Homework 13

Scaling Theory of Polyelectrolytes[1]

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 11, 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. Because of the screening of counterions, at length scales larger than l_D electrostatics again plays a secondary role, so that entropy wins again. However, this late statement is true only if the "Debye blobs" do not overlap. What is the correct polymer statistics followed by the polyelectrolyte at such scales?

   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.*[2] for the behavior of the radius of gyration of a syntethic polymer as a function of salt concentration! (Turn page)

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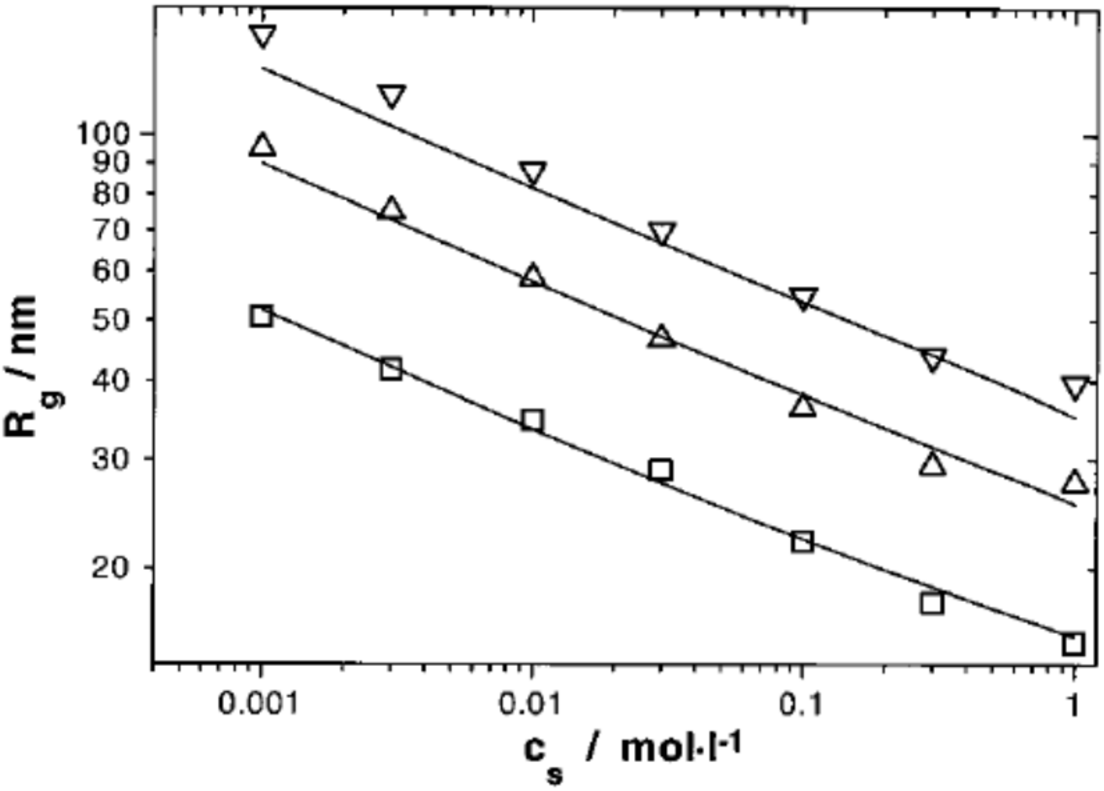
[1] De Gennes et al., J. Phys. (Paris) 37,1461 (1976); Barrat and Joanny, Europhys. Lett. 24, 333-338 (1993);Dobrynin and Rubinstein, Prog. Polym. Sci. vol 30, 1049-1118 (2005)

[2] Beer et al., Macromolecules 30, 8375-8385 (1997)



R_g / nm
100
90
80
70
60
50
40
30
20
0.001
0.01
0.1
1
c_s / mol·l^{-1}