Flexible Polyelectrolytes with Monovalent Salt

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Abstract

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.

Key words:

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1 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]. Besides, a large class of synthetic polyelectrolytes are present in the chemical industry. For instance, poly-

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acrylic acid is the main ingredient for diapers [2] and dispersions of copolymers of acrylamide or methacrylamide and acrylic or methacrylic acid are fundamental for cleaning water [3]. Even though the tremendous interest in polyelectrolyte, unlike neutral polymers [4], 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]. Recent molecular simulations of salt-free systems [6] were able to obtain the end to end distance of strong electrolytes below Manning parameter [1]. The picture provided by these simulations have shown to be more complicated than early analytic theories have predicted [7]. Past theoretical works tended to neglect entropy. For stiff chains, such as DNA, entropy is a small contribution to the free energy and, in principle, can be disregarded. In contrast, for flexible polyelectrolytes, treating entropy along 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 [8]. The end to end distance and pressure calculated using this method show good agreement with simulations [6].

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 [9], Manning condensation [1] and Flory elasticity for polymers [4]. We show that 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 polyion becomes relevant and the chain stretches. At even lower temperatures, above the Manning condensation threshold, counterions condense into the polyion. The polymer chain net charge decreases and the polyion collapses. The addition of salt screen the electrostatic interactions and the polymer contracts. Our results show a good quantitative agreement with simulations [10].

2 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 $-Z q < 0$, 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 referred as counterions and the negative as coions. Thus if $m$ is the
fraction of associated ions, $\rho_+ = Z(1-m)\rho_p + \rho_s$, $\rho_- = \rho_s$ are the density of
counterions and coions respectively. 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 $\beta = 1/k_BT$. 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 [1] $\xi = \beta q^2/\lambda B$. Hence $\xi = \sigma/b T^*$ and $\xi = \lambda B/b$. For
simplicity, macroion does not assume any preferential orientation. Hence, the
distance between monomers $i$ and $j$ is represented by $r_{ij} = b|i - j|^\gamma$ as usual
[4]. The end to end distance $R_e$ is the distance between monomers 1 and $Z$
and it is represented by $R_e = b(Z - 1)^\gamma$

The electrostatic interaction between the chain and the counterions leads the
formation of a complex made of one macromolecule and $n = Zm$ 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, $n$ and the end to end distance characterized by $\gamma$.
The system is, therefore, composed by complexes made of one polion and
$n$ counterions, free counterions 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 $f = f_{ELEC} +
 f_{HC} + f_{ENT}$ where $f_{ELEC}$ contains all the electrostatic interactions, $f_{HC}$ has
the hard core contribution between the different species and $f_{ENT}$ has the
entropic contributions for the free energy density.

The electrostatic free energy density is split into $f_{ELEC} = f_{pc} + f_{ff} + f_{d}$
where $f_{pc}$ accounts for the electrostatic interaction between the polyelectrolyte
chain and the free electrolyte, $f_{ff}$ takes care of the electrostatic interaction
between the counterions e coions and $f_d$ includes the dipole-ion interaction
between the dipole pairs along the chain and both charged monomers and free
counterions and coions \[8\]. The hard core free energy density is divided into
two contributions given by $f_{HC} = f_{hc} + f_{cs}$ where $f_{hc}$ takes care of hard core
interaction between monomers along the chain and $f_{cs}$ includes the hard core
interaction between free ions. Here $cs$ 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 $f_{ENT} = f_{ei} + f_{ig}$ where $f_{ei}$ is
the elastic free energy of the flexible chain, $f_{ig}$ is the ideal gas free energy for
the mixture of the different species present in the solution.

The electrostatic free energy density between the complex made of a poly-
electrolyte and $n$ counterions associated to it and the free ions in the solu-
tion can be derived in the framework of the Debye-Hückel theory yielding
[12]$$\beta f_{pc} = \xi p_z^2 bI/2$$ where $$p_z = -1 + m = -1 + Z/n$$ and

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

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

For the interaction between free ions we employ the Debye-Hückel free energy for electrolytes [9]. 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 the free energy density in reference [11][12].

The polyelectrolyte will be considered to be in a good solvent. Therefore, hard-core repulsion between monomers is approximated by a virial coefficient from Flory-de Gennes theory [4],$$\beta f_{hc} = Z W_1 \bar{\rho} / 2$$ where $$W_1 = 4\pi \sigma^3 / 3$$ is the second virial coefficient for hard spheres of diameter $$\sigma$$, and $$\bar{\rho} = Z/V_c$$ with $$V_c = 4\pi R_c^3 / 3$$. The hard-core repulsion between free ions is approximated by the Carnahan-Starling free energy [13].

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 [4][12]$$\beta f_{el} = \frac{3}{2} \left( \alpha^2 - 1 \right) - 3 \ln \alpha$$ where $$\alpha = R_c / R_0$$, where $$R_0 = b \sqrt{Z - 1}$$ is the end to end distance of a polymer in a Θ solvent.

Another important entropic 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 [11][12][8]:

$$\beta f_{ig} = \frac{1}{\tilde{\rho}_p} \left[ \rho_+ \ln \rho_+ \Lambda^3 - \rho_+ + \rho_- \ln \rho_- \Lambda^3 - \rho_- \right] + \ln \rho_p \Lambda^3 - 1 + \beta f_{ig}^c$$ \hspace{1cm} (2)

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

$$\beta f_{ig}^c = Z (1 - m) \ln \left[ \frac{Z (1 - m)}{V_c} \Lambda^3 - 1 \right]$$ \hspace{1cm} (3)
\[ + Zm[\ln \frac{Zm}{V_e} \Lambda^6 - 1] - Z[\ln \frac{Z}{V_e} \Lambda^3 - 1] + \beta f_{ig}^{\text{int}}. \]

Since the monomers along the chain are mobile, the first two brackets in Eq. (3) 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 the elastic energy. The last term is the internal partition function of the complex in its internal reference frame. The internal partition function of the dipoles, \( \zeta_2 \), was explicitly calculated in references [11].

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 polyelectrolyte. This last term is already included in Eq. (3) while the electrostatic term is given by:

\[ \beta f_{ig}^{\text{int}} = \xi p_z^2 b \sum_{i=1}^{Z-1} \frac{1}{r(i)}, \]

with \( r(i) = bi^\gamma \).

3 Results and Conclusions

The equilibrium configuration of the polyelectrolyte is obtained by minimizing the free energy \( f \) described in the last session with respect to the number of associated counterions, \( n \) and \( \gamma \) that is related to the end to end distance. The behavior of the polyelectrolyte under temperature for \( Z = 32 \), density of monomers, \( \rho_m^* = 0.001 \), and density of salt, \( \rho_s^* = 0 - 0.008 \) (from top to bottom), 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 \( R_c = b(Z - 1)^{0.588} \). For \( Z = 32 \) and \( b = 2^{1/6} \sigma \) the end to end distance is given by \( R_c \approx 8.45\sigma \). 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 [10] (the circles in the graph). 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,
$R^*$ depends only on the value of the bare inverse of screening length, $\kappa_0 = \sqrt{4\pi(\rho_m + 2\rho_s)\lambda_B}$, and not on the density of polyelectrolytes. In Figure 3 the renormalized end to end distance given $R^* = R_e / b(Z/32)^{0.588}$ is plotted against $\ln \kappa_0 \sigma$ for $Z = 32, 64$, various densities of monomers and for $\lambda_B = 0.83\sigma$ ($\xi = 0.75$). 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. Our results are compared with simulations [10] (the squares and circles in the graph).

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

In summary, we studied the end to end distance of polyelectrolytes with added
We found that \( R_e \) 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 \( R_e \). For fixed values of \( Z \), \( \rho_p \) and \( \rho_s \), as the temperature is decreased, \( R_e \) exhibits three distinct behaviors: stretched, extended and collapsed. This three regimes are related to the stretched polymer, fully extended polyelectrolyte and collapsed polymer behavior.

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**References**


