Polyelectrolyte Solutions between Charged Surfaces.

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Abstract. – The effect of electrostatic interactions on the distribution of polymers in a good solvent is investigated for semi-dilute solutions containing charged polymers (polyelectrolytes) and small ions. A *mean field* approach is used to derive two coupled differential equations: a modified *Poisson-Boltzmann* equation for the electrostatic potential, and a *self-consistent field* equation for the polymer order parameter. We compare several monomer charge distributions: smeared, annealed and quenched. The polymers are confined between two charged surfaces, and are in contact with a reservoir of polymers and electrolyte. This makes the annealed and quenched cases equivalent. Non-monotonous profiles are obtained for the case of competing surface interactions: electrostatic adsorption *vs.* short-range desorption.

The motivation for studying the behaviour of polyelectrolyte solutions between charged surfaces stems from at least two sources. On the one hand, the presence of polymers (in many cases charged) in a solution has a prominent effect on the stability of colloidal suspensions[1,2]. Industrial applications range from stabilization of ink and paint to waste water treatment and paper making[3]. On the other hand, the presence of proteins and other partially charged biopolymers in the intercellular fluid (aqueous solution) affects the interactions between adjacent membranes[4].

Our model system consists of weakly (positively) charged polymers and small ions in a good solvent between two parallel and uniformly charged surfaces. The small ions are of three kinds: (negative) counter-ions and a 1:1 electrolyte composed of (positive) co-ions and (negative) counter-ions. We take all the counter-ions to be identical, but this assumption does not affect the results.

The system can be viewed as a combination of two coupled problems[5,6]. The first

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consists of an electrolyte solution between two charged surfaces and was investigated extensively in the framework of the Gouy-Chapman theory[7], extending from the *Poisson-Boltzmann* equation. The second consists of adsorption (or depletion) of neutral polymers immersed in solution between two walls. This problem was investigated for the last twenty years, and good understanding was reached[8,9].

One approach to treat the full polyelectrolyte problem is the *multi-Stern-layer model* [10], in which the spacing between the two surfaces is divided into parallel and discrete lattice layers. A set of discrete self-consistent equations are then solved numerically, *e.g.* by iterations. Another approach used in the present work is a self-consistent mean field[5], where continuous and spatially varying functions such as the electrostatic potential are used to describe the free energy of the system. The thermodynamic equilibrium of the system is then determined by a set of differential equations obtained using a variational principle.

Taking the monomer concentration $\varrho_m(r)$, the ion concentrations $c^+(r)$ and $c^-(r)$, and the electrostatic potential $\psi(r)$ as continuous and local functions of the position, and assuming ground-state dominance[11,12], the monomer concentration $\varrho_m(r)$ is replaced by the so-called *polymer order parameter* $\phi(r)$, where $|\phi(r)|^2 = \varrho_m(r)$. The system is in contact with a reservoir of polymers and electrolyte characterized by their respective bulk values: ϕ_b, c_b^+, c_b^-. The bulk value of the electric potential is set to zero ($\psi_b \equiv 0$).

We limit ourselves to weakly charged polymers, for which the chains remain flexible. Three types of charge distribution (for the polymer) are considered: i) *Smeared*: the charge is distributed uniformly along the chain. Each monomer carries a fractional charge equal to pe where e is the elementary charge unit and $p \ll 1$. ii) *Annealed*: each monomer can acquire one elementary charge with a *nominal* probability p. However, the *effective* charge configuration can change dynamically as it depends on the local electric potential at equilibrium. Experimentally, the annealed case can be realized by synthesizing weak acidic (or basic) polymers. The pH of the solution controls the dissociation of ions from the polymer[13]. iii) *Quenched*: each monomer can have one elementary charge with a fixed (quenched) probability p. Here, the charge configuration is frozen in contrast with the annealed case. The quenched case can be obtained experimentally by synthesizing a random heteropolymer from charged and uncharged monomers[13]. However, as was previously noted[14], the reservoir allows the system to choose only those chains with charge distribution best adapted to the local potential. In this sense it is equivalent to the annealed case, and indeed a detailed calculation verifies this conclusion[15]. The dynamics of reaching this state might be different, but, as we consider only equilibrium properties, we will treat only the smeared and annealed cases.

In the smeared case the excess free energy with respect to the bulk is an integral over space of the free-energy density: $f(r) = f_{pol}(r) + f_{ent}(r) + f_{el}(r)$, where

$$f_{pol}(r) = k_B T \left[\frac{a^2}{6} |\nabla\phi|^2 + \frac{1}{2} v(\phi^4 - \phi_b^4) \right] - \mu_p(\phi^2 - \phi_b^2), \qquad (1)$$

$$f_{ent}(r) = \sum_{i=\pm} k_B T [c^i \log(c^i) - c^i - c_b^i \log(c_b^i) + c_b^i] - \mu^i(c^i - c_b^i), \qquad (2)$$

$$f_{el}(r) = pe\phi^2\psi + ec^+\psi - ec^-\psi - \frac{\varepsilon}{8\pi} |\nabla\psi|^2 . \qquad (3)$$

The free energy $f_{pol}(r)$ is the contribution of the semi-dilute polymer solution in good-solvent conditions [12]. It includes a chain elasticity term, where a is the Kuhn step length and $k_B T$ is the thermal energy, and an excluded-volume interaction term v (with units of a volume). The last term represents the coupling with the polymer reservoir, μ_p being the chemical potential

of the polymer. The entropic contribution of the small ions is represented by $f_{ent}(r)$. It includes the change in the entropy of the ions with respect to the bulk, and the chemical potential μ^i of the i-type ion. Finally, f_{el} is the electrostatic energy of the system. The first three terms are the interaction energies of the charges with the local electric field, while the last term represents the self-energy of the electric field, where ε is the dielectric constant of the solution.

Using the variational principle on the smeared free energy, eqs. (1)-(3), with respect to ϕ, $c^\pm$ and ψ: $\delta f/\delta\phi = \delta f/\delta c^\pm = \delta f/\delta\psi = 0$, we obtain four equations. Using, in addition, the charge neutrality condition leads to

$$\frac{a^2}{6}\nabla^2\phi(r) = v(\phi^3 - \phi_b^2\phi) + p\phi\beta e\psi\,, \tag{4}$$

$$\nabla^2\psi(r) = \frac{8\pi e}{\varepsilon}c_b\sinh(\beta e\psi) - \frac{4\pi e}{\varepsilon}(p\phi^2 - p\phi_b^2\exp[\beta e\psi])\,, \tag{5}$$

where the ion distributions are given by the Boltzmann factors: $c^+ = c_b\exp[-\beta e\psi]$ and $c^- = (c_b + p\phi_b^2)\exp[\beta e\psi]$. Equation (4) is the *self-consistent field* equation in the presence of an external electrostatic potential, and eq. (5) is the Poisson-Boltzmann equation with the charged polymer as an additional charge carrier. Similar equations applied only for smeared charges were introduced previously without the excluded-volume term [5,10].

We turn now to the annealed case where one has to average the partition function over all charge configurations. As a result, the above two equations become

$$\frac{a^2}{6}\nabla^2\phi(r) = v(\phi^3 - \phi_b^2\phi) - \phi\log(1 - p + p\exp[-\beta e\psi])\,, \tag{6}$$

$$\nabla^2\psi(r) = \frac{8\pi e}{\varepsilon}c_b\sinh(\beta e\psi) - \frac{4\pi e}{\varepsilon}(p_a\phi^2 - p\phi_b^2\exp[\beta e\psi])\,, \tag{7}$$

where $p_a = p\exp[-\beta e\psi]/(1 - p + p\exp[-\beta e\psi])$ can be interpreted as a Boltzmann weighted-charge probability. Note that in the limit of low charge probability ($p \ll 1$) and low electrostatic potentials ($\beta e\psi \ll 1$), the annealed and smeared cases become identical.

The structure function $S(q)$ and its Fourier transform (the concentration fluctuation) have been calculated by several authors [16-19] using the random phase approximation (RPA). We would like to note that exactly the same expressions for $S(q)$ can also be obtained by linearizing eqs. (4), (5) around the bulk values [15].

The chosen boundary conditions consist of two flat uniformly charged parallel surfaces. We have chosen Neumann boundary condition where the surface charge density σ is given ([1]). The electrostatic boundary condition is $\hat{n}\cdot\nabla\psi|_s = -4\pi\sigma/\varepsilon$, where $\hat{n}$ is the normal to the surface. To model the polymer surface adsorption we use the Cahn boundary condition [8]: $(\hat{n}\cdot\nabla\phi)/\phi|_s = 1/D$, where D is the polymer adsorption length inversely proportional to the strength of the short-range interaction of the monomer with the surface. D is negative (positive) for an attractive (repulsive) surface.

The set of differential equations (4), (5) or (6), (7) with their boundary conditions were solved numerically for, respectively, smeared and annealed cases. Several useful characteristic lengths can be defined in the problem: the Edwards correlation length $\xi =$

([1]) Alternatively, Dirichlet boundary condition where the surface potential ψ_s is fixed can be used.

Fig. 1. – The effect of competing surface and electrostatic interactions on the polymer concentration profile for the smeared (solid line) and annealed (filled circles) models. The monomers of size $a = 5$ Å and with $v = a^3 = 125$ Å^3 are positively charged with a fractional charge $p = 0.01$. The surfaces are negatively charged with a charge density of $-3000e/$Å^2, while the short-range repulsion is characterized by a desorption length $D = 20$ Å. All charges are monovalent, $T = 300$ K and $\varepsilon = 80$ (water). The distance between the plates is $d = 550$ Å. The electrostatic screening lengths are $\kappa_s^{-1} = = 44$ Å for the salt and $\kappa_p^{-1} = 106$ Å for the polymer. These values correspond to polymer and electrolyte bulk concentrations of $c_b = 5 \cdot 10^{-3}$ M and $\phi_b^2 = 10^{-6}$ Å^{-3}, respectively. The polymer correlation length is $\xi = 260$ Å. The electrostatic potential decays roughly in an exponential manner from its surface value ($\beta e \psi_s \approx -1$) towards its mid-plane value. The inset shows the neutral monomer concentration profile, with the same surface interaction. Note the high values of polymer adsorption in the charged cases vs. the neutral one (inset). The dashed horizontal line corresponds to the bulk polymer value.

$= a/\sqrt{3v\phi_b^2}$ for neutral polymers; the Debye-Hückel screening length $\kappa_s^{-1} = (\varepsilon k_B T/8\pi e^2 c_b)^{1/2}$ coming from the screening by the salt and, similarly, $\kappa_p^{-1} = (\varepsilon k_B T/4\pi e^2 \phi_b^2)^{1/2}$ which depends on the bulk concentration of the (charged) polymers. Two other lengths are the surface separation d and the adsorption length D. At high polymer (salt) concentration $\xi(\kappa^{-1})$ decreases, thus limiting the range of the polymer (electrostatic) interaction. A strong coupling of polymer and electrostatic effects is expected when the two length scales are of similar range. In addition, the two surfaces will interact strongly when the inter-surface distance is less than or of the same order of magnitude as the screening lengths.

Since we do not consider any inhomogeneities in the directions parallel to the surface, the only relevant spatial coordinate is the distance from the surfaces, x, whose origin is taken at the mid-plane between the two surfaces.

In fig. 1 we present an interesting case of competing surface interactions: short-range repulsion ($D > 0$) vs. electrostatic attraction (negative surface charge). We compare the reduced monomer concentration profiles $u^2(x) \equiv \phi^2(x)/\phi_b^2$ for the smeared case (solid line) and annealed case (circles) with the same set of physical parameters. The inset of fig. 1 shows the concentration profile for neutral polymers having the same adsorption characteristics. The relatively small surface charge ($\sigma = -e/3000$ Å) is enough to substantially increase the average monomer concentration (in rescaled units) $\langle u^2 \rangle \equiv \int u^2(x) \, dx/d$, from 0.04 for neutral polymers to 11.1 (14.3) for smeared (annealed) polymer charges, where $d = 550$ Å is the

chosen inter-surface distance. This effect is mainly due to the longer range of the charged surfaces. A depletion layer, whose width is about the adsorption length $D = 20$ Å, has appeared near the surfaces as a result of the short-range repulsion. We note that non-monotonous profiles have been previously obtained. However, we believe that they were due either to the constraint on the amount of polymer between the plates, or to discretization effects [6, 10].

The electrostatic potential is maximal near the surfaces (where $|\beta e\psi| \simeq 1$) and decays to its mid-plane value due to screening. The electrostatic screening is dominated by the electrolyte, whose screening length $\kappa_s^{-1} = 44$ Å is shorter than the screening due to the polymer charges (and their counter-ions), $\kappa_p^{-1} = 106$ Å. As a result, the electrostatic-potential profile (smeared and annealed) is very similar to that of a pure electrolyte solution (no polymers). The difference between the smeared and annealed cases is most pronounced near the surface where the electrostatic potential is high. When the electrostatic potential is small, the difference between the two cases diminishes. This can be demonstrated by expanding the electrostatic free energy in the annealed case $f_{\text{el}}^{(a)}$ in powers of $\beta e\psi$:

$$f_{\text{el}}^{(a)} = -k_B T\phi^2 \log(1 - p + p\exp[-\beta e\psi]) \approx f_{\text{el}}^{(s)} - \frac{1}{2}k_B T p\phi^2(\beta e\psi)^2 + \dots, \qquad (8)$$

where $f_{\text{el}}^{(s)}$ is the contribution of the charged monomers to the smeared case, eq. (3). Another point is that the annealed free energy is lower than the smeared one. This can be easily understood since the annealed charges can adjust according to the local electrostatic potential, and allow a better optimization of the free energy. As can be seen from fig. 1, the polymer concentration in the annealed case is higher than in the smeared case, especially close to the wall where $|\beta e\psi| \geqslant 1$.

In conclusion, we have investigated the behaviour of charged-polymer solutions in the presence of salt for several monomer charge distributions. We have seen that the difference between the smeared and annealed cases depends on the electrostatic potential. At low electrostatic potentials ($|\beta e\psi| \ll 1$), the simplified smeared case is a good approximation for the more realistic annealed case, while at high electrostatic potentials ($|\beta e\psi| \geqslant 1$), the difference between the two cases becomes more evident. This difference is in particular large close to the surfaces. In our annealed example, although p is very small ($p = 0.01$), the effective dissociation close to the surface is $p_a \sim 0.17$ due to the large electric potential there. The effect of surface charges on the surface excess of polymer between the surfaces can be very large. As was demonstrated, even a moderate surface charge density may increase the amount of polymer between the surfaces by three orders of magnitude.

Several extensions to this research can be of interest. For example, the expression for the local free energy, eqs. (1)-(3), allows the calculation of the osmotic pressure between the two surfaces for a given profile. Such measurements for polyelectrolyte solutions are available [20, 21] using a surface force apparatus [22] and can be used to test our results [15]. Another direction might be extending the formalism beyond one dimension, either by considering non-flat geometries such as charged spheres in a solution, or by allowing the surfaces to become non-homogeneous.

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