Force Equilibria Between Charged Surfaces with Confined Polyelectrolyte Chains

R. Podgornik

J. Stefan Institute, Theoretical Physics Department,
P.O.B. 100, 61111 Ljubljana, Slovenia

Abstract. The forces in a system composed of two charged (membrane) surfaces are studied, effected by the addition of an infinitely long, flexible polymeric chain carrying charges of the sign opposite to the sign of the fixed surface charges. The conformation of the polymeric chain as a function of the intermembrane separation clearly displays the onset of the unbinding transition of the polymer analogous to the one observed in a system of deformable, fluid membranes. This transition couples with the usual double layer forces in such a way that the total intermembrane force can become attractive.

Stabilization of colloidal dispersions is an important field not only in chemistry but also in biology where different self - assembly mechanisms, generating aggregates of different geometry such as membranes, micelles or vesicles, are dependent on the nature of the interactions between the aggregates [1]. These interactions are usually subsummed under the heading of the DLVO theory where they are thought of as being composed of an attractive van der Waals component and an often repulsive stabilising double - layer electrostatic component. Only recently has it been realized that the DLVO theory misses an important facet of the (bio)colloidal interactions connected with the flexibility of the interacting surfaces [2]. The thermally excited undulations of the interacting membrane surfaces can lead to drastic modifications in the nature of the intersurface forces introducing an additional stabilizing interaction into the total force equilibrium. This interaction is seen as stemming from the sterical exclusion of all thermal undulation modes of the apposed membranes that would violate the impenetrability of the interacting surfaces and leads to the prediction of the s.c. unbinding transition for a stack of suspended membranes under vanishing external (osmotic) stress [2].

Recently we have further extended the framework of the DLVO theory by considering the modifications in the intersurface forces brought about by exchanging (point) counterions confined between the interacting surfaces with flexible, charged polyelectrolyte chains [3]. Flexible polymers can provide additional stabilization to the (bio)colloidal systems [1] in somewhat the same vein as the steric interaction between the undu-

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lating membrane surfaces enhances the repulsion provided by the double - layer electrostatic (or equivalently the hydration) forces [2]. However, with polymers bearing charges of the oposite sign to those residing on the bounding (membrane) surfaces, an attractive component to the total interaction may also be introduced because the polymer segments can adsorb to the surfaces thus enabling the formation of bridges between them. The magnitude of this bridging attraction can be significant if compared to the van der Waals attraction or the double - layer repulsion and can thus alter the force equilibria in a colloidal system [3].

The case of confined flexible polyelectrolyte chains has been treated by various authors on different approximation levels starting from the seminal work of Wiegel [4]. The different approaches mainly belong to the continuous - chain models in external field , lattice self - consistent field (SCF) theories or computer simulations [5]. In order to formulate the problem in a language that would be close to the Poisson - Boltzmann formulation of the confined electrolyte problem we recently introduced the self-consistent field Poisson-Boltzmann approximation for polyelectrolytes [3] that allowed us to compare in a most direct manner the double - layer forces with and without the presence of flexible polyelectrolyte counterions.

Here we consider the statistical properties of a confined polyelectrolyte chain related to the connection between the conformation of the polymeric chain and the nature of forces between the charged bounding surfaces. In the case that a polymeric chain is confined from one side only (semiinfinite confinement) it has been argued recently [6] that it undergoes unbinding transitions as the strength of the wall potential is varied. In the case that the wall potential is electrostatic in nature (screened Debye - Hückel form) the existence of an unbinding transition for semiinfinite confinement has been demonstrated quite some time ago [4]. Most notably the unbinding of the polymer can in this case be triggered by varying the surface charge density.

We consider a continuum (Gaussian) model for a charged polymeric chain confined between two charged surfaces separated by $2a$. The charges of magnitude τ residing on the polymer segments of length l are assumed to be of a sign different from the charges of surface charge density σ fixed on the bounding hard walls. In the limit of the ground - state dominance the transverse polymer Green's function can be written as $G(z, z'; N) \approx \psi(z)\psi(z')e^{-E_N N}$ where z is the transverse coordinate limited to $|z| \leq a$, while E_N is the part of the total free energy stemming from the polymer configurations alone. In this case the SCF equations reduce to the one dimensional Hartree equation [3] of a form

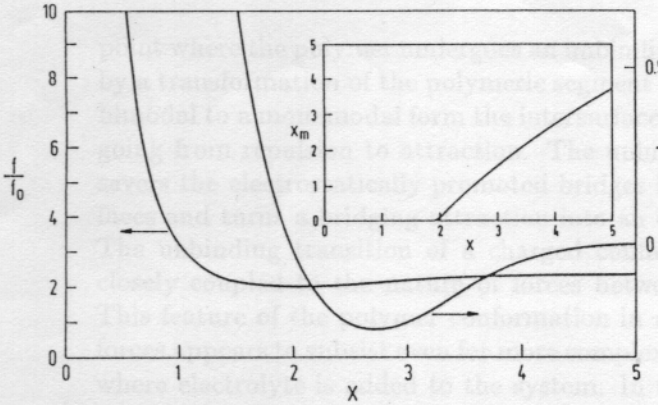

Fig.1 The dimensionless surface free energy density f/f_0, where $f_0 = \sigma^2/(\epsilon\epsilon_0\lambda_B{}^{\frac{1}{3}})$ and $\lambda_B = 6\beta\tau\sigma/(l^2\epsilon\epsilon_0)$, as a function of dimensionless separation $x = \lambda_B{}^{1/3}a$. The dimensionless pressure is defined as $p/p_0 = -\frac{\partial}{\partial x}(f/f_0)$. The inset shows the position of the maximum of the segment density distribution function (x_m) as a function of x. When $x_m = 0$ the density distribution is monomodal with a single maximum at the midpoint of the intersurface space and depletion layers in the vicinity of the bounding surfaces. On the other hand when $x_m \neq 0$ the polymer is in the bound state with its segment density distribution of a bimodal form with two maxima located close to the bounding surfaces at $x = \pm x_m$ and a broad depletion layer in the middle of the intersurface space. The unbinding transition sets in at $x \approx 1.986$.

$$\frac{l^2}{6}\frac{d^2\psi(z)}{dz^2} + E_N\psi(z) + \frac{\beta\tau\sigma}{\epsilon\epsilon_0}\int_{-a}^{+a}|z-z'|\psi^2(z')dz'\psi(z) = 0 \qquad (1)$$

where β is the inverse thermal energy while the SCF potential has the form $V(z) = \int_{-a}^{+a}|z-z'|\psi^2(z')dz'$. We were able to obtain analytical solutions to this equation in the case where we approximate the SCF potential by a linearized form $V(z) \approx |z|$ which is accurate close to the walls, where the SCF potential is the largest, but fails in the vicinity of $z = 0$, where the expansion starts as $V(z) \approx \langle z\rangle + \psi^2(z=0)z^2$ [3]. In the linearized case the solution of Eq.(1) can be given in terms of the Airy functions and leads to a form of the free energy and pressure as a function of the dimensionless intersurface separation presented in Fig.1.

The most interesting feature of this dependence can be extracted if we monitor the conformation of the polymeric chain together with the pressure acting between the bounding surfaces. Clearly exactly at the

point where the polymer undergoes an unbinding transition, characterised by a transformation of the polymeric segment density distribution from a bimodal to a monomodal form the intersurface pressure changes sign thus going from repulsion to attraction. The unbinding of the polymer thus severs the electrostatically promoted bridges between the bounding surfaces and turns a bridging attraction into an essentially steric repulsion. The unbinding transition of a charged confined polymer chain is thus closely coupled to the nature of forces between the confining surfaces. This feature of the polymer conformation in relation to the intersurface forces appears to subsist even for more complex situations as in e.g. a case where electrolyte is added to the system. In this case, which represents a generalization of the semiinfinite confinement model studied by Wiegel [4], the connection between intersurface pressure and the conformation of the polymeric chain is somewhat more complicated, though. The reason being that the total free energy of the system is composed of a polymeric part as well as of a contribution of the ionic double-layer overlap which has the same form as in the DLVO theory.

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