close enough that the depletion zones can start to overlap. The polymer then pushes the colloids together further until they aggregate.

## Problem 12

a)

$$\begin{aligned}
 R_F &= bN^{3/5} \\
 \xi &= bg^{3/5} & g &= (\xi/b)^{5/3} \\
 R_x &= \xi \left( \frac{N}{g} \right) = \xi \left( \frac{Nb^{5/3}}{\xi^{5/3}} \right) = \frac{R_F^{5/3}}{\xi^{2/3}} \\
 \xi^{2/3} &= \frac{R_F^{5/3}}{R_x} & \xi &= \frac{R_F^{5/2}}{R_x^{3/2}} \\
 F_{\text{str}} &= k_B T \left( \frac{N}{g} \right) = k_B T \frac{R_x}{\xi} = k_B T \left( \frac{R_x}{R_F} \right)^{5/2} \\
 f(R_x) &= \frac{\partial F}{\partial R_x} = \frac{5}{2} k_B T \left( \frac{1}{R_F} \right) \left( \frac{R_x}{R_F} \right)^{3/2}
 \end{aligned}$$

b) No, it is a power law spring with exponent 3/2.

c) Compare  $fb/k_B T$ , the dimensionless force.

$$\begin{aligned}
 \text{Ideal : } \frac{fb}{k_B T} &= \frac{3R_x}{Nb} \\
 \text{Real : } \frac{fb}{k_B T} &= \frac{5}{2} \left( \frac{R_x}{Nb} \right)^{3/2}
 \end{aligned}$$

$$\text{These are equal for : } \sqrt{R_x} = \frac{6}{5} \sqrt{Nb} \quad R_x \approx Nb$$

The forces are equal when the chain is stretched to its maximum end-to-end distance (the contour length,  $Nb$ ).