Thermodynamic properties of ring polyelectrolytes in thebinding mean spherical approximation.

Olivier Bernard, J.-P. Simonin

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O. Bernard[a] [1], J.-P. Simonin[a]

[a] UPMC Univ. Paris 06, CNRS, Laboratoire PHENIX UMR 8234, Sorbonne Universités, 75005 Paris, France

Abstract

A simple model for charged ring polyelectrolyte is proposed, to describe their thermodynamic properties. Starting from an analytical expressions previously obtained for charged chains within the binding mean spherical approximation, we present a method to determine suitable modifications in order to describe charged rings. It is shown that the electrostatic excess thermodynamic properties can still be computed from relatively simple formulas which involve a screening parameter Γ^B.

1 Introduction

We are pleased and honored to contribute to the Festschrift dedicated to the 70th birthday of Vojko Vlachy, a well-known expert in the modelling of the structural and thermodynamic properties of polyelectrolytes. The description of the thermodynamic properties of polymers has made great progress with the various models developed by Wertheim [1, 2]. In these models, it was assumed that the polymers can be described as a set of spherical sub-units linked together to form chains, rings, star polymers, etc. A thermodynamic perturbation theory (TPT) was developed in order to calculate the free energy of polymers from the reference free energy of its dissociated constituents. From these free energies other thermodynamic quantities such as the pressure can be deduced by differentiation. This approach enabled one to develop analytical models of polymer properties. The statistical associating fluid theory (SAFT) is based on this approach [3, 4]. Thus, if neutral polymers are assumed to be composed of hard spheres, the reference free energy is that of a system of hard spheres for which accurate expressions are available.

Moreover, integral equations have also been developed to describe polymer chains from the interactions between their subunits. This complementary approach allows one to derive thermodynamic quantities such as the pressure, but also permits to describe

[1] to whom any correspondence should be addressed, E-mail: olivier.bernard@upmc.fr

the structure in terms of the radial distribution function between the various elementary constituents of these polymers. This approach is particularly useful when the subunits constituent of the polymer interact through a long-range potential . In this case the fact that these subunits are linked together has a profound influence on these interactions, which significantly changes the structure and thermodynamics of these systems. In particular, the integral equations were used to describe the properties of polyelectrolytes made up of charged hard spheres in chain assemblies [5, 6, 7, 8, 9]. Important contributions to the development and application of this approach have been made by V. Vlachy *et al.*, particularly for spherical [10, 11] and flexible polyelectrolytes in explicit solvent [12]. To solve these integral equations analytically, the mean spherical approximation (MSA) was used as a closure relationship [13, 14, 15, 16]. For these charged hard sphere chains, explicit expressions were established for the electrostatic contributions to the various thermodynamic properties [8, 9]. The pressure computed using these expressions was compared to those derived from simulation. These pressure can describe those deduced from simulation for weakly charged polyelectrolytes [17].

Integral equations can also be applied to the description of polymers with other structures than simple chain: branched polymers or star polymers. However these equations are not suitable to describe ring polymers. For uncharged rings, modifications of the thermodynamic perturbation theory have been developed [18, 19, 20, 21, 22]. By contrast, for charged rings, there is currently no suitable expression for the electrostatic contributions to the various thermodynamic properties usually calculated using integral equations. In this article we present a method to obtain such expressions from suitable modifications of the expressions established previously for charged chains.

We present in the next section how to obtain these expressions. In the following section these expressions are applied to calculate the osmotic pressure for charged rings in solution. A comparison is made with a similar calculation made for charged chains. Finally, prospects of this work are presented.

2 Theory

The development of expressions for the electrostatic contributions to the various thermodynamic quantities (internal energy, Helmholtz energy, pressure) is carried out from expressions previously obtained in the case of polyelectrolytes represented as chains of charged hard spheres. These previous expressions were obtained from Wertheim Ornstein-Zernike (WOZ) integral equations solved using the MSA approximation as a closure relationship. We first present the model and the expressions. Then, changes to these terms are presented in order to describe polyelectrolyte rings.

2.1 The model of fixed length polyelectrolyte

We consider a system with an arbitrary number of components m, with number density ρ_i, charge ez_i, (e is the elementary charge) and hard core diameter σ_i in a solvent viewed

as a continuum of relative permitivity ϵ_r. We consider that the particles 1, 2, $\cdots n$ with $z_1 = z_2 = \cdots = z_n$ and $\sigma_1 = \sigma_2 = \cdots = \sigma_n$ are the constituents of the polyelectrolyte chain. There is also counterions c of charge z_c, diameter σ_c and number density ρ_c such that the system is electroneutral. Possibly the system also contains coions of arbitrary sizes and charges. The set of particles with indices 1, 2, $\cdots n$ are participating in the bonding to form the polyelectrolyte chains, while those with $n+1, \cdots m$ are not. The temperature of the system is T, Boltzmann's constant is k_B and we use $\beta = 1/k_BT$ throughout. Each hard sphere of the set of particles 2, $\cdots n-1$ has two sticky points, A and B, randomly positioned on its surface. In contrast, spheres 1 and n have only one sticky point and the counterions and coions have no sticky points. The pair potential for this model is given by

$$u_{ij}(12) = u_{ij}^{HS}(r) + u_{ij}^{el}(r) + \sum_{K,L} U_{ij}^{KL}(12) \tag{1}$$

where 1 and 2 stand for the spatial and orientational coordinates of two ions, i and j are the indexes for the ionic species, $u_{ij}^{HS}(r)$ is the hard-sphere potential, $u_{ij}^{el}(r)$ is the Coulomb potential, and $U_{ij}^{KL}(12)$ is the short-ranged site-site potential responsible for association. Hereafter K and L take the values A and B and denote the type of site. The short-ranged site-site potential $U_{ij}^{KL}(r)$ between sites K and L on ions i and j are defined in terms of the Mayer function, $f_{ij}^{KL}(r)$, as

$$f_{ij}^{KL}(r) = \exp\left[-\beta U_{ij}^{KL}(r)\right] - 1 = \mathcal{B}_{ij}^{KL}\delta(r - \sigma_{ij}^{-}) \tag{2}$$

where $\mathcal{B}_{ij}^{KL}$ is an element of the matrix of the sticky interactions. The Coulomb potential, $u_{ij}^{el}(r)$, is given by

$$u_{ij}^{el}(r) = \frac{e^2 z_i z_j}{\varepsilon r} \tag{3}$$

with $\varepsilon = 4\pi\epsilon_0\epsilon_r$ and ϵ_0 the permittivity of vacuum.

The thermodynamic properties of this model can be evaluated by using thermodynamic perturbation theories [23, 24, 25, 26, 27] or by using the WOZ integral equations [8, 9, 28, 29, 30, 31]. In both case it has been shown, that the thermodynamic properties like the excess Helmholtz free energy ΔA, may be decomposed in three terms as

$$\Delta A = \Delta A^{HS} + \Delta A^{chain} + \Delta A^{el} \tag{4}$$

in which ΔA^{HS} is the contribution from uncharged dissociated hard spheres, which was computed using a classic expression [32]. ΔA^{chain} is a contribution arising from association between the subunits 1, 2, $\cdots n$ of the chain regarded as being uncharged, and ΔA^{el} is the electrostatic contribution from charged associated hard spheres. The relation giving the chain part of the free energy ΔA^{chain}, is identical to that obtained in TPT1 or SAFT approximations [1, 2, 3, 4].

The electrostatic contribution from charged hard sphere chains and counterions ΔA^{el}, have been determined from the WOZ integral equations. By averaging the correlation functions over the orientations of each site, the orientation dependence of the site-site potentials can be eliminated to obtain the total orientation-averaged pair correlation function, $h_{ij}(r)$. As an outcome of the attractive potentials defined in Eq. (2), the functions

$h_{ij}(r)$ have additional short range attractive contributions proportional to the orientation-averaged Mayer functions, $f_{ij}^{KL}(r)$. Initially, Wertheim developed his integral equations for particles with binding off-center sites with fixed positions. So the corresponding correlation functions are orientation dependent. As a simplification, the orientation-averaged total pair correlation functions $h_{ij}(r)$ can be coupled with the orientation-averaged direct correlation functions $c_{ij}(r)$ through a set of approximate orientation-averaged integral equations [1, 2] called Wertheim-Ornstein-Zernike (WOZ) equations. This procedure has been proposed and used initially to describe flexible polymers [33, 34]. WOZ equations couple total correlation functions $\mathbf{h}_{ij}(r)$ and direct correlation functions $\mathbf{c}_{ij}(r)$. For each pair of particles of species i and j, $\mathbf{h}_{ij}(r)$ and $\mathbf{c}_{ij}(r)$ are matrices, consisting of the partial correlation functions for the different bonding states. Partial correlations corresponding to species i and j simultaneously unbound (denoted with superscript 00) have a special role in the definition of the closure relations for the integral equations. In particular, a MSA-like closure relation has been used to solve these equations, namely for the direct correlation functions one set $c_{ij}^{00}(r) = u_{ij}^{el}(r)$ for $r > \sigma_{ij}$ [35, 36]. The analytic solution of this Binding (or Associative) Mean Spherical Approximation (BiMSA) was obtained in the case of polyelectrolytes represented as charged hard sphere chains [5, 6, 7, 8, 9]. Explicit expressions were obtained for the thermodynamic properties in terms of a scaling parameter[8, 9], Γ^B, similar to the Debye-Hückel κ screening parameter. The electrostatic contribution to the internal energy ΔE^{el} can be deduced from the solution of the WOZ equations. From the thermodynamic relation $\partial\beta A/\partial\beta = E$, the electrostatic contribution to the Helmholtz energy ΔA^{el}, can be deduced by thermodynamic integration. Then, the osmotic and mean activity coefficients can be calculated by differentiation of the Helmholtz energy ΔA^{el}. To simplify the presentation of the equations, we will now consider that all the sub-units forming the chain have the same diameter. The generalization to chains made of subunits of arbitrary size is straighforward but tedious. In previous work different closure relations have been studied. A chain approximation that takes 3 body hard core exclusion into account has been introduced [8]. It has been shown that this triplet exclusion chain approximation (TECA) satisfies explicitly the Debye Hückel limiting law for all lengths n, and also for all charge combinations. Now we will consider only the results obtained with this closure.

2.2 Thermodynamic properties of polyelectrolyte chains

Hereafter, we will consider the case of the charged chains constitued of the hard spheres 1, 2, $\cdots$ n having the same diameter σ and with counterions and coions of arbitrary sizes and charges. In this case, the internal energy is given by [8]

$$\Delta E^{el} = \frac{e^2}{\varepsilon}\left[\sum_k \rho_k z_k M_k^0 + \rho_p \sum_{k=1}^{n-1}\sum_{i=1}^{n-k} \frac{z_k \mathcal{X}_{k+i}^0}{(i+1)\sigma}\, y^i + \rho_p \sum_{k=2}^{n}\sum_{i=1}^{k-1} \frac{z_k \mathcal{X}_{k-i}^0}{(i+1)\sigma}\, y^i\right] \tag{5}$$

where $\rho_p = \rho_1 = \cdot = \rho_n$ and $\mathcal{X}_k^0$ and M_k^0 are given by

$$\mathcal{X}_k^0 = \frac{z_k - \eta^T \sigma_k^2}{1 + \Gamma^B \sigma_k} \tag{6}$$

$$M_k^0 = \frac{1}{\sigma_k}\left[\mathcal{X}_k^0 - z_k\right] = -\frac{\Gamma^B z_k + \eta^T \sigma_k}{1+\Gamma^B \sigma_k} \tag{7}$$

and with

$$y = \frac{1}{1+\Gamma^B \sigma} \tag{8}$$

The screening parameter is given by

$$\left[\Gamma^B\right]^2 = \frac{\pi e^2 \beta}{\varepsilon}\left[\sum_k \rho_k \left(\mathcal{X}_k^0\right)^2 + \rho_p \sum_{k=1}^{n-1}\sum_{i=1}^{n-k} \mathcal{X}_k^0 \mathcal{X}_{k+i}^0\, y^i + \rho_p \sum_{k=2}^{n}\sum_{i=1}^{k-1} \mathcal{X}_k^0 \mathcal{X}_{k-i}^0\, y^i\right] \tag{9}$$

with

$$\eta^T = \frac{\pi}{2\Delta}\left[\sum_k \rho_k \sigma_k \mathcal{X}_k^0 + \rho_p \sum_{k=1}^{n-1}\sum_{i=1}^{n-k} \frac{\sigma \mathcal{X}_{k+i}^0}{(i+1)}\, y^i + \rho_p \sum_{k=2}^{n}\sum_{i=1}^{k-1} \frac{\sigma \mathcal{X}_{k-i}^0}{(i+1)}\, y^i\right] \tag{10}$$

we have used the usual notation [14, 15, 16]

$$\Delta = 1 - \pi\zeta_3/6 \tag{11}$$

$$\zeta_n = \sum_k \rho_k \sigma_k^n \tag{12}$$

The electrostatic part of the Helmholtz free energy has been calculate by charging up the system of the discharged chains and counterions, which leads to:

$$\beta \Delta A^{el} = \beta \Delta E^{el} + \frac{[\Gamma^B]^3}{3\pi} \tag{13}$$

From the above equations, the excess osmotic coefficient ϕ^{el} is obtained by differentiation

$$\phi^{el} = -\frac{\left[\Gamma^B\right]^3}{3\pi\zeta_0} - \frac{e^2\beta}{\varepsilon\zeta_0}\,\frac{2}{\pi}\left[\eta^T\right]^2 \tag{14}$$

where ζ_0 is given by Eq.(12).

Simplifications occur when the chain is composed of particles with the same charge $z_1 = z_2 = \cdots = z_n$, it is a polyelectrolyte with a charge $z_p = nz_1$. In this case we have [8]:

$$\Delta E^{el} = \frac{e^2}{\varepsilon}\left[\rho_p z_1 \left(nM_1^0 + 2\mathcal{X}_1^0 \sum_{i=1}^{n-1} \frac{n-i}{(i+1)\sigma} y^i\right) + \sum_{c=n+1}^{m} \rho_c z_c M_c^0\right] \tag{15}$$

$$\left[\Gamma^B\right]^2 = \frac{\pi e^2 \beta}{\varepsilon}\left[\rho_p \left(\mathcal{X}_1^0\right)^2 \left(n + 2\sum_{i=1}^{n-1}(n-i)y^i\right) + \sum_{c=n+1}^{m} \rho_c \left(\mathcal{X}_c^0\right)^2\right] \tag{16}$$

The sum involved in this eq. can be express in a more explicit form, which leads to

$$\left[\Gamma^B\right]^2 = \frac{\pi e^2 \beta}{\varepsilon}\left[\rho_p \left(\mathcal{X}_1^0\right)^2 \left(n + \frac{2y}{1-y}\left(n-1\ - \frac{y-y^n}{1-y}\right)\right) + \sum_{c=n+1}^{m} \rho_c \left(\mathcal{X}_c^0\right)^2\right] \tag{17}$$

with

$$\eta^T = \frac{\pi}{2\Delta}\left[\rho_p\sigma_1\mathcal{X}_1^0\left(n + 2\sum_{i=1}^{n-1}\frac{n-i}{i+1}y^i\right) + \sum_{c=n+1}^{m}\rho_c\sigma_c\mathcal{X}_c^0\right] \tag{18}$$

In practice, the Γ^B parameter is evaluated first using Eq. (9). Then the various thermodynamic quantities can be deduced. Eqs. (5)-(18) constitute a set of expressions specifically adapted to the description of linear polyelectrolyte solutions. Our goal now is to modify these expressions for a description of solutions of a polyelectrolyte made up of rings. For this, we will first characterize each of the contributions introduced earlier. Thus, eq. (5), giving the internal energy of a polyelectrolyte solution, consists of three contributions. The first is the classic contribution to the MSA approximation when considering a dissociated electrolyte [15] . The following two contributions are double sums on the constituents of the chains. The first double sum describes the interactions between the components k and constituents $k+i$, with $1 \leq i \leq n-k$. The second double sum describes the interactions between the constituents k and $k-i$, with $1 \leq i \leq k-1$. All the components k are included in these double sums.

To give more physical meaning to the various parameters involved in these equations we consider the limit of great dilution. In this limit $\Gamma^B\sigma \ll 1$, $\mathcal{X}_k^0 \to z_k$, and the $y \to 1$. Within this limit, the first double sum runs over $z_k z_{k+i}e^2/(\varepsilon(i+1)\sigma)$ which is the Coulomb interaction energy between ions k and $k+i$ separated by distance $(i+1)\sigma$. Similarly, the second double sum is applied to $z_k z_{k-i}e^2/(\varepsilon(i+1)\sigma)$ which is the Coulomb interaction energy between ion k and $k-i$ at distance $(i+1)\sigma$. Then, the doubles sums, involved in the expression of ΔE^{el}, account for the Coulomb interactions between all the components within a chain. At finite concentration, when all the constituents of the chains have the same size σ, we note that all interactions between nearest neighbors are equal to $(e^2/\epsilon)(z_k\mathcal{X}_{k+1}^0/(2\sigma)$. Similarly, all the interactions between second neighbors are equal to $(e^2/\epsilon)(z_k\mathcal{X}_{k+2}^0/(3\sigma)$, and so on ...

2.3 Thermodynamic properties of polyelectrolyte rings

Now we will consider the amendments to the internal energy when the chains are closed rings. To perform this conversion, we add a connection between the particles 1 and n in each of the chains. We assume that this induces no modification on the first term in the expression for ΔE^{el}. By contrast, we will modify the following two terms to account for connectivity changes occurring during the transformation of a polyelectrolyte chain into a ring. This has the effect of changing all the interactions between the components k such that $1 \leq k \leq n$. Thus for chains, in the first double sum one finds the term $z_1\mathcal{X}_n^0 y^{n-1}/(n\sigma)$ in eq. (5), which accounts for the interaction between the components 1 and n. In the rings, the particles 1 and n are bonded. To more realistically describe the interactions between these particles in a ring, we consider that the term associated with this pair is of the same form as that between 1 and 2. Then, we replace the previous term by $z_1\mathcal{X}_n^0 y/(2\sigma)$. Similarly for each of the pairs (k and $k+i$ in the first double sum, and k and $k-i$ in the second double sum) we assume that the shortest distance in the ring

is the most realistic. Similarly, all interactions between the polyelectrolyte components of pairs are changed. We assume for simplicity that interactions between first, second, ..., i-th neighbors within the polyelectrolyte keep the same forms they have in the case of polyelectrolytes chains.

So, for chains, at finite concentration, when all the constituents of the chains have the same size σ, we note that all interactions involved in eq. (5) between nearest neighbors are equal to $(e^2/\epsilon)(z_k\mathcal{X}^0_{k+1}/(2\sigma)$. Similarly, all the interactions between second neighbors are equal to $(e^2/\epsilon)(z_k\mathcal{X}^0_{k+2}/(3\sigma)$, and so on ... To be more specific, in the equation (5) for ΔE^{el}, the interaction between the i-th neighbors uses the term $z_k\mathcal{X}^0_{k\pm i}y^i/((i+1)\sigma))$. Similarly, in the eq. (9) for $[\Gamma^B]^2$, the interaction between the i-th neighbors uses the term $\mathcal{X}_k\mathcal{X}^0_{k\pm i}y^i$. And finally, in the eq. (10) for η^T, the interaction between the i-th neighbors uses the term $\sigma\mathcal{X}^0_{k\pm i}y^i/(i+1))$. We keep the same terms in the corresponding equations for the rings.

Then, in order to determine the sums involved in the expressions of ΔE^{el}, Γ^B and η^T for charged rings, we must first count the number of first neighbors, second neighbors, etc, for a n components ring. For a ring containing n particles there are $n(n-1)/2$ interactions. When counting the neighbors, we first count the number of first neighbors which form a first group of interactions. Next we count the number of second neighbors which constitute a second group, and so on. We call v the total number of groups, for a given n.
When n is odd, all the groups contain n pairs of interactions. Knowing the total number of interactions between pairs and the number of interactions in each group, we deduce that $v=(n-1)/2$ when n is odd.
When n is even, the group of interactions between the most distant pairs contains $n/2$ interactions. This leaves $n(n-2)/2$ interactions spread in the $v-1$ other groups, that contain n pairs of interactions. So, $v=n/2$ when n is even.

Now for simplicity, we consider rings made of particles with the same diameter and the same charge z_1. This introduces the simplification $\mathcal{X}^0_1=\mathcal{X}^0_2=\cdots=\mathcal{X}^0_n$. In the case of chains, the double sums involved in the expressions for ΔE^{el}, $\left[\Gamma^B\right]^2$ and η^T, are replaced by simple sums (see eqs. (15, 16, 18)). Similarly, for the rings, the double sums are also replaced by simple sums on the interactions between the i-th neighbors, with $1\leq i\leq v$.

When n is odd, we obtain

$$\Delta E^{el}=\frac{e^2}{\varepsilon}\left[n\rho_p z_1\left(M^0_1+2\mathcal{X}^0_1\sum_{i=1}^{(n-1)/2}\frac{1}{(i+1)\sigma}y^i\right)+\sum_{c=n+1}^{m}\rho_c z_c M^0_c\right] \tag{19}$$

$$\left[\Gamma^B\right]^2=\frac{\pi e^2\beta}{\varepsilon}\left[n\rho_p\left(\mathcal{X}^0_1\right)^2\left(1+2\sum_{i=1}^{(n-1)/2}y^i\right)+\sum_{c=n+1}^{m}\rho_c\left(\mathcal{X}^0_c\right)^2\right] \tag{20}$$

with

$$\eta^T=\frac{\pi}{2\Delta}\left[n\rho_p\sigma_1\mathcal{X}^0_1\left(1+2\sum_{i=1}^{(n-1)/2}\frac{1}{i+1}y^i\right)+\sum_{c=n+1}^{m}\rho_c\sigma_c\mathcal{X}^0_c\right] \tag{21}$$

In the same way, when n is even, we obtain

$$\Delta E^{el} = \frac{e^2}{\varepsilon}\left[n\rho_p z_1\left(M_1^0 + 2\mathcal{X}_1^0\sum_{i=1}^{(n-2)/2}\frac{1}{(i+1)\sigma}y^i + 2\frac{\mathcal{X}_1^0\, y^{n/2}}{(n+2)\sigma}\right) + \sum_{c=n+1}^{m}\rho_c z_c M_c^0\right] \tag{22}$$

$$\left[\Gamma^B\right]^2 = \frac{\pi e^2\beta}{\varepsilon}\left[n\rho_p\left(\mathcal{X}_1^0\right)^2\left(1 + 2\sum_{i=1}^{(n-2)/2}y^i + y^{n/2}\right) + \sum_{c=n+1}^{m}\rho_c\left(\mathcal{X}_c^0\right)^2\right] \tag{23}$$

with

$$\eta^T = \frac{\pi}{2\Delta}\left[n\rho_p\sigma_1\mathcal{X}_1^0\left(1 + 2\sum_{i=1}^{(n-2)/2}\frac{1}{i+1}y^i + 2\frac{y^{n/2}}{(n+2)}\right) + \sum_{c=n+1}^{m}\rho_c\sigma_c\mathcal{X}_c^0\right] \tag{24}$$

We note that the new equations (19, 22), obtained for ΔE^{el} satisfies the relation

$$\beta\frac{\partial\Delta E^{el}}{\partial\Gamma^B} = -\frac{[\Gamma^B]^2}{\pi} \tag{25}$$

This property allows us to deduce expressions of the Helmholtz free energy and pressure, as in the case of charged chains. We find similar expressions for the free energy given by eq. (13) , and the pressure given by eq. (14). However, the parameters Γ^B and η^T must be calculated either with eqs (20, 21) if n is odd, or with eqs. (23, 24) if n is even.

3 Application

The osmotic pressure can be computed from the previous equations. The uncharged part of the osmotic pressure can be calculated with the hard sphere term given in [32] and the TPT theory for the rings [18, 19, 20, 21]. In the case of charged chains, the uncharged contribution seems to be the dominant part of the computed osmotic pressure. In order to show the difference between the results obtained for polyelectrolyte chains and rings, we present the electrostatic contribution to the osmotic coefficient in Figure 1. The Debye Hückel limiting law previously computed [8] is also reported. We present the result for polyelectrolytes with 32 monomers of equal valency $z_1 = -1$ and diameters $\sigma_1 = 0.857$ nm. The counterions have a valency $z_c = 1$ and the same diameter. The Bjerrum length is related to the diameter by: $L_B = 0.833\sigma$. By comparing the curves calculated for chains and rings we see that they tend towards the same limit for large dilutions and high concentration. In both cases the Debye Huckel limiting law is satisfied. The term proportional to $[\Gamma^B]^3$ is generally dominant in the expression of the pressure (14). The expressions of the screening parameter Γ^B, given by eq. (16) for chains, and by eq. (23) for rings, take similar values. At intermediate concentrations, the electrostatic contribution is more important for the rings because the charged sites interact more with the other charges than in the case of a linear chain. The number of nearest neighbors is greater for rings for chains, the electrostatic repulsion is probably more important in the case of the rings.

4 Conclusion

In this work, we have studied the thermodynamics of ring polyelectrolytes in solution. The development of expressions for the electrostatic contributions to the various thermodynamic quantities has been carried out from amendments to expressions previously obtained in the case of chains of charged hard spheres. Expressions for the Helmholtz energy, internal energy, and activity and osmotic coefficients have been obtained. It is shown that the electrostatic excess thermodynamic properties can still be computed from relatively simple formulas which involve a screening parameter Γ^B. The electrostatic contribution to the osmotic coefficient has been computed for polyelectrolyte rings and compared with the corresponding expression for chains. As was said earlier, simulations of linear polyelectrolytes have already been carried out. There are also simulations of rings whose subunits interact through Lennard-Jones potentials [22]. But there are currently no numerical simulations of the type of system considered in this article. They could not be achieved in the present work, but it would be interesting to make such simulations in future work.

This work could be applied to the description of small cyclic molecules uniformly charged such as the benzene-hexacarboxylic (mellitic) acid and its neutral and acidic salts. On a ring polyelectrolyte, when the distance between charged subunits is small compared to the Bjerrum's length , the condensation of counterion could probably be considered in the same way as for a linear polyelectrolyte. This phenomenon may be taken into account in the integral equations, by considering on each of the charged sub-units, an additional site allowing the association of a counterion, as was done in previous work using thermodynamic perturbation theory [37]. The inclusion of additional sites, for specifically binding counterions, has recently been described for spherical polyelectrolytes [38]. The extension of this work to linear polyelectrolyte is currently being studied. The expressions describing the thermodynamic properties of linear polyelectrolyte with association of counterions, could also be suitable to the description of cyclic polyelectrolytes. Moreover, the method used in this study to derive the thermodynamic expressions adapted to uniformly charged rings, may also be applied subsequently to the case of cyclic molecules comprising only one or two charged groups, which case is much more common in solution chemistry.

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We spare a thought for Lesser Blum who passed away last April - a good friend and an excellent scientist. He introduced us to the MSA theory and made significant contributions to the resolution of the WOZ equations within this approximation, e.g. in the case of linear polyelectrolytes [8, 31].

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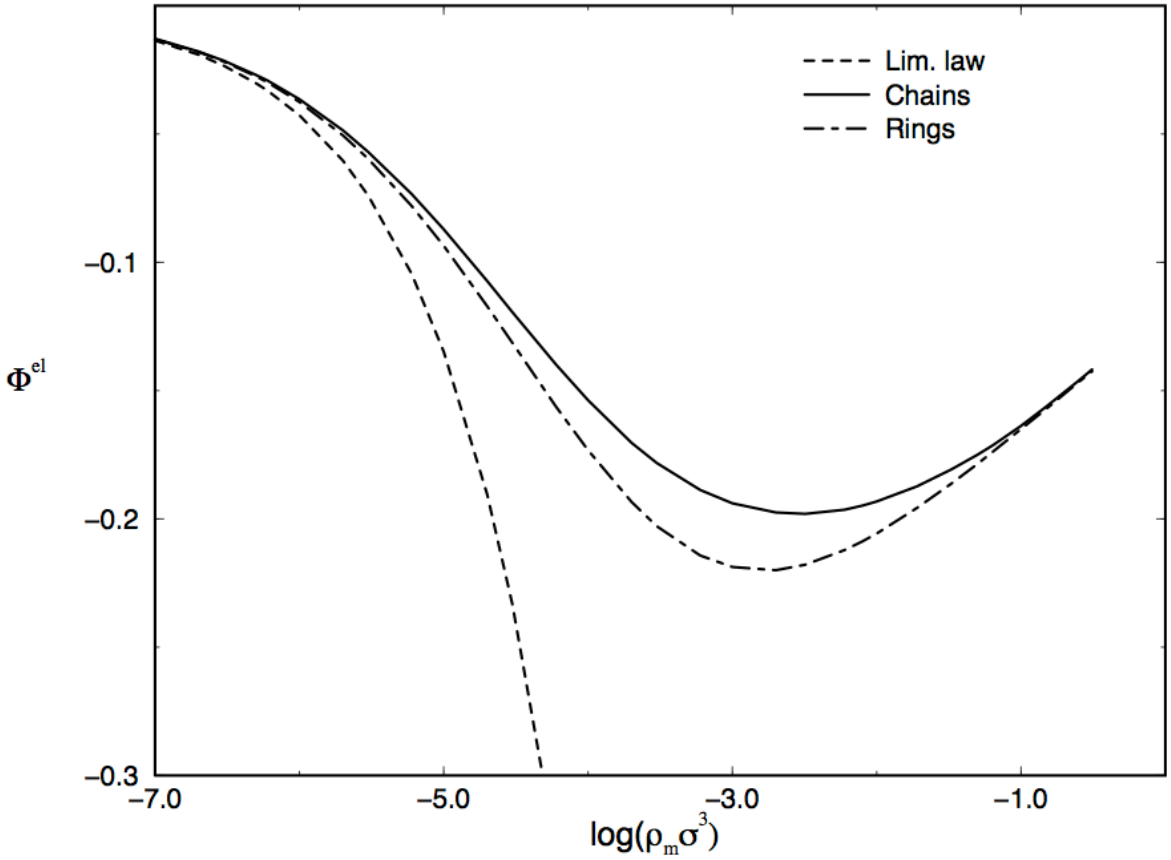

Figure 1: The electrostatic part of the osmotic coefficient of polyelectrolyte solution . Solid line: result for chains. Dash-dotted line: result for rings. Dashed line: the limiting law.

Highlights

- A model for the thermodynamics of charged ring polyelectrolytes is proposed.
- We modify expressions for charged chains within BiMSA, in order to describe rings.
- The electrostatic contribution to the osmotic coefficient has been computed.