060428 Quiz 5 Polymer Properties

A polymer coil can accommodate to changing thermodynamic conditions because it is a molecule which spans several orders of size. Thermodynamic conditions on a small scale can differ from conditions at a large scale. This concept is the basis for the definition of a "blob".

1) a) Define a "blob".

b) Give the temperature dependence of the *thermal* blob for a polymer coil.

c) How can this temperature dependence describe structural changes that occur to a polymer in dilute solution? (Discuss these structural changes perhaps using scattering curves or using schematic magnification of the structure)

d) Sketch the dependence of R_g and R_H on temperature.

e) Is the concept of a thermal blob needed to explain this dependence?

2) The Flory-Krigbaum model is based on the concept of excluded volume.

a) For an ideal gas what is the excluded volume?

b) A Gaussian chain is sometimes called an ideal chain or ideal coil. Explain why this term might be used.

c) Why would you expect enthalpy to play a role in excluded volume? (Give an example of what enthalpy is in a model system and how it could effect excluded volume.)

d) Give the Flory-Krigbaum expression for excluded volume. And sketch a plot of excluded volume versus temperature.

e) Explain the logic of the equation in part "d" by considering the limits in temperature.

3) In addition to the thermal blob we began to discuss the concentration blob in class. The concentration blob involves a fundamental feature of interacting systems as their concentration is increased; termed "screening" by Debye in his book "Polar Molecules" (cited in his Nobel Prize).

a) Consider a human interaction such as a mother and child who are separated but enthalpically attracted in a large hall by the "*enthalpy of maternal instinct*". How will this interaction be effected if a large number of similar mothers and children are crowded into the same hall?

b) As the population density increases in the hall can you think of a characteristic distance or length-scale vital to the mother and child that changes with population density?

c) Last week's quiz considered pairwise interactions briefly. Explain how the concept of pairwise interactions might be important to the depiction of "screening" in question "a"? Comment on this.

d) In a crystal, enthalpic interactions are strong but screening of binary (pairwise) enthalpic interactions is not seen. Explain in your own words (guess) why this might be the case.

e) Consider a polymer solution. At what concentration would you expect the coils to just begin interpenetration? Write an expression for this concentration (mass/volume) using only the molar mass N and the coil size R_F.

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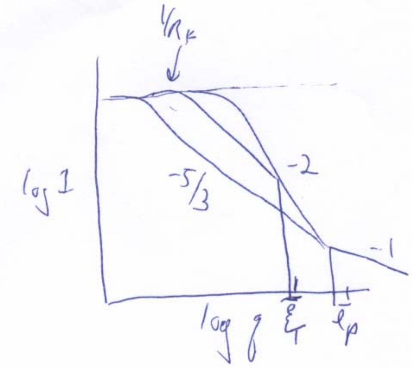
1) a) A blob is a size scale associated with a change in structural scaling. It is used to renormalize a chain structure.

b) $\xi_T = l_p/(1-2\chi) = l_p/(1-2z\Delta\varepsilon/kT)$

c)

(c)



As T drops χ approaches 1/2 $\xi_T \Rightarrow R_F$ & the coil becomes Gaussian. R_F drops. At High magnifications the coil appears Gaussian; at low magnifications it is a SAW.

d)

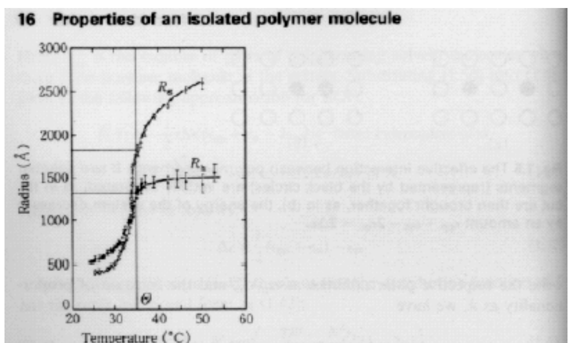


Fig. 1.6 The coil–globule transition in a solution of polystyrene in cyclohexane. The radius of gyration R_g and the hydrodynamic radius R_h of the polymer show a dramatic change as temperature passes through the Θ temperature. The hydrodynamic radius R_h is defined by $R_h = k_B T/6\pi\eta D$, where D is the diffusion constant of the polymer and η is the viscosity of the solvent. (Sun, S.T., Nishio, I., Swislow, G., and Tanaka, T. (1980). *J. Chem. Phys.*, 73, 5971, Fig.2.)

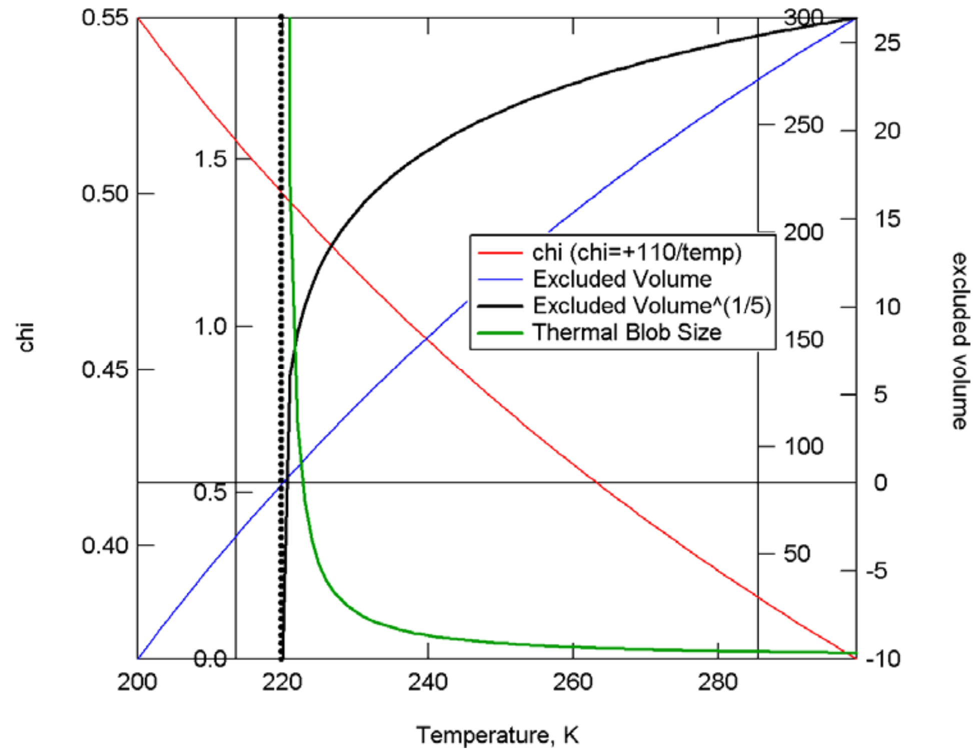
e) No, the dependence can be shown just using the Flory-Krigbaum function. The thermal blob model is needed to explain the structural meaning of the Flory-Krigbaum function.

2) a) An ideal gas is composed of molecules of no volume so there is no excluded volume.

b) A Gaussian chain is called an ideal chain in analogy to an ideal gas since a Gaussian chain displays no excluded volume.

c) Enthalpy involves binary interactions between molecules in a system. The simplest binary interaction involves the volume that is excluded from one molecule by the presence of another. More complicated interactions might involve bonding, electrostatic charge forces, and van der Waals and London forces. There is little or no distinction between the kind of ineraction involved in excluded volume and the kind of interaction involved in enthalpy.

d) $V = V_0(1-2\chi)$



e) As temperature drops the excluded volume decreases until it is 0 at the theta temperature (about 220 K above). At high temperature the excluded volume gradually approaches V_0.

3) a) The interaction is effected in terms of the spatial distance over which it can have an effect. Crowding makes the attraction only effective at short distances. The higher the crowding the shorter the distance over which the attraction is functional. The strength of the attraction is not effected.

b) The length at which the child is first "lost" is analogous to the screening length. This length becomes smaller with higher concentration.

c) The pairwise distribution function considers the probability that given you are at one of a pair, what is the probability of finding the other of the pair at a distance "r". This function is plotted as a function of "r", the separation distance and it is a mean value over all beginning points and over all ending points a distance "r" away. Attractive interactions would lead to a shift of the pairwise distribution function to higher values at smaller "r". Screening would lead to a characteristic shift of this function, reducing the value especially at intermediate "r". No attraction would be seen beyond r = the screening length.

d) In a crystal the binary units are held in position enthalpically and are at closest approach. The presence of screening apparently relies on thermal Brownian motion of the binary pair.

e) The overlap concentration $c^* = N/R_F^3$.