Chemical physics of polymer solutions

Exercise 5

15 December 2003

A polyelectrolyte is a polymer whose monomers may be charged. Consider a polyelectrolyte chain consisting of N monomers of length a, an average fraction φ of which are monovalently charged.

- 1. Apply the Flory argument to write down the free energy of the chain. Note that the electrostatic interaction is long-ranged and, hence, we cannot use the virial expansion to describe it. Instead, recall that the energy associated with a charged object of size R (e.g., a charged sphere of radius R) is $\sim Q^2/(\varepsilon R)$, where Q is the total charge of the object and ε the dielectric constant of the medium.
- 2. Calculate the equilibrium extent of the chain, R, as a function of N, φ , and a.
- 3. What is the value of the swelling exponent ν and the dimensionality D? What is the meaning of this result?

Remark: In real polyelectrolyte solutions there are always mobile ions that screen electrostatic interactions beyond a certain screening length λ . The result that you have obtained is valid, therefore, only as long as $R < \lambda$.