

Question 1 (4p)

When deriving the conformational entropy as function of end to end distance r for a theoretical freely jointed chain one gets the expression:

$$S(r) = \text{constant} - \frac{3k_B r^2}{2Na^2}$$

If a is the physical length of a monomer and N is degree of polymerization, why is this not an accurate model? What is the next step to get an accurate model and which parameter is introduced?

The model is not sufficient because a monomer does not behave as a freely jointed chain segment. The next step is to introduce Kuhn length b instead of a and change N to number of Kuhn steps aN/b , which gives:

$$S(r) = \text{constant} - \frac{3k_B r^2}{2abN}$$

Question 2 (4p)

An alternative way to write the Flory radius is:

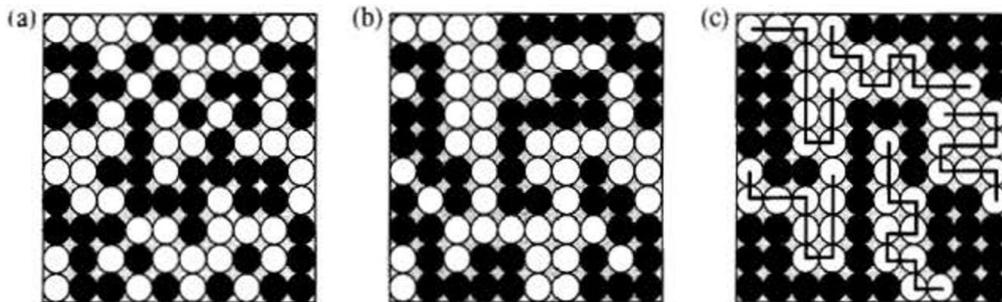
$$R_F = [abv[1 - \chi]]^{1/5} N^{3/5}$$

What does the χ parameter represent? What is the physical meaning of $\chi = 1$ and what is this state called?

The χ parameter represents energetic interactions with the surrounding solvent molecules. When $\chi = 1$ the interaction energies perfectly compensate the excluded volume entropy, which gives a random walk behavior ($R \propto N^{1/2}$). This is the theta solvent condition.

Question 3 (4p)

Why is it hard to mix polymers with each other (even when they are not glassy or crystalline)? Explain with help of this drawing if you prefer:



The configurational entropy of mixing is reduced due to restrictions from the fact that monomers in a chain must be neighboring. The white and black balls illustrate this. In (a) both are monomers, in (b) the black ones are connected and in (c) they are both connected chains, which leads to much fewer possible configurations on the lattice.

Question 3 (3p)

Sketch the stress relaxation of two polymer melts with different molecular weights. (An instant strain event occurs at time zero.)

