Flexible Polyelectrolytes with Monovalent Salt

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We present a model for describing flexible polyelectrolytes in a good solvent and in the presence of monovalent salt. The molecule composed by $N$ monomers is characterized by the end to end distance $R_e = b(Z-1)\gamma$ and the number of associated counterions $n$. At high temperatures the polyelectrolyte behaves as a neutral polymer ($\gamma = 0.588$). Decreasing the temperature, the macromolecule changes from this extended configuration ($\gamma = 0.588$) to a stretched form ($\gamma \approx 1$). At even lower temperatures, above the Manning condensation threshold, the polyelectrolyte collapses ($\gamma \approx 0.3$). Our results show good agreement with simulations.

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I. INTRODUCTION

Polyelectrolytes represent a very interesting class of materials. Biological systems abound with polyelectrolytes. Two of the most well known of all polymers, DNA and RNA, are charged polymers [1][2]. Besides, a large class of synthetic polyelectrolytes are present in the chemical industry. For instance, polyacrylic acid is the main ingredient for diapers [3] and dispersions of copolymers of acrylamide or methacrylamide and acrylic or methacrylic acid are fundamental for cleaning water [4]. Even though the tremendous interest in polyelectrolyte, unlike neutral polymers [5][6], the understanding of the behavior of electrically charged macromolecules is still rather poor.

The contrast between our understanding of charged and neutral polymers results from the long range nature of the electrostatic interactions that introduces new length and time scales that render the analytical description very complicated [5]. The presence of charges introduces more than one new length scale making the scaling theories used for no longer as simple and applicable. Besides the length scale associated with the strength of the Coulomb interaction, there is also lengths associated with the mean separation of the counterions required by the charge neutrality. The association of these free ions to the polyon, renormalizing its charge, is another factor that has to be taken into account.

Therefore, simulations seems to be a good technique to overcome these major difficulties. Recent molecular simulations of salt-free systems [8]-[10] were able to obtain the end to end distance of strong electrolytes below Manning parameter [11]. The picture provided by these simulations have shown to be more complicated than early analytic theories have predicted [12]-[22]. Past theoretical works tended to neglect entropy. For stiff chains, such as DNA, entropy is an small contribution to the free energy and, in principle, can be disregarded. In contrast, for flexible polyelectrolytes, treating entropy along with with the Coulomb interactions is essential. Acknowledging that, one of us developed a theory for describing the thermodynamics of salt-free polyelectrolytes in a good solvent. Within this approach both entropy and electrostatic interactions are taken into account [23][24]. The end to end distance and pressure calculated using this method show good agreement with simulations [8][9][25].

The addition of salt is a key factor both in biological and industrial applications. However, including new charged species in the system, adds another scale to this already very complicated problem. In this work we develop a simple theory for studying a dilute polyelectrolyte solution in the presence of monovalent salt in the framework of three theories: Debye and Bjerrum for electrolytes [26]-[28], Manning condensation [11] and Flory elasticity for polymers [5].

Unlike neutral polymers, the polyelectrolyte in salt solution exhibits three distinct behaviors. At high temperatures the chain is extended. As the temperature is decreased, the electrostatic repulsion between the monomers along the polyon becomes relevant and the chain stretches. At even lower temperatures, above the Manning condensation threshold, counterions condense into the polyon. The polymer chain net charge decreases and the polyelectrolyte collapses. The addition of salt screen the electrostatic interactions and the polymer contracts. Our results show a good quantitative agreement with simulat-
In section II, our model is presented in detail. In section III, the free energy of the system is constructed and minimized with respect to two parameters: number of ions associated to the polyion and end to end distance. The results are presented in section IV. Conclusions end this session.

II. THE MODEL

We consider a dilute polyelectrolyte solution of concentration \( \rho_p \) (see Figure 1). The chains are immersed in a continuum solvent with dielectric constant \( D \) and monovalent salt. There are \( Z \) charged groups of diameter \( \sigma \) along the polymer chain. \( b = 2^{1/6} \sigma \) is the distance between adjacent monomers. The total charge of the completely ionized molecule is \( -Zq < 0 \), where \( q \) is the proton charge. The counterions that neutralizes the solution have charge \(+q\), diameter \( \sigma \) and concentration \( \rho_m = Z \rho_p \). The salt ions have charge \(+q\) or \(-q\), diameter \( \sigma \) and density \( \rho_s \). For simplicity the positive ions of salt will be refereed as counterions and the negative as coions. Thus

\[
\rho_+ = Z(1-m)\rho_p + \rho_s \quad (1)
\]

\[
\rho_- = \rho_s \quad (2)
\]

are the density of counterions and coions. The inverse Debye screening length \( \kappa \) is defined in the usual way by \( \kappa = \sqrt{4 \pi \rho_1 \lambda_B} \), where \( \lambda_B = \beta q^2/D \) is the Bjerrum length, the distance between two ions where the electrostatic energy equals the thermal energy, \( \rho_1 = \rho_+ + \rho_- \), and \( \beta = 1/k_B T \). The reduced density for species \( j \) is \( \rho^*_j = \rho_j \sigma^3 \), the reduced temperature is \( T^* = D\sigma/\beta q^2 \).

The Manning charge parameter is \( \xi = \beta q^2/Db \). Hence \( \xi = \sigma/b T^* \) and \( \xi = \lambda_B/b \). For simplicity, macroion does not assume any preferential geometry.

Hence, the distance between monomers \( i \) and \( j \) is represented by \( r_{ij} = |i - j|^\gamma \) as usual. The end to end distance \( R_e \) is the distance between monomers \( 1 \) and \( Z \) and it is represented by:

\[
R_e = b(Z-1)^\gamma . \quad (3)
\]

The electrostatic interaction between the chain and the counterions leads the formation of a complexes made of one macromolecule and \( n \) associated microions. At a given temperature \( T \), monomer density \( \rho_m = Z/V \) and salt density \( \rho_s \), the system reaches the equilibrium characterized by a number of associated counterions, \( m \) and the end to end distance characterized by \( \gamma \).

III. THE HELMHOLTZ FREE ENERGY

The system is, therefore, composed by complexes made of one polyion and \( n \) countenions, free countenions and free coions. The end to end distance of the complex is \( R_e \). The equilibrium configuration is found by minimizing the Helmholtz free energy density with respect to \( n \) and \( R_e \). The free energy density, \( f = F/N_p \) is composed by three contributions, namely

\[
f = \text{f}_{\text{elec}} + \text{f}_{\text{hc}} + \text{f}_{\text{ent}} \quad (4)
\]

where \( \text{f}_{\text{elec}} \) contains all the electrostatic interactions, \( \text{f}_{\text{hc}} \) has the hard core contribution between the different species and \( \text{f}_{\text{ent}} \) has the entropic contributions for the free energy density.

The electrostatic free energy density is splitted into:

\[
\text{f}_{\text{elec}} = \text{f}_{\text{pc}} + \text{f}_{\text{ff}} + \text{f}_{\text{di}} \quad (5)
\]

where \( \text{f}_{\text{pc}} \) accounts for the electrostatic interaction between the polyelectrolyte chain and the free electrolyte, \( \text{f}_{\text{ff}} \) takes care of the electrostatic interaction between the counterions e coions and \( \text{f}_{\text{di}} \) includes the dipole-ion interaction between the dipole pairs along the chain and both charged monomers and free countenions and coions.

The hard core free energy density is divided into two contributions given by:

\[
\text{f}_{\text{hc}} = \text{f}_{\text{hc}} + \text{f}_{\text{cs}} \quad (6)
\]

where \( \text{f}_{\text{hc}} \) takes care of hard core interaction between monomers along the chain and \( \text{f}_{\text{cs}} \) includes the hard core interaction between free ions. Here \( \text{f}_{\text{cs}} \) represents the free energy of Carnahan-Starling, the hard core term between free ions.

Finally, the free energy density terms that contains entropic contributions are:

\[
\text{f}_{\text{ent}} = \text{f}_{\text{el}} + \text{f}_{\text{ig}} \quad (7)
\]

where \( \text{f}_{\text{el}} \) is the elastic free energy of the flexible chain, \( \text{f}_{\text{ig}} \) is the ideal gas free energy for the mixture of the different species present in the solution.
A. The polyion-free ions electrostatic free energy density $f_{pc}$

The electrostatic free energy density between the complex made of a polyelectrolyte and $n$ counterions associated to it and the free ions in the solution can be derived in the framework of the Debye-Hückel theory yielding (see appendix A):

$$\beta f_{pc} = \frac{\xi p_z^2 b \mathcal{I}}{2},$$  \hspace{1cm} (8)

where $p_z = -1 + m = -1 + Z/n$ and

$$\mathcal{I} = 2 \int_0^Z dx (Z - x) e^{-\kappa r(x)} - 1$$  \hspace{1cm} (9)

where $r(x) = bx^\gamma$.

These ideas have been successful in describing charged systems, including simple electrolyte solutions \cite{30,31}, charged rods \cite{32,33}, charged spherical colloids \cite{34}, and flexible charged chains \cite{23,24,35}. In particular, the binding isotherms of DNA with surfactant molecules have been found in good agreement with experiment \cite{36}.

The integral $\mathcal{I}$ might also be written using the incomplete gamma function \cite{37}.

$$\gamma_{inc}(\alpha, x) = \int_0^x dt e^{-\alpha t}\alpha^{-1}, \text{Re} \alpha > 0. \hspace{1cm} (10)$$

The suffix $inc$ is used to avoid confusion with the exponent $\gamma$. In this case, we get

$$\mathcal{I} = \frac{Z \kappa}{(kb)^{1/\gamma}} \gamma_{inc}(-1 + 1/\gamma, \kappa b Z^\gamma)$$  \hspace{1cm} (11)

$$- \frac{\kappa}{(kb)^{2/\gamma}} \gamma_{inc}(-1 + 2/\gamma, \kappa b Z^\gamma)$$  \hspace{1cm} (12)

where $\rho = Z/V_e$ and $\kappa$ is the Debye-Hückel reciprocal screening length.

B. Free ion-free ion electrostatic free energy density $f_{ff}$

For the interaction between free ions we employ the Debye-Hückel free energy for electrolytes \cite{26,27}.

$$\beta f_{ff} = \frac{1}{4\pi \rho_p^2} \ln(1 + \kappa \sigma) - \kappa \sigma + (\kappa \sigma)^2/2. \hspace{1cm} (13)$$

C. The dipole-ion electrostatic free energy density $f_{di}$

When a counterion associate to a negative monomer of the polyelectrolyte, it forms dipole. The interaction between these dipoles formed by association and the monopoles consisting of free counterions and coions and non-associated monomers along the chain is given by the usual dipole-ion interaction originally derived for the coulomb gas and given by \cite{30,31}:

$$\beta f_{di} = -\frac{1}{T^2} Z m (\sigma/a_2)^3 x^2 \omega_2(x), \hspace{1cm} (14)$$

where $x = \tilde{\kappa} a_2, \tilde{\kappa} \sigma = \sqrt{\frac{4\pi x (\tilde{\kappa} + \tilde{\kappa}^2)}{x}}, \tilde{\rho}_c^+ = Z (1-m) \sigma^3/V_e, V_e = 4\pi R_e^3/3, a_2 = 1.1619\sigma$, and

$$\omega_2(x) = 3[\ln(1 + x + x^2/3) - x + x^2/6]/x^4. \hspace{1cm} (15)$$

Note that we use here $\tilde{\kappa}$ in order to take the interactions between the dipoles formed on the chain and the charged monomers and free ions. It is essential for the attractive forces that lead to collapse of the chain at low temperatures. The density $\tilde{\rho}_c^+$ is the density of charged monomers not associated in the volume $V_e$ occupied by the chain.

D. The excluded volume free energy densities $f_{hc}$ and $f_{cs}$

The polyelectrolyte will be consider to be in a good solvent. Therefore, hard-core repulsion between monomers is approximated by a virial coefficient from Flory-de Gennes theory \cite{3,4,38,39},

$$\beta f_{hc} = \frac{Z}{2} W_1 \bar{\rho}, \hspace{1cm} (16)$$

where $W_1 = 4\pi \sigma^3/3$ is the second virial coefficient for hard spheres of diameter $\sigma$, and $\bar{\rho} = Z/V_e$ with $V_e = 4\pi R_e^3/3$.

The hard-core repulsion between free ions is approximated by the Carnahan-Starling free energy \cite{40},

$$\beta f_{cs} = V \rho_1 y \frac{4 - 3y}{(1 - y)^2}, \hspace{1cm} (17)$$

where $y = \pi \rho_1^3/6$ is the volume fraction occupied by the free positive and negative ions.

E. The elastic free energy density $f_{el}$

We are considering here flexible polyelectrolytes. The entropic contribution of the elastic free energy density is the same of a neutral polymer and it is given by \cite{3,35,41,42,43}:

$$\beta f_{el} = \frac{3}{2} (\alpha^2 - 1) - 3 \ln \alpha, \hspace{1cm} (18)$$

where $\alpha = R_e/R_0$, where $R_0 = b\sqrt{Z-1}$ is the end to end distance of a polymer in a $\Theta$ solvent.
F. The ideal gas free energy density $f_{ig}$

Another important entropic free contribution is due to the mixing of the different species, complexes, counterions and coions. The free energy density associated with the mixing of ideal particles is given by [30, 31]:

$$
\beta f_{ig}^e = \frac{1}{\rho_p} [\rho_+ \ln \rho_+^* \Lambda^3 - \rho_+ + \rho_- \ln \rho_-^* \Lambda^3 - \rho_- + \ln \rho_p \Lambda^3 - 1 + \beta f_{ig}^\text{int}] + \int_0^{R_B} \frac{Zm \ln \frac{Zm}{V_e \zeta_2} \Lambda^3 - 1} \frac{r^2 e^{\sigma/r} dr}{V e} = K(T),
$$

where $\Lambda = \frac{h}{2\pi m k_BT}$ is the thermal wavelength. $f_{ig}^e$ includes the internal degrees of freedom of the complex made of a polyelectrolyte and the associated ions and it is given by:

$$
\beta f_{ig}^e = Z(1-m)[\frac{Z(1-m)}{V_e} \Lambda^3 - 1] + Zm[\frac{Zm}{V_e \zeta_2} \Lambda^3 - 1] - Z[\frac{Z}{V_e} \Lambda - 1] + \beta f_{ig}^\text{int}.
$$

Since the monomers along the chain are mobile, the first two brackets in Eq. (20) account for the entropy of mixing of charged monomers and dipoles along the chain. The third bracket discounts the overcounting since the entropy of a neutral polymer was already accounted in Eq. (18). The last term is the internal partition function of the complex in its internal reference frame. The internal partition function of the dipoles, $\zeta_2$, is given by:

$$
\zeta_2 = 4\pi \int_0^{R_B} \frac{r^2 e^{\sigma/r} dr}{V e} = K(T),
$$

where $R_B$ is chosen according to Bjerrum to be $\sigma/2T^*$, the location of the minimum of the integrand. Thus the association constant is different from zero for $T^* < 0.5$. Above this temperature there is no counterion association and no dipole formation on the chain. We have then [28, 31, 31]

$$
K(T) = 4\pi^3 Q_0 e^{1/T^*} T^*,
$$

with

$$
Q_0 = \frac{1}{6T^*} e^{-1/T^*} [Ei(1/T^*) - Ei(2) + e^2] - \frac{1}{6T^*} \left( \frac{1}{T^*} + \frac{1}{T^*} + 2 \right).
$$

The internal partition function of a n-complex contains: one electrostatic term due to the interaction between the monomers and associated ions and one term due to the different ways $n$ ions can associate into $Z$ monomers in a polycions. The additions of these two parcels gives:

$$
\beta f_{ig}^\text{int} = \xi p_b^2 b \sum_{i=1}^{Z-1} (Z-i) \frac{1}{r(i)} + Z m \ln m + Z (1-m) \ln (1-m) + \xi \gamma.
$$

IV. RESULTS AND CONCLUSIONS

The behavior of the polyelectrolyte under the variation of temperature is illustrated in Figure 2. At high temperatures (low Bjerrum length) the end to end distance approaches the one of a neutral polymer in a good solvent and $R_e = b(Z-1)\rho$, For $Z = 32$ and $b = 2^{1/6} \sigma_e$ the end to end distance is given by $R_e \approx 8.45 \sigma_e$. As the temperature decreases, the electrostatic interactions become dominant, the polymer stretches and the end to end distance is given by $\gamma \approx 1$. Above the Manning condensation threshold, the counterions associate to the monomers along the chain, decreasing the electrostatic interactions. The elastic energy becomes dominant and the polymer collapses. Our results are compared with simulations [29]. The actually salt density used for that simulation is not specified in the manuscript but is within the interval $\rho^*_s = 0.001$ and $\rho^*_s = 0.008$.

Figures 3 and 4 show that for a given $Z$, the radius of end to end distance, $R_e$, depends only on the value of the bare inverse of screening length, $\kappa_0 = \sqrt{4\pi (\rho_m + 2\rho_e) \lambda_B}$, and not on the density of polyelectrolytes. In Figure 3 the renormalized end to end distance given by

$$
R^* = \frac{R_e}{b(Z/32)0.588}
$$

is plotted against $\ln \kappa_0 \sigma$ for $Z = 32, 64$ for various densities and for $\lambda_B = 0.83\sigma_e (\xi = 0.75)$. The decrease of the end to end distance is, in this case, due to the screening of the salt present in the solution. Note that here there is no condensation. The renormalized end to end distance, $R^*$, was constructed as follows. $R$ was divided by the end to end distance of an equivalent neutral polymer in a good solvent $R_0 \approx bZ^{0.588}$. In order to keep both $Z = 32$ and $Z = 64$ in the same scale, $N$ was also divided by $Z = 32$. Our results agree with simulations performed in the scale [29].

In Figure 4 we show $R^*$ for $\lambda_B = 3.2 \sigma_e (\xi = 2.9)$. In this case, since the system is above the Manning threshold, condensation is present and the polyelectrolyte should form a more compact form than for $\lambda_B = 0.83\sigma_e (\xi = 0.75)$. Comparison with Figure 3 shows that for $\ln \kappa_0 \sigma > -0.5$ larger $\lambda_B$ has larger $R$. Part of this effect is due to plotting versus $\ln \kappa_0 \sigma$. For the same $\rho_m$ and $\rho_e$, the end to end distance is surely smaller for $\lambda_B = 0.83\sigma_e$ than for $\lambda_B = 3.2 \sigma_e (\xi = 2.9)$ as indicated by Figure 2.

In summary, we studied the end to end distance of polyelectrolytes with added salt. We found that $R$ for a fixed $Z$ and $\lambda_B$ depends only on the amount of salt in solution. In this case, the main effect of the electrolytes is to screen the interactions and decreasing $R$. For fixed values of $Z$, $\rho_m$ and $\rho_e$, as the temperature is decreased, $R$ exhibits three distinct behaviors: stretched, extended and collapsed. This three regimes are related to the stretched polymer, fully extended polyelectrolyte and collapsed polymer behavior.
FIG. 2: Plot of end to end distance as a function of $\lambda_B$ for $Z = 32$, $\rho^*_m = 0.001$, and from top to bottom $\rho_s = 0 - 0.008$. The circles are the simulational results extracted from ref. [29].

FIG. 3: Plot of the renormalized end to end distance $R^*$ as a function of $\ln \sigma \kappa_0$ for $Z = 32$ (solid line) and $Z = 64$ (dashed line), for $\rho^*_m = 0.0001, 0.001, 0.01, 0.02$ and $\xi = 0.75$. The points for different densities fall in the same line. The symbols are the simulation results for the same $\rho^*_m$ and $Z = 32$ (circles) and $Z = 64$ (squares) extracted from ref. [29].

FIG. 4: Same as in Figure 3 but for $\xi = 2.9$.

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APPENDIX A: CALCULATION OF $f_{pc}$

In order to compute the free energy density associated with the polycation-free ions interaction, let us start by calculating the electrostatic potential at a point $P$ due to the charged chains and electrolytes. Each chain has a linear charge density $\lambda' = -(Z - n)q/L$. The coordinates on the molecule are denote by a prime, and the coordinates of the point $P$ where we want to evaluate the electrostatic potential are $P = (x, y, z)$. The electrostatic potential at a point $P$ located in an ionic solution, due to a charge element $\lambda' ds'$ on the molecule, is given by the Debye-Hückel expression,

$$d\phi = \lambda' ds' e^{-\kappa r}/Dr,$$  \hspace{1cm} (A1) 

where $r$ is the distance of the charge element to the point $P$. Integrating the expression above, the electrostatic total potential at $P$ becomes:

$$\phi(x, y, z) = \int d\phi = \frac{\lambda'}{D} \int_0^L ds' e^{-\kappa r}/r,$$  \hspace{1cm} (A2) 

where $L = b(Z - 1)$ is the contour length. The electrostatic potential at $P$ due to the chain when there is no electrolyte is given by:

$$\phi_{pr}(x, y, z) = \int d\phi_{pr} = \frac{\lambda'}{D} \int_0^L ds' 1/r,$$  \hspace{1cm} (A3) 

the suffix $pr$ meaning proper.

The potential due to the ionic solution discounting the chain is given by $\psi = \phi - \phi_{pr}$. The free energy is then evaluated by using the charging process of Debye [20, 27] in this potential.

The electrostatic energy of a charge element $dq$ at $(x, y, z)$ in the potential $\psi$ is

$$dU = dq(x,y,z) \psi(x,y,z).$$  \hspace{1cm} (A4)
The electrostatic energy of the entire molecule is obtained integrating the above expression, what gives

\[ U = \frac{1}{2} \int dU = \frac{1}{2} \int dq(x, y, z) \psi(x, y, z) = \frac{1}{2} \int \lambda \psi ds, \]

\[ = \frac{\lambda^2}{2D} \int_0^L ds \int_0^L ds' \frac{e^{-\kappa r}}{r} - 1, \quad (A5) \]

where \( r = r(s - s') = r(s' - s) \) denotes the distance between line elements \( ds \) and \( ds' \), both on the molecule. The factor 1/2 is included to avoid double counting. Now we substitute \( q \) by \( \zeta q \) in \( U \) and integrate in \( \zeta \) from 0 to 1. We obtain

\[ F_{pc} = \int_0^1 2U(\zeta) d\zeta = 2U \int_0^1 \zeta d\zeta = 2U \left( \frac{1}{2} - 0 \right) = U. \quad (A6) \]

Therefore,

\[ F_{pc} = U = \frac{\lambda^2}{2D} \int_0^L ds \int_0^L ds' \frac{e^{-\kappa r}}{r} - 1. \quad (A7) \]

We now change from \( s \) to a dimensionless variable \( t \), with

\[ L = \int_0^L ds = \int_0^b dt. \quad (A8) \]

Hence,

\[ f_{pc} = \frac{\lambda^2 b^2}{2D} \int_0^\infty dt \int_0^\infty d\tau \frac{e^{-\kappa(r - \tau)}}{r(t - \tau)} - 1. \quad (A9) \]

Changing variables again, \( x = t - \tau' \), and integrating by parts, the free energy becomes

\[ f_{pc} = \frac{\lambda^2 b^2}{2D} \int_0^\infty dx \left( \frac{Z - x}{e^{-\kappa r(x)}} - 1 \right). \quad (A10) \]

Defining \( p_z = -1 + m \) and substituting \( \lambda = (-1 + m)q/b \), we may write

\[ \beta f_{pc} = \frac{\beta}{2} \int_0^\infty dx \left( \frac{Z - x}{e^{-\kappa r(x)}} - 1 \right). \quad (A11) \]

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