The Osmotic Behavior of Short Stiff Polyelectrolytes

Dmytro Antypov,[1,2] *Christian Holm*[*1,3]

Summary: We report our recent advances in understanding when a simple cell model of a single, short polyelectrolyte is able to correctly reproduce the osmotic coefficient of a bulk solution. To this end we proposed a self-consistent geometry optimized cell model. In contrast to the usual monotonic Poisson-Boltzmann prediction, the cell model predicts the correct non-monotonic dependence of the osmotic coefficient on concentration. A lower degree of polymerization is found to reduce significantly the counterion condensation for a typical dilute strong polyelectrolyte solution, thus increasing the osmotic coefficient. The results agree quantitatively with simulations of a corresponding many-body bulk system up to a dense semi-dilute regime. We investigate the effect of chain flexibility and on residual salt on the osmotic properties, and give a short overview about other effects which might be responsible for the observed discrepancy to recent experimental results on a PPP polyelectrolyte system.

Keywords: computer modeling; molecular dynamics; Poisson-Boltzmann; polyelectrolytes; solution properties

Introduction

Polyelectrolytes are macromolecules that can dissociate into a highly charged macroion and oppositely charged small counterions in a polar solvent. Unlike flexible-chain polyelectrolytes, rod-like polyelectrolytes do not change their conformation upon changing concentration and thus serve as excellent model systems to study the underlying physics of counterion condensation and the counterion contribution to the osmotic properties. Aqueous solutions of short DNA fragments[1] and rigid synthetic polyelectrolytes[2] are good examples of such systems, since their contour length is of the order of their persistence length. Due to a great number of free counterions, the osmotic pressure in a dilute polyelectrolyte solution is much higher than that of neutral polymers at similar concentrations. However, not all counterions are osmotically active - some of them are bound to the macroion by electrostatic forces. The reduced thermodynamic activity of counterions can be expressed in terms of the osmotic coefficient ϕ:

$$\phi = \frac{\Pi}{\Pi_{\mathrm{id}}}, \tag{1}$$

where Π is the osmotic pressure and $\Pi_{\mathrm{id}} = c_c k_B T$ is the ideal gas pressure at a given counterion concentration c_c and temperature T, with k_B being the Boltzmann constant. Many experimental studies of strongly charged polyelectrolytes have shown that ϕ is of order of 0.2 to 0.3 for monovalent counterions in the dilute salt-free regime (see Ref. [2–4] and references therein). A similar value can also be obtained using the mean field Poisson-Boltzmann (PB) theory for an infinite rod cell model.[1–5] Within this approach, an infinitely long linear macroion and its counterions are confined inside a cylindrical

---

[1] Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany
Fax: (+49) 6131379100
E-mail: holm@mpip-mainz.mpg.de

[2] Department of Materials Science and Metallurgy, Pembroke St., Cam-bridge, CB2 3QZ, UK

[3] Frankfurt Institute for Advanced Studies (FIAS), Max-von-Laue-Straße 1, 60438 Frankfurt, Germany
Fax: (+49) 6979847611
E-mail: c.holm@fias.uni-frankfurt.de

cell and the counterion density distribution $\rho(r)$, which satisfies both the Poisson equation and the Boltzmann distribution, can be found analytically (see Ref. [6] and references therein). Despite the reported agreement with experimental data, this model is restricted at low salt solutions to the semi-dilute regime, where the distance between the macroions is much smaller than their length. Indeed, any finite macroion loses all its counterions upon infinite dilution resulting in $\phi = 1$, whereas, for an infinitely long charged rod, the osmotic coefficient monotonically approaches the Manning limit.[7] Extension of Manning arguments to a finite chain[8] fixes the limiting value to unity but results in monotonic *decrease* of osmotic coefficient with concentration. While there are some non-cell model analytical approaches[9–11] which capture the qualitatively correct non-monotonic concentration dependence of the osmotic coefficient, the cell-model approach is appealing due to its simplicity and the possibility to obtain exact results.[12] A dual cell model approach has recently been put forward to study a very dilute polyelectrolyte solution, and an analytical solution to the PB theory was used to describe it.[13] However, the theoretical description of a polyelectrolyte solution at moderate concentrations is still a complicated matter. Recently we proposed a model which bridges between the spherical cell at low polymer concentrations and an infinitely long cell at high concentrations[14] which we would like to present in the following.

The main idea of the cell model is to treat a polyelectrolyte solution as a set of identical non-interacting, electrically neutral cells each of which contains one finite rod-like macroion and the corresponding number of counterions (Fig. 1). The macroscopic polymer concentration c_p sets the cell volume at $1/c_p$. The choice of the shape of the cell is not as obvious as, for example, in the case of a spherically symmetric macroion. Here, the cell is expected to be nearly spherical at very low polymer concentrations and it should resemble the shape of the macroion, i.e. be rod-like, at high concentrations. The shape of the *optimal* cell would always coincide with the equipotential surface of electrostatic potential, as it is in the case of a spherical or infinitely long linear macroion. Due to such tinfoil-like boundary conditions and cell electroneutrality, the electrical field is perpendicular to the cell surface at every point and is zero outside the cell. The direct consequence of this is that two such cells do not interact with one another, which in turn justifies the usage of the cell model. The constant electrostatic potential at the cell surface also results, at least within the PB mean-field approximation, in a constant surface density ρ_0. The osmotic pressure can therefore easily be evaluated as $\rho_0 k_B T$.

Below we demonstrate that for a rod-like polyelectrolyte the cell shape can be successfully approximated by a simple cylinder. Consider a cylindrical cell of volume V, length L, and radius R, and define its aspect ratio as $\alpha = L/R$, see Fig. 1. The cell walls are electrically neutral and act merely as a space constraint for our point-like counterions. Among all cylindrical cells of volume V, let us choose the one which has the lowest free energy $F(V, \alpha)$, i.e.

$$\left(\frac{\partial F(V,\alpha)}{\partial \alpha}\right)_V = 0. \tag{2}$$

Here $F(V, \alpha) = -k_B T \ln Z$, where

$$Z = \prod_{i=1}^{N} \int_0^{2\pi} d\phi_i \int_0^L dz_i \int_0^R r_i dr_i \exp\left(-\frac{U}{k_B T}\right), \tag{3}$$

is the canonical partition function and U is the total potential energy which depends on particle coordinates and also includes the macroion interaction potential. Both the volume and shape of the cell enter Eq. (3) only via the integration limits L and R which are well-defined functions of V and α. After substituting Eq. (3) to Eq. (2), it reduces to

$$\langle\rho\rangle_{r=R} = \langle\rho\rangle_{z=L}, \tag{4}$$

where $\langle\rho\rangle_{r=R} 1/L \int_0^L \rho(R,z)dz$ is the average counterion density at the side surface of the cell and $\langle\rho\rangle_{z=L} = 2/R^2 \int_0^R \rho(r,L)rdr$ is the average density at the top of the cell.

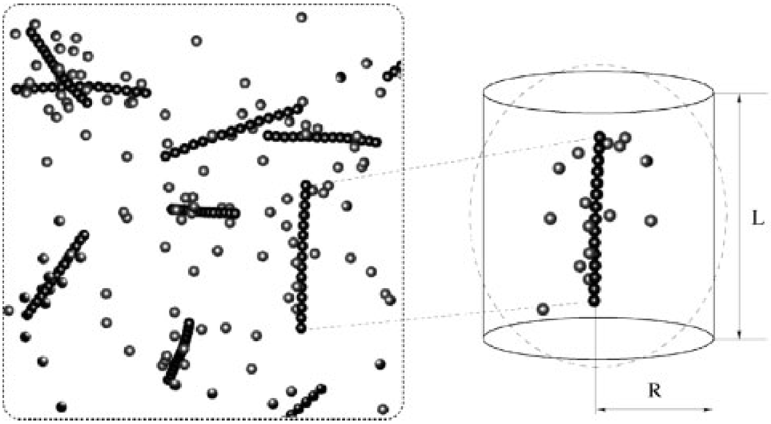

Figure 1.
Dilute solution of stiff-chain polyelectrolyte. The snapshot on the left shows a typical bulk arrangement of rod-like macroions and oppositely charged spherical counterisee text for details).

The counterion density is different across the cell surface and condition (4) is a weaker version of the constant surface density requirement for the *optimal* cell. The thermodynamic definition of the pressure as minus the partial derivative of the free energy with respect to volume gives some average pressure which in general depends on the way the cell volume is varied. For example, variation of R at fixed L gives $p_R = k_B T \langle \rho \rangle_{r=R}$, the average pressure at the side surface of the cell, and analogously, variation of L at fixed R gives $p_L = k_B T \langle \rho \rangle_{z=L}$. It can also be shown that for independent variation of both L and R the result can be anything between p_R and p_L. Since $p_R = p_L$ for the minimum free energy cell, the cell pressure is uniquely defined and can be equated to the osmotic pressure in the bulk. For other cell shapes we adopt the isotropic volume variation which does not change the aspect ratio α, and define the osmotic pressure as

$$\begin{aligned} p &= -\left(\frac{\partial F(V,\alpha)}{\partial V}\right)_{\alpha} \\ &= k_B T \left(\frac{2\langle \rho \rangle_{r=R} + \langle \rho \rangle_{z=L}}{3}\right). \end{aligned} \tag{5}$$

Note that the osmotic pressure is proportional to the *average* counterion density at the cell surface. The same conclusion can be drawn from an analogous calculations made for a spherical cell containing a macroion of arbitrary shape.

To test our optimized cylindrical cell model at different polymer concentrations we performed standard Monte Carlo (MC) simulations in the canonical ensemble for a typical strong polyelectrolyte which was also used in Refs. [9] and [15]. The macroion contained $N = 30$ unit charges, one charge per monomer of unit length σ. The Bjerrum length was set to 3σ, meaning that the electrostatic energy was k_BT when the separation between two unit charges was 3σ. This value yields a Manning parameter $\xi = 3$, and a limiting osmotic coefficient $(2\xi)^{-1} \approx 0.167$ at infinite dilution. The counterions were treated as point charges which could approach the monomers as close as 1σ. For each given polymer concentration c_p, the cell volume was fixed at $1/c_p$, and average densities $\langle \rho \rangle_{r=R}$ and $\langle \rho \rangle_{z=L}$ were measured for a series of aspect ratios α. The minimum free energy configuration and the corresponding osmotic pressure were defined by Eq. (4). The same procedure was repeated for shorter and longer macroions to assess how the osmotic pressure depends on the degree of polymerization. All main results are summarized in Fig. 2. The fraction of free counterions increases as the polymer chain

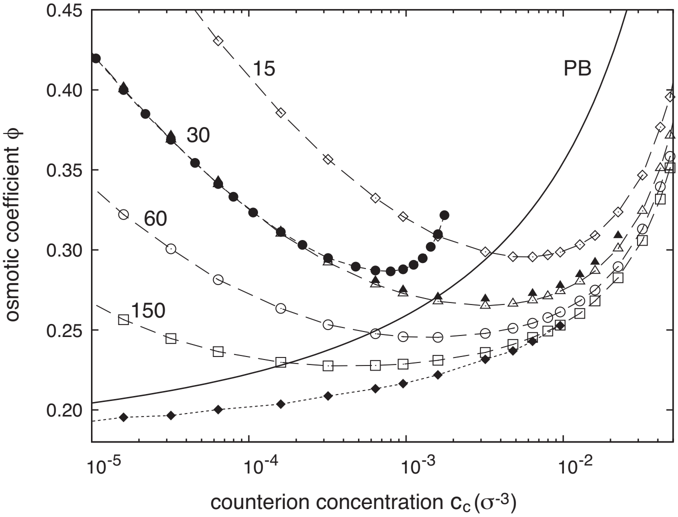

Figure 2.
The concentration dependence of the osmotic coefficient of a typical strong polyelectrolyte (see text for details). All open symbols are the results of MC simulations of the cylindrical cell model for different polymer lengths $15 \leq N \leq 150$. We further included spherical cell model simulations for $N = 30$ (●), bulk MD simulations for $N = 30$(▲), and results of MD simulations of an infinitely long polymer (◆). The solid line is a prediction of the PB theory for the infinite charged rod cell model.

length is decreased and the osmotic coefficient is always higher for shorter chains at a given bulk concentration of counterions. Unlike the PB solution for an infinite rod, shown in Fig. 2 as a solid line, which monotonically increases with concentration, each curve calculated for a finite rod has a characteristic minimum. This mini-

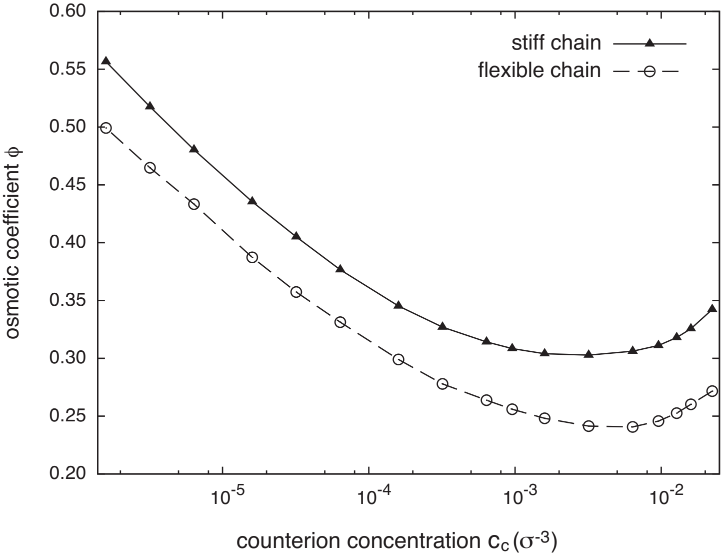

Figure 3.
Influence of chain flexibility on the osmotic coefficient. Shown is the osmotic coefficient φ for a completely rigid (▲) and totally flexible (o) chain of length $N = 30$ as a function of counterion concentration c_c.

mum corresponds to the situation when the gain of entropy due to more uniform distribution of the counterions starts rto exceed the electrostatic energy penalty. Indeed, the electrostatic potential of a finite charged rod behaves as $1/r$ at large distances and as $\ln r$ at short distances, while the entropic gain is always logarithmic We would like to remark that the simulation results at moderate concentrations can be fitted remarkably well with a quadratic polynomial of $\ln c_c$. At sufficiently high counterion screening, finite rods behave similar to an infinite rod. In order to locate this curve, a 1*D*-periodic system, mimicking an infinitely long cell, was simulated via molecular dynamics (MD) using the MMM1D algorithm[16] for the electrostatic interactions. Filled diamonds in Fig. 2 are the results of these MD simulations. The difference between the pressure profile for the infinite rod and any of the finite rod profiles yields exactly the contribution of the end effects. The difference between the PB curve and the MD simulations of the infinite rod is informative of the effect of counterion correlations, which are neglected within the mean-field PB framework. This effect is almost negligible at low concentrations ($\approx 5\%$ at $10^{-5}\sigma^3$), but very significant ($\approx 50\%$ at $10^{-2}\sigma^{-3}$) in the semi-dilute regime. Here, integral equations,[10,11] strong coupling theories,[17] or modifications to the usual PB theory[18] can be used to improve on the mean-field treatment.

To answer the question of how well the optimized cylindrical cell model predicts the actual osmotic pressure, we compare the above results with bulk MD simulations. A 3*D*-periodic system of 50 polymer chains, 30 monomers each, and their corresponding counterions, was simulated in the constant *NVT* ensemble using standard numerical methods:[19] velocity Verlet algorithm, Langevin thermostat, and the P3M algorithm for calculating the electrostatic interactions. The monomers were modeled as charged, purely repulsive Lennard-Jones spheres connected by stiff harmonic bonds. This, together with a stiff bending potential, provided a rod-like conformation of each chain. The total pressure Π, which includes an ideal gas contribution, the usual virial expression for short-range forces and the electrostatic contribution taken as a third of the average electrostatic energy per unit volume,[20] was calculated at different counterion concentrations and then divided into two terms

$$\Pi = \Pi_p + \Pi_c \tag{6}$$

where Π_p is the osmotic contribution of the macroions, taken as the ideal gas pressure $c_p k_B T$, and Π_c is the pressure due to the free counterions. The second component, Π_c is plotted for $N = 30$ in Fig. 2 and found in excellent agreement with the predictions of the optimized cylindrical cell model. Therefore, the two main conclusions can be drawn: a) the osmotic pressure of a polyelectrolyte solution is mainly controlled by free counterions and (a small correction Π_p of order *1/N)* osmotically active macroions together with condensed counterions b) the macroion-macroion correlations have a very weak effect on the osmotic pressure at the studied concentrations.

All cell models predict almost the same pressure at very low counterion concentrations (at $\lesssim$ the cell shape is not critical to the pressure). As the concentration is increased, the spherical cell starts to overestimate the pressure and completely fails when the cell diameter becomes equal to the rod's length at overlap concentration $\sigma^3 c^* = 6/\pi\ N^2 \approx 2 \times 10^{-3}$. Both cylindrical cells predict similar pressures up to $\sigma^3 \approx 0.03$ which is much higher than c^*. The bulk pressure was found to be always slightly higher than the prediction of the cell models. This is attributed to the small effect of macroion-macroion correlations which was found to be a weak function of density. In other words, Π_p in Eq. (6) in addition to the ideal component $c_p k_B T$, also includes a virial term which corresponds to the repulsion between the cells.

We have also measured the effect of the chain flexibility. Even for $N = 30$, replacing stiff chains with completely flexible ones causes the reduction of bulk pressure from 10% at low concentrations to 20% in the semi-dilute regime, compare 3. This effect is more profound for longer chains. The position of the minimum of the osmotic coefficient versus concentration curve (see Fig. 2) depends on chain flexibility and was found to scale proportional to $N^{-1.2}$ for rigid rods and N^{-2} for flexible chains.[15]

Comparison with Experiments

We now want to study to what extent our results are relevant for short rod-like polyelectrolytes. As a reference system we use a water solution of synthetic rod-like poly(p-phenylenes) (PPP) that has been intensively studied[2,3,21] by means of different experimental techniques including electric birefringence measurements, membrane osmometry and X-ray scattering. At 40° C this highly charged polyelectrolyte is characterized by Manning parameter $\xi = 3.4$. The monomer length was taken to be 4.3 Å with two unit charges per monomer. The counterions were treated as point charges and could approach the backbone as close as $r_0 = 7.0$ Å. Three essentially different types of models were studied at these parameters: (a) an infinitely long rod (b) one finite rod consisting of $N = 40$ monomers (c) a bulk system of 30 very stiff chains. The polymer chain length is $L = 17.2$ nm which is less than the experimentally measured persistence length of 22 nm. All simulations were performed in the range of counterion concentrations $0.2 < c_c < 14$ mmol/L for which experimental data are available.

In Fig. 2 we can infer that the ionic interactions are already significant for strongly charged polyelectrolytes at moderate concentrations.[14] This effect was found to decrease the osmotic pressure by approximately 7%[4] at low concentrations for the PPPs we study here, and this decrease could also be obtained by using the modified PB functional of Ref. [18]. To assess how the finiteness of the chain affects the osmotic coefficient at a given polymer concentration we performed a series of simulations for PPP parameters using a spherical and cylindrical cell model as well as bulk MD simulations. Figure 4 summarizes the results of these simulations.

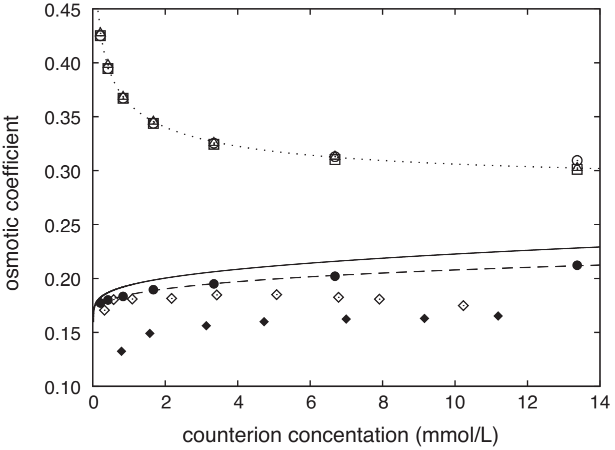

Figure 4.

The osmotic coefficient calculated at different counterion concentrations using various models. The results for a finite rod calculated using the spherical cell model (empty circles), cylindrical cell with adjustable geometry (empty squares) and bulk system (empty triangles) are found in a very good agreement. The dotted line is a numerical fit to the bulk data drawn to guide the eye. The solid line is the prediction of the PB theory and the dashed line fits the results obtained from MMM1D simulations for an infinitely long rod (filled circles). Experimentally measured osmotic coefficient for iodide (open diamonds) and chloride (filled diamonds) counterions[3] are also shown.

The osmotic coefficients measured using the finite cell models are corrected by the $1/N$ term to obtain the bulk pressure, see[22] for more details. All finite rod methods yield similar results which are significantly higher than both theoretical and simulation predictions of the osmotic coefficient for an infinite rod. The small deviation between the cylindrical and spherical cells at higher densities is due to the fact that application of the latter is limited to very low densities, when the polymer chain is considerably smaller than the cell diameter. The optimal cylindrical cell, on the contrary, can be successfully applied up to the semi-dilute regime.[14]

The correlation effects discussed above are all small in comparison to the large difference between the pressure obtained for a finite and an infinite polymer chain. The finiteness of the chain therefore plays the leading role in the studied concentration range. The $\Pi(c_c)$ curve obtained for the finite macroion does not only decrease monotonically, as would in-deed be expected at very low density, but also goes well above the curve obtained for an infinite rod. Compared to our previous findings[4] we face the fact the we found now an even bigger difference between the simulation and the experimental data of Ref. [3] for finite rods. Other issues like chain flexibility, residual salt, charge distribution on the back-bone and specific interactions between the backbone and counterions as possible candidates to close the gap between calculated and measured data have been thoroughly examined, and in the following we just give a short summary of the most important findings, the full account will appear elsewhere.[22]

In the following we will discuss the effect of residual salt, since a small amount of resid-ual salt is known to be present even in deionized water, of the order of 1 μmol, depending on the experimental setup, and if the osmotic pressure is measured in a membrane osmometer against pure water this will influence the resulting osmotic measurements. Salt results in a non-zero Donnan potential across the membrane separating the polymer solution from the pure water cell. The corresponding electric field affects the distribution of charged particles in the system,[4,6] resulting in a *decrease* of the measured osmotic pressure. For sim-plicity we consider a PPP solution with a trace of a monovalent salt at bulk concentration c_b. Using the formalism of an electrically neutral spherical cell model with added positive and negative salt ions we can write down the condition of Donnan equilibrium in terms of charge balance at the cell boundary:

$$\rho_+(R)\rho_-(R) = c_{b,}^2 \tag{7}$$

where $\rho_+(R)$ and $\rho_-(R)$ are the total boundary densities of positive and negative charges respectively. Note that both counterions and salt anions contribute to $\rho_-(R)$. The resulting osmotic pressure is given by the difference between the osmotic pressures at the cell boundary acting from inside and from outside:

$$\Pi = (\rho_+(R) + \rho_-(R) - 2c_b)k_BT. \tag{8}$$

The bulk salt concentration c_b cannot be set *a priori* in the cell simulation. However, the effects of the residual salt can still be incorporated by including a fixed amount of salt in the cell and then measuring the equilibrium values of the charge densities at the cell boundary. Then using Eq. (7) and Eq. (8) both the bulk salt content and corresponding osmotic pressure can be calculated. Repeating this procedure for different amounts of salt at a fixed polymer concentration we obtained $\Pi(c_b)$ curves at several polymer concentrations studied previously. The resultant values of the osmotic pressure as a function of both polymer and salt concentrations are summarized in Fig. 5. As it is expected, the effect of the residual salt is more pronounced at low polymer concentrations. It is the residual salt that is responsible for suppressing the asymptotic increase of the osmotic coefficient at lower polymer concentrations in experiments. However, as the polymer concentration is increased, this effect becomes relatively weak. Thus, to achieve an experimentally observed osmo-

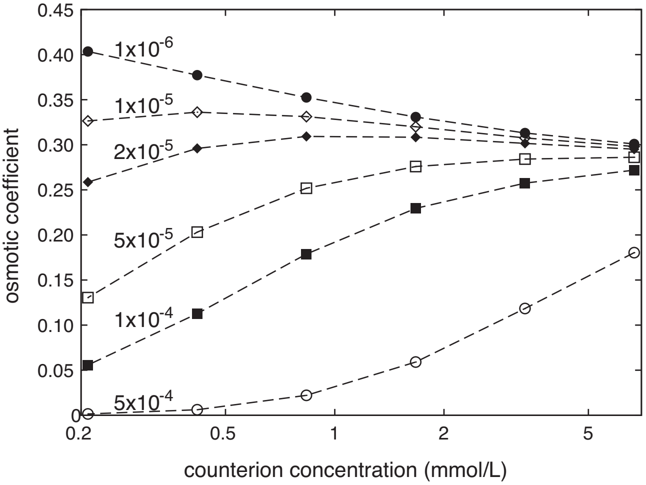

Figure 5.

Osmotic coefficient as a function of polymer concentration measured at different salt content. The upper curve (open triangles) is the salt free case. The salt concentration then increases along the shown arrow as follows: 1 μmol (filled triangles), 10 μmol (open diamonds), 20 μmol (filled diamonds), 50 μmol (open squares), 100 μmol (filled squares), 200 μmol (open circles), 500 μmol (filled circles).

tic pressure at moderate polymer content approximately 0.5 mmol/L of salt is needed. This is already 500 times higher than what is thought to be the usual residual salt concentration. Therefore, for sufficiently low residual salt concentrations, one should observe the increase of the osmotic coefficient experimentally for short polyelectrolyte chains. In this case, upon lowering the concentration the increase of the osmotic pressure due to the finiteness of the macroions might be seen before the residual salt brings it down to zero. We are not aware of any experiments that have observed this effect so far, although the experimentally data for iodide in Fig. 4 seem to indicate this trend.

Conclusions

In summary, a geometry optimized cell model approach was proposed that is able to predict the osmotic pressure of a solution of rod-like polyelectrolytes from a very dilute to a dense semi-dilute concentration range. An exact route was derived to find the aspect ratio that minimizes the free energy of a cylindrical cell. The predictions of the cell model agree very well with our complementary bulk simulations in a wide range of concentrations, enhancing the applicability of the previous cell model approaches greatly. We further showed that the PB approach for the infinite rod fails at low concentrations due to the finite chain length and also misses the effect of counterion correlations which is very significant at high concentrations. For a stiff-chain PPP polyelectrolyte with well defined parameters we found that the finiteness of the macroion plays the most important role in the range of experimental concentrations. Not only the macroion itself contributes to the total osmotic pressure but it also has a distinctively lower fraction of condensed counterions compared to an infinite chain. Both effects therefore increase the pressure in the system. The contribution of macroion-macroion correlations to the pressure was found to be positive but small which means that an appropriate cell model containing a single macroion and its counterions is a good tool to predict the pressure. From the analysis of varying the flexibility of the PE

Table 1.
Different effects and their contribution to the osmotic coefficient calculated for parameters of PPP polyelectrolyte at counterion concentration $c_c = 6.7$ mmol/L.

Effect	Contribution
mean-field PB condensation	0.216
electrostatic correlations	-0.014
excluded volume correlations	$+0.001$
macroion-macroion correlations	$+0.004$
macroion osmotic contribution	$+0.013$
residual salt 1 μmol/L	-0.0003
finite chain length	$+0.100$
finite chain stiffness	-0.007
off-center ion distribution	$+0.028$

backbone it was concluded that finite chain stiffness has a small effect on the osmotic properties, but higher flexibility reduces the pressure. Another effect which was found to reduce the pressure slightly was the effect of electrostatic correlations which is basically the difference between the PB solution and the simulation results. Other effects like ion specificity, backbone ion distribution on the macroion, or excluded volume correlations were also treated in Ref. [22], but either large unphysical values (ion specificity) are needed to reduce significantly the osmotic coefficient, or the effects were small. Table 1 gives an approximate contribution of each effect studied. If all effects are incorporated into the simple cell model to make it resemble the experimental system more closely the resultant osmotic coefficient almost twice exceeds the experimentally observed value of $\phi_{exp} \approx 0.18$.[3] It is not clear what the reason for this discrepancy is. It might be that the experimental system did not have such an ideal composition as was assumed, and that some larger aggregates might have been present. Another experimental data set on small stiff polyelectrolytes in salt free environment would be desirable to test our results, or to give further hints on what the difference between our computer model and the experimental system might be.

All the model systems considered in this paper were based on the assumption of pure Coulomb interactions in a uniform dielectric background. We do not believe, however, that this is the main cause of the mismatch to the experimental results. In light of our recent tests of the dielectric continuum model versus a simulation with an explicit water solvent[23] the explicit water simulations might show a lowering, due to the decrease of the local relative dielectric constant near the macroion, but probably only on the order of a few percent.

Summarizing again, we used simple geometric arguments to improve the model system from a single infinitely long rod to a solution of finite semi-flexible polyelectrolyte macro-molecules. The latter, however, gives the osmotic pressure about twice higher than that predicted by experiment. We hope that our results will stimulate more experimental studies and computer simulations with explicit solvent to address this issue.

Acknowledgements: We thank M. Ballauff, M. Deserno and E. Trizac for useful discussions and acknowledge financial support from the DFG under grants Ho 1108/11-2, SFB 625 and TR6.

[1] E. Raspaud, M. da Conceicao, and F. Livolant, *Phys. Rev. Lett.* **2000**, *84*, 2533.
[2] C. Holm, M. Rehahn, W. Oppermann, and M. Ballauff, *Adv. Polym. Sci.* **2004**, *166*, 1.
[3] J. Blaul, M. Wittemann, M. Ballauff, and M. Rehahn, *J. Phys. Chem. B* **2000**, *104*, 7077.
[4] M. Deserno, C. Holm, J. Blaul, M. Ballauff, M. Rehahn, *Eur. Phys. J. E* **2001**, *5*, 97.
[5] P. L. Hansen, R. Podgornik, and V. A. Parsegian, *Phys. Rev. E* **2001**, *64*, 021907.
[6] M. Deserno and C. Holm, in: *Electrostatic Effects in Soft Matter and Biophysics*, Vol. *46* of *NATO Science Series II - Mathematics, Physics and Chemistry*, C. Holm, P. Kékicheff, and R. Podgornik, Eds., Kluwer Academic Publishers, Dordrecht **2001**.
[7] G. Manning, *J. Chem. Phys.* **1969**, *51*, 924.
[8] P. González-Mozuelos and M. O. de la Cruz, *J. Chem. Phys.* **1995**, *103*, 3145.
[9] R. M. Nyquist, B. Ha, and A. J. Liu, *Macromolecules* **1999**, *32*, 3481.
[10] C. Shew and A. Yethiraj, *J. Chem. Phys.* **1999**, *110*, 11599.
[11] T. Hofmann, R. Winkler, and P. Reineker, *J. Chem. Phys.* **2001**, *114*, 10181.
[12] H. Wennerström, B. Jönsson, and P. Linse, *J. Chem. Phys.* **1982**, *76*, 4665.
[13] A. Deshkovski, S. Obukhov, and M. Rubinstein, *Phys. Rev. Lett.* **2001**, *86*, 2341.

[14] D. Antypov and C. Holm, *Phys. Rev. Lett.* **2006**, *96*, 088302.

[15] Q. Liao, V. Dobrynin, and M. Rubinstein, *Macromolecules* **2003**, *36*, 3399.

[16] A. Arnold and C. Holm, *J. Chem. Phys.* **2005**, *123*, 144103.

[17] A. Naji and R. R. Netz, *Phys. Rev. Lett.* **2005**, *95*, 185703.

[18] M. C. Barbosa, M. Deserno, and C. Holm, *Europhys. Lett.* **2000**, *52*, 80.

[19] H.-J. Limbach, A. Arnold, B. A. Mann, and C. Holm, *Comp. Phys. Comm.* **2006**, *174*, 704.

[20] G. Hummer, L. R. Pratt, and A. E. García, *J. Phys. Chem. A* **1998**, *102*, 7885.

[21] M. Ballauff, J. Blaul, B. Guilleaume, M. Rehahn, S. Traser, M. Wittemann, P. Wittmeyer, *Macromol. Symp.* **2004**, *211*, 1.

[22] D. Antypov, C. Holm, submitted.

[23] B. Hess, C. Holm, and N. van der Vegt, *Phys. Rev. Lett.* **2006**, *96*, 147801; *J. Chem. Phys.* **2006**, *124*, 164509.