Introduction to Macromolecular Physics

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Homework 4

Polymer Solutions and Blends

We consider here the Flory-Huggis theory for polymer solutions and blends. The internal energy for a solution of a polymer (chains of N_1 segments) in a low molecular weight solvent (monomer concentration Φ) and for a blend of two polymers with monomer concentrations Φ and $1-\Phi$ (chain lengths N_1 and $N_2 < N_1$) is given in a lattice model by the same expression. The forms of the entropy however differ.

- Give the expressions for the free energy of the solution and of the blend.
- Derive the equations for spinodals on a (Φ, χ) plane for both cases and sketch the corresponding curves for the case $N_1 = 10000$ and $N_2 = 100$.
- Determine the position of a critical point for the blend.

Single Molecule in a Solvent

To describe the behavior of a single molecule in a dilute polymer solution we use the following approach based on a lattice model. The space within the size (end-to-end distance) R of the molecule of length N is considered to contain $N_0 = R^3/a^3$ lattice sites. We take this space to be homogeneously filled by monomers at concentration $\Phi = Na^3/R^3$. The internal energy in this system is calculated in the way parallel to a Flory-Huggins approach.

- Find the expression for the internal energy in this model.

The entropic contribution consists of the translational entropy of solvent molecules, $S_s = k_B N_0 (1-\Phi)\ln(1-\Phi)$ and the entropy S_c of the swollen (shrunk) chain which is put into the form $S_c = S_{c,0} - k_B(\alpha^2 + \alpha^{-2})$ with the swelling coefficient $\alpha = R/R_0 = R/(aN^{1/2})$.

- Find the expression for the free energy of the polymer. Show that it can be put down in the form $F = F_0 + k_B T(B\alpha^{-3} + C\alpha^{-6} + \alpha^2 + \alpha^{-2})$.
- Find the expressions for the coefficients B and C.
- Discuss the case of a good solvent and find an approximate dependence of the size of the molecule R on the Flory parameter χ.