080227 Quiz 7 Polymer Properties

1) Electrostatic screening involves the reduction in the energy, dU, associated with two charges separated by a distance r associated with a change in separation distance dr.
   a) Show that a linear dependence of the change in energy on the energy and the change in distance, $dU \sim -U\, dr$, can lead to the expression used by Debye for the Debye screening length, λ_D.
   b) How does the Debye screening length depend on concentration of ions and why does it have this dependence?
   c) Sketch U(r) versus r for two charges in a vacuum, two charges in a dielectric media and two charges in a sea of other charges that display screening. Is screening long range or short range effect?

2) Polymers also display screening as concentration is increased.
   a) Sketch a log-log plot of neutron scattering from a polymer chain in a good solvent at three concentrations in the dilute, semi-dilute and concentrated regimes.
   b) Does screening in this polymer system display a long or a short range effect? Compare the effect with your answer to question1c.
   c) Show that the dependence of this screening length, ξ_c, on concentration, c, follows, $\xi_c \sim R_0 \left(c / c^* \right)^{-3/4}$.

3) In class we discussed the relationship between a virial expansion in concentration for a non-ideal gas and the Flory-Huggins expression for the osmotic pressure.
   a) Explain this relationship and give an expression for the non-ideal gas pressure, P, and the osmotic pressure, Π, for a Gaussian polymer in solution.
   b) If the Flory function is followed sketch a plot of $\Pi/(c\ kT)$ versus c for several different molecular weight polymers.
   c) It is found that a universal curve is produced (that is all of the molecular weights you plotted in b fall on the same curve) when $(\Pi\ N)/(c\ kT)$ is plotted against (c/c^*). A power-law of $\Pi/(kT) \sim (c/c^*)^{9/4}$ is followed at high (c/c^*). Explain why this might be the case.

ANSWERS: 080227 Quiz 7 Polymer Properties

1) a) $dU = -U \frac{dr}{\lambda_D}$

$\int \frac{dU}{U} = \int -\frac{dr}{\lambda_D}$

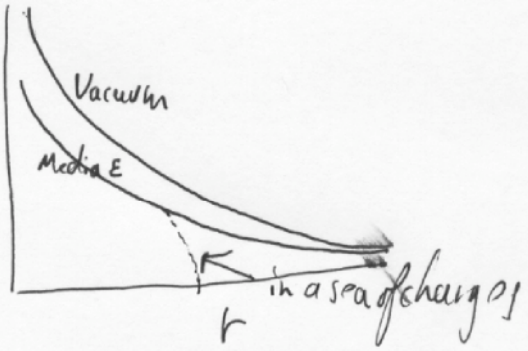
$U(r) = U_0 \exp\left(\frac{-r}{\lambda_D}\right)$

$U_0 = k \frac{q_1 \cdot q_2}{\varepsilon r}$

b) $\lambda_D = \frac{\varepsilon k_B T}{4\pi k e^2 \sum \rho_i z_i^2}$

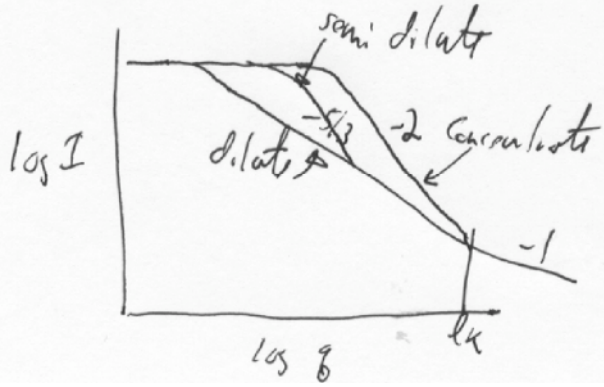
ρ is concentration of ions
z is number of charges

c) $U(r)$



Screening has a large "r" or long-range effect

2) a)



b) Screening has a long-range effect. This is similar to Debye screening in that large distance interactions are blocked while short distances are still observed.

c)

① At c^* $\xi_c \sim R_0 \sim N^{3/5} l_K$

② - above c^* $\xi_c \sim N^0$

③ ξ_c must depend on $\left(\frac{c}{c^*}\right)^p$

So using ① & ③ we write

$$\xi_c \cong R_0 \left(\frac{c}{c^*}\right)^p$$

& using $c^* \sim \frac{N}{R_0^3} \sim N^{-4/5}$

$$R_0 \sim N^{3/5}$$

$$N^{3/5} N^{p4/5} = N^0$$

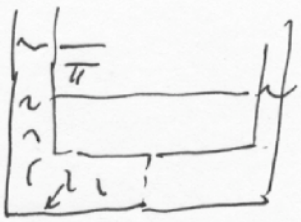
so $\frac{3}{5} + \frac{p4}{5} = 0$ & $p = -\frac{3}{4}$

$$\xi_c \cong R_0 \left(\frac{c}{c^*}\right)^{-3/4}$$

(3) a)

each moves with kT

$$P = kT\left(\frac{N}{V}\right) = kTc$$



each chain moves with kT

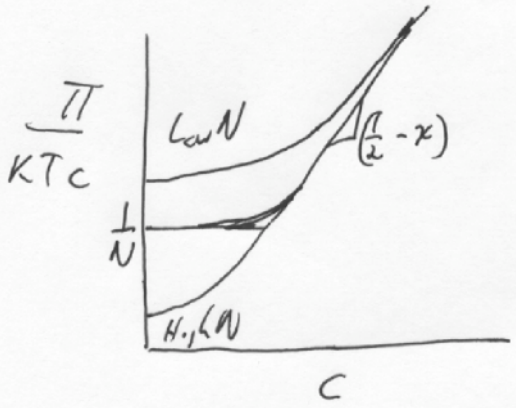
$$\pi = kT\left(\frac{\text{mass}}{\text{vol}}\right)\frac{1}{N}$$

Virial Expansion

$$P = kTc\,(1 + B_2 c)$$

$$\pi = kTc\left(\frac{1}{N} + \underbrace{\left(\frac{1}{2} - \chi\right)}_{\text{per mer unit}} c + \ldots\right)$$

b)



c) $\left(\frac{\pi}{KTc}\right)N$ Removes N intercept dependence

$\left(\frac{c}{c^*}\right)$ Removes shift in power law region due to N corrections

We know that

① $\Pi \sim \frac{kT\phi}{N}$ from Flory's first term.

② & above ϕ^* $\Pi \sim \left(\frac{\phi}{\phi^*}\right)^{P_2}$

③ also $\Pi \sim N^0$ above ϕ^* at high ϕ

So $\Pi \sim \frac{kT\phi}{N}\left(\frac{\phi}{\phi^*}\right)^{P_2}$

$\phi^* \sim N^{-4/5}$ from 2c)

$$N^{-1} N^{P_2(4/5)} = N^0$$

$$\therefore \quad P_2 = \frac{5}{4}$$

So ϕ dependence is 9/4 power.