080317 Final Polymer Properties

Q1.3) In class we discussed the Gaussian distribution function.

a) Write the normalized 1-d Gaussian probability function, $P_{1d}(R,n,l)$ and show how $\langle R \rangle$, $\langle R^2 \rangle$, and $\langle R^3 \rangle$ are calculated using this function.

b) Sketch the distribution curves corresponding to $P_{1d}(R,n,l)$ and the three moments given above and give the value for these three moments and the integral of $P_{1d}(R,n,l)$.

c) Show how the value for $\langle R^2 \rangle$ as a function of n and l can be obtained from summations. Show how a similar scaling relationship can be obtained from the plot of the second moment distribution curve.

Q2.3) a) Describe the difference between short range interactions (SRI) and long range interactions (LRI). For a balled sheet of paper and a balled sheet of aluminum foil, consider that balls of paper spring open when pressure is released while balls of aluminum foil do not. Is this springiness associated with short range or long-range interactions in paper?

b) Describe the differences between i) statistical segment length, ii) chemical unit length, iii) Kuhn length, and iv) persistence length.

c) Explain how you would apply the idea of a Kuhn unit in linear chains to the crumpled sheets. (see for example Kantor et al. *Phys. Rev. A* **35** 3056-3071 (1987)).

The characteristic ratio, C_n, is the ratio of observed end-to-end distance, and the end-to-end distance of a freely jointed chain composed of n bonds of step length l_{chem},

$$C_n = \frac{\langle r^2 \rangle_0}{n_{chem} l_{chem}^2} = \frac{l^2_{\text{stat. seg. length}}}{l^2_{chem}}$$

The extrapolation of this value to infinite molecular weight is called C_∞.

The coil expansion factor, α, is defined as the square root of the ratio of the coil end-to-end distance to that of the coil in a Gaussian state (in the melt),

$$\alpha^2 = \frac{\langle r^2 \rangle_{Experimental}}{\langle r^2 \rangle_{GaussianState}}$$

α varies with the temperature for a polymer in solution.

Q3.1) a) In class we considered the simplest case for short range interactions (SRI) where the chain is prevented from back-tracking. Explain how this SRI might effect C_n as well as α.

b) The derivation for back-tracking relied on conversion of an infinite power series, $\sum_{\alpha=0}^{\infty} x^\alpha = \frac{1}{1-x}$ for -1<x<1. Show that this equality is true by using a recursive relationship (that is by defining the function in terms of itself, $\sum_{\alpha=0}^{\infty} x^\alpha = 1 + x\sum_{\alpha=0}^{\infty} x^\alpha$).

c) The derivation in class resulted in a simple function for the dependence of Kuhn length on coordination number, z. Give this relationship, sketch the dependence on z by drawing a graph of Kuhn length versus z and explain why this dependence makes sense.

Q3.2) One technique to measure the hydrodynamic size of a polymer or colloid involves determination of the intrinsic viscosity, [η].

a) Describe how the shear viscosity can be obtained from the force applied to and the velocity of a fluid. (A sketch is OK to describe this.)

b) Explain why the intrinsic viscosity represents a first order approximation (associated with dilute conditions).

c) Explain the dependence of intrinsic viscosity on molecular weight and hydrodynamic radius for a sphere, rod and Gaussian coil.

Q4.1&2) The radius of gyration for an object made of discrete steps, such as a freely jointed chain, can be obtained with summation. For continuous objects, such as disks and rods, an integration over all points must be made to determine R_g.

a) Obtain the radius of gyration for a rod, R_g^2, by performing a normalized double integral over length and radius using a coordinate system with an origin at the center of mass for the rod. You need to use cylindrical coordinates so the integral for a function f(r,y) is $\int_{r=0}^{R}\int_{y=-H}^{H} 2\pi r f(r,y)\,dr\,dy$. (Remember to normalize by an integral with f(r,y) = 1.)

b) What equation is used to determine the radius of gyration and sketch the appearance of this function on a log-log plot.

c) In what way is this equation a Gaussian function and why might this be true?

Q5.3) The second virial coefficient depends on the excluded volume.

a) Explain why this is the case for a gas composed of spheres.

b) Write an expression for the conformational free energy, E, of an isolated chain in terms of the excluded volume, V_c, chain end-to-end distance, R, and temperature, T, by comparing an exponential expression for the probability of a chain of end-to-end distance R with the Boltzman probability for a chain of end-to-end distance R, $P_{Boltzman}(R) = \exp(-E/kT)$

c) Sketch a plot of the isolated chain energy, E, versus excluded volume, V_c, and explain the behavior and limits to this plot. Is there a minimum excluded volume? Why can't a maximum excluded volume be reached?

Q6.2) a) Write an expression for the energy of an isolated chain as a function of temperature using the chi-parameter.

b) Use this expression for a SAW chain and the expression for a Gaussian chain to calculate the spring constant, k_{spr}, for these two chains, $F = k_{spr} R$.

c) Does the non-linearity of the spring constant for the SAW become larger or smaller with higher deformation, R? Does it become larger or smaller as T drops? Explain these.

PNIPAM (poly-N-isopropyl acrylamide) is used as a drug release polymer because it displays an LSCT in water with a critical temperature at around 35º C close to the temperature of the human body. Through adjustment of the PNIPAM structure in aqueous gels a drug can be selectively released from the gel when it approaches diseased tissue that is hotter than the surrounding tissue.

Q8.1) A researcher began studies of PNIPAM polymer in solution by making a series of solutions and measuring the cloud point to construct a phase diagram.

a) Describe what a cloud point is and sketch an LSCT phase diagram.

b) If the molecular weight of the PNIPAM is known how could the interaction parameter be determined using the cloud point? (You will need to take a derivative to obtain an equation for the cloud point using $d\ln\phi/d\phi = 1/\phi$ and $d\ln(1-\phi)/d\phi = -1/\phi$.)

c) What functionality would you expect the chi parameter to have in temperature? Explain.

Q8.3) a) Explain the terms critical slowing-down and critical point using the words fluctuation and free-energy space in the context of the Flory-Huggins equation.

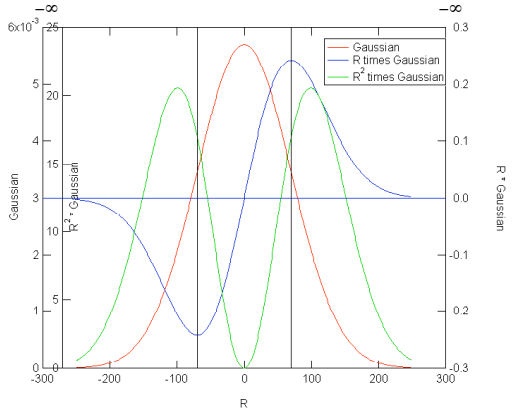
b) Give a generic expression for the critical interaction parameter and critical composition then show the values for a blend of gases, a polymer/solvent mixture and a symmetric polymer blend.

c) It is often said that polymers do not mix. Use the Flory-Huggins equation to explain why this is the case. (Show what part of the Flory-Huggins equation drives miscibility and which part drives phase separation; explain why they favor or disfavor miscibility; and show the dependence of these terms on molecular weight.)

Answers: Final Polymer Properties

Q1.3) a) $P_{1d}(R,n,l) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{R^2}{2nl^2}\right)$; $\langle R\rangle = \int_{-\infty}^{\infty} RP_{1d}(R,n,l)dR = 0$;

$\langle R^2\rangle = \int_{-\infty}^{\infty} R^2 P_{1d}(R,n,l)dR = nl^2$; $\langle R^3\rangle = \int_{-\infty}^{\infty} R^3 P_{1d}(R,n,l)dR = 0$

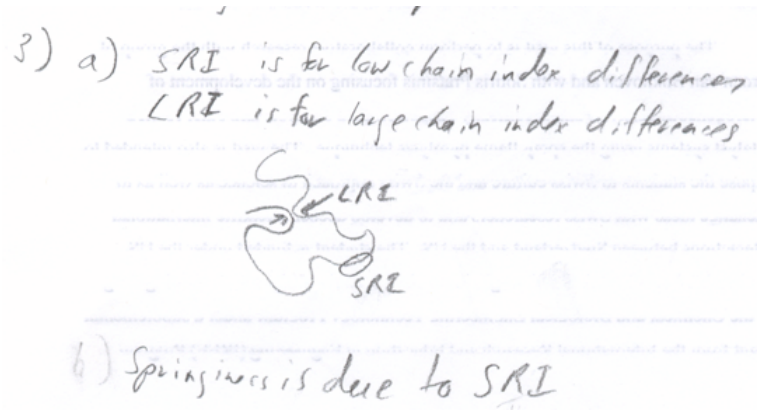


b) <R^3> is similar to <R>

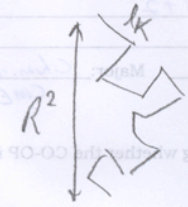
Values are given in a)

c) $\langle R^2\rangle = \langle r_i \bullet r_j\rangle = \sum_{1}^{n} r_i^2 + \sum_{i=0}^{n}\sum_{j=0\neq i}^{n} r_i \bullet r_j = nl^2$ where the second summation is 0 because there is no correlation between i and j vectors.

A similar result can be obtained by setting the derivative at the maximum of the R^2 curve above to 0 resulting in $R^{*2} = 2nl^2$.



3C) Kuhn unit is basically jointed chain model



$R^2 = n_K l_K^2$

For ball of foil consider a slice and find the end to end distance R. Consider that

this 2d projection of the sheet is a random walk similar to the 3-d walk of a polymer chain.

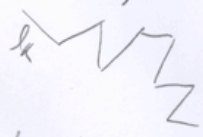
36)

i) statistical segment length is conversion factor chain size R_{end} to number of chemical units n_{chem}

$$R_{end}^2 = n_{chem} l_{SS}^2$$

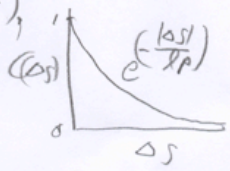
ii) Chemical unit length is just bond length or bond length plus bond angles to compose a chemical unit, l_{chem}.

iii) Kuhn length refers to a freely jointed chain, l_K



$$R^2 = n_K l_K^2$$

iv) Persist bond length refers to a worm-like chain & describes the decay in orientational correlation $C(\Delta s)$,



$$2 l_p = l_K$$

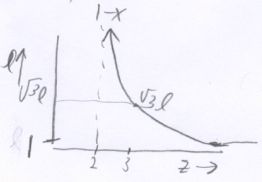
1) "C_∞" is intended to reflect SRI while "α" is intended to reflect LRI. Both were developed by Flory in the late 1950's to early 1960's. Then we expect that SRI will change C_∞ & C_∞ but will have no affect on α. This is because changes in l_K (Kuhn length) already affect $\langle r^2 \rangle_{Gaussian}$. There is little temperature dependence to l_K. On the other hand, C_∞ is a direct measure of the consequences of SRI and changes in l_K due to RISM & bond angle restrictions and the like.

b) $\sum_0^\infty x = A$

$A = 1 + xA$ so $1 = \frac{1}{A} + x$ or $\frac{1}{A} = 1 - x$

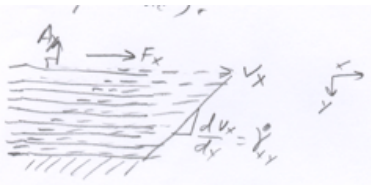
$\therefore A = \frac{1}{1-x}$

c) $\left(\frac{z}{z-2}\right)^{1/2} l = l_{eff}$



As z becomes larger the fraction of chains that are excluded become smaller so the affect on l_{eff} is smaller. With only 2 chains the walk is a ballistic walk (like a bullet) and the persistence is infinite (straight line).

2) a)



$$\tau_{xy} = \frac{dF_x}{dA_y} = \eta \dot{\gamma}_{xy}$$

b) $\eta_{solution} = \eta_0 \left(1 + [\eta]_{solvent} c + A_3 c^2 + A_4 c^3 \ldots\right)$

(A_1: first power of c; A_2, A_3, A_4: for dilute)

For dilute conditions higher orders in c go to 0.
It is first order because c is to the power "1".

c) $[\eta] = \frac{R_H^2}{z}$ ← Mass

using a fractal law $R_f \sim z$

$[\eta] = R_H^{3-d_f} = z^{3/d_f - 1}$

object	d_f	$R_H^{3-d_f}$	z^{3/d_f-1}
sphere	3	$R_H^0 = 1$	$z^0 = 1$
rod	1	R_H^2	z^2
coil	2	R_H^1	$z^{0.5}$

a) $\int_{r=0}^{R}\int_{-H}^{H} 2\pi r (r^2 + y^2)\, dr\, dy = 2\pi \int_{-H}^{H} \left[\frac{r^4}{4} + \frac{r^2 y^2}{2}\right]_0^R dy$

$= \pi \int_{-H}^{H} \left[\frac{R^4}{2} + \frac{R^2 y^2}{2}\right] dy$

$= \pi \left[\frac{R^4 y}{2} + \frac{R^2 y^3}{3}\right]_{-H}^{H}$

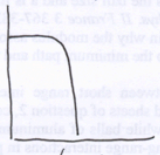
$= \pi \left(R^4 H + \frac{2R^2 H^3}{3}\right)$

$\int_{r=0}^{R}\int_{-H}^{H} 2\pi r\, dr\, dy = 2\pi R^2 H$

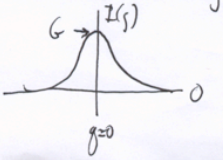
$R_g^2 = \frac{\int_V (r^2 + y^2)\, dr\, dy}{\int_V dr\, dy} = \frac{R^2}{2} + \frac{H^2}{3}$

b) Guinier's law

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

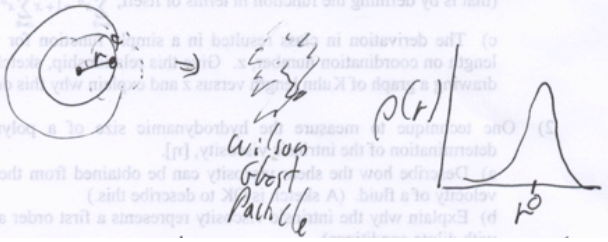


c) Guinier's law is a gaussian distribution about $q = 0$



The Fourier Transform of a gaussian is another gaussian so the correlation function is a Gaussian

The Gaussian correlation function is related to the Wilson Ghost particle. For any structure we can depict the probability of 2 points separated by a distance "r" being in the particle by rotating the particle about any point in the particle so that a probability density cloud is created whose density distribution function is a Gaussian for any object.



3) a) $\frac{P}{KT} = C + B_2 C^2 + \cdots$

Virial expansion

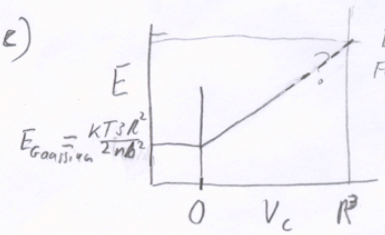
B_2 is the excluded volume per gas atom

Since this accounts for hard core interactions

$B_2 = 4V_0$ for spheres

b) $E = KT\left(\frac{3}{2}\frac{R^2}{Nb^2} + \frac{V_c N^2}{R^3 2}\right)$

c)



$E = KT\left(\frac{3}{2}\frac{R^2}{Nb^2} + \frac{N^2}{2}\right)$

Function fails at large V_c since it assumes $\frac{V_c}{R^3}$ is small in the derivation.

V_c is a measure of energy (enthalpy)

When $V_c = 0$ the chain is wholly entropic; Enthalpy $= 0$

2) a) $E = KT\left(\frac{3R^2}{2nl^2} + \frac{N^2}{2}\frac{V_0}{R^3}(1-2\chi)\right)$

$\chi = \frac{2A\sqrt{\varepsilon}}{KT}$

b) $F = \frac{dE}{dR} = \left(\frac{3kT}{nl^2}\right)R$ For Gaussian

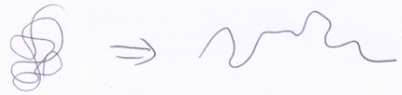
$K_{spring} = \left(\frac{3kT}{nl^2}\right)$

SAW

$F = \frac{dE}{dR} = KT\left(\frac{3}{nl^2} - \frac{3N^2}{2}\frac{V_0(1-2\chi)}{R5}\right)R$

c) Smaller with larger R & smaller as T drops.

as R increases self-overlap becomes less likely

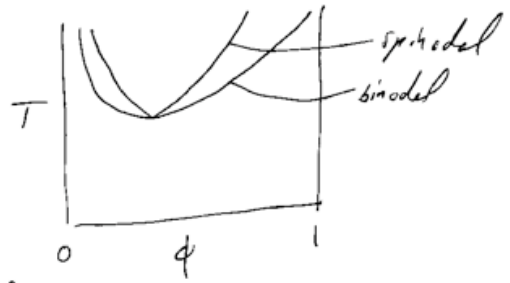


so the excluded volume term becomes less important.

Similarly, as T drops $(\tfrac{1}{2}-\chi) \Rightarrow 0$

& the chain appears to lose self-avoidance & excluded volume.

1) a) for a mixture the cloud point is the temperature where the system first phase separates with rising (UCST) or decreasing (LCST) temperatures. It refers to the binodal point.



b) The binodal occurs when $\frac{df}{d\phi} = 0$

We use the Flory Huggins Equation

$$f = \frac{\phi \ln\phi}{N} + (1-\phi)\ln(1-\phi) + \phi(1-\phi)\chi$$

$$\frac{df}{d\phi} = \frac{\ln\phi}{N} + \frac{1}{N} + \frac{1}{\phi} - \ln(1-\phi) + 1 + \chi - 2\phi\chi \equiv 0$$

if you know ϕ & N you can solve for χ

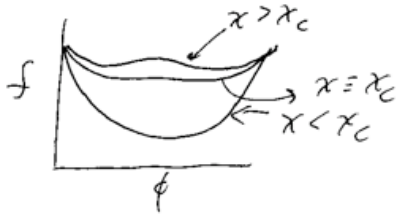
c) $\chi = A - \frac{B}{T}$ because this is an LCST system.

As $T \uparrow$ χ is positive & larger than $\left(\frac{\phi \ln\phi}{N} + (1-\phi)\ln(1-\phi)\right)$

As $T \downarrow$ χ is less than this term due to "A"

(3) a)

A plot of the Flory Huggins equation in free energy space



fluctuations in composition picks those curves where $\pm\Delta\phi = -\Delta\phi$ so $\langle\phi\rangle$ remains the same. At the critical χ there is no difference in f for different ϕ so there is no preference for

which fluctuations are stable & fluctuations of all sites & compositions are possible. Here is no driving force to form fluctuations so the kinetics (rate) of phase separation goes to 0. This is called "critical slowing-down"

(b)

	General	Gasses $N_A = N_B = 1$	Polymer Sol'n $N_A \neq N_B = 1$	Symmetric Polymer Blend $N_A = N_B = N$
ϕ_{Ac}	$\frac{\sqrt{N_B}}{\sqrt{N_B}+\sqrt{N_A}}$	$\frac{1}{2}$	$\frac{1}{1+\sqrt{N_A}} \sim \frac{1}{\sqrt{N_A}}$	$\frac{1}{2}$
χ_c	$\frac{1}{2}\left(\frac{1}{\sqrt{N_A}}+\frac{1}{\sqrt{N_B}}\right)^2$	2	$\frac{1}{2}\left(\frac{1}{\sqrt{N_A}}+1\right)^2 \sim \frac{1}{2}$	$\frac{2}{N}$

(c)

$$f = \underbrace{\frac{\phi \ln \phi}{N_A} + \frac{(1-\phi)\ln(1-\phi)}{N_B}}_{\text{Entropy}} + \underbrace{\phi(1-\phi)\chi}_{\text{Positive}}$$

(Negative, Negative)

Entropy
Favors Miscibility
Negative Term
High Molecular Weight Makes This Term Small

Enthalpy
Favors Phase Separation
Positive Term
No Molecular Weight Dependence