

# Coulomb Correlation Between Counterions in the Double Layer Around Cylindrical Polyions<sup>†</sup>

Jesus Piñero<sup>a</sup>, Lutful B. Bhuiyan<sup>a</sup>, Jurij Reščič<sup>b</sup> and Vojko Vlachy<sup>b\*</sup>

<sup>a</sup>Laboratory of Theoretical Physics Department of Physics, University of Puerto Rico San Juan, Puerto Rico 00931-3343

<sup>b</sup>Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia

Received 03-05-2006

<sup>†</sup> Dedicated to the memory of Prof. Dr. Davorin Dolar

## Abstract

Monte Carlo simulation and theoretical results on some aspects of structure and thermodynamics of polyelectrolyte solutions at room temperature are presented. The solution is mimicked by an infinitely long cylindrical polyion surrounded by point counterions. Both standard histogram method and Widom's particle insertion method are utilized in the simulations based on the cylindrical cell model. The osmotic coefficient is determined via different equations (approaches) to determine the internal consistency of the equations as also the numerical accuracy of the calculations. Contributions to the osmotic coefficient arising out of polyion-counterion and counterion-counterion interactions are explicitly evaluated. The study clearly demonstrates (i) that the good agreement between the Poisson-Boltzmann predictions and the simulations is partly due to some serendipitous cancellation of errors, and (ii) that it is the neglect of the inter-ionic correlations in the mean field approach that leads to a partial compensation of the shortcomings of the Poisson-Boltzmann osmotic equation. Simulations results are also reported for the ion-ion correlations in the inhomogeneous diffuse double layer surrounding the polyion.

**Keywords:** polyelectrolyte solution, Monte Carlo, Poisson-Boltzmann, osmotic coefficient, heat of dilution

## 1. Introduction

Quantitative understanding of the various inter-particle correlations that govern the distribution of the charge cloud in the double layer around a linear polyelectrolyte is of great importance for life sciences and technology.<sup>1</sup> Despite many experimental and theoretical studies performed over the past four decades, the predictions for equilibrium and non-equilibrium properties of these solutions are, in general, at best semi-quantitative.<sup>(2-7)</sup> For example, some recent experimental results for the osmotic pressure of ionene solutions as a function of polyion charge have re-confirmed significant deviations from electrostatic models.<sup>8</sup> The deviations are larger for weakly charged polyelectrolytes, which manifest in osmotic pressures that are about 25% lower than predicted. More complex behaviour is exhibited by the enthalpies of dilution  $\Delta H^9$ , which for ionenes<sup>10</sup> and some other polycations in water<sup>11</sup> are endothermic. This is in complete contrast to the predictions of the established electrostatic theories. Similarly, measurements of the heats of dilution of the salts of poly(styrenesulphonic)acid indicates that  $\Delta H < 0$  in most cases, but changes sign from negative to positive for 'structure breaking' ions ( $\text{Cs}^+$ ) above

room temperatures.<sup>12</sup> There is presently no quantitative explanation of these results, though presumably the effects are solvent (water in this case) induced. Clearly, further theoretical and experimental studies are needed to understand these solutions.

Interpretation of measurable quantities of polyelectrolyte systems is most often based on the Poisson-Boltzmann (PB) equation (see for example, references [2], [3], and [4]) and/or the Manning condensation theory.<sup>13</sup> These two approaches are really the cornerstones of the polyelectrolyte theory their appealing features being (i) the ease of use that is convenient for routine, everyday analysis of experimental data, and (ii) their intuitive simplicity. Over the last few decades, more formal approaches based on statistical mechanics have been advanced to describe the electric double layer around a cylindrical polyion. Notable among these are the modified Poisson-Boltzmann (MPB) theory,<sup>14,15</sup> the hypernetted chain/mean spherical approximation (HNC/MSA)<sup>16,17</sup> (see also the references listed in [4]), and the density functional (DFT) theory.<sup>18</sup>

A rigorous examination of the shortcomings of the PB equation as applied to cylindrical polyelectrolyte solutions was first carried out by Fixman.<sup>19</sup> Later, the

theory was tested against ‘exact’ Monte Carlo (MC) simulation data in numerous publications (see for example, references [16, 20–23]). The list is long, with the most recent contribution to the subject being the work of Wang and coworkers.<sup>24</sup> The general consensus that emerges out of the simulation studies is that the PB theory yields a semi-quantitative agreement overall with the simulations, the level of agreement being perhaps better for some properties, while being worse for others. It has been suggested that the semi-quantitative nature of the PB predictions might be a consequence of some fortuitous cancellation of errors. Our interest in the present paper is to examine to what degree is the ‘good’ agreement between the PB theory and the MC simulations a result of cancellation of intrinsic errors of the theory. Towards this goal, we have performed extensive MC simulations and carefully examined some properties that have not been so studied earlier in the literature. The new simulations are based on the cylindrical cell model with the polyion being treated as a uniformly charged rigid cylinder that models DNA molecule. An important feature of the present simulation that distinguishes it from previous such simulations is that we treat the counterions as point particles – an aspect that allows meaningful comparisons with the PB theory. Since ions do not have size in the physical model treated here, discrepancies between the PB predictions and the ‘exact’ MC results can be ascribed to the absence of Coulomb correlations in the former.

In the part of the work concerned with osmotic properties we build on some previous work by one of us<sup>25,26</sup> and explore various contributions to the osmotic pressure. The distribution of the counterions will be determined using both histogram and Widom’s method<sup>27</sup>, while the osmotic pressure will be calculated using different equations to check the internal consistency of the equations and the numerical accuracy of the calculations. We will show how the neglect of the ion-ion correlations in the PB principles leads to a partial compensation of the deficiencies in the osmotic equation derived from the PB theory. We will present the results for enthalpies of dilution comparing the MC data with the cell model PB calculations, which, to best of our knowledge, has not been done before. The last but not the least important part of the paper is concerned with correlation between pointlike counterions in the ion atmosphere surrounding a polyion.

## 2. Model and Methods

In accordance with the concept of the cell model, the polyelectrolyte solution is viewed as an assembly of mutually independent, electroneutral cylindrical cells of radius  $R$  and length  $h$ . We focus our attention

on one such cell. The cylindrical polyion with radius  $a$  and length  $h$  is placed along the long cell axis. It is assumed that each of the  $N$  monomer units of length  $b$  ( $h = Nb$ ) carries one elementary charge. The cell radius is determined by polyelectrolyte concentration given in the basemol units (moles of monomer units per  $\text{dm}^3$ ),  $c_m^{-1} = \pi(R^2 - a^2)N_A h$  where  $N_A$  denotes the Avogadro’s number. We also assume that counterions are the only ionic species present and are represented by point-like charges embedded in a continuum dielectric with relative permittivity  $\epsilon_r$ . The pair interaction between two monovalent counterions separated by a distance  $r$  is

$$u_{cc}(r) = \frac{L_B}{\beta r} \quad (1)$$

Where the Bjerrum length  $L_B$  is given by

$$L_B = \frac{\beta e^2}{4\pi\epsilon_0\epsilon_r} \quad (2)$$

In these equations,  $\beta = 1/(k_B T)$ , where  $k_B$  is the Boltzmann’s constant,  $T$  is the absolute temperature,  $\epsilon_0$  and  $\epsilon_r$  are the vacuum and relative permittivity, respectively, and  $e$  the proton charge. The polyion-counterion interaction potential is given by

$$u_{pc}(r) = \frac{2\lambda}{\beta} \log_e \left[ \frac{h}{2r} + \left\{ 1 + \left( \frac{h}{2r} \right)^2 \right\}^{1/2} \right] \quad (3)$$

where  $\lambda = L_B / b$  and  $r$  is here the radial distance from the polyion long axis. Note that for  $h \gg r$ ,  $u_{pc}(r)$  reduces to the familiar form for an infinitely long polyion, namely,  $u_{pc}(r) \sim \log_e(r)$ .

### 2.1 Monte-Carlo Simulations

The Metropolis MC simulations were performed utilizing two independent codes similar to the ones utilized in references [14] and [28], respectively, and on different computers to ascertain the influence of random number generators, get a better estimate of statistical errors, and to check for other sources of errors. The programs were modified to incorporate the Widom’s method<sup>27</sup> of calculating the counterion distribution around the polyions. The method has the following advantages, viz., (i) it is more accurate than the standard practice of collecting histograms where the ‘bin’ size affects results, and (ii) the counterion concentrations at  $r = a$  and  $r = R$ , needed in calculations of quantities like the osmotic coefficient, can be obtained without the uncertainties associated with an interpolation procedure.

In the first of the programmes, the correction for the finite length  $h = Nb$  of the polyion was done as described before,<sup>14</sup> viz., the central MC cell with  $N$  monomer units was replicated along the cylinder axis.

In the second, no such correction was made but a much longer polyion was used. The polyion length dependence was checked by performing well converged calculations for  $N = 1000, 2000$ , and  $5000$ . The results obtained this way are given in Tables 1 and 2. In all the calculations reported in this paper we made equilibration runs with around  $16 \times 10^3$  passes (number of trial moves per particle) and long, production runs with around  $144 \times 10^3$  passes. The results in Table 1 show very good consistency between results obtained by different codes and on different machines. Furthermore, the effects of the finite length or of periodicity in distribution imposed by using replicas<sup>14</sup> seem to be quite small and well within the stochastic uncertainties of simulations. It is worth noting also that good agreement with earlier results for polyion-counterion contact values and osmotic coefficients<sup>25</sup> were obtained.

The PB equation was solved numerically using a 4<sup>th</sup> order Runge-Kutta method. The boundary condition at the surface of the polyion,  $r = a$ , given by Gauss Law was satisfied by a trial and error procedure sometimes known as the ‘shooting method’.<sup>20</sup>

## 2.2 Osmotic Coefficient

The osmotic coefficient is defined as  $\phi = \Pi / \Pi_{id}$ , where  $\Pi$  is the measured pressure and  $\Pi_{id}$  is the ideal pressure. In this work we have obtained the osmotic coefficient using two different equations. The first one is the usual expression valid within the cell model approximation

$$\phi = \frac{c(R)}{\langle c \rangle} \quad (4)$$

where  $c(R)$  is the local concentration of counterions at the cell boundary,  $r = R$ , and  $\langle c \rangle$  is the average concentration of the counterions in the polyion free volume of the cell. For monovalent counterions as in the present case,  $\langle c \rangle = c_m$ . The concentration of counterions at the cell boundary was calculated using the Widom’s method and by collecting the histogram of densities (number concentrations) within the distances  $r$  and  $r + \delta r$ , with  $\delta r$  being the width of a bin. Numerical agreement between the two ways of collecting the data is good (see also the subsection on polyion-counterion distribution). Results for different concentrations and  $N$ -values are tabulated in Table 1.

The osmotic coefficients were also calculated using the virial equation in cylindrical symmetry derived earlier by one of us.<sup>25</sup> For completeness we outline here the basic equations in the derivation. The osmotic equation reads

$$\phi = 1 - \frac{V}{Nk_B T} \int \frac{\partial u_{pc}}{\partial V} \rho(\vec{r}) d\vec{r} - \frac{V}{2Nk_B T} \iint \frac{\partial u_{cc}}{\partial V} \rho^{(2)}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (5)$$

**Table 1.** The  $N$ -dependence<sup>a</sup> and the consistency of the two Monte-Carlo routines used in characterizing thermodynamics.

| $C_m(M)$ | $N$  | osmotic coefficient    |                    |                    | energy<br>(in units of $k_B T$ ) |                      |                      |
|----------|------|------------------------|--------------------|--------------------|----------------------------------|----------------------|----------------------|
|          |      | Histogram <sup>a</sup> | Widom <sup>a</sup> | Viral <sup>a</sup> | Histogram <sup>b</sup>           | routine <sup>a</sup> | routine <sup>b</sup> |
| 0.002    | 1000 | 0.1635                 | 0.1641             | 0.1215             | 0.1614                           | -20.0726             | -20.0881             |
|          | 2000 | 0.1630                 | 0.1624             | 0.1666             |                                  | -22.9712             |                      |
|          | 5000 | 0.1627                 | 0.1619             | 0.1664             |                                  | -26.8252             |                      |
| 0.005    | 1000 | 0.1711                 | 0.1725             | 0.1541             | 0.1706                           | -20.2266             | -20.2491             |
|          | 2000 | 0.1715                 | 0.1706             | 0.1678             |                                  | -23.1273             |                      |
|          | 5000 | 0.1713                 | 0.1725             | 0.1736             |                                  | -26.9835             |                      |
| 0.01     | 1000 | 0.1797                 | 0.1804             | 0.1627             | 0.1802                           | -20.3513             | -20.3669             |
|          | 2000 | 0.1805                 | 0.1801             | 0.1672             |                                  | -23.2620             |                      |
|          | 5000 | 0.1798                 | 0.1799             | 0.1769             |                                  | -27.1096             |                      |
| 0.05     | 1000 | 0.2116                 | 0.2129             | 0.2071             | 0.2118                           | -20.6624             | -20.6759             |
|          | 2000 | 0.2114                 | 0.2115             | 0.2111             |                                  | -23.5706             |                      |
|          | 5000 | 0.2122                 | 0.2121             | 0.2138             |                                  | -27.4203             |                      |
| 0.1      | 1000 | 0.2325                 | 0.2330             | 0.2319             | 0.2324                           | -20.8154             | -20.8611             |
|          | 2000 | 0.2341                 | 0.2322             | 0.2310             |                                  | -23.7246             |                      |
|          | 5000 | 0.2325                 | 0.2329             | 0.2318             |                                  | -27.5744             |                      |
| 0.2      | 1000 | 0.2615                 | 0.2623             | 0.2605             | 0.2598                           | -20.9870             | -20.9956             |
|          | 2000 | 0.2622                 | 0.2609             | 0.2604             |                                  | -23.8964             |                      |
|          | 5000 | 0.2616                 | 0.2609             | 0.2608             |                                  | -27.7466             |                      |

<sup>a</sup> MC programme (A) (see for example, reference [28]).

<sup>b</sup> MC programme (B) (see for example, references [14] and [15]).

The second term is the polyion-counterion (p-c) contribution as it contains the p-c interaction  $u_{pc}(r)$  with  $\rho(r)$  being the singlet polyion-counterion distribution function (number density profile). It has been shown<sup>25</sup> that this term yields a simple expression

$$-\lambda + v_m [\rho(a) - \rho(R)] \quad (6)$$

Here,  $\rho(a)$  and  $\rho(R)$  are the contact values of the polyion-counterion distribution function at the polyion and cell surfaces, respectively.<sup>25,26</sup> The quantity  $v_m$  is the volume of the monomer unit,  $v_m = \pi a^2 b$ .

The third term is due to the counterion-counterion (c-c) interaction. It contains the two-particle (doublet) distribution function,  $\rho^{(2)}(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2)g(\vec{r}_1, \vec{r}_2)$ , where  $g(\vec{r}_1, \vec{r}_2)$  is the ion-ion pair distribution function in the inhomogeneous double layer.<sup>29</sup> By writing  $\rho^{(2)}(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2)$ , that is by putting  $g(\vec{r}_1, \vec{r}_2) = 1$ , this term can be integrated to yield a simple result,  $\lambda/2$ . It has been demonstrated<sup>25</sup> by invoking the Bogoliubov-Born-Green-Yvon hierarchy of equations that the approximation is essentially equivalent to the approximations inherent in the PB theory.

The virial equation (Eq. 5) for the osmotic coefficient thus approximates to

$$\phi = 1 - \lambda / 2 + v_m [\rho(a) - \rho(R)] \quad (7)$$

This expression is valid within the framework of the mean field PB approximation and is numerically equivalent to the better known result given by Eq. 4. The terms in Eq. 5 can, however, be calculated ‘exactly’ by the MC method and we will present these results in the next Chapter.

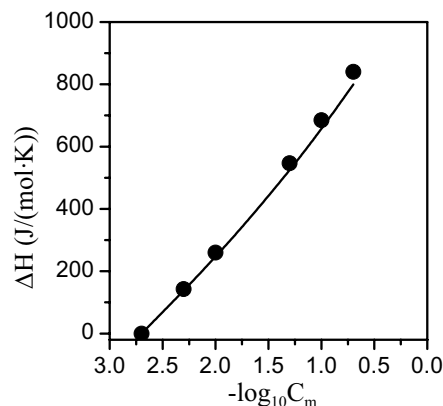
### 3. Results and Discussion

#### 3.1 Thermodynamic Properties

In all the calculations presented in this study, the polyion radius  $a = 10 \times 10^{-10}$  m,  $b = 1.7 \times 10^{-10}$  m,  $\lambda = 4.2$ , and  $L_B = 7.14 \times 10^{-10}$  m, which corresponds to a water-like solvent at  $T = 298$  K. The values of  $b$ ,  $\lambda$  are also the usually accepted parameters for double-stranded DNA solution.

##### 3.1.1 Enthalpies of Dilution

We begin this discussion by presenting the results for enthalpies of dilution approximated here by the energy difference between the two given concentrations. In the present calculations we have taken  $c_m = 0.002$  M to be the final (diluted) state, so that for an initial (concentrated) state specified by the concentration  $c_m$  we have,  $\Delta H_{c_m \rightarrow 0.002M} \approx E(c_m = 0.002M) - E(c_m)$ , where  $E$  is the excess internal energy, calculated in the usual way. Note that the configurational energies obtained from the MC or the PB theories have to be multiplied by the factor  $(1 + \frac{d \log_e \epsilon_r}{d \log_e T})$ , which for water at 298 K equals  $-0.368$ . Some results for  $\Delta H$  (in J/mole.K) are given in Figure 1. As expected from the electrostatic model  $\Delta H$  is negative, with the agreement between the simulations and the PB predictions reasonably good, especially for the lower initial concentrations. It is noted that the numerical uncertainties in the  $\Delta H$  obtained by MC are necessarily large as they result from subtraction of a large number from another large number. Absolute values of energies are much bigger than the differences  $\Delta H$ . The numerical errors are estimated to be within 5%. As can be seen, the PB  $\Delta H$ 's are slightly less negative relative to the corresponding MC values and the discrepancies are generally larger than the statistical uncertainties. We would like to mention that both the MC programmes were utilized to calculate  $\Delta H$  and the results were consistent and indistinguishable on the graphical scale of Figure 1. To our knowledge MC calculation of this property has not been done earlier in the literature, so that it is for the first time that PB results for enthalpies of dilution are confronted with the computer simulation data.



**Figure 1.** Enthalpy of dilution of a cylindrical polyelectrolyte solution as a function of logarithm of polyion concentration. The symbols denote MC simulations, while the line denotes PB results. All calculations are for a cylindrical cell model with monovalent point-like counterions and polyion radius  $a = 10 \times 10^{-10}$  m, Manning's parameter  $\lambda = 4.2$ , Bjerrum length  $L_B = 7.14 \times 10^{-10}$  m, monomer unit length  $b = 1.7 \times 10^{-10}$  m, and temperature  $T = 298$  K. The values of  $\lambda$  and  $b$  are apropos of double-stranded DNA.

##### 3.1.2 Osmotic Properties

In the MC simulation the osmotic coefficient  $\phi$  was calculated from Eqns. (4) and (5). In the former case the agreement between the two ways of collecting data – Widom's method and using the standard histogram method – for evaluating  $\phi$  are quite consistent as can be seen from Table 1. In the latter case the integral terms of Eq. 5 can be calculated exactly (see also, Eq. 8 of reference [25]). The MC and PB results for the full osmotic coefficient (Eq. 5) together with the individual p-c contribution (Eq. 6) and c-c contribution (the third term in Eq. 5) are given in Table 2 for several polyion concentrations. Numerical uncertainties in the MC calculation of the osmotic coefficient depend on the equation used. For the results obtained via Eq. 4 (Widom's method is slightly more accurate than histogram approach), we estimate the error bars to be  $\pm 1\%$ , and for the virial equation (Eq. 6) the uncertainties are around  $\pm 5\%$ . Eq. (5) yields larger numerical uncertainties than Eq. (4) since it obtains from adding three terms of order of unity to obtain the term (osmotic coefficient) in the magnitude range 0.1 to 0.3. As we see from the  $\phi$  results presented in Table 1, the agreement between the results given by Eqs. 4 and 5 is actually better than suggested by the numerical uncertainty of these calculations. In passing, we note that although the optimum confidence in the data in the tables is probably up to three significant digits, more digits after decimal are given for the benefit of the reader that might be interested in using the data for calculations. Indeed the two sets of MC data are virtually the same to three significant digits as can be seen in the tables.

**Table 2.** The counterion-counterion (c-c) and polyion-counterion (p-c) contributions (Eq. 6) to the virial osmotic coefficient (Eq. 5). The PB results are calculated via Eq. 7.

| $c_m(M)$ | N    | MC <sup>a</sup> |         |                      | PB   |         |        |
|----------|------|-----------------|---------|----------------------|------|---------|--------|
|          |      | c-c             | p-c     | $\phi(\text{viria})$ | c-c  | p-c     | $\phi$ |
| 0.002    | 1000 | 1.9706          | -2.8491 | 0.1215               | 2.10 | -2.9315 | 0.1684 |
|          | 2000 | 1.9990          | -2.8324 | 0.1666               |      |         |        |
|          | 5000 | 2.0070          | -2.8406 | 0.1664               |      |         |        |
| 0.005    | 1000 | 1.9888          | -2.8347 | 0.1541               | 2.10 | -2.9200 | 0.1797 |
|          | 2000 | 2.0015          | -2.8337 | 0.1678               |      |         |        |
|          | 5000 | 2.0043          | -2.8307 | 0.1736               |      |         |        |
| 0.01     | 1000 | 1.9942          | -2.8315 | 0.1627               | 2.10 | -2.9086 | 0.1908 |
|          | 2000 | 2.0000          | -2.8327 | 0.1672               |      |         |        |
|          | 5000 | 2.0023          | -2.8254 | 0.1769               |      |         |        |
| 0.05     | 1000 | 1.9905          | -2.7834 | 0.2071               | 2.10 | -2.8637 | 0.2326 |
|          | 2000 | 1.9916          | -2.7805 | 0.2111               |      |         |        |
|          | 5000 | 1.9916          | -2.7778 | 0.2138               |      |         |        |
| 0.1      | 1000 | 1.9842          | -2.7523 | 0.2319               | 2.10 | -2.8294 | 0.2622 |
|          | 2000 | 1.9846          | -2.7536 | 0.2310               |      |         |        |
|          | 5000 | 1.9841          | -2.7523 | 0.2318               |      |         |        |
| 0.2      | 1000 | 1.9743          | -2.7138 | 0.2605               | 2.10 | -2.7730 | 0.3036 |
|          | 2000 | 1.9744          | -2.7140 | 0.2604               |      |         |        |
|          | 5000 | 1.9740          | -2.7132 | 0.2608               |      |         |        |

<sup>a</sup> MC programme (A) ( see for example, reference [28])

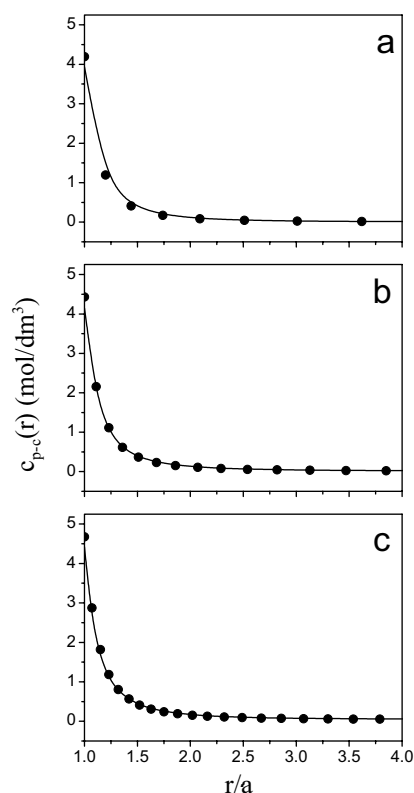
It is evident from Table 2 that the PB theory overestimates the c-c contribution where it has the constant value  $\lambda/2 = 2.1$ . On the other hand, this theory underestimates the p-c contribution. The overall effect is a partial compensation of errors leading to relatively better agreement with the full ‘exact’ MC osmotic coefficient for pointlike counterions. This is part of the reason why PB theory yields relatively good agreement with the experimental results for this quantity.

### 3.2 Spatial Distributions of Counterions

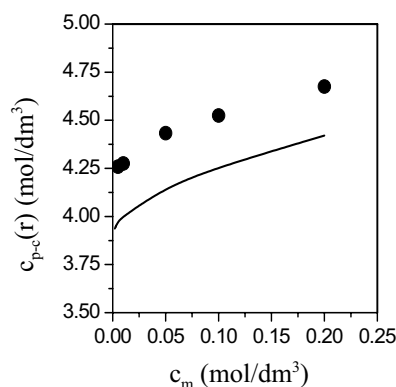
#### 3.2.1 Polyion-Counterion Correlation

We present these results in Figures 2 and 3. First in Figure 2 we show the local polyion-counterion concentration profile  $c_{p-c}(r)$  for three polyelectrolyte concentrations (from top panel to bottom panel)  $c_m = 0.002, 0.05$ , and  $0.2 \text{ mol/dm}^3$ , respectively, obtained by the Widom’s method (symbols) and the PB theory (line). We have also obtained  $c_{p-c}(r)$  using the histogram method, which was found to be virtually the same as that from the Widom’s method and is hence not shown. As indicated earlier, the advantage of the Widom’s

method is that there is no uncertainty associated with the extrapolation to  $r = a$  and  $r = R$ . The figure indicates relatively good agreement between the computer simulations (symbols) and PB results (line). However, a closer look reveals that MC electrical double layer is thinner and the contact values higher (viz., top panel).



**Figure 2.** Polyion-counterion (singlet) distribution at different polyion concentrations in the cylindrical cell model. The symbols denote MC (Widom) simulations, while the line denotes the PB results. From top to bottom, (a)  $c_m = 0.002 \text{ mol/dm}^3$ ,  $R = 394.42 \times 10^{-10} \text{ m}$ , (b)  $c_m = 0.05 \text{ mol/dm}^3$ ,  $R = 79.48 \times 10^{-10} \text{ m}$ , and (c)  $c_m = 0.2 \text{ mol/dm}^3$ ,  $R = 40.68 \times 10^{-10} \text{ m}$ . The model parameters are given in the caption of Figure 1.



**Figure 3.** Contact value of the polyion-counterion (singlet) distribution at the polyion surface, as a function of polyelectrolyte concentration. The symbols denote MC (Widom) simulations, while the line denotes PB results. The model parameters are given in the caption of Figure 1.

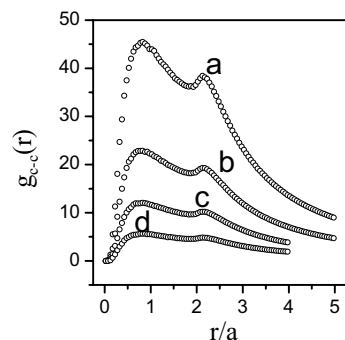
Further evidence of this is seen in the Figure 3, where the concentration of counterions at contact,  $c_{p-c}(a)$ , is presented as a function of the polyelectrolyte concentration  $c_m$ . Again, the MC (Widom's method) results are shown by symbols and PB calculations as a continuous line.

### 3.2.2 Counterion-Counterion Correlation

The doublet correlation function  $\rho^{(2)}(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2)g(\vec{r}_1, \vec{r}_2)$  is very difficult to calculate accurately even for a simpler planar case<sup>30</sup>. Fortunately, a somewhat more restricted information,  $\langle g(r_{12}) \rangle$ , the average being taken over the free volume of the cell, is readily obtained by the MC method. This function is simply a volume average of the probability of finding two ions in the range of distances  $r$  and  $r + \delta r$ . In the isotropic system this is the usual pair correlation function  $g(r)$ , but for the anisotropic case studied here, however, the contributions to  $\langle g(r_{12}) \rangle$  coming from different parts of the cylindrical cell are different, and hence a volume average. Information about the correlation between counterions in the electrical double-layer around cylindrical polyion, as reflected in  $\langle g(r_{12}) \rangle$ , is given in Figure 4. In this figure the  $\langle g(r_{12}) \rangle$  results are shown for four different concentrations; from top to bottom  $c_m$  is 0.005, 0.01, 0.02 and 0.05 mol/dm<sup>3</sup>.

We can see from this figure that the counterion-counterion correlation functions exhibit two peaks. The first peak is located around  $r \approx 8 \times 10^{-10}$  m. We can assume that this value represents the upper limit of the radius of the 'correlation hole', that is, the sphere from which all other counterions are excluded. This value exceeds the diameter of the most of the ions in their hydrated state. It is very likely therefore, that the excluded volume of the ion, here they are treated as point-like, will not affect much the thermodynamic results. This is consistent with the experimental data for the osmotic coefficient, which are only slightly dependent on the size of the monovalent counterion.

The shape of the distribution functions given in Figure 4 is the consequence of the fact that the counterions tend to cluster around the highly charged polyion, but at the same time are trying to avoid, as much as possible, contact with each other. This accounts for the fact that the second peak is located around  $r \approx 2a = 20 \times 10^{-10}$  m. Also, the plots reveal that the effect does not vanish with dilution; on the contrary, the correlations between counterions are stronger for dilute solutions. It is confirmed here that  $\langle g(r_{12}) \rangle$  departs from unity in a substantial part of the MC cell, what accounts for the deviations of the PB theory from simulations. Note that similar shape of the counterion-counterion distribution function has previously been obtained for spherical macroions.<sup>31</sup> Strong correlation between the ions of the same sign, caused by presence



**Figure 4.** Counterion-counterion (doublet) distribution function  $\langle g(r_{12}) \rangle$  in the double layer around a polyion. The plots are, from top to bottom, (a)  $c_m = 0.005$  mol/dm<sup>3</sup>, (b)  $c_m = 0.01$  mol/dm<sup>3</sup>, (c)  $c_m = 0.02$  mol/dm<sup>3</sup>, and (d)  $c_m = 0.05$  mol/dm<sup>3</sup>. The symbols represent results of MC simulations and the model parameters are given in the caption of Figure 1.

of polyelectrolyte has been utilized to catalyze some hydrolysis reactions<sup>32</sup>, and to study ionic distributions in DNA solutions.<sup>33</sup>

## 4. Concluding Remarks

The combined MC – PB study is presented for a model polyelectrolyte solution with point-like counterions with the polyions modelled as uniformly charged cylinders. This way, the shortcomings of the PB approximation, resulting from the neglect of the Coulomb correlation, can be examined independently from the excluded volume effect. Various thermodynamic and structural properties were investigated; for the first time we present the MC results for enthalpies of dilution and compare these data with the PB values. Relatively good agreement between the two calculations was obtained.

Osmotic coefficients were calculated using two different equations. We have shown that both expressions yield, within numerical accuracy, the same result. One of the osmotic equations, the so-called virial equation, permits evaluation of the separate contributions stemming from the counterion-counterion and polyion-counterion interactions. The conclusion is that PB theory overestimates the counterion-counterion term and underestimates the polyion-counterion contribution to the osmotic coefficient. The compensation of the two separate errors yields relatively good agreement of the PB osmotic coefficient with the MC data.

The above conclusion is supported by plots showing the counterion profiles (singlet distributions) around the polyion. In agreement with previous studies we have found that the PB theory underestimates the concentration of counterions at contact with the polyion. The effect of the Coulomb correlation is to make the electrical double layer thinner. These conclusions are further borne out by the results obtained

for the counterion-counterion correlation (doublet distributions). The volume average of the counterion-counterion correlation function in the electrical double layer around polyion was calculated for different polyelectrolyte concentrations. This function departs from unity (that is, from the PB approximation) in the part of the cell next to the polyion. Furthermore, the correlations between counterions are stronger for dilute solutions. This is suggestive of the fact that, in contrast to simple electrolyte solutions, the polyelectrolytes do not approach ideal state, but rather depart from it by dilution.

Some comments on the relevance and suitability of the cell model vis-a-vis practical situations, especially DNA solutions, are in order. The model has proved useful over the years in predicting equilibrium properties of many polyelectrolyte solutions. For example, Bratko and Vlachy<sup>34</sup> had earlier found that their MC simulated osmotic coefficients of some poly(styrenesulfonate) (PSS) solutions using the cylindrical cell model agreed fairly well with the corresponding experimental values. More recently, structural properties of salt-free, rodlike DNA in presence of polyamine counterions (at DNA concentrations of 0.05 mol/dm<sup>3</sup> and 0.1 mol/dm<sup>3</sup>) predicted by MC simulations, again on the cell model, have been found to correspond well to the experimental small-angle-neutron-scattering (SANS) results.<sup>35</sup> It is therefore plausible that the cell model will be useful for other thermodynamic properties such as heats of dilution. Unfortunately, to our best knowledge, no such experimental measurements of  $\Delta H$  for DNA seem to have been reported.

For stability reasons DNA is often studied in presence of added simple electrolytes and not in salt-free conditions as examined in this work. One such example is given in reference [33] where the effect of DNA on rates of bimolecular energy transfer between ions is measured. The energy transfer from luminescent lanthanide ions probes collision frequencies that are dependent on concentration of DNA. Two generalization are needed in order to simulate this experiment: (i) the ions need to be modelled as (bulky) lanthanides (and not point-like as in the present calculations), and (ii) an additional ionic species, so-called co-ions, needs to be introduced into the model. The cell model indeed allows for such extensions.<sup>14,15</sup> We hope to present the results of such a study in the near future.

## 5. Acknowledgement

This work was supported by the Slovenian Research Agency through Physical Chemistry Research Program 0103-0201, Research Project J1-6653, and US-SLO Joint grant BI-US/06-07-008. LBB acknowledges support through a National Science Foundation Grant

0137271, and an institutional grant through Fondo Institucional Para Investigacion (FIPI), University of Puerto Rico.

## 6. References

1. H. Dautzenberg, W. Jaeger, J. Kötze, B. Phillip, C. Seidel, D. Stscherbina, *Polyelectrolytes, Formation, Characterization and Application* 1994 (Hanser, Munich).
2. A. Katchalsky, Z. Alexandrowicz and O. Kedem in : *Chemical Physics of Ionic Solutions*, eds. B. E. Conway, R. G. Barradas, 1966 (Wiley, New York), pp.295–346.
3. D. Dolar in : *Polyelectrolytes*, eds. E. Selegny, M. Mandel, U. P. Strauss, 1972 (Reidel, Dordrecht), pp. 97–113.
4. K. S. Schmitz, *Macroions in Solutions and Colloidal Dispersion*, 1993 (VCH Publishers Inc., New York).
5. C. Wandrey, D. Hunkeler, U. Wendler, W. Jaeger, *Macromolecules* 2004, 33, 7136–7143.
6. J. Blaul, M. Wittemann, M. Ballauff, M. Rehahn, *J. Phys. Chem. B* 2000, 104, 7077–7081.
7. C. Holm, M. Rehahn, W. Opperman, M. Ballauff, *Adv. Polymer Sci.* 2004, 166, 1–27.
8. K. Arh, C. Pohar, V. Vlachy, *J. Phys. Chem. B* 2002, 106, 9967–9973.
9. G. E. Boyd, D. P. Wilson, *J. Phys. Chem.* 1976, 80, 805–808.
10. K. Arh, C. Pohar, *Acta. Chim. Slov.* 2001, 48, 385–394.
11. M. Keller, R. N. Lichtenthaler, A. Heintz, *Ber. Bunsengesell. Phys. Chem.* 1996, 100, 776–779.
12. G. Vesnaver, M. Rudez, C. Pohar, J. Skerjanc, *J. Phys. Chem.* 1984, 88, 2411–2418.
13. G. S. Manning, J. Ray, *J. Biomol. Struct. Dyn.* 1998, 16, 461–476.
14. T. Das, D. Bratko, L. B. Bhuiyan, C. W. Outhwaite, *J. Phys. Chem.* 1995, 99, 410–418.
15. T. Das, D. Bratko, L. B. Bhuiyan, C. W. Outhwaite, *J. Chem. Phys.* 1997, 107, 9197–9207.
16. V. Vlachy, D. A. McQuarrie, *J. Chem. Phys.* 1985, 83, 1927–1932.
17. E. Gonzales Tovar, M. Lozada-Cassou, D. Henderson, *J. Chem. Phys.* 1985, 83, 361–372.
18. C. N. Patra, L. B. Bhuiyan, *Condens. Matter Phys.* 2005, 8, 425–446.
19. M. Fixman, *J. Chem. Phys.* 1979, 70, 4995–5005.
20. D. Bratko, V. Vlachy, *Chem. Phys. Lett.* 1982, 90, 434–438.
21. M. Le Bret, B. H. Zimm, *Biopolymers* 1984, 23, 271–285.
22. R. Bacquet, P. J. Rossky, *J. Phys. Chem.* 1984, 88, 2660–2669.
23. C. F. Anderson, M. T. Record, *Annu. Rev. Biophys. Biochem.* 1990, 19, 423–465.
24. K. Wang, Y.-X. Yu, G.-H. Gao, G.-S. Luo, *J. Chem. Phys.* 2005, 123, art. no. 234904.
25. V. Vlachy, *J. Chem. Phys.* 1982, 77, 5823–5825.

26. V. Vlachy, D. Bratko, *J. Chem. Phys.* **1981**, 75, 4612–4614.
27. D. Frenkel, B. Smit, *Understanding Molecular Simulation, From Algorithms to Applications*, **1996** (Academic Press, London).
28. V. Vlachy, A. D. J. Haymet, *J. Chem. Phys.* **1986**, 84, 4612–4614.
29. T. L. Hill, *Statistical Mechanics* **1956**, (McGraw Hill, New York).
30. H. Greberg, R. Kjellander, T. Akesson, *J. Chem. Phys.* **1996**, 87, 407–422.
31. V. Vlachy, C. H. Marshall, A. D. J. Haymet, *J. Am. Chem. Soc.* **1989**, 111, 4160–4166.
32. H. Morawetz, *J. Polymer Sci. Part B-Polymer Phys.* **2002**, 40, 1080–1086.
33. T. G. Wensel, C. F. Meares, V. Vlachy, J. B. Matthew, *Proc. Natl. Acad. Sci. U.S.A.* **1986**, 83, 3267–3271.
34. D. Bratko, V. Vlachy, *Chem. Phys. Lett.* **1982**, 90, 434–438.
35. S. S. Zakharova, S. U. Egelhaaf, L. B. Bhuiyan, C. W. Outhwaite, D. Bratko, J. R. C. van der Maarel, *J. Chem. Phys.* **1999**, 111, 10706–10716.

## Povzetek

V tem delu podajamo teoretične rezultate in rezultate Monte Carlo simulacij nekaterih lastnosti modelne raztopine polielektrolita pri sobni temperaturi. Polielektrolit obravnavamo kot neskončno dolg in enakomerno nabit valj, okoli katerega so porazdeljeni točkasti protiioni. Za izračun porazdelitve protiionov v valjasti celici okoli poliiona smo uporabili tako običajno metodo tvorjenja histograma kot tudi Widomovo enačbo. Da bi preverili usklajenost termodinamičnih enačb in numerično natančnost izračunov, smo osmozni koeficient izračunali na več različnih načinov. Posebej smo izračunali prispevke, ki izvirajo iz interakcij med poliionom in protiioni kot tudi med samimi protiioni. Raziskava dokazuje (i), da je sorazmerno dobro ujemanje med rezultati Poisson-Boltzmannove enačbe in simulacijami v veliki meri naključno ter (ii), da poenostavljeno obravnavanje korelacij med protiioni v Poisson-Boltzmannovi enačbi vodi do delne kompenzacije napak pri računanju osmoznega koeficienta. Kot pomemben rezultat tega dela podajamo tudi pravilno parsko porazdelitveno funkcijo za točkaste protiione v električni dvojni plasti okoli valjastega poliiona.