CROATICA CHEMICA ACTA CCACAA **65** (2) 285–295 (1992)

ISSN 0011-1643
UDC 541.1
CCA—2059 *Original Scientific Paper*

Conformational Transition of a Charged Polymer Chain Between Two Oppositely Charged Surfaces

Rudi Podgornik

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

Received September 6, 1991

The paper deals with the intersurface forces in a system composed of two charged (membrane) surfaces immersed in a uni-uni valent electrolyte, effected by addition of an infinitely long, flexible polymeric chain carrying charges of the sign opposite to the one fixed on the surfaces. The conformation of the polymeric chain as a function of the intermembrane separation clearly displays the onset of an adsorption transition of the polymer characterized by a bimodal polymer segment distribution function. Polymer adsorption in a confined system leads to formation of bridges between the boundary surfaces that, in turn, contribute an attractive force component to the intersurface forces. This bridging attraction couples with the usual electrostatic double-layer forces in such a way that the total intermembrane force can become attractive or can even show two-phase equilibria.

INTRODUCTION

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 double-layer electrostatic component.[2] The latter is held to be the major stabilizing factor for these systems. Only recently, it has been realized that the DLVO theory misses an important facet of the (bio)colloidal interactions connected with the flexibility of the interacting surfaces, as is the case of *e.g.* a system of suspended planar membranes under osmotic stress.[3] The thermally excited undulations of the interacting membrane surfaces usually 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 which would violate the impenetrability of the interacting surfaces. It leads to novel features in the intermembrane forces, of which the most important one is the prediction of the so called unbinding transition for a stack of suspended membranes under vanishing external (osmotic) stress.[4]

In this contribution, we shall further extend the framework of the DLVO theory by considering modifications in the intersurface forces, brought about by exchanging (point) counterions confined between the interacting surfaces with a flexible, charged polyelectrolyte chain. Flexible polymers are usually thought of as conferring additional stability to the (bio)colloidal systems[5] in somewhat the same vein as the steric interaction between the undulating membrane surfaces enhances the repulsion provided by the double-layer electrostatic (or, equivalently, hydration) forces. This stabilizing effect of confined polymers is again a consequence of the steric exclusion of polymer configurations that would violate the impenetrability of the bounding (membrane) surfaces. However, with polymers bearing charges of the opposite sign to those residing on the bounding surfaces, an attractive component to the total interaction may also be introduced because the polymer segments can adsorb to the surfaces, thus enabling 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.

The case of a flexible polyelectrolyte chain confined between charged surfaces has been treated by various authors on different approximation levels starting from the seminal work of Wiegel[6] where and adsorption transition of the charged polymer was clearly established. The different approaches mainly belong to the continuous chain models in external field,[7] lattice self-consistent field (SCF) theories[8] or computer simulations.[9] 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 (SCF-PBP),[10] being essentially a continuous chain SCF method that allowed us to compare, in a most direct manner, the double-layer forces with and without the presence of long, flexible polyelectrolyte counterions. Thus, we were able to assess the consequences of the intramolecular forces (polymer flexibility) on the interactions between macroscopic colloid aggregates. In what follows, we shall mostly follow the detailed presentation given in ref. 10 where the reader can find all the relevant formal details presented in unabridged form.

BASIC MODEL AND AN OUTLINE OF THE SCF THEORY

A combined model is utilized to specify the system under study, Figure 1. The uni-uni valent electrolyte is described in terms of the primitive model with ionic charge e_0, dielectric constant ε and bulk activity ζ. For the level of subsequent approximations, the hard core radius is not important. The polyelectrolyte chain is described in the frame of a modified continuum version of the Baumgärtner model[11] with the proper inclusion of the polyelectrolyte-ion interactions. In this framework, the polyelectrolyte chain is described in terms of freely joined links of charge τ per bead of length l, with a total contour length equal to Nl. The electrolyte as well as the polyelectrolyte chain are confined between two impenetrable surfaces of surface area S separated by $2a$ and each carrying a surface charge density σ (presumed negative) of a sign opposite to τ. All the electrostatic interactions are mediated by a Coulomb potential of the form $u(\mathbf{r},\mathbf{r}') = 1/4\pi\varepsilon\varepsilon_0|\mathbf{r}-\mathbf{r}'|$. The configurational part of the Hamiltonian for this model system can be written in the form

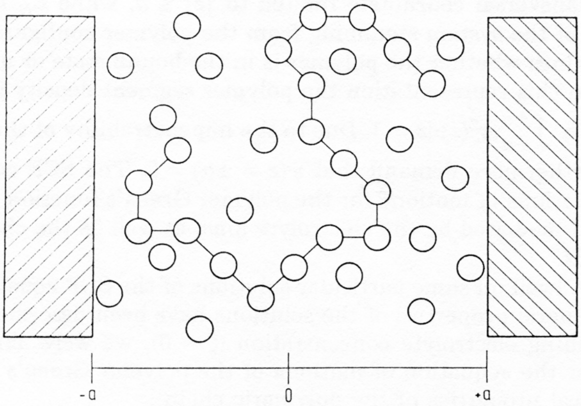

Figure 1. The model system. Two charged surfaces (surface charge density σ) at a separation $2a$ with a uni-uni valent electrolyte and a charged polyelectrolyte chain (charge per bead τ) in-between. The dielectric constant ε is supposed to be the same in all regions of the space. Surfaces are impenetrable to ions as well as to the polyelectrolyte chain. The sign of the charges residing on the polymer beads is opposite to the sign of the fixed charges on the bounding surfaces.

$$H = \frac{3kT}{2l^2} \int_0^N \left(\frac{d\mathbf{r}(n)}{dn}\right)^2 dn + \frac{1}{2}\sum_{i \neq j} e_i e_j u(\mathbf{r}_i,\mathbf{r}_j) + \sum_i e_i \phi_e(\mathbf{r}_i).$$

In the above equation, n runs over all the polymer beads with coordinates $\mathbf{r}(n)$ along the chain of a length N. Indices i and j run over all polymer beads ($e_i = \tau$), all anions ($e_i = -e_0$) and all cations ($e_i = e_0$). $\phi_e(\mathbf{r})$ is the external electrostatic potential due to the charges on the surfaces. In the above form of the Hamiltonian, the possibility of discrete surface charges, as well as the presence of dielectric discontinuities, was disregarded since they rarely have any qualitative effects.[12]

The statistical properties of a system specified by the above Hamiltonian were investigated in the framework of the SCF theory with an additional proviso that the polymeric chain is infinitely long and the ground-state dominance ansatz is applicable.[13] We shall not dwell on the formalities of the SCF theory, which have been described in all the relevant detail elsewhere.[10] Let us just note here that the SCF equations are derived in the form of three coupled equations. The first of them is a modified Poisson-Boltzmann equation that, besides a term corresponding to the local charge densities of electrolyte ions, also contains a term proportional to the local charge density of the polymer. The second equation is a diffusion type equation for the polymer Green's function in the mean electrostatic potential. The third equation is an electroneutrality constraint in the form of a boundary condition for the derivative of the electrostatic potential at the charged boundaries.

The basic information on the statistical properties of the polymeric chain is contained in the polymer Green's function specifying the probability that a chain starting from $\mathbf{r}$ will arrive to $\mathbf{r}'$ after N segments (polymer links). In plan parallel geometry it can be represented in the following form[13]

$$G(\mathbf{r},\mathbf{r}';N) = G(z,z';N) \approx \psi(z)\psi(z')e^{-E_N N}$$

where z is the transversal coordinate limited to $|z| \leq a$, while E_N is the part of the total free energy of the system stemming from the polymer configurations alone. The sign of E_N determines whether the polymer is in the bound state or not. ψ is the »density field« since in this representation the polymer segment density is given simply as $\rho(z) = \frac{N}{S}\psi^{2(z)}$ with $\int_{-a}^{+a}\psi^2(z)\mathrm{d}z = 1$. Due to the impenetrability of the boundary surfaces, one must furthermore demand that $\psi(z = \pm a) = 0$. The SCF equations can also be viewed as »equations of motion« for the polymer Green's function in the mean electrostatic potential mediated by the electrolyte ions, as well as the charges residing on the polymer beads.

We shall now dwell on some particular solutions of the SCF equations for different limiting cases. General properties of the solutions have been described elsewhere.[10] In the case of vanishing electrolyte concentration ($\zeta \to 0$), we were able to derive[10] the following form for the »equation of motion« of the polymer Green's function that governs the statistical properties of the polymeric chain

$$\frac{l^2}{6}\frac{\mathrm{d}^2\psi(z)}{\mathrm{d}z^2} + E_N\psi(z) + \frac{\beta\tau\sigma}{\varepsilon\varepsilon_0}\int_{-a}^{+a}|z-z'|\psi^2(z')\mathrm{d}z'\psi(z) = 0 \tag{1}$$

It has the form of a one dimensional Hartree equation, where the range of the SCF potential, defined as $V(z) = \int_{-a}^{+a}|z-z'|\psi^2(z')\mathrm{d}z'$, is the same as the dimensions of the system. This makes it quite difficult to solve it in general since the SCF potential cannot be approximated by its zero-th Fourier component as is often the case.[14] We were, however, able to find an approximate analytical solution to the above equation in the limit where the linearization of the SCF potential is possible.[10] A numerical solution is, nevertheless, needed to assess the soundness of the approximate analytical results.

The Hartree equation is solved numerically after introducing the dimensionless variables $y = \frac{6E_N}{l^2\lambda_B^{2/3}}$ and $x = \lambda_B^{1/3}z$, where $\lambda_B = \frac{\beta\tau\sigma}{l^2\varepsilon\varepsilon_0}$. In terms of these variables, the total surface free energy density of the system (F/S) can be obtained as

$$\frac{F}{S} = kTE_N\frac{N}{S} + \frac{\sigma^2}{\varepsilon\varepsilon_0}a = \frac{\sigma^2}{\varepsilon\varepsilon_0\lambda_B^{1/3}}(y(x_0)+x_0) = f_0\,(y(x_0)+x_0) \tag{2}$$

where we took account of the electroneutrality condition, $\tau\frac{N}{S} = \sigma$, while $x_0 = \lambda_B^{1/3}a$. The second term in the above relation $\left(\frac{\sigma^2}{\varepsilon\varepsilon_0}a\right)$ clearly takes account of the electrostatic self-energy of the system.

The numerical solutions for this particular limiting case are now presented in Figure 2. The forces between the bounding surfaces are clearly seen to be either repulsive (at small intersurface separations) or attractive (at larger intersurface separations). Approximate analytical form of the intersurface forces was given elsewhere[10] and is apparently quite accurate for small and intermediate separations, if we compare it with numerical results of Figure 2. The most important characteristic of the system is obtained if one monitors simultaneously the conformation of the polymeric chain between the surfaces and the forces. The inset to Figure 2 shows the position of the maximum of the segment density distribution function (w_{max}) as a function of w_0. When

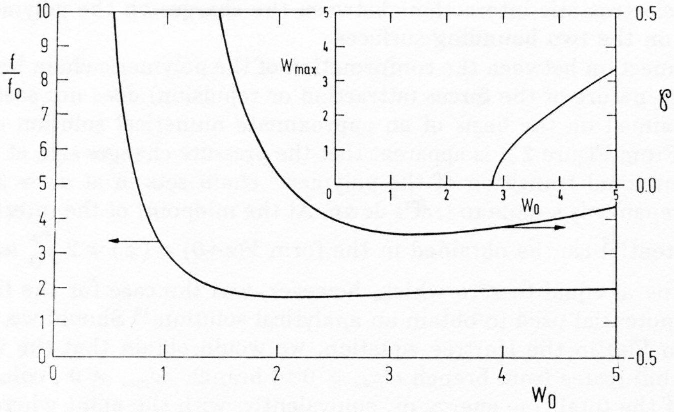

Figure 2. The dimensionless surface free energy density $\frac{f}{f_0}$, where $f = \frac{F}{S}$ and f_0 are defined in Eq. (2), as a function of dimensionless separation $w_0 = \lambda_B^{1/3} a$. The dimensionless pressure is defined as $\wp * = -\frac{\partial}{\partial w_0}\left(\frac{f}{f_0}\right)$. Positive pressure corresponds to repulsive intersurface forces and negative pressure to attractive forces. The inset shows the position of the maximum of the segment density distribution function ($w_{\max}$) as a function of w_0. When $w_{\max} = 0$, the density distribution is monomodal with a single maximum in the middle of the intersurface space and depletion layers in the vicinity of the bounding surfaces. On the other hand, when $w_{\max} \neq 0$, the distribution of the polymer is bimodal with two maxima located close to the bounding surfaces at $w = \pm w_{\max}$ and a broad depletion layer in the middle of the intersurface space.

$w_{\max} = 0$, the density distribution is monomodal with a single maximum in the middle of the intersurface space and depletion layers in the vicinity of the bounding surfaces. This means that the conformation of the polymeric chain in this region of the intersurface separations is mainly governed by the steric exclusion of the polymer from the regions close to the bounding surfaces located at $w = \pm w_0$. On the other hand, for sufficiently large intersurface separations when $w_{\max} \neq 0$, the distribution of the polymer is bimodal with the maxima located close to the bounding surfaces at $w = \pm w_{\max}$ and a broad depletion layer in the middle of the intersurface space. Thus, the electrostatic attraction between the charges on the polymeric chain and those fixed to the bounding surfaces promotes a soft adsorption of the chain to the surfaces. While most of the chain is now in the vicinity of both bounding surfaces, those parts of the chain that span the intersurface region act as polymer bridges that, due to their connectivity, pull the surfaces towards each other. The adsorbed (or surface bound) conformation of the polymeric chain is, thus, the physical cause for the (bridging) attraction between equally charged surfaces. The transition from the monomodal (unbound polymer) to bimodal (surface bound polymer) distribution function shows all the characteristic of a second order phase transition where the order parameter is the location of the maximum of the segment density distribution. The role of the temperature is played by the separation between the bounding surfaces. This conformational transition of a confined charged polymer bears considerable similarity to the coil-stretch transition in the bulk, studied by Mansfield,[15] which is accomplished by varying the strength of an external field stretching the polymer. In our case, this field would correspond to electrostatic interactions between the charges on the polymeric chain and those fixed on the two bounding surfaces.

The connection between the conformation of the polymeric chain between the surfaces and the nature of the forces (attraction or repulsion) does not seem to be direct, as it was claimed on the basis of an approximate numerical solution of the Hartree equation.[10] From Figure 2 it is apparent that the pressure changes sign at $w_0 \approx 2.0$ while the conformational transition of the polymeric chain sets in at $w_0 \approx 2.8$. The origin of this discrepancy is simple to track down. At the midpoint of the intersurface region, the SCF potential can be obtained in the form $V(z \to 0) = \langle z \rangle = 2\int_0^a u\psi^2(u)\mathrm{d}u$ and it is not in general equal to zero which, however, was the case for the linearized form of the SCF potential used to obtain an analytical solution.[10] Should we, thus, subtract $V(z=0)$ from $V(z)$ in the Hartree equation, we would obtain that the value of w_0, at which $w_{\max}$ bifurcates from branch $w_{\max} = 0$ to branch $w_{\max} \neq 0$, coincides with the minimum of the total free energy or, equivalently, with the point where the intersurface pressure changes sign. This observation would then lead to the general conclusion that the change from repulsion to attraction is driven by the conformational transition of the confined polymeric chain between two different states, characterized by monomodal and bimodal forms of the polymer segment density between the surfaces. This transition enables creation of polymer bridges between the surfaces and, thus, promotes effective attraction between the bounding surfaces.

The emergence of bridging attraction in this system is not the only thing that sets it quite apart from the usual DLVO behavior.[2] One could argue that the peculiarities of the interaction forces described above are due to the vanishing of the electrolyte concentration and that, at finite values of electrolyte concentration, more standard double-layer repulsive forces would overwhelm the attraction due to the electrostatic polymer bridge formation. We have shown that this is not the case for a very broad range of the system parametres.[10] Polymer bridging and the associated attractive forces appear to remain the salient feature of the system's behavior but they do not show distinctive peculiarities in different regions of the parameter space. One of them, connected with the existence of a »two-phase« equilibrium, will be given separate attention later on.

In the case of non-vanishing electrolyte concentration, there are additional effects that govern interactions between the charged bounding surfaces of the system. Here, the SCF theory with the ground-state dominance ansatz leads to a set of two coupled non-linear equations for the local mean electrostatic potential $\phi(z)$ and the polymer »density field« $\psi(z)$

$$\frac{l^2}{6}\frac{\mathrm{d}^2\psi}{\mathrm{d}z^2} + (E_N - \beta\tau\phi)\psi = 0 \tag{3}$$

and

$$\varepsilon\varepsilon_0\frac{\mathrm{d}^2\phi}{\mathrm{d}z^2} - 2\zeta e_0\sinh(\beta e_0\phi) + \tau\frac{N}{S}\psi^2 = 0. \tag{4}$$

Impenetrability of these surfaces to polymer beads is again reduced to the boundary condition $\psi(z = \pm a) = 0$, while the appropriate boundary condition for the electrostatic potential can be deduced from the electroneutrality condition. Clearly, in the absence of the polymeric chain, the above two equations reduce to the standard Poisson-Boltzmann equation fro a uni-uni valent electrolyte.[1,2] Also, for vanishing electrolyte concentration ($\zeta \to 0$), they reduce to Eq. (1). With the polymeric chain present, we can view Eq. (4) as a modified Poisson-Boltzmann equation, where the dependence of the polymeric charge density on the mean electrostatic potential has to be determined self-consistently, *via* the dependence of the polymer »density field« $\psi(\mathbf{r})$ on the electrostatic potential.

It is quite straightforward to deduce that the solution of Eqs. (3) and (4) is governed by the value of dimensionless separation $w_0 = (\kappa a)$, where κ is the inverse Debye screening length for a one-one electrolyte, *viz.* $\kappa^2 = \frac{2\zeta\beta e_0^2}{\varepsilon\varepsilon_0}$, the value of the dimensionless surface charge $\Gamma = \frac{\beta e_0 \sigma}{\varepsilon\varepsilon_0\kappa}$, the value of the electrostatic coupling between the polyelectrolyte chain density and the mean total charge density $\lambda = \frac{\beta e_0^2}{\varepsilon\varepsilon_0\kappa}\frac{N}{S}$ and the product κl. The solution of the SCF equations is quite complicated in the space defined by these parameters and we shall delimit ourselves only to a very special case, a general analysis of the solutions being available elsewhere.[10] The free energy of the system described by Eqs. (3) and (4) can be obtained analogously to the case of vanishing electrolyte concentration Eq. (2) in the form

$$\frac{F}{S} = kTE_N\frac{N}{S} + F_{\mathrm{dl}} \tag{5}$$

where F_{dl} is now the electric double-layer free energy[2] that has exactly the same form in terms of the mean electrostatic potential $\phi(z)$ as in the standard Gouy-Chapman theory, except that the mean electrostatic potential is not a solution of the Poisson-Boltzmann equation but of Eq. (4).

The consequences of the above two equations in terms of the forces between the charged bounding surfaces are varied and have been described in detail.[10] The upshoot is, however, the same as in the simpler case of vanishing electrolyte concentration, *viz.* that the polymer bridge formation introduces an additional attractive component into the total force that can, for a fairly broad range of the system parameters, overwhelm either the polymer steric exclusion forces or the more familiar double-layer repulsion. There is an additional facet to the presence of the polymer chain in the confined region, which we address below.

The scaling behavior of various components of the total interaction with respect to the separation between the bounding surfaces is different.[10] The steric exclusion of the polymer at the surfaces has the scaling form of $p(a \to 0) \sim a^{-3}$.[5] The polymer bridging attraction was shown to have an approximate limiting form of $p(a \to \infty) \sim -e^{-\mathrm{const.}a^{3/2}}$,[10] while the double-layer repulsion has the standard Gouy-Chapman limiting form $p(a \to \infty) \sim -e^{-2\kappa a}$.[2] A glance at the scaling forms of these three components of the total interaction pressure opens a possibility for a case where the interaction could go from (steric) repulsion at small separation to (bridging) attraction at intermediate separations and then back to (double-layer) repulsion at very large separation. Such a behaviour has indeed been observed in numerical solutions of Eqs. (3) and (4) and is presented in Figure 3. The dependence of pressure on the intersurface separation has a form similar to the isotherms of a van der Waals gas, if we identify λ (the dimensionless polymer charge) as the parameter playing the role of temperature. This formal similarity of the force curves with the van der Waals isotherms opens a possibility of thermodynamic equilibrium for the polymer system characterized by the fact that it can show stable minima at two different separations for the same value of intersurface pressure.

The pressure corresponding to this equilibrium, p_{eq}, can be obtained from the Maxwell construction (see Figure 3) applied to the pressure curve between separations w_α and w_β or by analyzing the dependence of the free enthalpy (chemical potential) on the pressure.[19] The form of the free enthalpy as a function of pressure is shown in the inset of Figure 3 and clearly exhibits a loop structure typical of a first-order phase transition. Thus, we could say that at p_{eq} we have a coexistence of two »phases« in thermodynamic equilibrium.

The first one, corresponding to a range of separations $w_0 < w_\alpha$, is characterized by the fact that the total interaction between the surfaces is dominated by steric exclusion of the polymers at the two bounding surfaces. Disregarding a region in close proximity of p_{eq}, the scaling form of the pressure in this »phase« is $p(a) \sim a^{-3}$. The polymer is in the unbound conformation (monomodal density distribution) and is, thus, mainly concentrated in the middle of the intersurface space, leaving depletion regions close to the boundary surfaces. The second phase, $w_0 > w_\beta$, is characterized by the dominating contribution of the double-layer repulsion between the surfaces to the total interaction pressure. The scaling form of the total pressure is $p(a) \sim a^{-2\kappa a}$ but its

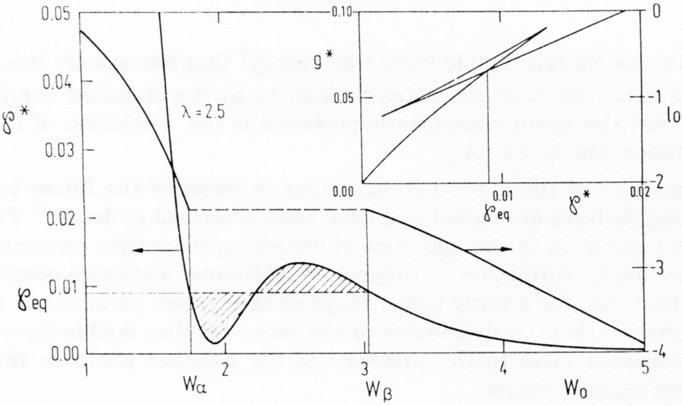

Figure 3. Dimensionless pressure $\wp^* = \dfrac{p}{p_0}$, where $p = -\dfrac{\partial}{\partial w_0}\left(\dfrac{F}{S}\right)$ and $p_0 = \dfrac{\varepsilon\varepsilon_0\kappa^2}{(\beta e_0)^2}$, for a system with nonvanishing electrolyte concentration as a function of dimensionless separation $w_0 = \kappa a$. The free energy density $\dfrac{F}{S}$ for this system is defined in Eq. (5). The values of parameters λ and Γ are: $\lambda = 2.5$ and $\Gamma = 5.45$, corresponding to a surface charge density of one electron charge per 2 nm^2 and $\kappa^{-1} = 1.2$ nm.[10] The van der Waals like form of the pressure curve is clearly displayed and the Maxwell construction between separations w_α and w_β determines the equilibrium pressure $\wp_{eq}$ at which a first order transition between the two »phases« sets in. The log-scale displays the exponential behavior of the pressure in the region $w_0 > w_\beta$. The inset show the dimensionless free enthalpy (g^*) as a function of the dimensionless pressure. The crossing point of the loop is equivalent to the equilibrium pressure obtained from the Maxwell construction.

magnitude depends on the length of the polymer confined between the surfaces (*i.e.* on λ). The longer the polymer, the smaller is this effective double-layer interaction (see Figure 4). This is a simple consequence of the fact that in this »phase« the polymer is in the bound configuration (bimodal density distribution) and, thus, effectively screens the fixed surface charges, diminishing them in overall magnitude. The contribution of bridging attraction in this »phase« is not large enough to overwhelm the double-layer repulsion.

Just like in the case of van der Waals isotherms, the pressure-intersurface separation curves show a »coexistence region« where the first order transition from w_α to w_β can take place, Figure 4. The necessary condition for the emergence of the »coexistence region« is that the pressure at $w_0 \to \infty$ is repulsive. This means that the dimensionless surface charge Γ has to be above a certain minimal value[10] and, in fact, the larger Γ the larger is the interval of λ values that defines the »coexistence region«. One can conclude that the first order phase transition, characterized by a discontinuous change in the intersurface separation, would be present for a wide range of λ (polymer charge) if only the fixed surface charges were large enough.

Also, it is exactly in the region $w_\alpha < w_0 < w_\beta$ that the confined polymeric chain goes from a unimodal to a bimodal configuration. The structure of the $w_\alpha \to w_\beta$ transition is quite extraordinary. First, we have a first order transition between two »phases« characterized by two different values of intersurface separation. On top of this, we have a second order of transition of the polymeric chain between a conformation described by a monomodal segment density distribution and a bimodal density distribution. This is indeed quite a complex state of affairs, brought about simply by the connectivity of the polymeric chain and the interaction of its charges with the charges residing on the bounding surfaces of the system. It has no relation to the for-

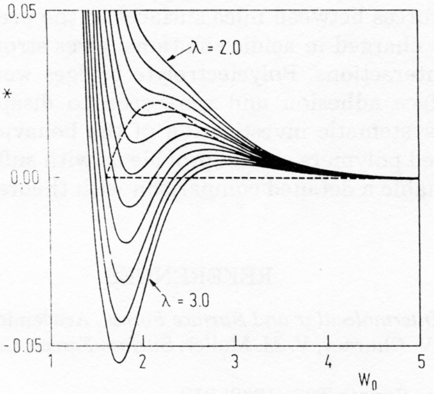

Figure 4. Dimensionless pressure (see Figure 3) as a function of the dimensionless separation for Γ = 5.45 and $2.0 \le \lambda \le 3.0$. The coexistence region of the $\wp * - w_0$ diagram, where the first order transition between the two »phases« described in the main text can take place, is bounded by the dashed curve. It corresponds to values of λ such that $2.25 \le \lambda \le 2.6$, the larger the dimensionless surface charge Γ, the larger is the region of λ values where one can observe this first order phase transition. The similarity with the van der Waals isotherms is apparent while the value of temperature is played by parameter λ (dimensionless polymer charge). The pressure decays exponentially with w_0 in the limits of large w_0 but its magnitude depends on the value of

ces that are usually incorporated into the ordinary DLVO theory. It appears that polymers can confer a much more varied behavior to colloidal systems than provide them solely with a means for simple steric stabilization.

CONCLUSIONS

Attraction promoted by the bridging of the polymeric chain between the two bounding surfaces appears to be the single most important feature of the system under study. It has no correlates in the standard forces entering the DLVO theory and is solely a consequence of the connectivity of the polymeric chain.

In general. there are three tendencies that govern the interactions between charged surfaces in the presence of a confined polyelectrolyte chain. First of all, there is the entropic contribution of sterically excluded polymer configurations, amounting to a repulsion between the surfaces. Direct electrostatic interactions between the surfaces correspond to the changes in free energy due to the electrostatic double-layer overlap on approach of the two charged boundaries. Lastly, the soft adsorption of the polymeric chain to the surfaces also stems from electrostatic interactions between the polymeric charges and the charges fixed to the walls. However, in spite of the electrostatic nature of this effect, it promotes (bridging) attraction between the bounding surfaces, which can in certain cases overwhelm the other two repulsive contributions.

Finally, one should add a note on the experimental situation. At this point we were not able to find any systematic investigation of forces between charged surfaces in the presence of polyelectrolytes that could be used for a direct comparison with our theoretical predictions. However, investigations of the short range order of silica particles in the presence of cationic polymers[16] or direct measurements of forces between mica surfaces in the presence of polypeptides[17] do suggest that strong attractions exist between charged particles in a solution of oppositely charged polyelectrolyte. Furthermore, a study of the forces between mica surfaces in the presence of Poly-(2-vinylpyridine),[18] which is fully charged in acidic solutions, gives strong support to the bridging origin of attractive interactions. Polyelectrolyte bridges were inferred from the force curves following surface adhesion and were seen to disappear for shorter polymer chain lengths. More systematic investigation of the behavior of a colloidal system in the presence of charged polymers should provide us with sufficiently varied experimental data that would enable a detailed comparison with theoretical predictions described in this contribution.

REFERENCES

1. J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press: New York, 1985.
2. B. V. Derjaguin, N. V. Churaev, V. M. Muller, *Surface Forces*, Consultants Bureau: New York, 1987.
3. R. Lipowsky, *Physica Scripta* **T29** (1989) 259.
4. S. Leibler and R. Lipowsky, *Phys. Rev.* **B35** (1987) 7004.
5. D. H. Napper, *Polymeric Stabilization of Colloidal Dispersions*, Academic Press: New York, 1983.
6. F. W. Wiegel, *J. Phys.* **A10** (1977) 290.
7. M. Muthukumar, *J. Chem. Phys.* **86** (1987) 7230.
8. M. R. Boehmer, O. A. Evers and J. M. H. M. Scheutjens, *Macromolecules* **23** (1990) 2288.
   R. Israelis, J. M. H. M. Scheutjens, G. Fleer and F. Leermakers (personal communication).
9. T. Åkesson, C. Woodward and B Jönsson, *J. Chem. Phys.* **91** (1989) 2461.
   T. Åkesson, C. Woodward and B. Jönsson, *Physica Scripta* **T33** (1990) 32.

10. R. Podgornik, *Chem. Phys. Lett.* **174** (1990) 191.
R. Podgornik, *J. Phys. Chem.* **95** (1991) 5249.
R. Podgornik, *J. Phys. Chem.* (1991) submitted.
11. A. Baumgärtner, *J. Physique Lett.* **45** (1984) L515.
12. H. Wennerström and B. Jönsson, *J Phys. Chem.* **29** (1988) 6044.
13. P.-G. de Gennes, *Scaling Concepts in Polymer Physics* Cornell University Press: Ithaca, 1979.
14. F. W. Wiegel, *Introduction to Path-Integral Methods in Physics and Polymer Science*, World Scientific: Singapore, 1986.
15. M. L. Mansfield, *J. Chem. Phys.* **88** (1988) 6570.
16. B. Cabane, K. Wong, T. K. Wang, F. Lafuma and R. Duplessix, *Colloid and Polymer Sci.* **266** (1988)101.
17. T. Afshar-Rad, A. I. Bailey, P. F. Luckham, W. Macnaughtan and D. Chapman, *Colloids and Surfaces* **31** (1988) 125.
18. J. Marra and M. L. Hair, *J. Phys. Chem.* **92** (1988) 6044.
19. H. Wennerström, in *Physics of Amphiphilic Layers*, Eds. D. Langevin and N. Boccara, Springer: New York, 1987, p. 171.

SAŽETAK

Konformacijski prijelaz nabijenoga polimernog lanca između dviju suprotno nabijenih površina

R. Podgornik

Proučavane su međupovršinske sile u sustavu sastavljenom od dviju nabijenih (membranskih) površina uronjenih u 1:1 valentni elektrolit, što je postignuto dodatkom vrlo dugog fleksibilnog polimernog lanca, čiji su naboji suprotnog predznaka onima fiksiranim na površinama.

Konfiguracija polimernog lanca kao funkcija međumembranske udaljenosti jasno otkriva postojanje adsorpcijskog prijelaza polimera, koji je karakteriziran bimodalnom raspodjelnom funkcijom polimernog segmenta. Adsorpcija polimera u omeđenim sustavima uzrokuje stvaranje mostova između graničnih površina, što predstavlje jednu komponentu međupovršinskih privlačnih sila. Ta »mostovna privlačnost« spreže se s uobičajenim elektrostatskim silama dvostrukog sloja, tako da ukupna međumembranska sila može biti privlačna ili može pokazivati čak dvofaznu ravnotežu.