

POLYELECTROLYTE SOLUTIONS BETWEEN TWO CHARGED SURFACES

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We investigate the distribution of polyelectrolytes in solution between two charged walls. Such a situation arises, for example, in colloidal suspensions where the polyelectrolytes affect both the aggregation and the stability of the colloidal particles. We consider the case of a good solvent, i.e. in the presence of excluded volume interactions among the monomers. The system is confined between two infinite flat charged walls, making the problem effectively one dimensional. The polyelectrolytes are weakly charged, and several models for the charge distribution are considered. We use a mean field approach to derive two coupled differential equations: a modified *Poisson-Boltzmann* equation for the electrostatic potential, and a *self consistent field* equation for the polymer concentration. The equations are solved numerically. As an example we present a case of competing surface interactions: electrostatic attraction vs. chemical repulsion resulting in a non-monotonic concentration profile. We discuss also the difference between a polymer with a uniform “smeared” charge and one in which the charges are annealed and can redistribute themselves at thermodynamical equilibrium.

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We consider an aqueous solution containing charged polymers (*polyelectrolytes*) and small ions (electrolyte) between charged surfaces (Fig. 1). The polymers are positively charged, while the surfaces can be either positive or negative. In addition to electrostatic interactions, we consider excluded volume repulsion between the monomers, and short range (chemical) interactions of the monomers with the surfaces, which can be either attractive or repulsive.

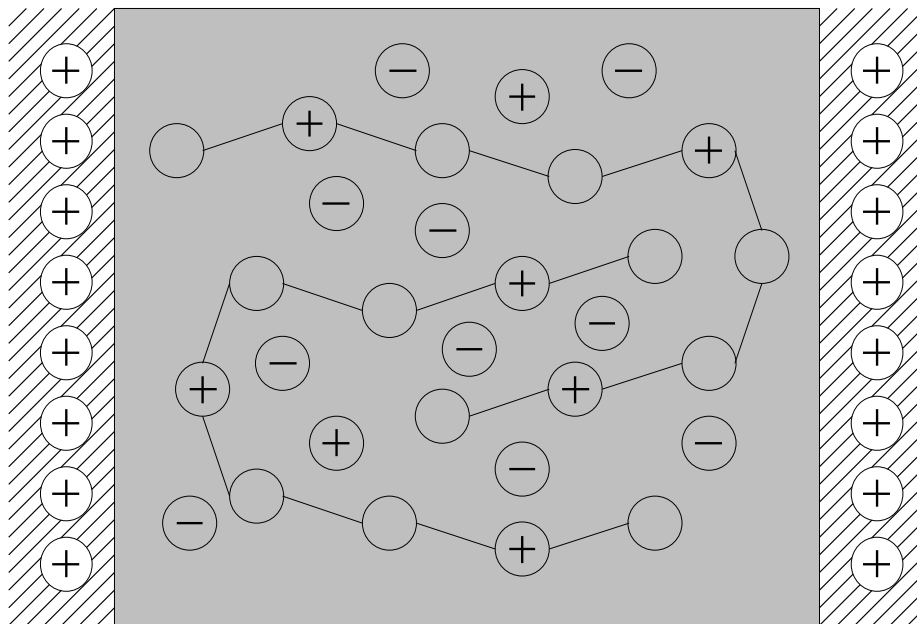


Figure 1: Schematic view of the system.

The motivation for such systems comes from two main sources. The first related system is a colloidal suspension [1, 2, 3], that is, solid particles immersed in an aqueous solution. Polymers may be added to the solution in order to modify the inter-colloidal forces. Some processes, such as waste water treatment and mineral processing, require attraction between the colloids, while other processes, such as ink and paint stabilization, require repulsion [3]. Another related system is a biological one in which proteins (charged macromolecules) affect the interactions between lipid bilayer (biological membranes).

The electrostatics of an *electrolyte* solution between two flat and charged surfaces has been investigated extensively in the frame work of the Gouy–Chapman theory [4], whose starting point is the Poisson–Boltzmann equation. On the other hand, the adsorption (depletion) of *neutral* polymers to (from) one surface and between two surfaces has been also investigated thoroughly, and good understanding was reached [5, 6, 7]. The combination of electrostatic interactions, together with the connectivity of the polymer chain [8], proves to be a complex problem due to the interplay between the short range “chemical” interactions, the polymer conformations (entropy) and the long range (though often screened) electrostatic interactions.

We describe the system in a mean field approach through the local electrostatic potential $\psi(\vec{r})$ and the polymer order parameter $\phi(\vec{r})$, related to, $\rho(\vec{r})$, the polymer concentration by $\rho(\vec{r}) = \phi^2(\vec{r})$ [10, 11, 12].

The electrostatic potential is determined by the *Poisson–Boltzmann equation*. For a monovalent electrolyte solution assumed here it can be written as:

$$\nabla^2\psi(\vec{r}) = -\frac{4\pi}{\varepsilon}q(\vec{r}) = \frac{8\pi e}{\varepsilon}c_b \sinh(\beta e\psi) \quad (1)$$

where $q(\vec{r})$ is the charge density determined by the Boltzmann distribution for ions in an electric potential $\psi(\vec{r})$; c_b is the bulk electrolyte concentration, $\beta = 1/k_B T$ where k_B is Boltzmann constant and T is the temperature; e is the elementary charge unit, and ε is the dielectric constant of the solution. Charged polymers and their counter-ions will appear as additional terms on the right hand side of equ. (1).

One way of deriving the Poisson–Boltzmann equation is by writing the free energy as a sum of the electrostatic and entropy of mixing contributions, and then performing a variational procedure [13, 14]. The advantage of this approach is that one can also add the polymer contribution to the free energy and perform the same variational procedure on the total free energy.

At the surfaces, the electrostatic boundary conditions are chosen as fixed surface charge density σ : $\psi'|_s = -\frac{4\pi}{\varepsilon}\sigma$. In a similar way, and depending on the system in mind, one can also choose fixed surface potential as the electrostatic boundary conditions. The effect of the surfaces is screened on a length scale of the Debye–Hückel screening length κ^{-1} (proportional to $1/c_b^{1/2}$), due to the presence of the electrolyte.

For a semidilute solution of polymers the local free energy of the system can be described by [11, 12]:

$$\beta f_{pol}(\vec{r}) = \frac{a^2}{6}|\nabla\phi|^2 + V(\phi^2) - \mu_p\phi^2 \quad (2)$$

The first term represents the connectivity of the polymer chains, where a is the effective length of one monomer and is roughly of the order of a few Angstroms. The second term represents the polymer interactions. It includes the electrostatic interaction as well as the excluded volume repulsion $\frac{1}{2}v\phi^4$, where $v > 0$ has units of volume and is the excluded volume parameter in good solvent conditions. The last term represents the contact of the system with a polymer reservoir and μ_p is the chemical potential of the polymers.

A variation of the free energy yields the *self consistent field* equation for *neutral* polymers:

$$\frac{a^2}{6}\nabla^2\phi(\vec{r}) = v(\phi^3 - \phi_b^2\phi) \quad (3)$$

where ϕ_b^2 is the bulk polymer concentration. The Edwards correlation length of neutral polymer solutions, as is apparent from equ. (3), is equal to $a/\sqrt{3v\phi_b^2}$ and characterizes the polymer concentration variations in the solution (e.g., close to the wall).

interaction of monomers with the surface:

$$\left. \frac{1}{\phi} \phi' \right|_s = \frac{1}{D} \quad (4)$$

The adsorption length D is inversely proportional to the strength of the surface interaction and is negative (positive) for attractive (repulsive) surfaces.

We return now to the problem of polyelectrolytes where all the contributions to electrostatic and polymer free energy are included. Details are given elsewhere [13, 14].

The contributions of the polymer charges are computed for three models:

- *Smearred*: The charges are uniformly distributed (hence the name “smearred”) over the polymer chains. Each monomer has a fractional charge equal to $p e$. In this case the contribution to the free energy is

$$f_{el}^{(s)} = p \phi^2 e \psi \quad (5)$$

- *Annealed*: Each monomer has a probability p to carry one elementary charge e (and $1 - p$ to be neutral). The monomers can ionize or de-ionize dynamically, and thus adjust to the local electrostatic potential [9]. Tracing over the monomer charge degrees of freedom in the partition function results in the following contribution to the free energy:

$$f_{el}^{(a)} = -k_B T \phi^2 \log(1 - p + p e^{-\beta e \psi}) \quad (6)$$

- *Quenched*: As in the annealed case, each monomer has a probability p to be charged. However, the distribution of the polymer charged is “frozen” (quenched). We will not further discuss here this more difficult case [14] but in many respects we expect this case to be intermediate between the smearred and the annealed cases.

From a variational procedure performed on the full free energy, two coupled equations for the electrostatic potential ψ and polymer order parameter ϕ can be obtained and will replace equ. (1) and equ. (3).

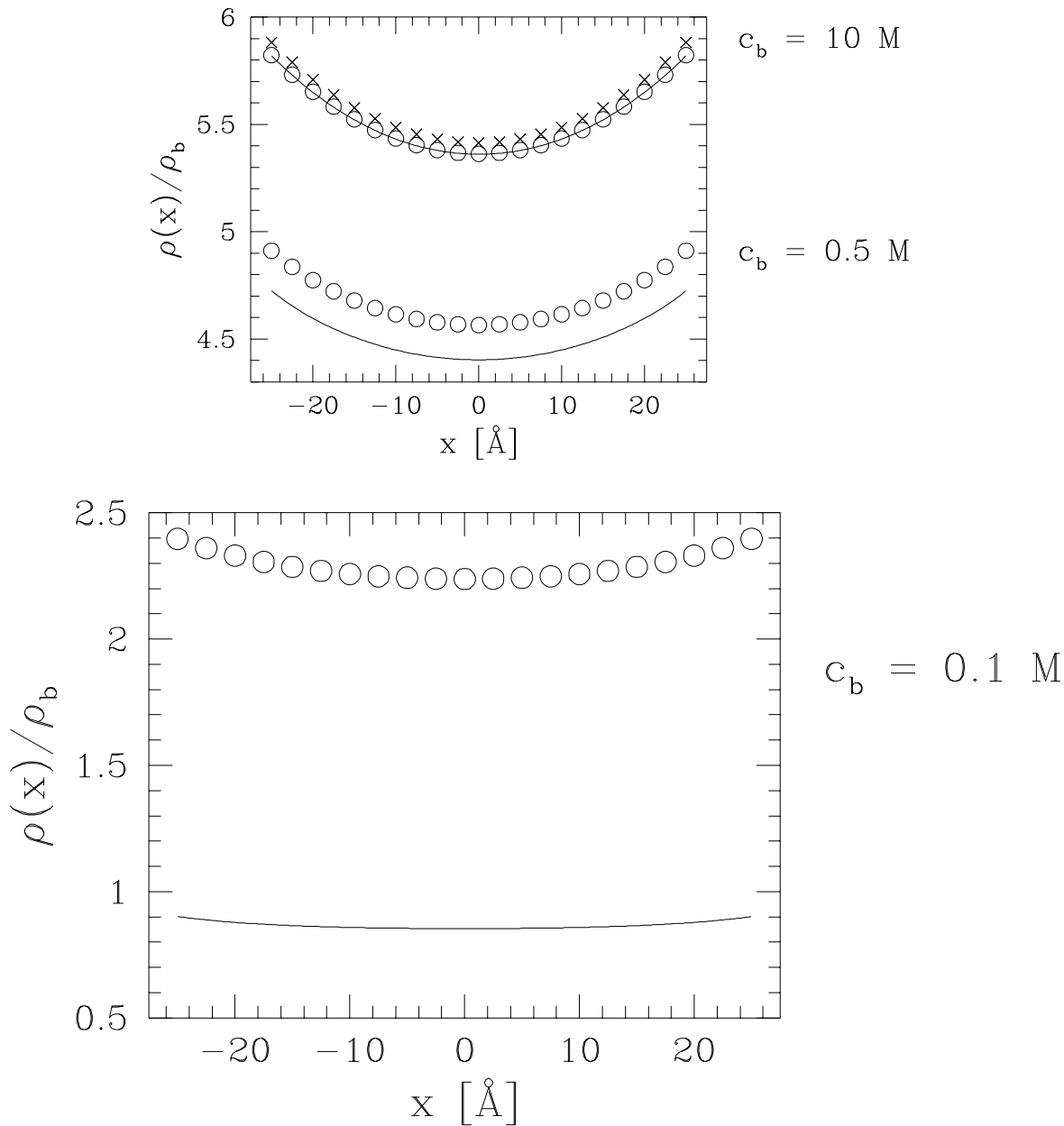
In the smearred case, for example, the Poisson–Boltzmann and the self consistent field equations are modified to become:

$$\nabla^2 \psi(\vec{r}) = \frac{8\pi e}{\varepsilon} c_b \sinh(\beta e \psi) - \frac{4\pi e}{\varepsilon} (p \phi^2 - p \phi_b^2 e^{\beta e \psi}) \quad (7)$$

$$\frac{a^2}{6} \nabla^2 \phi(\vec{r}) = v(\phi^3 - \phi_b^2 \phi) + p e \psi \phi \quad (8)$$

Similar equations have been derived for the quenched and annealed cases [14].

We present two numerical examples of polymer concentration profiles. As our model is effectively one dimensional, the only spatial coordinate left is the distance from the surfaces x whose origin is taken at the mid-plane between the two surfaces.



In the first example (Fig. 2) we compare the polymer concentration profiles of the smeared model (solid line) and annealed model (circles) for three salt concentrations measured in units of mole/litter [M]. The top two pairs of profiles in the figure correspond to high salt concentrations (strong electrostatic screening) while the bottom pair corresponds to a lower salt concentration (weaker electrostatic screening). Beside the three different values of c_b , all other phenomenological parameters used to evaluate the profiles are the same (their values are given

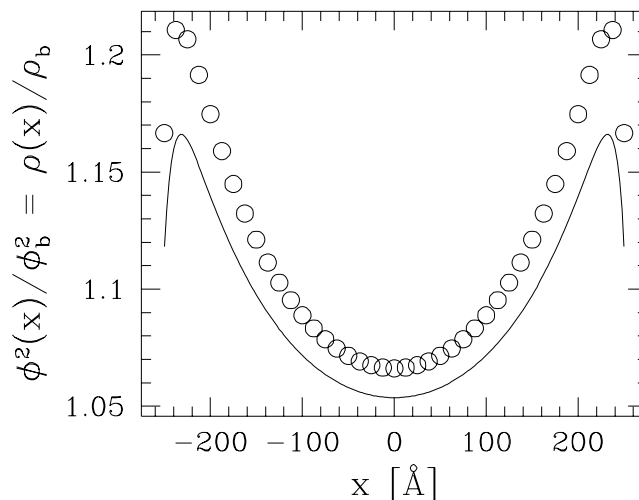
polymers with the same adsorption characteristics but which, obviously, is independent of the salt concentration, c_b .

The parameters of Fig. 2 are chosen such that the electrostatic potential is affected only in a negligible way by the presence of polymers [13]. This can be demonstrated by comparing the Debye–Hückel screening length, which varies between $1\ \bar{r}A$ and $10\bar{r}A$, to the Edwards correlation length q^{-1} .

The differences between the smeared and annealed models comes from the electrostatic contribution to the polymer part of the free energy (Sec. 2). At low charge density ($p \ll 1$) and low potentials ($\beta e\psi \ll 1$), one can expand the annealed free energy in powers of $\beta e\psi$:

$$f_{el}^{(a)} \approx k_B T p \phi^2 (\beta e\psi) - k_B T p \phi^2 (\beta e\psi)^2 = f_{el}^{(s)} - k_B T p \phi^2 (\beta e\psi)^2 \quad (9)$$

Note that the difference between the two free energies is second order in ψ and makes the annealed free energy *lower* than the smeared one. This can be understood simply by observing that the annealing of the polymer charges adds a new effective degree of freedom to the system. Those charge degrees of freedom can adjust according to the local electrostatic potential, and allow a better optimization of the free energy.



In the second example (Fig. 3) we show the result of a competition between short range (chemical) repulsive interactions ($D > 0$) and electrostatic attractive interactions (negative surface charge). We observe a depletion layer near the surface, whereas at larger distances the surface induces an effective adsorption. In this case too, the model parameters have been chosen in such a way so that the electrostatic profile is barely affected by the presence of charged polymers.

Since the difference between the smeared and annealed models is only minor (see Fig. 3), we can consider the simpler smeared case. The polymer behavior can be understood by considering the one dimensional self consistent field equation, equ. (8):

$$\frac{a^2}{6} \phi''(x) = v(\phi^3 - \phi_b^2 \phi) + p e \psi \phi \quad (10)$$

should be accompanied by a change of sign in the right hand side of equ. (10). Near the surface the sign of the first derivative of the polymer concentration $\rho(x)$ (which is the same as the sign of the polymer order parameter $\phi(x)$) is determined through the Cahn boundary condition, equ. (5) by the sign of D . For a depletion case, $D > 0$ and $\phi'(x) > 0$ near the left surface. The electrostatic potential is negative at the negatively charged surface, and decays exponentially on a length scale of $\kappa^{-1} = 10 \bar{r} A$. *At short distances from the surface the electrostatic part dominates the right hand side of the equation. In the limit of large distances the electrostatic part is screened and the right hand side of the equation is dominated by the depletion term. At short distances from the surface the first derivative is zero due to the symmetry of the two surfaces. If the distance between the two surfaces is large compared to the Debye length the electrostatic part is screened and the right hand side of the equation is dominated by the depletion term.*

4 Conclusions

In this work, we have investigated concentration profiles of charged polymer chains between two surfaces. We have introduced three models for the charge distribution along the chain. The simplified smeared model is used extensively in the literature as it is easier to handle analytically, but the annealed and quenched models provide a more realistic description of experimental systems. At low electrostatic potentials ($\beta e \psi \ll 1$) the smeared model provides a good approximation for the annealed model. However, at high electrostatic potentials the difference between the models become significant (see Fig. 2) and should be taken into account. Generally speaking, the annealed charges are less sensitive to the electrostatic conditions, as they can redistribute themselves over the chains according to the local electrostatic potential. The quenched model is considered in more detail elsewhere [14].

We have also investigated the interplay between electrostatic and other interactions such as excluded volume effects in the bulk and short-range interactions between the polymers and the surfaces. In particular, the effect of competing repulsive short-ranged interactions vs. attractive electrostatic interactions has been explored (Fig. 3). We have also seen that further away from the wall the electrostatic interactions dominate as long as they are not screened.

Some possible future directions of research can follow the present study. For example, the osmotic pressure between the two surfaces can be calculated [14] from the local free energy as was done for neutral polymers [6], and compared with experiments. One might also want to extend this work to non-flat geometries, in order to improve the modeling of polyelectrolyte adsorption on colloidal particles. We have considered here fixed surface charge densities, having in mind charged colloids or surfaces. One can also consider situations where the surface potential is externally fixed and induces a variable surface charge density. Finally, it will be interesting to look at polyelectrolyte solutions in a potential gradient (e.g., electrophoresis or electro-osmosis).

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