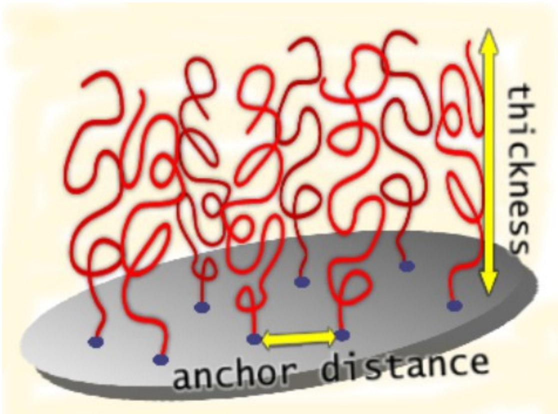
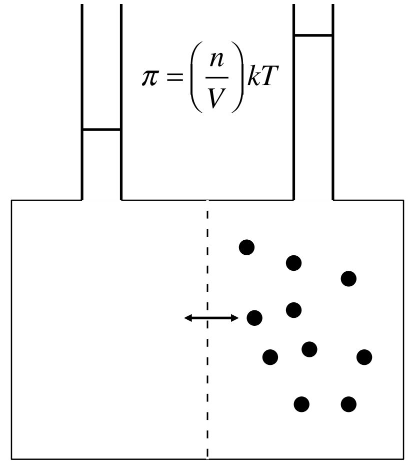
120517 Quiz 5 Polymer Properties



a) Question 1



b) Question 2

1) The graphic in "a)" depicts polymer chains at thermal equilibrium grafted to a surface, The chains are subjected to thermal randomization in a good solvent that are constrained by the tethered end and by crowding.

   a) What scaling regimes would you expect in this situation? Explain why.

   b) If you proposed a blob model to describe these chains would you expect the blob size to increase or decrease with chain surface packing density. Would the blob size increase or decrease with molecular weight?

   c) Write a scaling expression for the blob size in terms of molecular weight and packing density (number of chain tether sites per area, ρ) then use a geometric argument to determine the scaling constants of blob size with molecular weight and packing density.

   d) Can your model predict the polymer layer thickness? Determine an equation to explain how.

   e) What experiments would you propose to test your blob model?

2) Figure "b)" above shows a model for an osmotic pressure measurement.

   a) What assumptions are necessary for the black dots in order for the equation to hold? (These are the same assumptions that are needed for an ideal gas.)

   b) Under what conditions would these assumptions be appropriate to describe a polymer in solution?

   c) How could this expression be modified if we wanted to consider binary interactions for a polymer?

Based on Flory's work, Stockmayer and Fixman[2] developed an intrinsic viscosity relationship for high molecular weight flexible-chain polymers, neglecting solvent draining effects:

$$[\eta] = K_\theta\sqrt{M} + \frac{0.51\Phi_0 M}{N_A V_s \rho_p^2}(1 - 2\chi) \qquad (1)$$

In eq. (1), K_θ is the Mark–Houwink–Sakurada K value at the theta temperature; M, the weight-average polymer molecular weight; χ, the polymer–solvent interaction parameter; V_s, the solvent molar volume; ρ_p, the polymer density; Φ_O, the Flory constant (2.8×10^{23}); and N_A, Avogadro's number.

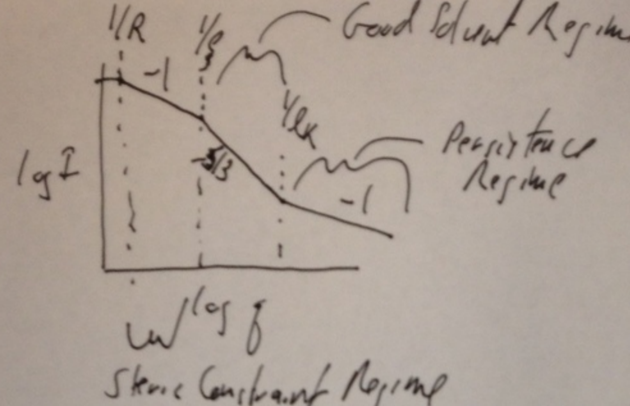
Journal of Applied Polymer Science, Vol. 89, 2831–2835 (2003)

d) Equation (1), above, indicates that the second virial coefficient could be obtained from the intrinsic viscosity. Use this equation to write an expression for the second virial coefficient using the intrinsic viscosity.

e) Do you agree with the hypothesis that it is possible to calculate the second virial coefficient from the intrinsic viscosity. (You will need to define the second virial coefficient, specifying the interacting entities and other features, and the intrinsic viscosity in order to answer this question.)

Answers: 120517 Quiz 5 Polymer Properties

1) a)



Chain Crowding could lead to an extended chain regime at low q. $d_f = 1$

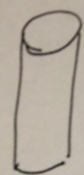
At larger q a regime of good solvent scaling Might be observed $d_f = 5/3$

At high q the persistence regime is seen $d_f = 1$

b) Blob size ξ should decrease with N since chain crowding would increase with N

ξ should decrease with chain packing density ρ due to increased chain crowding

c) Consider the chain forms a rod or cylinder



of volume $R^3 = (N^{3/5})^3$

Diameter of cylinder is spacing of chains $= D$

$$\rho = \frac{\#\text{ of chain stems}}{\text{Area}}$$

$$D \cong \frac{1}{\sqrt{\rho}} \cong \xi$$

Height of chain $t = \frac{R^3}{D^2} \sim \rho N^{9/5}$

Blob size doesn't depend on N

Blob size depends on $\frac{1}{\sqrt{\rho}}$

$$\xi \sim \frac{1}{\sqrt{\rho}}$$

d) $t \sim \rho N^{9/5}$

e) Vary ρ & N & measure t using ellipsometry or reflectivity (Neutron or X-ray)

2) a) Black dots pass through each other
Phantom dots
Each dot has kT energy

b) dilute conditions Low η_0 (solvent viscosity)

c)
$$\frac{\Pi}{\phi kT} = \frac{1}{N} + \underbrace{\left(\frac{1}{2}-\chi\right)}_{(A_2)}\phi$$

d)
$$A_2 = \left([\eta]-[\eta]_\theta\right)\frac{N_A V_s \rho_p^2}{2(0.51)\Phi_0 M}$$

e) Second virial coefficient describes the interaction energy for binary interactions of ~~polymer chains in~~ monomers & solvents in solution.

Intrinsic viscosity reflects the effect of adding a chain on the viscosity of a solution. $[\eta]$ reflects dynamics of whole chain interactions.

4

There is no direct link between A_2 & $[\eta]$

A_2 Statics; site-site

$[\eta]$ Dynamics; chain-chain