Osmotic pressure acting on a semipermeable shell immersed in a solution of polyions

Roumen Tsekov,[1,2] Mikhail R. Stukan,[3,a)] and Olga I. Vinogradova[1]

[1]*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 31 Leninsky Prospect, 119991 Moscow, Russia*
[2]*DWI, RWTH Aachen, Pauwelsstr. 8, 52056 Aachen, Germany*
[3]*Department of Physics, Moscow State University, 119992 Moscow, Russia*

We study theoretically the osmotic equilibria for a shell immersed in a suspension of polyions (e.g., colloids, polyelectrolytes, etc.). The shell is treated as impermeable for polyions, but allowing free diffusion of counterions that permeate inside the shell. From the solution of linearized Poisson–Boltzmann equation, we obtain the distribution of a potential and concentration profiles for polyions and counterions. We then obtain an explicit formula for the excess osmotic pressure of a polyion solution exerted on the shell, which includes a quadratic term in order to provide a self-consistency of a linear theory. As a result this pressure is larger than given by a concentration of polyions at the outer shell boundary obtained within linearized theory. It is, however, always smaller than or equal to the bulk osmotic pressure. This difference is attributed to a repulsive electrostatic disjoining pressure due to an overlap of counterion clouds inside the shell. A comparison with molecular dynamics simulations is provided and demonstrates that although the concentration profiles obtained within a linear theory deviate from simulation data at large potential, the theoretical and simulation pressures are in surprisingly good harmony. © *2008 American Institute of Physics.*
[DOI: 10.1063/1.3046679]

I. INTRODUCTION

In this paper we study a shell in osmotic equilibrium with an outer suspension of charged colloids or polyelectrolytes. The shell represents a semipermeable membrane, being impermeable to large polyions, but allowing diffusion of solvent molecules and small counterions (Fig. 1). This situation is traditionally referred to as a Donnan equilibrium.[1] Examples of such systems abound in our everyday life. Such solutions are charged colloidal particles, dendrimers, micelles, polyelectrolytes, proteins, and more. They play tremendous role in life science, since proteins and DNAs represent polyions. Such shells are vesicles and liposomes with ionic channels,[2,3] various types of micro-and nanocapsules,[4–7] cell,[8,9] and bacterial[10–12] membranes, viral capsids.[13,14] Similar system has been employed for a determination of elastic modulus of shells[15] and selective encapsulation.[16–18] Depending on the applications the collapse of the shells due to high external pressure should be avoided[19] or desired.[15]

A great deal of research has been devoted to understanding the Donnan equilibria and the pressure exerted on a semipermeable membrane at the various level of sophistication. One of the most convenient approaches employs the mean-field Poisson–Boltzmann (PB) theory for calculating ionic profiles,[20] and using then the thermodynamic boundary density rule,[21] according to which the osmotic pressure is given by the value of the polyion density at the membrane, since this rule holds in the PB approach[20,22,23] (and is actually beyond the mean-field approximation[24]). However, there is no known exact solution of the PB equation for a spherical geometry, so that this should be commonly substituted by a linearized version. The linearized PB for a sphere can be then solved analytically, however, since the boundary density rule does not hold in a linearized theory[20,23,25] the calculation of osmotic pressure acting on small spherical membranes, which represent enormous interests for many biological and materials science problems[26,27] remains an open question.

In our previous papers[23,28] we made an attempt to calculate an inner excess pressure on a semipermeable shell filled with a solution of polyions. Although the main concentration trends predicted by theory reproduced results obtained in a simulation[29] a direct comparison with the simulation data was not possible due to a different geometry of configuration used in a simulation study. Beside that, pressure on the shell was evaluated only theoretically.

Our present paper solves a pressure problem for a geometry shown in Fig. 1. In other words, we now address the inverse problem of a shell immersed into a polyion solution. We first use a linearized PB theory to evaluate the concentration profiles at the low potential limit (as we prove this condition is not dramatically violated in our system even at large concentrations). We then derive an explicit expression for a pressure on the shell and demonstrate that the result for a pressure from the nonlinear PB theory should not be used together with ionic profiles computed within linearized theory since it does not satisfy the conditions for mechanical and thermodynamic equilibria. Since there are usually two

---

a)Present address: Schlumberger Dhahran Center for Carbonate Research, Dhahran Techno Park-KFUPM, P.O. Box 2836, Al Khobar 31952, Kingdom of Saudi Arabia.
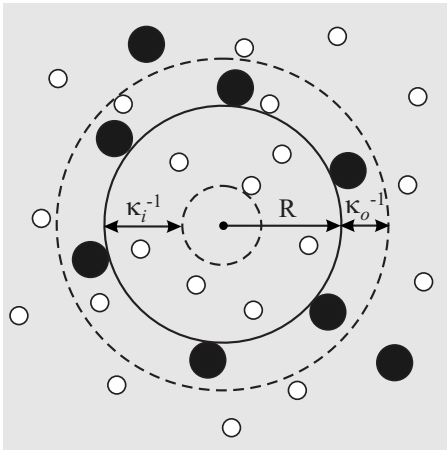
FIG. 1. Schematic of an ion distribution inside and outside of a semiperme-able shell immersed in a polyion solution. The shell is permeable for small counterions only and has to support an excess osmotic pressure Δp. The polyions are depicted as spherical (as appropriate, for instance, for "conventional" charged colloids or micelles), but our conclusions are general. They could also apply for cylindrical (e.g., DNA, viruses, actin filaments) or planar objects (e.g., clay particles) and polyelectrolytes.

main concerns with the use of the continuum mean-field PB approach for large and multivalent ions, namely connected with steric effects[30,31] and statistical correlations,[32–34] we then perform molecular dynamics (MD) simulations to evaluate the importance of these for our system and to estab-lish the region of validity of our theoretical formulas. Our simulations show that both effects are unimportant at low concentrations of polyions. At large concentrations, the ionic profiles, as expected, are affected by correlations and finite size of the polyions. However, and surprisingly, simulation data fully support the validity of our mean-field linearized theory for an evaluation of an osmotic pressure on the shell, suggesting that finite size effects and correlations are not so important, in contrast to many other systems. This remark-able conclusion opens enormous possibilities in using simple continuum analytical formulas for treatment of complex sys-tems and interpreting experiments.

II. THEORY

A. Model

We start with the theoretical consideration of a shell of radius R immersed in a solution of electrolyte composed of polyions with an effective charge Z and concentration C and small free counterions with charge z and concentration c (Fig. 1). We keep our theoretical description at the simplest possible level by using the linearized PB approach. This means that we treat polyions as pointlike particles and ne-glect their correlations. We consider the shell to be rigid and a neutral interface (see Refs. 23, 29, 35, and 36, for more discussions) and assume it is infinitesimally thin.[37] Our ap-proach is general. However, for all numerical examples we will use $Z=-15$ and $z=1$. These values correspond to our recent simulation study,[29] where they were suggested to be the parameters of a coarse-grained colloidal model describ-ing real polyelectrolyte coils (in dilute and semidilute bulk solutions[38]), so that Z is already an effective renormalized

quantity that incorporates some nonlinear effects (see Appen-dix A for more details). Our strategy of a derivation will follow the ideas and approach formulated in Ref. 23.

Away from the shell the solution is electroneutral, so that $ZC_\infty + zc_\infty = 0$.[39] The linearized PB equation for polyions and small ions in spherical geometry reads

$$\epsilon_0 \epsilon \partial_r(r^2 \partial_r \phi)/r^2 = -ZeC - zec, \tag{1}$$

where ϵ_0 and ϵ are dielectric constants of vacuum and sol-vent, respectively, e is the elementary charge, and r is the distance from the center of the shell. The local concentra-tions C and c in the frames of low electric potential acquire the form

$$c_{i,o} = c_\infty \left(1 - \frac{ze\phi_{i,o}}{k_B T}\right), \tag{2}$$

$$C_i = 0, \quad C_o = C_\infty \left(1 - \frac{Ze\phi_o}{k_B T}\right), \tag{3}$$

where k_B is the Boltzmann constant and T is the temperature. Here and below subscripts i and o indicate inner ($r < R$) and outer ($r > R$) region, correspondingly. The first expression in Eq. (3) accounts for the fact that the shell is impermeable for polyions.

Note that the validity of the linearized PB approach is justified provided the potential (Coulomb) energy of ions is small compared to their thermal energy. In other words, con-ditions

$$ze\phi/k_B T \ll 1 \quad \text{and} \quad -Ze\phi/k_B T \ll 1 \tag{4}$$

should be fulfilled for counterions and polyions, correspond-ingly, to expect accurate descriptions of the concentration profiles, Eqs. (2) and (3). Therefore, strictly speaking we should also limit ourselves by a relatively low potential, es-pecially in the case of highly charged multivalent polyions. This restriction and its possible relaxation will be discussed below, after the calculation of the potential and concentration profiles.

B. Potential

The outer solution of Eq. (1) is given by

$$\phi_o = \phi_s \frac{R}{r} \exp[\kappa_o(R - r)], \tag{5}$$

where ϕ_s is the surface potential, and an outer inverse Debye (electrostatic screening) length is defined as $\kappa_o = \sqrt{e^2(Z^2 C_\infty + z^2 c_\infty)/\epsilon_0 \epsilon k_B T}$. To derive Eq. (5) we have used that $\phi_o(r \to \infty) = 0$.

The inner solution of Eq. (1) is

$$\phi_i = \frac{k_B T}{ze} + \left(\phi_s - \frac{k_B T}{ze}\right) \frac{R}{r} \frac{\sinh(\kappa_i r)}{\sinh(\kappa_i R)}, \tag{6}$$

with an inner inverse Debye length $\kappa_i = \sqrt{e^2 z^2 c_\infty/\epsilon_0 \epsilon k_B T}$. Note that the electroneutrality implies that $\kappa_o/\kappa_i = \sqrt{1 - Z/z}$.

Since there is no attraction between the shell and ions, the latter do not adsorb. Hence, the surface charge density is zero which corresponds to continuity of the electric field at the surface,
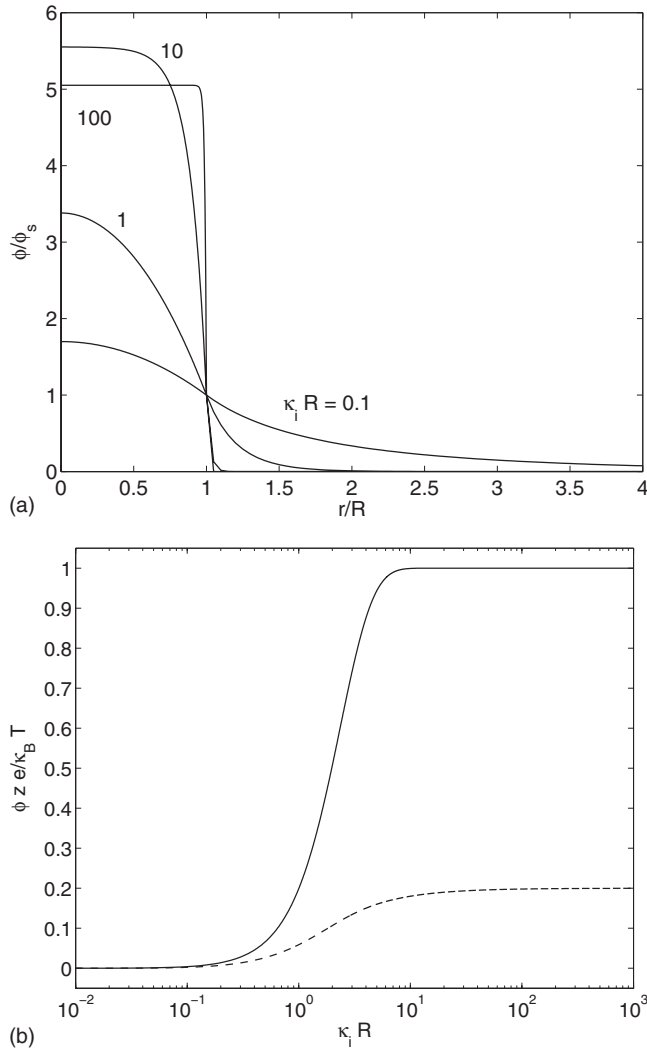
FIG. 2. (Top) A radial distribution of a potential at different $\kappa_i R$ normalized by a surface potential ϕ_s. (Bottom) Central, ϕ_c (solid curve), and surface, ϕ_s (dashed curve), potentials as a function of $\kappa_i R$. $Z/z = -15$.

$$(\partial_r \phi_o)_R = (\partial_r \phi_i)_R. \tag{7}$$

The solution of this equation yields the dependence of the surface potential on the shell radius

$$\phi_s = \frac{k_B T}{ze} \frac{\kappa_i R \coth(\kappa_i R) - 1}{\kappa_o R + \kappa_i R \coth(\kappa_i R)}. \tag{8}$$

The radial distribution of a potential calculated for different $\kappa_i R$ is shown in Fig. 2(top). All curves are normalized to the corresponding value of ϕ_s. It can be seen that the potential turns to zero at infinity and takes the maximum value at the center of the shell. The relative value of the potential at the center, $\phi_c = \phi_i(r=0)$, exhibits a maximum at intermediate values of $\kappa_i R$ and then, at large $\kappa_i R$, asymptotically decays to 5 with our $-Z/z = 15$. To examine this behavior more closely, ϕ_s and ϕ_c as a function of $\kappa_i R$ are shown in Fig. 2 (bottom). Note that at $\kappa_i R \ll 1$ (a weak variation in the potential in the inner region), $\phi_s ze/k_B T \to (\kappa_i R)^2/3$, so that the surface potential vanishes. Such a situation would be realistic for very dilute solutions and/or very small shells. Another asymptotic limit of large shells and/or concentrated solutions, $\kappa_i R \gg 1$ (fast decay of the potential close to the

surface), gives $\phi_s ze/k_B T \to \kappa_i/(\kappa_i + \kappa_o) = 1/(1 + \sqrt{1 - Z/z})$. This result is identical to the Donnan potential at a flat semipermeable membrane in the given polyion solution.

Now we can evaluate the validity of conditions of low Coulomb energy of ions as compared with $k_B T$, Eq. (4). Figure 2 (bottom) suggests that the condition for counterions, Eq. (4), is satisfied everywhere provided $\kappa_i R < 1$. For $\kappa_i R > 1$ it is valid in the outer region [since $\phi_o \ll \phi_s$ due to a fast decay of a potential in this situation as seen in Fig. 2 (top)] and is never significantly violated at the vicinity of the shell. The Coulomb energy, however, becomes of the order of thermal one at the center of the inner region, so that the theoretical concentration profiles of counterions can deviate from exact ones (being qualitatively correct). The same arguments suggest that the condition for a low potential energy of polyions is satisfied in most of situations, and only violations are possible at large $\kappa_i R$ being confined into the immediate vicinity of the shell, with an extension of κ_o^{-1}. Note, however, that the PB theory itself is known to overestimate the concentration of multivalent ions near highly charged surfaces due to an assumption of pointlike ions, so that this shortcoming of a linearization may, in reality, be not so pronounced for our system.[30]

C. Concentration profiles

The concentration profiles read

$$c_i = c_\infty \frac{\kappa_o R + 1}{\kappa_o R + \kappa_i R \coth(\kappa_i R)} \frac{R}{r} \frac{\sinh(\kappa_i r)}{\sinh(\kappa_i R)}, \tag{9}$$

$$c_o = c_\infty \left[1 - \frac{\kappa_i R \coth(\kappa_i R) - 1}{\kappa_o R + \kappa_i R \coth(\kappa_i R)} \frac{R}{r} \exp[\kappa_o(R - r)] \right], \tag{10}$$

$$C_o = C_\infty + c_\infty \frac{\kappa_i R \coth(\kappa_i R) - 1}{\kappa_o R + \kappa_i R \coth(\kappa_i R)} \frac{R}{r} \exp[\kappa_o(R - r)]. \tag{11}$$

In what follows the concentration of polyions at an outer shell boundary is

$$C_o(R) = C_\infty + c_\infty \frac{\kappa_i R \coth(\kappa_i R) - 1}{\kappa_o R + \kappa_i R \coth(\kappa_i R)} \geqslant C_\infty, \tag{12}$$

so one observes an increase in concentration of polyions at the shell. We should note that this effect is neither adsorption (driven by an attraction of ions to the shell) nor condensation (driven by an attraction between ions). None of these phenomena is present in our case, so that we deal with another effect, where the local saturation is caused by attraction of polyions to inner counterions. This, in turn, is the consequence of a counterion leakage leading to an excess charge of inner and outer regions.

The typical concentration profiles are shown in Fig. 3. One can see that at $\kappa_i R \ll 1$ the concentration of counterions in the whole system is uniform, $c_i \approx c_o \approx c_\infty$. So is the distribution of polyions in the outer region. If $\kappa_i R \gg 1$, the counterions penetrate the shell, but are concentrated in the vicinity of it. In this case, the polyions are concentrated near the shells, which is reflected by a very sharp concentration peak.
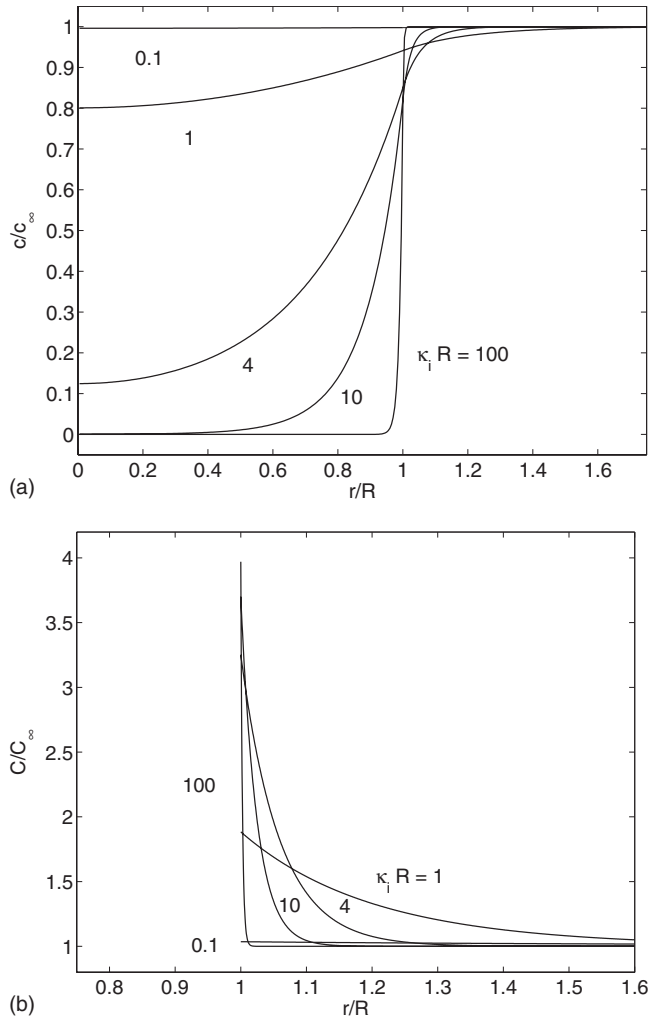
244707-4

FIG. 3. Concentration profiles of counterions (top) and polyions (bottom) in the vicinity of a semipermeable shell calculated with Eqs. (9)–(11) for $Z/z = -15$ and different $\kappa_i R$.

As we have discussed above, at large $\kappa_i R$ the value of this peak calculated within linearized approach might differ significantly from the mean-field value, which, in turns, might strongly overestimate the exact concentration of polyions.

D. Pressure

The outer and inner solutions exert a contact pressure. The normal and tangential components of the pressure tensor in the liquid read

$$P_N = p - \frac{\epsilon_0 \epsilon (\partial_r \phi)^2}{2}, \quad P_T = p + \frac{\epsilon_0 \epsilon (\partial_r \phi)^2}{2}, \quad (13)$$

respectively, where p is the local pressure of polyion solution at point r. The pressure components from Eq. (13) should satisfy the equilibrium condition $\partial_r P_N = 2(P_T - P_N)/r$, which gives

$$\partial_r p = \epsilon_0 \epsilon (\partial_r \phi)[\partial_r(r^2 \partial_r \phi)/r^2]. \quad (14)$$

The substitution of Eq. (14) into Eq. (1) leads to the following Gibbs–Duhem relation:

$$\partial_r p = (-ZeC - zec)\partial_r \phi. \quad (15)$$

With the local concentrations described by Eqs. (2) and (3) this gives

$$p_o = p_L + k_B T(C_\infty + c_\infty) + \frac{\epsilon_0 \epsilon \kappa_o^2 \phi_o^2}{2}, \quad (16)$$

$$p_i = p_L + k_B T c_c - zec_\infty(\phi_i - \phi_c) + \frac{\epsilon_0 \epsilon \kappa_i^2 (\phi_i^2 - \phi_c^2)}{2}. \quad (17)$$

Here p_L is the pressure of pure solvent and $c_c = c(r=0)$. Note that at infinity ϕ_o vanishes, so that Eq. (16) transforms to an equation for an osmotic pressure of a bulk polyion solution, $p_o \to p_L + k_B T(C_\infty + c_\infty)$.[21,40,41]

The continuity of an electric field implies that the shell supports an excess osmotic pressure, which is given by

$$\Delta p = p_o - p_i$$

$$= k_B T C_\infty + k_B T c_\infty \left[1 - \frac{\kappa_o R + 1}{\kappa_o R + \kappa_i R \coth(\kappa_i R)} \frac{\kappa_i R}{\sinh(\kappa_i R)} \right.$$

$$+ \frac{1}{2} \left[\frac{\kappa_o}{\kappa_i} \frac{\kappa_i R \coth(\kappa_i R) - 1}{\kappa_o R + \kappa_i R \coth(\kappa_i R)} \right]^2$$

$$\left. - \frac{1}{2} \left[\frac{\kappa_o R + 1}{\kappa_o R + \kappa_i R \coth(\kappa_i R)} \right]^2 \left[1 - \frac{(\kappa_i R)^2}{\sinh^2(\kappa_i R)} \right] \right]. \quad (18)$$

We stress that it would be wrong to evaluate pressure as $k_B T C_o(R)$ since this would not satisfy the condition of mechanical and thermodynamic equilibria, which is the consequence of a linearization (see Appendix B). Similar conclusion has been derived before for different systems.[20,23]

Equation (18) indicates that an excess osmotic pressure exerted on the shell is always smaller than or equal to the excess osmotic pressure of the bulk polyion solution, $\Delta p^{id} = p_o - p_L = k_B T c_\infty (1 - z/Z) \approx k_B T c_\infty$. Indeed, at small $\kappa_i R$ the first term of Eq. (18) dominates. The pressure exerted on the shell is equal to the bulk osmotic pressure of polyions $\Delta p / \Delta p^{id} \approx (1 - Z/z)^{-1}$, which is normally considered as negligibly small, since the bulk pressure is given mostly by the concentration of counterions. In contrast, at large $\kappa_i R$, the main contribution to the pressure on the shell is given by the second term of Eq. (18). This, however, does not mean that counterions contribute to pressure on the shell directly. Their role is to charge the interior of the shell and thus attract polyions. Therefore, the pressure on the shell is due to increase in the concentration of polyions at the shell as compared with the bulk value. At very large value of $\kappa_i R$ the pressure supported by the shell is close to the osmotic pressure of the corresponding bulk solution, $\Delta p / \Delta p^{id} \approx 1$. In this case we deal with the standard bulk Donnan equilibrium. These trends are illustrated in Fig. 4. We remark and stress that despite the fact that in the limit of large $\kappa_i R$ our linearized theory is expected to be inaccurate in determination of the value of a polyion concentration at the shell, the nonlinear term in the expression for pressure allowed us to get its
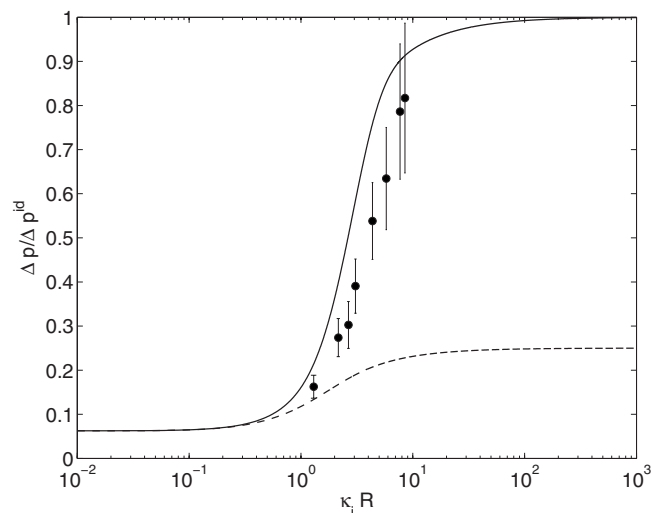
FIG. 4. A ratio of an osmotic pressure exerted on the shell to the osmotic pressure of the bulk solution as a function of $\kappa_i R$. As in the previous figures, $Z/z=-15$. Solid curve shows the results obtained with Eq. (18). Dashed curve corresponds to osmotic pressure estimated as $k_B T C_o(R)$ with C_o from Eq. (12). Included are the value of pressure $k_B T C_o$ obtained from simulations (filled circles with the error bar).

correct asymptotic value [which is for our numerical example four times larger than a pressure estimated as $k_B T C_o(R)$!].

III. COMPARISON WITH MD SIMULATION

In this section we provide a comparison of the theoretical expressions with the results from a MD computer simulation, which is intended to test the predictions of our simple analytical approach. We also aim here to investigate more closely the reasons for possible discrepancies between simulations and a linearized theory. In particular, we address the question whether and when deviations are due to linearization or a mean-field character of a theory (which ignores correlations and/or finite size effects). Simulations were performed on the level of the coarse-grained model with explicit polyions and counterions using the ESPResSo molecular simulation package.[42,43] We used the cell model setup with two concentric spherical walls: the smaller one represents the shell and the larger one fixes the volume of the system and thus the concentration of charged species. The inner spherical wall (the shell) was made impermeable for the polyions but "invisible" for the counterions. This construction therefore is an inverted version of a polyion-filled shell, which we studied previously.[29] The polyions were modeled as soft spheres with a repulsive potential holding apart the counterions and fixing their closest approach distance to the capsule center (see Appendix A for more details).

We first computed the concentration profiles for polyions and counterions at different values of $\kappa_i R$. The variation in $\kappa_i R$ has been achieved by changing the ratio between the size of the semipermeable shell and an external impermeable spherical constraint and by variation in number of ions. This allowed us to vary this parameter in the range from 1 to 10. As argued above, at smaller values of $\kappa_i R$ we expect linear theory to be very precise. Typical simulation results are shown in Fig. 5. Also included are the theoretical curves
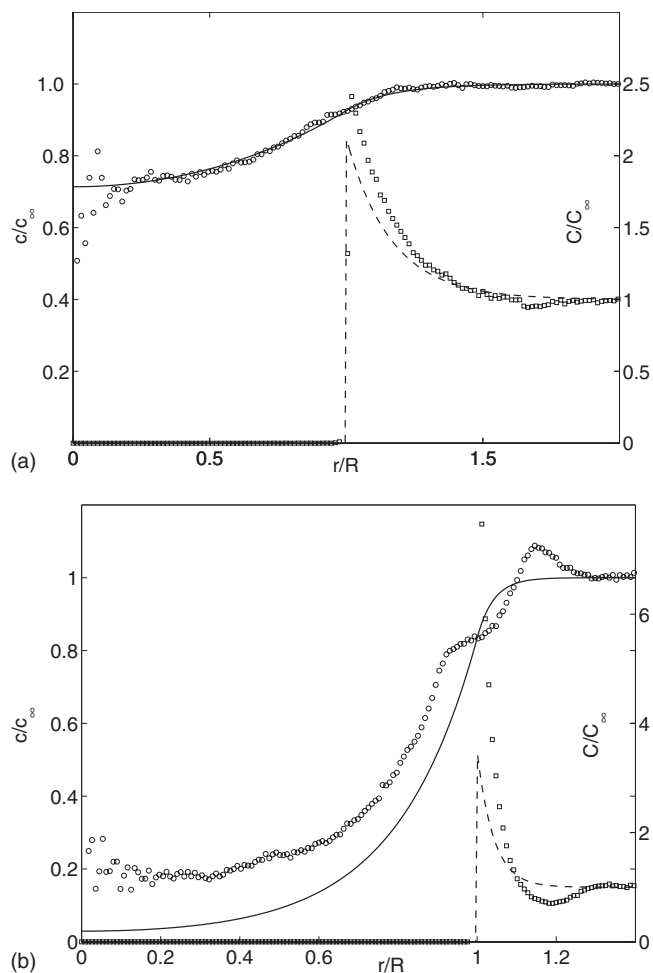

FIG. 5. Theoretical concentration profiles for counterions (solid curve) and polyions (dashed curve) calculated at $\kappa_i R=1.3$ (top) and $\kappa_i R=5.8$ (bottom). Symbols represent the MD simulation results for counterion (circles) and polyion (squares) distributions.

calculated according to Eqs. (9)–(11). The results we show as representative correspond to $\kappa_i R=1.3[\approx 1]$ (Fig. 5, top) and $\kappa_i R=5.8[\gg 1]$ (Fig. 5, bottom). Since we are interested mostly in the calculation of pressure through the height of the polyion peak, we have scaled the simulation results on $R+R_g$ rather than R (this, in particular, means that observed at large $\kappa_i R$ oscillations in concentrations of counterions near the shell are, in fact, outside of it). For $\kappa_i R \approx 1$ the agreement between the theory and simulation is very good, except as a small quantitative discrepancy in the value of a polyion peak at the shell. For $\kappa_i R \gg 1$ the agreement is good at large r/R, where the potential is low, but there are significant discrepancies near the shell boundary ($r/R \approx 1$) for polyions and inside the shell for counterions ($r/R \ll 1$). One of the reasons for the observed discrepancies is the linearization. Indeed, the linear model, Eqs. (2) and (3), being formally applied at large potentials will underestimate mean-field concentrations (this is in agreement with the concentration trends shown Fig. 5). Note, however, that the exact mean-field C at the shell would, in turn, overestimate its value obtained in simulations. The reason is that the nonlinear PB approach leads to extremely high and unphysical values of concentrations of large multivalent ions at the vicinity of charged surfaces. In

reality, the region near the shell can become saturated, leading to pronounced deviations from the PB theory for large ions, and making a real (simulation) value of their concentration closer to predicted within the linearized approach.[30,31] Although with our parameters these steric effects are not as important as in Refs. 30 and 31, they are also expected to decrease the values of PB concentration peaks. Figure 5 also shows oscillations of the local concentration of polyions and even counterions near the shell, which are an indication to ionic correlations in the system neglected in the mean-field theory. (It is interesting to note that a similar structure of concentration profiles near a semipermeable shell is also expected in the case of uncharged solutes and solvents.[44]) We therefore conclude that at large $\kappa_i R$ the finite size and correlation effects are discernible in a very narrow region close to the shell. They do not affect values of concentrations significantly and may even partly reduce a discrepancy in concentrations due to the linearization, but in a general case they are neither zero nor negligible.

Since the exact pressure on the shell is given by the value of the polyion concentration at the outer shell boundary, we have to calculate the exact values of the height of the concentration peak for polyions. The discrete nature of the profiles obtained in the simulation normally does not allow us to fall exactly to the shell boundary. Therefore, to get the height of the peak we have used the (polynomial) extrapolation procedure of our simulation profiles. These values were used to calculate the osmotic pressure. The values of $\Delta p / \Delta p^{id}$ obtained in the simulation are included in Fig. 4. Remarkably, the results for a pressure obtained in the theory and simulation are in a very good harmony despite the obvious discrepancies in concentration profiles at large $\kappa_i R$. In other words, the error in evaluation of a pressure in the linearized theory is not only smaller than in calculations of concentrations (see Appendix B for more discussion) but even extremely small if not negligible. We note, however, that (see Fig. 4) our theory always predicts the value of pressure which is slightly larger than given by simulations. Still, theoretical and simulation pressures are in surprisingly good harmony, especially taking into account the simplicity of the model and the complexity of the system. One can speculate that the effects are somehow included in the quadratic term of the expression for a pressure which provided a self-consistency of the theory. It is interesting to note that there are other examples of successful applications of simple formulas for an osmotic pressure (that also include a kind of quadratic terms) for different types of complex ionic systems,[30,45] and this is not fully understood yet. All these questions, however, deserve further investigations and remain a subject for future work.

IV. CONCLUDING REMARKS

Several aspects of our work warrant more comments. This concerns first of all our main finding that the semipermeability of the shell should lead in some conditions to a dramatic reduction in an excess osmotic pressure as compared with what would be expected for large systems within a standard (bulk) Donnan approach. On a practical side, this result might have implications for many systems, and we would like to mention briefly some of them. Note that an experimental configuration similar to one considered here was used to measure Young's modulus of synthetic semipermeable shells[15] since the modulus is proportional to a critical osmotic pressure, which causes the buckling. Since a pressure exerted on a shell might be much smaller than the bulk osmotic pressure, Young's modulus reported in Ref. 15 can be in reality much smaller and closer to the result obtained with alternative methods.[19,46] Another practical conclusion might concern the mechanical stability of micro- and nanoshells used as a delivery system in the high osmotic pressure environment. As it follows from our results, the efficient way to provide the mechanical stability and the resistance to a compression is to make the shell membrane semipermeable and to adjust the size. Moreover, our results suggest that many data on a pressure acting in truly small nanosystems such as viral capsids and microvilles should be reanalyzed. However, we have proven that a pressure acting to a large membrane indeed reflects an osmotic pressure of a bulk polyion solution (which, in particular, suggests that one can safely use the membrane osmometers to probe the osmotic pressure of bulk polyion solutions[47]).

On a more fundamental level, we would like to remark that the difference between the bulk osmotic pressure and the pressure on the shell we found here can be interpreted as a disjoining pressure in the spherical confined volume. The inner disjoining pressure is positive indicating an electrostatic repulsion, and acts against a compressing osmotic pressure of polyelectrolyte solution. The concept of disjoining pressure is usually used for a description of the equilibria of a thin gap confined between flat or curved surfaces,[48] although there has recently been some theoretical attempts to justify its existence inside a spherical volume (e.g., droplets[49] and charged membranes[50]). Our results are fully consistent with the idea of a disjoining pressure inside a sphere, being now obtained for a new physical situation of a semipermeable shell immersed into a solution of polyions. It is difficult to overestimate a role the disjoining pressure plays in determining the stability of colloid suspensions and thin films.[48,51] One can surmise that it will be of the same importance in the spherically symmetric systems.

In summary, we have presented the linear PB theory and MD simulation data on pressure on the semipermeable shell immersed in a solution of polyions. According to our theoretical derivation, thermodynamic and mechanic consistencies require the boundary density rule to be replaced by a more accurate formula for a pressure, which depending on the conditions can be smaller then or equal to the bulk osmotic pressure. A comparison with the simulation data has shown that while the linearized continuum PB theory often fails to describe accurately the concentration profiles (due to linearization, mean-field character, and an assumption of pointlike ions), the results for a pressure remain reasonably accurate. Thus, the theoretical approach to pressure calculation developed here opens enormous possibilities in solving a large class of problems of soft matter and biophysics, material science, and more.

ACKNOWLEDGMENTS

APPENDIX A: PARAMETERS OF THE COLLOIDAL MODEL OF POLYELECTROLYTES

Here we give a brief summary of the simulation model and setup. The polyelectrolyte solution is treated on the level of the coarse-grained model, where polyions and counterions are represented by Lennard-Jones spheres with central charge according to their valencies. The solvent is considered as a homogeneous medium with dielectric constant ϵ, so that at a given temperature T it is characterized by the Bjerrum length

$$\lambda_B = \frac{e^2}{4\pi\epsilon_0\epsilon k_B T}. \tag{A1}$$

The electrostatic interaction between the ionic species was given by the Coulomb potential,

$$U_{\text{Coul}}(\rho_{ij}) = k_B T \frac{\lambda_B q_i q_j}{\rho_{ij}}, \tag{A2}$$

where $q_i=Z$ for the polyions and $q_i=z$ for the counterions. To model the excluded volume interactions we used repulsive Lennard-Jones (RLJ) potential with the cutoff distance $\rho_c=2^{1/6}\sigma$,

$$U_{\text{LJ}}(\rho) = \begin{cases} 4\varepsilon\left[\left(\dfrac{\sigma}{\rho}\right)^{12} - \left(\dfrac{\sigma}{\rho}\right)^{6} - \left(\dfrac{\sigma}{\rho_c}\right)^{12} + \left(\dfrac{\sigma}{\rho_c}\right)^{6}\right], & \rho \leqslant \rho_c, \\ 0, & \rho > \rho_c, \end{cases} \tag{A3}$$

where ρ is the distance between centers of two particles. The units of length and energy in all presented data were set by σ and ε, respectively (LJ units). The energy parameter ε controls the strength of the interaction, and its value was fixed to $\varepsilon=1.0k_B T$. The Bjerrum length was chosen to be $\lambda_B=2.65$, which gives $\kappa_i=2.16\times10^6\sqrt{c_\infty}$.

The parameters of the polyelectrolyte were taken from our previous work.[29] The polyions and their counterions had valencies $Z=-15$ and $z=+1$, respectively, the interactions between particles are determined by Eq. (A3). Lennard-Jones radii were $\sigma_{pc}=26.5$ polyion-counterion, $\sigma_{cc}=1$ counterion-counterion, $\sigma_{pp}=5$ polyion-polyion, so polyions in our model can overlap but the free counterions cannot go inside their soft cores (see Fig. 6).

The concentration of ionic species was set by means of a spherical cell of radius $R_{\text{ext}}=430$, with the number of polyions per cell ranging from $N_p=100$ to 400 and number of counterions from 1500 to 6000 for different concentrations. Interactions between the shell and polyions, and the outer constraint, which restricts the simulation cell with all particle in the system are described by the RLJ potential [Eq. (A3)], with interaction radii $\sigma_{\text{sh-p}}=\sigma_{\text{constr-p}}=\sigma_{\text{constr-c}}=1.0$. Thus, we use the same parameters of the colloidal model of the poly-
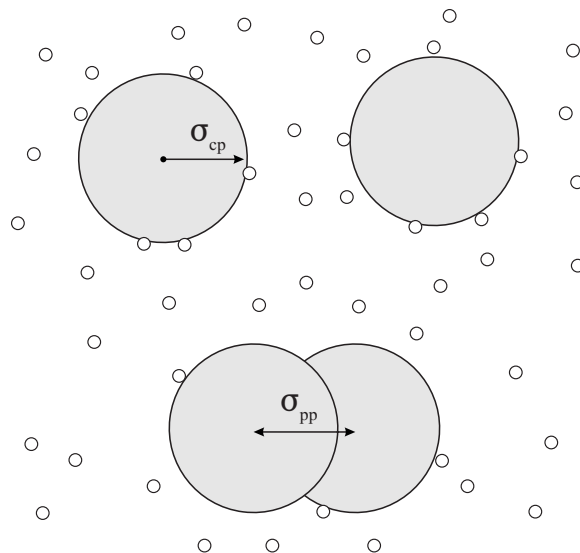

FIG. 6. Spatial distribution of polyions and counterions in the colloidal model with the illustration of the "overlap" of polyions.

electrolyte solution as in Ref. 29. These parameters correspond to a semidilute aqueous solution of polystyrene sulfonate (PSS) molecules with a degree of polymerization of about 200. The main difference with the previous setup is that now we consider a system, in which polyions are located outside of the shell. Generally, the effective parameters of relatively large polyelectrolyte coils can be estimated similar to colloidal particles.[52] The radius of gyration can be estimated as $R_g=\sqrt{l_p L/3}$, with l_p being the polymer persistence length and L the contour length. The saturated effective charge of a coil, Z, in a dilute or semidilute solution then can be estimated as $Z=(R_g/\lambda_B)(6+4\kappa_i R_g)$.[53] Here, we need that $l_p \ll L$ to approach a spherical coil shape. Finally, we should note that for comparison with theory, one should determine the shell radius from the shell-polyion closest approach distance (or radius of the shell constraint) R. Similar parameters can be used for a solution of globular proteins such as, for example, lysozyme.

APPENDIX B: PRESSURE IN THE LINEARIZED PB THEORY

Traditionally, it has been accepted that the computation of a pressure from the concentration profiles obtained in the linear theory can be based on the expressions from the nonlinear PB approach. However, it has recently been recognized that such an approach is incorrect, and a more complex nonlinear expression for a pressure is required to provide a self-consistency of the linear theory.[20] In attempts to justify the latter, different routes to calculate the pressure and the "optimal" linearization scheme have been suggested.[20] These led not only to an ambiguity in the pressure definition but also to a justification of a negative pressure and a consequent liquid-gas phase transition. These artifacts have even been attributed to a very nature of the linearized theory itself.[20,25] The aim of this appendix is to give a rigorous self-consistent derivation of the pressure in the linearized PB theory.

Our starting point is the Poisson equation,

$$\epsilon_0 \epsilon \Delta \phi = -\sum z_i e c_i, \tag{B1}$$

where ϵ is the dielectric constant of the medium and c_i is the local concentration of ions with charge z_i. In the case of dilute solutions the nonelectrostatic interactions between the ions can be neglected and thus the ion distribution obeys the Boltzmann law,

$$c_i = \langle c_i \rangle \frac{\exp(-z_i e \phi / k_B T)}{\langle \exp(-z_i e \phi / k_B T) \rangle}, \tag{B2}$$

where the brackets $\langle \rangle$ indicate a spatial average. The coupling of these two equations is known as the PB equation. Solving it under the relevant boundary conditions provide both the electric potential and the ion distribution.

The local pressure tensor can be written as

$$P = pI - \epsilon_0 \epsilon [\nabla \phi \nabla \phi - (\nabla \phi \cdot \nabla \phi / 2) I] \tag{B3}$$

where the last term is known as the Maxwell tensor and I is the unite tensor. The mechanical equilibrium of the system requires

$$\nabla \cdot P = 0. \tag{B4}$$

Substituting here Eq. (B3) this equation changes to

$$\nabla p = \epsilon_0 \epsilon \Delta \phi \nabla \phi = -\sum z_i e c_i \nabla \phi, \tag{B5}$$

where the last relation is derived by substituting Eq. (B1). Equation (B5) represents the Gibbs–Duhem relation at constant temperature and chemical potential. Substituting here Eq. (B2) and integrating the result one yields the pressure

$$p = p_L + k_B T \sum c_i, \tag{B6}$$

with p_L being the constant pressure of the solvent. It is not surprising that the derived pressure obeys the ideal solution law. According to Eq. (B6) pressure in the nonlinear theory is always positive and increases linearly with concentrations, which, in particular, means that the PB approach does not allow the liquid-gas coexistence.

In the case of small deviations of an electrostatic potential from its spacial average,[54] a very powerful approximation can be used. One can then expand the local concentration from Eq. (B2) in a series of the electric potential. Then by keeping only the first two terms one gets

$$\tilde{c}_i = \langle c_i \rangle \left[1 - \frac{z_i e (\tilde{\phi} - \langle \tilde{\phi} \rangle)}{k_B T} \right]. \tag{B7}$$

Hereafter the superscript $\tilde{\ }$ indicates quantities derived after the linearization of the concentration. Introducing this approximate expression into Eq. (B1) yields the linearized PB equation,

$$\Delta \tilde{\phi} = \kappa^2 (\tilde{\phi} - \langle \tilde{\phi} \rangle), \tag{B8}$$

where $\kappa = \sqrt{\sum z_i^2 e^2 \langle c_i \rangle / \epsilon_0 \epsilon k_B T}$ is the inverse Debye length. Equation (B8) can normally be solved analytically to get the electric potential and concentration profile.

Note that it would be wrong to calculate the local pressure by simple substitution of the concentration from Eq. (B7) in Eq. (B6) as it has been done in many publications.

Indeed, one can easily prove that constructed by such a manner pressure will not obey the Gibbs–Duhem relation. To satisfy the equilibrium condition, Eq. (B4), it is necessary to redefine the pressure in accordance with the approximation, Eq. (B7). The latter can be presented in the differential form as

$$\nabla \tilde{\phi} = -\frac{k_B T \nabla \tilde{c}_i}{z_i e \langle c_i \rangle}. \tag{B9}$$

Substituting this expression in the Gibbs–Duhem relation, Eq. (B5), yields

$$\nabla \tilde{p} = k_B T \sum \frac{\tilde{c}_i}{\langle c_i \rangle} \nabla \tilde{c}_i, \tag{B10}$$

which after integration provides the pressure distribution

$$\tilde{p} = p_L + \frac{k_B T}{2} \sum \tilde{c}_i \left[\frac{\tilde{c}_i}{\langle c_i \rangle} + \frac{\langle c_i \rangle}{\tilde{c}_i} \right]. \tag{B11}$$

We remark that Eq. (B11) coincides with our past result[23] and with the first of two alternative definitions derived in Ref. 20 by using different techniques. Obviously, their second definition allowing optimization along the average electric potential is erroneous.[55] Its incorrectness is also evident from the physically unacceptable results they have obtained using it such as negative pressure, etc.[20,25] It is evident from Eq. (B11) that the linearized theory cannot show any phase transition since $\tilde{p}$ increases monotonously with concentrations. This result is, of course, very reasonable. Since the real system represents an ideal solution [see Eq. (B6)], where the phase transitions are forbidden, the linearization should not allow them provided it has been performed correctly.

One can easily prove that the value of pressure calculated with Eq. (B11) is always larger than that calculated from Eq. (B6) by substituting the linearized concentration from Eq. (B7), i.e., $\tilde{p} \geq p_L + k_B T \sum \tilde{c}_i$. It is more difficult to conclude about the deviation of $\tilde{p}$ from the exact pressure since it depends on the concentration differences, which estimate requires a solution of the full PB equation. However, we argue that the error in the evaluation of pressure in the linear theory would normally be smaller than that of concentrations since $p - \tilde{p} \leq k_B T \sum (c_i - \tilde{c}_i)$.

Note that by combining Eqs. (B11) and (B7) one can get

$$\tilde{p} = p_L + k_B T \sum \langle c_i \rangle + \frac{\epsilon_0 \epsilon \kappa^2}{2} (\tilde{\phi} - \langle \tilde{\phi} \rangle)^2. \tag{B12}$$

As is seen from Eq. (B12) even at potentials small enough to take their linear contribution to the ion distribution the quadratic ϕ-terms in the pressure have to be taken into account in order to satisfy the mechanical equilibrium in the system. This is not surprising, however, since according to the Gibbs–Duhem relation, Eq. (B5), the pressure is an integral of the ion concentrations over the electric potential, which certainly will reflect in an order higher dependence on ϕ.

Thus, since the value of the average potential follows directly from the solution of the PB equation, it cannot be considered as a free parameter for an optimization of the linearization. An analytical expression for a pressure in the

linearized theory is essentially nonlinear and differs from the pressure definition in the exact PB theory. The pressure is positive and does not allow any phase transitions. Moreover, there are solid arguments to conclude that the accuracy of calculation of pressure in the linear theory exceeds that of concentrations.

[1] F. G. Donnan, Chem. Rev. (Washington, D.C.) **1**, 73 (1924).
[2] F. M. Menger and J. S. Keiper, Curr. Opin. Chem. Biol. **2**, 726 (1998).
[3] M. Lindemann and M. Winterhalter, IEE Proc. Sys. Biol. **153**, 107 (2006).
[4] E. Donath, G. B. Sukhorukov, F. Caruso, S. A. Davis, and H. Möhwald, Angew. Chem., Int. Ed. **37**, 2202 (1998).
[5] O. I. Vinogradova, O. V. Lebedeva, and B. S. Kim, Annu. Rev. Mater. Res. **36**, 143 (2006).
[6] V. V. Lulevich, I. L. Radtchenko, G. B. Sukhorukov, and O. I. Vinogradova, J. Phys. Chem. B **107**, 2735 (2003).
[7] B. S. Kim, V. Lobaskin, R. Tsekov, and O. I. Vinogradova, J. Chem. Phys. **126**, 244901 (2007).
[8] B. Alberts, D. Bray, J. Lewis, M. Raff, K. Roberts, and J. D. Watson, *Molecular Biology of the Cell* (Garland, New York, 1983).
[9] J. Darnell, H. Lodish, and D. Baltimore, *Molecular Cell Biology* (Scientific American Books, New York, 1986).
[10] K. Sen, J. Hellman, and H. Nikaido, J. Biol. Chem. **263**, 1182 (1988).
[11] J. B. Stock, B. Rauch, and S. Roseman, J. Biol. Chem. **252**, 7850 (1977).
[12] S. Sukharev, M. Betanzos, C.-S. Chiang, and H. R. Guy, Nature (London) **409**, 720 (2001).
[13] A. Cordova, M. Deserno, W. M. Gelbart, and A. Ben-Shaul, Biophys. J. **85**, 70 (2003).
[14] T. Odijk and F. Slok, J. Phys. Chem. B **107**, 8074 (2003).
[15] C. Gao, E. Donath, S. Moya, V. Dudnik, and H. Möhwald, Eur. Phys. J. E **5**, 21 (2001).
[16] Y. Lvov, A. A. Antipov, A. Mamedov, H. Möhwald, and G. B. Sukhorukov, Nano Lett. **1**, 125 (2001).
[17] O. V. Lebedeva, B. S. Kim, and O. I. Vinogradova, Langmuir **20**, 10685 (2004).
[18] O. V. Lebedeva, B. S. Kim, K. Vasilev, and O. I. Vinogradova, J. Colloid Interface Sci. **284**, 455 (2005).
[19] O. I. Vinogradova, D. Andrienko, V. V. Lulevich, S. Nordschild, and G. B. Sukhorukov, Macromolecules **37**, 1113 (2004).
[20] M. Deserno and H. H. von Grünberg, Phys. Rev. E **66**, 011401 (2002).
[21] R. A. Marcus, J. Chem. Phys. **23**, 1057 (1955).
[22] J. P. Hansen and H. Löwen, Annu. Rev. Phys. Chem. **51**, 209 (2000).
[23] R. Tsekov and O. I. Vinogradova, J. Chem. Phys. **126**, 094901 (2007).
[24] H. Wennerström, B. Jönsson, and P. Linse, J. Chem. Phys. **76**, 4665 (1982).
[25] M. N. Tamashiro and H. Schiessel, J. Chem. Phys. **119**, 1855 (2003).
[26] P. Sheeler and D. E. Bianchi, *Cell and Molecular Biology* (Willey, New York, 1987).
[27] O. I. Vinogradova, J. Phys.: Condens. Matter **16**, R1105 (2004).
[28] R. Tsekov and O. I. Vinogradova, Macromol. Symp. **252**, 149 (2007).
[29] M. R. Stukan, V. Lobaskin, C. Holm, and O. I. Vinogradova, Phys. Rev. E **73**, 021801 (2006).
[30] I. Borukhov, D. Andelman, and H. Orland, Phys. Rev. Lett. **79**, 435 (1997).
[31] M. S. Kilic, M. Bazant, and A. Ajdari, Phys. Rev. E **75**, 021502 (2007).
[32] P. Attard, Adv. Chem. Phys. **92**, 1 (1996).
[33] L. Joly, C. Ybert, E. Trizac, and L. Bocquet, Phys. Rev. Lett. **93**, 257805 (2004).
[34] R. Tsekov, J. Chem. Phys. **126**, 191110 (2007).
[35] K. S. Schmitz, Phys. Rev. E **65**, 061402 (2002).
[36] K. S. Schmitz and L. B. Bhuiyan, Langmuir **18**, 1457 (2002).
[37] The latter assumption is justified provided the shell thickness h is small as compared with its radius R and its dielectric constant is large [for example, shells representing polyelectrolyte multilayers, $\epsilon = 20-50$ (Ref. 56)]. Note, however, that in case of low dielectric constant of the membrane material (e.g., lipids, $\epsilon = 2-4$), especially when $h = O(R)$, the dielectric mismatch[57] can significantly affect the distribution of a potential as compared with predicted by our model.
[38] Note that in our system the radius of the shell is much larger than the size of polyelectrolyte molecules, which are outside of the shell. Therefore, effects related to the polymeric nature of the charged coil, which are crucial for highly confined polyelectrolyte molecules,[58] can be safely neglected.
[39] The condition of electroneutrality of the whole system means that the integral $r^2 dr$ of Eq. (1) is equal to zero. In other words it corresponds to $(r^2 d\phi/dr)_{r\to\infty} = 0$, which is satisfied in our theory.
[40] J. L. Barrat and J. F. Joanny, Adv. Chem. Phys. **94**, 1 (1996).
[41] A. V. Dobrynin and M. Rubinstein, Prog. Polym. Sci. **30**, 1049 (2005).
[42] A. Arnold and C. Holm, Comput. Phys. Commun. **117**, 2496 (2002).
[43] H. Limbach, A. Arnold, B. Mann, and C. Holm, Comput. Phys. Commun. **174**, 704 (2006).
[44] Y. Zhou and G. Stell, J. Chem. Phys. **89**, 7010 (1988).
[45] Y. Levin, E. Trizac, and L. Bocquet, J. Phys.: Condens. Matter **15**, S3523 (2003).
[46] V. V. Lulevich, D. Andrienko, and O. I. Vinogradova, J. Chem. Phys. **120**, 3822 (2004).
[47] A. Takahashi, N. Kato, and M. Nagasawa, J. Phys. Chem. **74**, 944 (1970).
[48] B. V. Derjaguin, N. V. Churaev, and V. M. Muller, *Surface Forces* (Plenum, New York, 1987).
[49] R. Tsekov, K. W. Stöckelhuber, and B. V. Toshev, Langmuir **16**, 3502 (2000).
[50] T. H. Fan and O. I. Vinogradova, Langmuir **22**, 9418 (2006).
[51] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1992).
[52] L. Bocquet, E. Trizac, and M. Aubouy, J. Chem. Phys. **117**, 8138 (2002).
[53] M. Aubouy, E. Trizac, and L. Bocquet, J. Phys. A **36**, 5835 (2003).
[54] Note that in contrast to a common belief the expansion should not necessarily be constructed around zero potential.
[55] Their mistake is hidden in the incorrect interpretation of the thermodynamic relation $p = -(\partial_V F)_{T,\mu,\phi}$. In their Eq. (22) the authors of Ref. 20 have considered also the average potential $\langle\phi\rangle$ as a variable since it depends on the volume V. However, since the thermodynamic definition above requires derivative at constant electric potential this automatically means that the average value of ϕ should also be considered as a constant.
[56] P. A. Neff, B. K. Wunderlich, R. V. Klitzing, and A. R. Bausch, Langmuir **23**, 4048 (2007).
[57] A. Parsegian, Nature (London) **221**, 844 (1969).
[58] R. Kumar and M. Muthukumar, J. Chem. Phys. **128**, 184902 (2008).