070502 Quiz 5 Polymer Properties

1) Consider a polymer coil with two terminal charge groups of opposite sign subject to a strong electric field in a dilute solution.
   a) How would you expect the coil to respond to this applied field? Electric force is calculated from the electric field times the charge.
   b) Give an expression for a blob size as a function of the applied field, E
   c) Give an expression for the extended length of the coil L as a function of the applied field, E.

2) Sketch the scattering pattern (I vs q) expected from your answer to question 1. Show several scattering patterns with no field and increasing field.

3) The following scattering function (the Ornstein-Zernike Function) has been proposed as a simplified Debye equation,

$$I(q) = \frac{\xi^2 / K^2}{1 + q^2 \xi^2}$$

   where ξ is the correlation length. Show that this function has similar limits to the Debye equation at high and low-q. (Is there a relationship between ξ, K and R_g?)

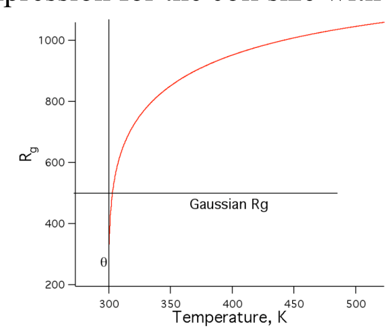
$$I(q) = \frac{2}{Q^2}\left(Q - 1 + \exp(-Q)\right) \quad \text{where} \quad Q = q^2 R_g^2 \qquad \text{Debye Equation.}$$

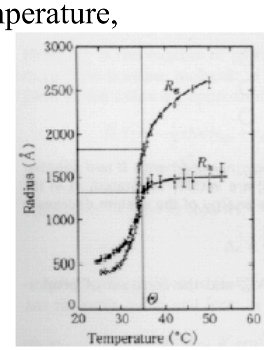
   At low x (x<<1), $\exp(+x) = 1 + x/1! + x^2/2! + x^3/3! + \ldots$ and $\exp(-x) = 1 - x/1! + x^2/2! - x^3/3! + \ldots$

4) The Flory-Krigbaum analysis results in an expression for the coil size with temperature,

$$R_F = N^{3/5} l_K^{2/5} \left(V_0(1-2\chi)\right)^{1/5} = N^{3/5} l_K \left(1 - \frac{2z\Delta\varepsilon}{kT}\right)^{1/5}$$

which is plotted to the right, next to experimental data.





   a) Why is a blob model needed to describe this behavior? (What is the structural model associated with the Flory-Krigbaum coil, that is what does it look like? What is the nature of the expanded to collapsed coil transition, what structural pathway does the chain take to the collapsed state?)
   b) Sketch the scattering pattern log I(q) vs log q showing the structural model for the thermal blob theory for this transition.
   c) Sketch a molecular model for this transition.
   d) Calculate the temperature (χ) dependence of the thermal blob size.

5) In class we discussed the screening of interactions with increase in concentration.

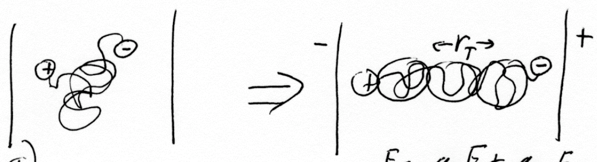
a) At what concentration should you begin to consider screening?

b) How would this concentration vary for coils of the same mass that were collapsed, R ~ $n^{1/3}$, Gaussian, SAW coils or extended rods, R ~ n?

c) What is the screening length?

d) For electrostatics the energy of interaction between two charges in dilute conditions is given by $U_{Dilute}(r) = \frac{kq_1q_2}{\varepsilon r}$. In concentrated conditions this energy is $U_{Concentrated}(r) = \frac{kq_1q_2}{\varepsilon r}\exp\left(-\frac{r}{\lambda_D}\right)$. Show that the two expressions are identical for small r.

① ①



a)

$F = q_\oplus E + q_\ominus E$

$= 2qE$

$U(R) = \frac{3}{2}\frac{R^2}{R_0^2} kT$

$F = \frac{du}{dR} = \frac{3R\,kT}{R_0^2}$

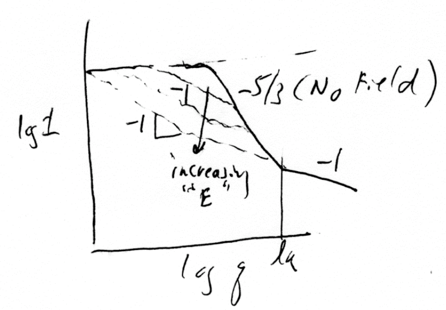
b) $\boxed{r_t \sim \frac{3kT}{F} = \left(\frac{3kT}{2qE}\right)}$

$L = N_t r_t \qquad r_t = n_t^{1/2} l_k$

$N_t = \frac{N}{n_t} = \frac{N l_k^2}{r_t^2}$

c) $\boxed{L = \frac{N l_k^2}{r_t} = \frac{2N l_k^2 |q| E}{3kT}}$

②



3

$$I(q) = \frac{\xi^2/k^2}{1+q^2\xi^2}$$

<u>at high q</u> $\quad q^2\xi^2 \gg 1$

$$I(q) \Rightarrow \frac{1}{k^2 q^2}$$

For Debye

$$I_{Debye}(q) \Rightarrow \frac{2}{q^2 R_g^2} \qquad \text{so} \quad \boxed{k^2 = \frac{R_g^2}{2}}$$

at low q

$$\exp(q^2\xi^2) \Rightarrow 1 + q^2\xi^2$$

$$I(q) = \frac{\xi^2}{k^2}\exp(-q^2\xi^2)$$

For Debye

$$I(q) \Rightarrow \exp\left(-\frac{q^2 R_g^2}{3}\right)$$

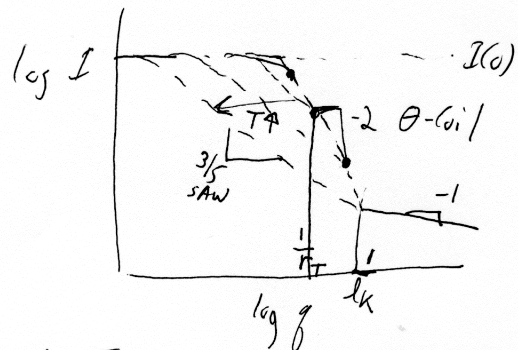
$$\text{so} \quad \boxed{\xi^2 = \frac{R_g^2}{3}}$$

$\boxed{\text{but } \frac{\xi^2}{k^2} \neq 1}$ so the two expressions are <u>Not</u> identical even in limits.

③

④ ⓐ A blob is needed because there is no structural basis for the transition from expanded coil to Gaussian & collapsed chain. Also the coil size does not reach the Gaussian R_g at the Θ temperature so the F-K expression is not accurate at the critical temperature.

ⓑ



As T increases r_T decreases in size (moves to the right in the plot).

ⓒ

4

(d) $R_T = r_T N_T^{3/5} = N^{3/5} l_K (1-2\chi)^{1/5}$

$r_T = l_K n_T^{1/2}$

$$N_T = \frac{N}{n_T} = \frac{N}{r_T^2} l_K^2$$

$$r_T N_T^{3/5} = N^{3/5} \frac{r_T \, l_K^{6/5}}{r_T^{6/5}} = \cancel{N^{3/5}} r_T^{-1/5} l_K^{6/5} = \cancel{N^{3/5}} \cancel{l_K} (1-2\chi)^{1/5}$$

$$r_T = \frac{l_K}{(1-2\chi)}$$

5 (a) Screening begins at the overlap concentration c^*.

$$c^* = \frac{N}{R_F^3}$$

(b)

	Collapsed	Gaussian	SAW	Rod
R	$N^{1/3}$	$N^{1/2}$	$N^{3/5}$	N^{1}
	$c^* = N^0$	$c^* \sim N^{-1/2}$	$c^* \sim N^{-4/5}$	$c^* \sim N^{-2}$

(c) As concentration increases long range interactions are screened by interference from other units. The distance where shielding of interactions dominates for the first time is the screening length. For shorter distances interactions are not screened.

5

(d) For small $r/\lambda_D << 1$

$$\exp\left(-\frac{r}{\lambda_D}\right) = 1 - \frac{r}{\lambda_D} + \left(\frac{r}{\lambda_D}\right)^2 \frac{1}{2!} - \cdots$$

$$\sim 1$$

So

$$U_{Dilute}(r) = U_{concentrated}(r)$$

for very small $\left(r/\lambda_D\right)$