

# Homework 14

## Scaling Theory of Polyelectrolytes<sup>1</sup>

In many experimental situations, when polymers are embedded in solutions they release some ionic groups, which can then wander throughout the solution. Naturally, the polymers themselves acquire in this way a net charge of opposite sign, thus ensuring a net electroneutrality for the solution. In this exercise we are going to see with some blob arguments how electrostatics changes the behavior of polymers.

As we saw in Homework 12, the electrostatic energy stored in a region increases with the size, and at small length scales we expect entropic effects to dominate over interaction. Let us consider an ideal polymer made of  $N$  segments of size  $b$  put in a solution with a concentration  $c$  of counterions (obtained e.g. by the dissociation of some chemical groups of the polymer itself and by putting salt into the solution), and that each monomer carries  $f$  elementary charges of the same sign (let's say positive).

1. According to what we said above at small length scales entropy dominates, so that usual polymer statistics is expected to hold in that case. What is the size  $D_e$  of a blob as a function of  $f$  and  $u \equiv l_B/b$  ( $l_B$  is the Bjerrum length)? Assume counterions to play a negligible role at this scale.
2. At length scales larger than  $D_e$  but lower than the Debye length  $l_D$ , electrostatics completely dominates the scene, so that the polymer takes the conformation which minimizes the interaction energy. What is it? How many monomers are there inside a Debye length?
3. By putting together all the previous results, show that the end-to-end distance  $R$  changes with concentration as  $R \propto c^{-1/5}$ .

Congratulations! You have quantitatively explained the experimental data found by Beer *et al.*<sup>2</sup> for the behavior of the radius of gyration of a synthetic polymer as a function of salt concentration! (Turn page)

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<sup>1</sup>De Gennes *et al.*, J. Phys. (Paris) 37,1461 (1976); Barrat and Joanny, Europhys. Lett. 24, 333-338 (1993); Dobrynin and Rubinstein, Prog. Polym. Sci. vol 30, 1049-1118 (2005)

<sup>2</sup>Beer *et al.*, Macromolecules 30, 8375-8385 (1997)

