Polyampholyte solutions between charged surfaces: Debye–Huckel theory

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We calculate the interaction between two identically charged surfaces immersed in a polyampholyte solution in the framework of the linear response approximation. In the case of the randomly charged polyampholyte with equal fractions of positively $f_+$ and negatively $f_-$ charged groups the interaction between charged surfaces is similar to that in electrolyte solutions. The screening of the surface potential in the linear response approximation is due to the charge redistribution on the length scales of the polymer coils without the excess of the polymers. In the solution of asymmetric polyampholytes ($f_+ \neq f_-$) the charge density fluctuations result in additional attractive interactions linearly proportional to the charge asymmetry. © 1998 American Institute of Physics.

I. INTRODUCTION

Charged polymers have recently attracted much attention due to their unique properties and their technological importance as rheology modifiers, dispersing aids, stabilizers, gelling agents, binders, etc. Common synthetic polyelectrolytes include polycrylic and methacrylic acids and their salts, cellulose derivatives, polypeptides, sulfonated polystyrene, and other strong polycylic and polybases. In most cases the charges on the polymers are fixed as either positive or negative. Other charged polymers (polyampholytes) are amphoritic in nature carrying both positive and negative charges. The net charge of polyampholytes (e.g., proteins) is determined by the pH of the aqueous solutions.

The development of the theory of the charged polymers near charged surfaces is an important step toward understanding their interactions with colloidal particles and biological membranes. Van der Scheer and Lyklema generalized the self-consistent-field theory of Scheutjens and Fleer to the case of electrostatic interactions in order to model the adsorption of polyelectrolytes. They have shown that the strong repulsion between charged monomers leads to very thin adsorbed layers. If this interaction is screened, by adding salt, the adsorbed amount increases and the adsorbed layer becomes thicker. The extension of the Van der Scheer and Lyklema approach to the case of weakly charged polyelectrolytes has been carried out by Evers et al. and Fleer et al.

Polyelectrolyte adsorption has also been studied using the mean-field approximation for the free energy that leads to the Poisson–Boltzmann equation. Using the linearized solution of the Poisson–Boltzmann equation Varoqui et al. have calculated the conformation of weakly charged polyelectrolytes at a liquid–solid interface, the adsorption isotherm and the concentration profile of the polymer near the interface. A numerical solution of the Poisson–Boltzmann equation was presented by Borukhov et al. They have calculated the concentration profile of weakly charged polyelectrolytes between two charged surfaces. The analytical results for the concentration profiles within the framework of the mean-field theory and in the limit of the weak adsorption were obtained by Chatellier and Joanny. It was shown that the concentration profile at low salt concentrations can show damped oscillations.

The theoretical studies of the interaction of polyelectrolytes with charged surfaces were limited to a single chain problem. However, such theory is needed in order to explain the results of numerous experiments and to guide the development of new technological applications. In the present note we apply the random phase approximation to describe the interaction between two identically charged surfaces immersed in polyampholyte solution.

II. POLYAMPHOLYTES BETWEEN CHARGED SURFACES

Consider a polyampholyte solution in a slab of thickness $D$ between two charged surfaces carrying $\sigma$ charges per unit area. The surfaces are parallel to the xy plane and located at $z = \pm D/2$. The solution in the slab is in equilibrium with a reservoir containing polyampholyte chains with a degree of polymerization $N$ and having the fraction $f_+$ of positive and negative charges randomly distributed along the chains. The average monomer density in the reservoir is $\rho$. The free energy of the system has three terms, which include the electrostatic interactions between charge-density fluctuations in the slab and the surface charges, $V_{\text{sib}}$, the electrostatic interactions between surface charges themselves, $V_{\text{sib}}$, and the free energy of polymers and counterions in the slab, $\Delta F_{\text{slab}}$.

$$\Delta F = V_{\text{sib}} + V_{\text{sib}} + \Delta F_{\text{slab}}.$$  \hspace{1cm} (2.1)

The part of the free energy describing the electrostatic interactions of the surface charges with the solution density fluctuations, $V_{\text{sib}}$, is
where \( \delta \rho_\alpha (r) \) is the local fluctuation of the density of the particles of type \( \alpha \) with valency \( q_\alpha \) from their average concentrations \( \rho_\alpha \). The number of charges on the surfaces is \( Q(r) = 2\alpha [\delta (z - D/2) + \delta (z + D/2)] \). The electrostatic interaction between charges on the surfaces, \( V_{s-s} \), has the form

\[
\frac{V_{s-s}}{kT} = \frac{l_B}{2} \int_{r_1} \int_{r_2} \frac{Q(r_1)Q(r_2)}{|r_1 - r_2|}.
\]

The contribution to the free energy due to the density fluctuations in the gap between two charged surfaces can be written in the RPA\(^{23-25}\) (quadratic in density fluctuations)

\[
\frac{\Delta F_{sab}}{kT} = \frac{1}{2} \int_{r_1} \int_{r_2} \delta \rho_\alpha (r_1) \left( G^{-1}_{\alpha\beta} (r_1 - r_2) + \frac{l_B q_\alpha q_\beta}{|r_1 - r_2|} \right) \delta \rho_\beta (r_2),
\]

where \( G_{\alpha\beta} (r_1 - r_2) \) is the correlation function of the polymer solution without electrostatic interactions. The last term in the right-hand side of Eq. (2.4) describes the electrostatic interaction between charge density fluctuations \( q_\alpha \delta \rho_\alpha (r_2) \) of the particles of type \( \alpha \) with valency \( q_\alpha \). The Bjerrum length \( l_B = e^2 / kT \) is the length scale on which the electrostatic interaction between two elementary charges \( e \) immersed into the medium of dielectric permeability \( \varepsilon \) is of the order of the thermal energy \( kT \). In Eq. (2.4) and below we use the Einstein rule for the summation over the repeated indices.

The interaction between the charged polymeric groups and counterions with the surface charges results in a redistribution of the charges in the slab in such a way that the opposite charges are closer to the surfaces while the similar ones are far away from the surfaces. The new equilibrium density distribution of the particles of type \( \alpha \) due to the interaction with the charged surfaces can be found by minimization of the free energy of the system with respect to the density fluctuations \( \delta \Delta F / \delta \rho_\alpha (r) = 0 \). This results in the following expression for the density of the \( \alpha \)th component:

\[
\delta \rho_\alpha (r) = - l_B \int_{r_1} \int_{r_2} \frac{M_{\alpha\beta} (r_1 - r) q_\beta Q(r_2)}{|r_1 - r_2|},
\]

where we introduced

\[
M^{-1}_{\alpha\beta} (r_1 - r_2) = G^{-1}_{\alpha\beta} (r_1 - r_2) + \frac{l_B q_\alpha q_\beta}{|r_1 - r_2|}.
\]

Using expression (2.5) for the density fluctuations we can calculate the charge distribution between two charged surfaces

\[
\delta Q(r) = \sum_{\alpha} q_\alpha \delta \rho_\alpha (r)
\]

\[
= -2\alpha \left( \frac{1}{D} + \frac{2}{D} \right) \sum_{n=1}^{\infty} (-1)^n \frac{\kappa^2 (2\pi n / D) \cos (2\pi n z / D)}{\kappa^2 (2\pi n / D) + (2\pi n / D)^2}.
\]

where we have introduced the inverse square Debye screening length \( \kappa^2 (2\pi n / D) = 4\pi l_B q_\alpha G_{\alpha\beta} (2\pi n / D) q_\beta \), which relates the screening of the electrostatic interaction with the correlation properties of the uncharged system. We have also used the cosine-Fourier transform in the \( z \) direction and continuous Fourier transform in the \( xy \) plane.

The change of the free energy of the polyampholyte solution in the gap between two charged surfaces can be obtained by the substitution of the expression for the density fluctuations, Eq. (2.5) into Eq. (2.1), followed by integration. The variation of the free energy is

\[
\frac{\Delta F (D)}{kT} = 8\pi l_B \sigma^2 S \left[ \frac{1}{D\kappa^2 (0)} \right. \\
+ \left. \frac{2}{D} \sum_{n=1}^{\infty} \frac{1}{\kappa^2 (2\pi n / D) + (2\pi n / D)^2} \right].
\]

where \( S \) is the surface area of the charged surfaces. The approach presented above is general. The specifics of the polyampholyte solutions appear only through the correlation function \( G_{\alpha\beta} \).

The correlation function of the neutral polymer solution \( G_{\alpha\beta} (q) \) is\(^{23}\)

\[
G_{\alpha\beta}^{-1} (q) = g_{\alpha\beta}^{-1} (q) - c_{\alpha\beta},
\]

where \( g_{\alpha\beta} (q) \) is the so-called structural matrix of the polymer system in the absence of the volume interactions, which describe the effect of connectivity of monomers in the polymer chains, and \( c_{\alpha\beta} \) is the matrix of the direct correlation functions. In the next section we will calculate matrix \( g_{\alpha\beta} (q) \) for different types of charge distributions along the polymer chains.

**A. Structural correlation function of a polyampholyte solution**

The synthetic polyampholytes are prepared during a random polymerization in the medium containing two or more distinct monomer units. For the simplest model of polyampholyte chain that contains only positively and negatively charged monomers, the polymerization reaction is described by the Markov process, with the average polyampholyte composition \( f_+ \) (the fraction of the positively charged monomers) and \( 2 \times 2 \) transfer matrix \( p_{\alpha\beta} \). (\( \alpha, \beta = +, - \)). The matrix elements \( p_{\alpha\beta} \) give the conditional probability that the charge of the monomer \( i + 1 \) is equal to \( \beta \) if the charge of monomer \( i \) is equal to \( \alpha \). Taking into account the conservation of probability, one obtains \( p_{++} + p_{-+} = 1, p_{++} + p_{+-} = 1, \) and \( f_+ = p_{++} + f_+ + p_{++} (1 - f_+) \). Under these conditions the matrix \( p_{\alpha\beta} \) has two eigenvalues 1 and \( \lambda = p_{++} + p_{+-} - 1 \). The coefficient \( \lambda \) varies between 1 and -1. The
value $\lambda = -1$ implies an alternating distribution of the positive and negative charges along the chain; $\lambda = 1$ corresponds to pure positively and negatively charged chains; $\lambda = 0$ is a random sequence of the charges.

The structural matrix $g_{\alpha\beta}(q)$ of the polyampholyte solution can be calculated by the transfer matrix method and the answer is\textsuperscript{26–28}

$$
\begin{align*}
g_{\alpha\beta}(q) &= \rho_a \delta_{\alpha\beta} + \frac{\rho}{N} \sum_{i\neq j} \langle \delta(i,\alpha) \delta(j,\beta) \rangle_{av} \\
&\quad \times \exp\left( -\frac{(qj)(i-j)}{6} \right),
\end{align*}
$$
\tag{2.9}

where the function $\delta(i,\alpha)$ is equal to unity if the $i$th monomer on the chain is of sort $\alpha$ and zero otherwise and the brackets $\langle \rangle_{av}$ denote the average over the charge distribution along the polyampholyte chains. The second term on the right-hand side of Eq. (2.9) describes the effect of connectivity of monomers in the polymer chain. For the Markov’s polyampholytes the correlation function is

$$
\langle \delta(i,\alpha) \delta(j,\beta) \rangle_{av} = f_{\alpha f_{\beta}} + (2 \delta_{\alpha\beta} - 1)f_{+f_{-}} \lambda^{i-j}.
$$
\tag{2.10}

After substitution of this expression into the equation for the structural matrix (2.9) we can write

$$
g_{\alpha\beta}(q) = \rho_a \delta_{\alpha\beta} + 2 \frac{\rho}{N} J_{\alpha\beta}(q),
$$
\tag{2.11}

where the matrix $J_{\alpha\beta}(q)$ is

$$
J_{\alpha\beta}(q) = f_{\alpha f_{\beta}} J(q,1) + (2 \delta_{\alpha\beta} - 1)f_{+f_{-}} J(q,\lambda),
$$
\tag{2.12}

and

$$
J(q,\lambda) = \frac{(N-1)\lambda q_j - N\lambda^2 J(q) + (\lambda J(q))^{N+1}}{(1-\lambda J(q))^2},
$$
\tag{2.13}

$$
j(q) = \exp(-q_j^2/6).
$$

One should note that the elements of the structural matrix $g_{\alpha\beta}$ for the nonpolymeric components such as counterions or salt ions have the first term $\rho_a \delta_{\alpha\beta}$ only.

**B. Symmetric polyampholytes**

In the case of the $\theta$-solutions ($G_{\alpha\beta}(q) = g_{\alpha\beta}(q)$) of symmetric polyampholyte chains with randomly distributed charges ($\lambda = 0$), the inverse Debye screening length $\kappa = [8 \pi l_B \rho (f_+ + f_-)]^{1/2}$, which has contribution from both charged monomers on the polyampholyte chains and their counterions are $n$ independent. This is due to the fact that the distribution of charges in the solution of random polyampholytes is the same as in electrolyte solutions. The variation of the free energy (2.7) in the slab between two charged surfaces is

$$
\frac{\Delta F(D)}{kT} = \frac{4 \pi l_B^2 \sigma^2 S}{\kappa} \coth \left( \frac{\kappa D}{2} \right).
$$
\tag{2.14}

The interaction energy $W$ per unit area between two charged surfaces is obtained by simple substraction from the free-energy $\Delta F(D)$ value for the infinite separation

$$
W(D) = \frac{8 \pi l_B^2 \sigma^2}{\kappa} \exp(-\kappa D) \\
\approx \frac{8 \pi l_B^2 \sigma^2}{\kappa} \exp(-\kappa D).
$$
\tag{2.15}

The interaction between the surfaces decays exponentially with distance. The characteristic decay length is the Debye length of the polyampholyte solution. Equation (2.15) is the well-known electrostatic part of the Derjaguin, Landau, Verwey, and Overbeek (DLVO) potential due to the double-layer repulsion.\textsuperscript{29} Using the Derjaguin approximation, we can write the repulsive part of the interaction between two spherical particles of size $R$ immersed in the solution of polyampholytes. The repulsive force is

$$
F(D) = \frac{8 \pi l_B^2 \sigma^2 R}{\kappa^2} \exp(-\kappa D),
$$
\tag{2.16}

from which one may obtain the interaction energy between two spherical particles

$$
W_{sp}(D) = \frac{8 \pi l_B^2 \sigma^2 R}{\kappa^2} \exp(-\kappa D).
$$
\tag{2.17}

The repulsive pressure $P$ between two identically charged surfaces in the polyampholyte solution can be calculated by taking the derivative of the free energy (2.14) with respect to the distance between surfaces $D$,

$$
P(D) = kT \frac{8 \pi l_B^2 \sigma^2 \exp(-\kappa D)}{[1 - \exp(-\kappa D)]^2} \\
\approx \frac{8 \pi l_B^2 \sigma^2 \epsilon^2}{\kappa^2} \exp(-\kappa D).
$$
\tag{2.18}

**C. Asymmetric polyampholytes**

Calculation similar to above can be performed for the asymmetric ($f_+ \neq f_-)$ random polyampholytes. The inverse Debye screening length in this case is

$$
\kappa^2 = 8 \pi l_B (f_+ + f_-) \rho + 8 \pi l_B (f_+ - f_-)^2 \frac{\rho}{N} J(q,1),
$$
\tag{2.19}

where the function $J(q,1)$ in the case $qa \ll 1$ reduces to the Debye function $g_D(q)$

$$
g_D(q) = N^2 \exp(-x) + x - 1 \\
x = q^2 R_g^2,
$$
\tag{2.20}

where $x = q^2 R_g^2$ and $R_g = bN^{1/2} \sigma^{1/2}$ is the gyration radius of the Gaussian chain. In the range of separations $D$ between charged plates $\kappa^{-1} < D < R_g$ the summation in Eq. (2.7) can be reduced to the integration

$$
\frac{\Delta F(D)}{kT} \approx 16 \pi l_B^2 \sigma^2 S \left[ \int_0^{\infty} dq \frac{q^2 [1 + \cos(Dq)]}{\pi q^4 + \kappa^2 q^2 + \Delta N^2 \kappa^2 / R_g^2} \right].
$$
\tag{2.21}
where the parameter \( \Delta N = (f_+ - f_-)^2 N/(f_+ + f_-) \) describes the charge asymmetry. It follows from the form of Eq. (2.21) that the asymmetric polyampholytes behave thus as weakly charged polyelectrolytes in salt solutions.\(^{12,23,24}\) The typical value of the parameter \( \Delta N/R_s \kappa \approx \frac{1}{2} \) after integration with respect to \( q \), we obtain the dependence of the interaction energy \( W \) per unit area on slab thickness \( D \)

\[
\frac{W(D)}{kT} = \frac{8 \pi l_B \sigma^2}{\kappa} \left[ \exp(\kappa D) - \frac{\Delta N}{R_s \kappa} \right] \times \exp\left( -\frac{\Delta ND}{R_s} \right).
\]

(2.22)

So, the charge asymmetry results in the additional effective attractive interaction between two similarly charged surfaces. In the opposite case \( \Delta N/R_s \kappa > \frac{1}{2} \), the interaction energy \( W(D) \) is

\[
\frac{W(D)}{kT} = \frac{\pi l_B \sigma^2}{\kappa z_1 z_2} \left( z_1 + \exp(-D \kappa z_2) - \frac{\Delta N}{R_s \kappa} \right) \times \left( z_1 \cos(D \kappa z_1) - z_2 \sin(D \kappa z_1) \right),
\]

(2.23)

where we have introduced the dimensionless parameters \( z_1 = 0.5\sqrt{2(\Delta N/R_s \kappa)} - 1 \) and \( z_2 = 0.5\sqrt{2(\Delta N/R_s \kappa)} + 1 \).

D. Polymer surface excess

An important experimentally observable quantity is the polymer surface excess

\[
\Gamma = \frac{1}{2} \int_{-D/2}^{D/2} dz \left[ \delta \rho_+(z) + \delta \rho_-(z) \right]
\]

\[
= -\frac{4 \pi l_B \sigma}{\kappa^2} \rho(f_+ - f_-).
\]

(2.24)

The polymer surface excess \( \Gamma \) is independent of the distance \( D \) between surfaces and is linearly proportional to the surface charge-density \( \sigma \). For symmetric polyampholyte chains there is no monomer excess near the charged surfaces. The local increase in concentration of positively charged monomers is exactly equal to the decrease of concentration of the negatively charged monomers. The zero excess of the monomers is the result of the linear response approximation. The second-order corrections will give the nonzero excess of monomers near the charged surfaces. The surface excess \( \Gamma \) is linearly proportional to the charge asymmetry \( (f_+ - f_-) \) on the chains.

E. DLVO potential for polyampholyte solutions

To calculate the total interaction between charged surfaces, one must also take into account the van der Waals attraction. This part of the interaction between the two surfaces separated by the distance \( D \) is

\[
W_{att} = -\frac{HS}{12\pi D^2},
\]

(2.25)

where \( H \) is the Hamaker constant. A typical value of the Hamaker constant for a liquid between two solids is \( 10^{-19} \) J. To illustrate the variation of the interaction between two charged surfaces we plot the total interaction between two similarly charged surfaces in the polyampholyte solutions for different values of the charge asymmetry \( \Delta N \) (see Fig. 1). The van der Waals attraction always exceeds the double-layer-like repulsion at small distances because it is inversely proportional to the square of the distance between surfaces while the repulsive part of the interaction increases more slowly. The energy barrier separating the primary and secondary minima decreases with increasing charge asymmetry \( \Delta N \). In fact, the asymmetric polyampholytes can be viewed as multivalent macromons. It is well known that even a relatively small amount of multivalent ions substantially screens the surface potential decreasing the energy barrier and results in faster coagulation of the colloidal systems.\(^{29}\)

III. DISCUSSION

Using the random phase approximation we have calculated the interaction between two charged surfaces in polyampholyte solutions. We found that for symmetric polampholytes the screening of the surface charge is due to the redistribution of the charged monomers without additional excess of the polymers (in the linear approximation). The interaction potential between charged surfaces is similar to that in the electrolyte solutions. For asymmetric polyampholytes there is an additional effective attraction linearly proportional to the charge asymmetry. Our predictions can be tested by direct measurements of the disjoining pressure between charged surfaces in the semidilute solutions of polyampholytes.

In our calculations we have assumed that the equilibrium conformation of the chains is almost Gaussian. This means that the electrostatic interactions are weak either due to the fact that the chains are weakly charged or that the electrostatic interactions are screened by the counterions. For symmetric polyampholytes this assumption is valid as long as the fraction of the charged monomers \( f_+ + f_- \) is smaller than
$N^{-1/2}$. For asymmetric polyampholytes our consideration can be applied at high enough polymer concentrations.\textsuperscript{23,27}

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