THE DYNAMICS OF POLYELECTROLYTES

Brina Črnko

Advisers: dr. Lea Spindler
doc. dr. Irena Drevenšek Olenik

University of Ljubljana
Faculty of Mathematics and Physics
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Abstract

Polyelectrolytes are macromolecules or aggregates that dissociate into large ions with many charges and small counterions when put in solution. An example of a natural polyelectrolyte is DNA, there also exist many synthetical polyelectrolytes. Their behaviour is largely influenced by electrostatic interactions, which lead to specific properties, such as counterion condensation. If we assume that only electrostatic forces govern the dynamics of polyelectrolytes, their dynamics can be described by coupled mode theory, which can provide us with diffusion coefficients for different ions in solution. Theoretical values of diffusion coefficients can be experimentally tested by methods, such as dynamic light scattering.

Contents

1   Introduction

Polyelectrolytes are macromolecules having many ionizable groups [1]. In solution they are dissociated into highly charged macroions (polyions) and many small ions of opposite charge, which we call counterions.

The high charge of the macroion produces a strong electric field which attracts counterions. The effect of the macroion is screened if, for example, an electrolyte, such as salt is added. In most polyelectrolyte solutions, there are charged species originating from macromolecules as well as from added salt. Among all these species there are electrostatic interactions which, due to the long range nature of Coulomb interaction, lead to characteristic properties of polyelectrolytes.

Over the past few decades, much work has focused on both theoretical and experimental aspects of polyelectrolyte solution dynamics. However, due to complexity of these systems, accurate theoretical description is difficult and there is still a lack of consensus on the fundamental aspects of polyelectrolyte behaviour [2].

Most of the biologically important molecules, such as DNA, RNA and proteins, are polyelectrolytes [3]. Polyelectrolyte properties of these compounds are expected to be in the background of various biological phenomena. There exist also many synthetical polyelectrolytes with important technological applications: they are used as process agents in paper production and water purification or as absorbers in diapers.

The complexity of the dynamics is due to large number of forces and processes that take place in polyelectrolyte solutions. The dynamics is influenced by electrostatic forces, by hydrodynamic forces, the interactions in solutions depend on the shape of the macromolecules, which itself changes.

The aim of this work is to introduce polyelectrolytes and explain their fundamental dynamic properties. We will assume that the dynamics is dependent mainly on the electrostatic interactions between the charged species, especially on the interaction between small ions and polyions. Their motions are entangled, hence the theory describing the dynamics of polyelectrolytes is called coupled mode theory. Coupled mode theory is based on the diffusion equation for ions in solution and provides diffusion coefficients for polyions, as well as small ions. Usually, numerical calculations have to be performed, however, limits can be introduced, which give analytical expressions for diffusion coefficients. In this paper, one limit, the Lin-Lee-Schurr approximation [2] will be described. Later, the concept of counterion condensation will be introduced. We will apply coupled mode theory, together with counterion condensation theory to the dynamics of short DNA oligonucleotides in solution, which can be accurately described as rigid rods. In conclusion, we will comment on the results and evaluate the theory.

2   Polyelectrolytes

Polyelectrolytes may widely be defined as highly charged macromolecules or aggregates formed in aqueous solutions by dissociation of charged units of these macromolecules.

- A regular **ELECTROLYTE,** such as table salt (NaCl), splits into positive sodium ions and negative chloride ions if put in water.

$$NaCl \longrightarrow Na^+ + Cl^-.$$

- A **POLYELECTROLYTE,** such as polyvinyl sulfonic acid (figure 1), completely dissociates into macroions having many negative charges and hydrogen ions when dissolved in water [4].
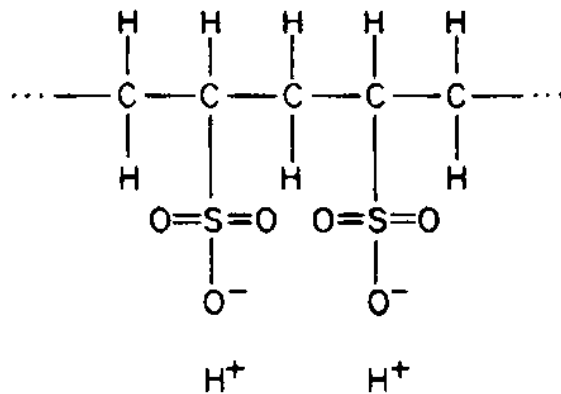
Figure 1: *Polyvinyl sulfonic acid completely dissociates into macroions having many negative charges and hydrogen ions when dissolved in water.*

- **CLASSIFICATION OF POLYELECTROLYTES**
  Polyelectrolytes can be natural, synthetic or little of both, the so called chemically modified biopolymers. Biopolymers are DNA, RNA and protein polymers.

  Polyelectrolytes form ions with any of the standard functional groups. The most important anionic functional groups are: carboxy, sulfate and phosphate. In solution, they form anions with negative charge. Cationic functional groups are: amino, ammonium and phosphonium. In solution, they form positively charged ions [5].

- **EXAMPLES**
  Natural polymers: nucleic acids (anionic), polypeptide and protein based.
  Chemically modified biopolymers: pectines (anionic), cellulose or starch based.

- **DNA**
  The most important example is the deoxyribonucleic acid, a natural polyelectrolyte. Each phosphate group of the sugar-phosphate backbone has one negative charge, which results in a highly charged double helix with two negative charges per 3.4 $\mathring{A}$ (figures 2 and 3).

2.1 Motivation to Perform Research in the Field of Polyelectrolytes

- Fundamental importance of prototypical polyelectrolytes, such as DNA. The polyelectrolyte properties of biopolymers are expected to be in the background of various biological phenomena [1].

- Polyelectrolytes remain one of the least understood states of condensed matter, in contrast to neutral polymer solutions. An understanding of the behaviour of polyelectrolytes is lacking.

- Broad application of chemically modified biopolymers and synthetic polyelectrolytes. Interaction of polyions with counterions is used in filter processes, dewatering... [5].
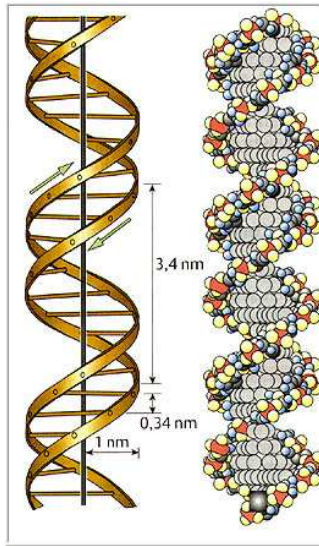
Figure 2: *DNA helix. Double helix, made up of two strands, held together by hydrogen bonds. Each strand of DNA consists of a large number of nucleotides. The two strands are wound around each other to form a double helix. The phosphate groups are marked yellow. The spacing between them is 0.34 nm [6].*
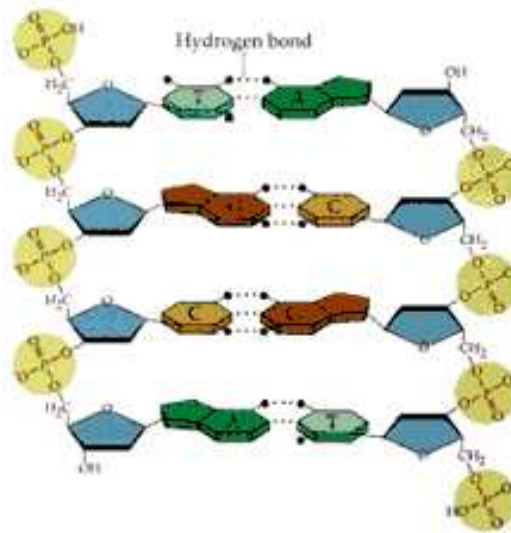

Figure 3: *Closeup of the DNA. Each nucleotide consists of a 5-carbon sugar (deoxyribose), a nitrogen containing base attached to the sugar, and a phosphate group. There are four different types of nucleotides found in DNA, differing only in the nitrogenous base. There are 4 kinds of nitrogenous bases, Thymine (T), Cytosine (C), Adenine (A), and Guanine (G). In the double stranded DNA, A always pairs with T and C always pairs with G. Phosphate groups in the sugar-phosphate backbone are negatively charged in solution. [7]*

2.2   General Properties of Polyelectrolytes

2.2.1   Effect of Electrostatic Interactions

Polyelectrolytes dissociate into polyions with many charges and small ions - counterions in solution. Usually, the solvent is water, but we often add simple electrolytes - salts in

the solution thus adding more charged particles and further complicating the dynamics. The charges originating from a regular electrolyte are called coions and are positively and negatively charged.

All ions in solution create a common electrostatic field, which fluctuates due to their motion and reversibly influences their dynamics. The motion of the polyions thus becomes coupled to the dynamics of the small and much faster counter- and coions [8].

Small ions of charge opposite to that of the polyion that are in the vicinity of the polyion screen the surface charge of the polyion. This long-range effect reduces the apparent charge on the polyion thereby reducing the magnitude of the direct polyion-polyion interactions [9].

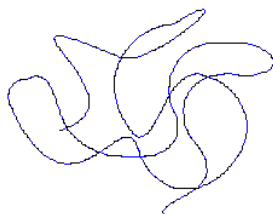### 2.2.2   Shape of Polyelectrolytes

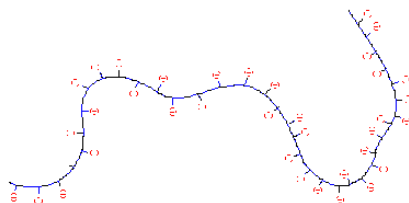Figure 4: *A polymer molecule tangled in random coil.*

Figure 5: *In solution, a polyelectrolyte expands because its like charges repel each other.*

Most polyelectrolytes, including DNA, change shape according to the conditions in solution. They are coiled when not in solution. In solution, they expand because the charges of the same sign repel each other. When salt is added, charges are screened and polyelectrolytes coil again (figures 4 and 5) [10]. Naturally, shape influences the dynamics and this causes difficulties in theoretical descriptions.

2.2.3   Other effects

In addition to electrostatic forces, there also act many other forces. For example, macromolecules have significant size and can hardly be described as point charges. They also cannot come too close together because of hard core repulsion.

3   The Diffusion of Polyelectrolytes

The approach in this paper will be as follows: all the forces except electrostatic will be neglected and many approximations will be made. The theory presented is a theory that works with molecular field approximation. All the ions in solution will be described as

point charges. Although the approach may appear overly simplified, it is a good indication of polyelectrolyte properties if one bears in mind all the simplifications and does not expect too much.

3.1 The Poisson-Boltzmann Equation

We consider a solution containing polyions and small ions of both charges. The fundamental equation that determines electrical properties is the Poisson equation. For s ionic species, it is written as [9]:

$$\nabla^2 \phi(\vec{r}, t) = -\frac{4\pi \rho(\vec{r}, t)}{\epsilon_0 \epsilon(\vec{r})} = -\frac{4\pi}{\epsilon_0 \epsilon(\vec{r})} \sum_{\alpha=1}^{s} Z_\alpha e_0 n_\alpha(\vec{r}, t), \tag{1}$$

where ∇^2 is the Laplacian operator, $\phi(\vec{r}, t)$ is the electric potential at position $\vec{r}$ and time t, ρ is charge density, ϵ is the local dielectric constant, $n_\alpha(\vec{r}, t) = N_\alpha(\vec{r}, t)/V$ is the local number density of ions of type α and Z_α is the valence of ion α.

Number density can be expressed by a Boltzmann distribution:

$$n_\alpha(\vec{r}, t) = <n_\alpha> e^{-\frac{Z_\alpha e_0 \phi(\vec{r}, t)}{k_B T}}, \tag{2}$$

where $<n_\alpha>$ is the average number density of ionic species α, k_B is the Boltzmann constant and T is the temperature. Assuming low potential, which means that $Z_\alpha e_0 \phi \ll k_B T$, we can expand number density as: $n_\alpha(\vec{r}, t) = <n_\alpha> \left(1 - \frac{Z_\alpha e_0 \phi(\vec{r}, t)}{k_B T}\right) = <n_\alpha> + \delta n_\alpha(\vec{r}, t)$. Number density fluctuates around average value $<n_\alpha>$ by $\delta n_\alpha(\vec{r}, t)$, which is a quantity one can measure in an experiment. The solution as a whole must be electrically neutral, so: $\sum_\alpha Z_\alpha e_0 <n_\alpha> = 0$. Substituting number density into the Poisson equation and accounting for the electroneutrality, one is left with a linearized Poisson-Boltzmann equation for ionic species in solution for low potential:

$$\nabla^2 \phi(\vec{r}, t) = -\frac{4\pi}{\epsilon_0 \epsilon} \sum_{\alpha=1}^{s} <n_\alpha> \frac{(Z_\alpha e_0)^2 \phi(\vec{r}, t)}{k_B T} = \kappa^2 \phi(\vec{r}, t), \tag{3}$$

where we defined Debye-Hückel screening length $1/\kappa$ as [9]: $\kappa^2 = \frac{4\pi e_0^2}{\epsilon \epsilon_0 k_B T} \sum_\alpha <n_\alpha> Z_\alpha^2$. The Debye-Hückel screening length is about $1\,\mu m$ in pure water, but it decreases with the addition of an electrolyte, such as NaCl. In case of $1\,M$ concentration of NaCl, $1/\kappa \approx 0.3\,nm$ [9]. For purposes of further calculation, partial screening parameter of species α can be defined:

$$\kappa^2 = \frac{4\pi e_0^2}{\epsilon \epsilon_0 k_B T} <n_\alpha> Z_\alpha^2. \tag{4}$$

In a polyelectrolyte solution, there are polyions (p) having charge $Z_p e_0$, cations (c) of charge $Z_c e_0$ and anions (a) of charge $Z_a e_0$. Cations and anions result from counterions and from added salt. We have assumed they have equal charge. Poisson equation then becomes:

$$\nabla^2 \phi(\vec{r}, t) = -\frac{4\pi e_0}{\epsilon_0 \epsilon} \left[Z_p \delta n_p(\vec{r}, t) + Z_a \delta n_a(\vec{r}, t) + Z_c \delta n_c(\vec{r}, t)\right]. \tag{5}$$

3.2 Diffusion Equation for Charged Particles in Solution

In a solution, where there are charged particles, the motion is due to ordinary diffusion and due to electric field, which is created by fluctuations of particles. The diffusion equation for number density for an ionic species α is [11]:

$$\frac{\partial n_\alpha(\vec{r},t)}{\partial t} = D_\alpha \nabla^2 \delta n_\alpha(\vec{r},t) + D_\alpha \frac{Z_\alpha e_0}{k_B T} <n_\alpha> \nabla^2 \phi(\vec{r}), \tag{6}$$

where D_α is the hydrodynamic diffusion coefficient of the ion and $\vec{E}$ is the electric field acting on the ion.

3.3   The Coupled Mode Theory

The aim of the coupled mode theory is to describe the dynamics of polyelectrolytes (which is strongly influenced by the coupling of the motions of polyions and small ions) by predicting the values of measurable quantities, namely the diffusion coefficients. The procedure begins with combining the equations that govern the dynamics in polyelectrolyte solutions, namely, the linearized Poisson-Boltzmann equation (5) and the diffusion equation for ionic species α (6). The equations are to be combined, then a Fourier transformation is performed [2]:

$$\nabla^2 \delta n_\alpha(\vec{r},t) \longrightarrow -q^2 \delta n_\alpha(\vec{q},t).$$

$\vec{q}$ is the wavevector of the fluctuation.

Fourier transformation of equations (5) and (6) leads to [8]:

$$\frac{\partial \delta \vec{n}(\vec{q},t)}{\partial t} = -\underline{\underline{M}}(q) \delta \vec{n}(\vec{q},t), \tag{7}$$

where

$$\delta \vec{n}(\vec{q},t) = [\delta n_p(\vec{q},t), \delta n_a(\vec{q},t), \delta n_c(\vec{q},t)]$$

and

$$\underline{\underline{M}}(q) = \begin{pmatrix} D_p(q^2 + \kappa_p^2) & \frac{D_p Z_a \kappa_p^2}{Z_p} & \frac{D_p Z_c \kappa_p^2}{Z_p} \\ \frac{D_a Z_p \kappa_a^2}{Z_a} & D_a(q^2 + \kappa_a^2) & \frac{D_a Z_c \kappa_a^2}{Z_a} \\ \frac{D_c Z_p \kappa_c^2}{Z_c} & \frac{D_c Z_a \kappa_c^2}{Z_c} & D_c(q^2 + \kappa_c^2) \end{pmatrix}. \tag{8}$$

κ_p, κ_a and κ_c are partial Debye-Hückel screening parameters of polyion, anions and cations, respectively and $\kappa^2 = \kappa_p^2 + \kappa_a^2 + \kappa_c^2$. Matrix $\underline{\underline{M}}(q)$ has three eigenvalues that represent the decay rates. We call the three eigenvalues λ_1, λ_2 and λ_3. λ_1 is the decay rate of charge fluctuation, the so-called Debye or plasmon mode and is independent of the scattering vector length q. λ_2 is associated with apparent polyion diffusion coefficient and is proportional to q^2 in the limit when $q \to 0$ [12]:

$$D_{app} = \frac{\lambda_2}{q^2}. \tag{9}$$

The third eigenvalue λ_3 is associated with small ion diffusion and is also proportional to q^2 for small values of q.

Both modes, λ_2 and λ_3 include coupling between the small ion and the polyion motions and are not purely polyion or small ion motions.

Eigenvalues of the matrix can be derived by analytical or numerical calculations using software such as Mathematica for analytical and MATLAB for numerical calculations.

3.3.1   Lin-Lee-Schurr Analytical Solution

Several attempts have been made to obtain simple analytical expressions for diffusion coefficients. The simplest way is to assume the following:

- Added salt is a 1:1 symmetrical electrolyte, where both ions have a single charge (again, table salt NaCl is an example).

- Added salt has common counterions with the polyion.

- Counterions and coions have the same charge and diffusion coefficient.

- We take the zero angle limit.

$$q = 0, \ D_a = D_c, \ Z_c = -Z_a = 1.$$

Under these conditions, the apparent polyion diffusion coefficient is [9]:

$$D_{app} = \frac{1}{2}\left[D_p\left(1 - \Omega\right) + D_s\left(1 + \Omega\right)\right], \tag{10}$$

where

$$\Omega = \frac{D_p Z_p - D_s\left(1 + \frac{2c_s}{Z_p c_p}\right)}{D_p Z_p + D_s\left(1 + \frac{2c_s}{Z_p c_p}\right)}, \tag{11}$$

where c_p is the molar concentration of the polyion and c_s is the molar concentration of small ions. This is so-called Lin-Lee-Schurr analytical solution.

Two limits are interesting. One is for high added salt concentrations:

$$D_{app} = D_p, \quad (\frac{2c_s}{c_p} \to \infty).$$

In high added salt conditions, there is strong screening of the polyion charge, so the polyions diffuse like uncharged particles with no coupling to the dynamics of small ions.

The other limit is for highly charged polyions $(D_p Z_p \gg D_s)$:

$$D_{app} \sim D_s, \quad (\frac{2c_s}{c_p} \to Z_p).$$

Highly charged polyions diffuse at the same rate as their counterions in the absence of added salt.

3.3.2 Assumptions of the Coupled Mode Theory

Coupled mode theory is based on molecular field approximation. It includes Coulomb interactions between polyions and the small ions, however, the forces between the polyions are not explicitly considered.

The theory is linearized with the condition $Ze_0\phi \ll k_B T$ being the basis of linearization.

4 Counterion Condensation

Counterion condensation is a characteristic phenomenon in highly charged polyelectrolytes. Polyions have a high charge density in the solution and the equilibrium distribution of the small ions is greatly affected by the polyion electric field [9].

When the numbers of charges and counterions are small, counterions are equally distributed in the solution. With the increase of the number of charges, the electric field becomes strong and relatively more counterions are retained near the polyion (figure 6).
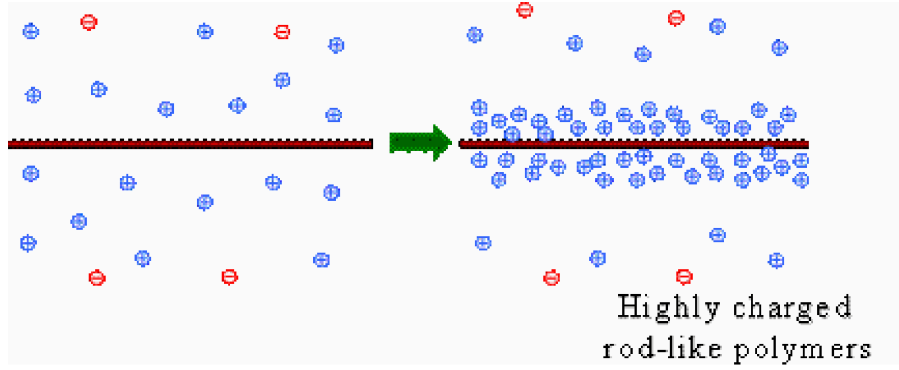
Figure 6: *Counterion condensation. If the charge of the polyion is smaller than the critical value, counterions are equally distributed in solution (left). If the charge density exceeds critical value, counterions condense onto the polyion and reduce its apparent charge to critical value (right).*
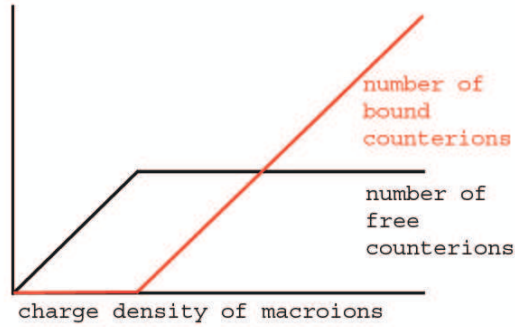

Figure 7: *Counterion condensation. The horizontal axis is the charge density of macroions. Black line represents the number of free counterions, while the red line represents the number of bound counterions.*

According to the Oosawa-Manning counterion condensation theory, that deals with linear polyelectrolytes, if the linear charge exceeds a critical value, counterions will condense onto the polyion and reduce the polyion charge density to the critical value [1].

When polyion charge density reaches a critical value, the number density of free counterions remains constant (figure 7). Increase of the polyion charge and counterion concentration results only in an increase of the number of counterions condensed onto the polyion.

A rodlike polyion has a linear charge density $\nu_L = \frac{Z_p}{L}$, where L is the length of the polyion and Z_p its charge. The critical density is given by [2]:

$$\nu_0 = \frac{1}{Z\lambda_B}, \tag{12}$$

where Z is the value of counterion charge and λ_B is the Bjerrum length [2]:

$$\lambda_B = \frac{e_0^2}{4\pi\epsilon\epsilon_0 k_B T}. \tag{13}$$

Bjerrum length is given by the characteristics of the solvent and represents the linear charge separation at which the electrostatic energy is equal to $k_B T$.

Bjerrum length for water solutions at $25°C$ is $0.7\,nm$. Polyions like DNA have charge densities that exceed critical density and counterion condensation takes place.

When the charge density of the polyion is less than ν_0, counterion condensation can be ignored. When the charge density of the polyion is greater than ν_0, counterions condense onto the polyion and the effective charge of the polyion reduces to $|Z_{eff}| = L\nu_0$ [2].

4.1 Approximations of the Counterion Condensation Theory

- Manning's linear polyelectrolyte approximation can be applied to polyions with a length much larger than the Debye-Hückel length ($L \gg 1/\kappa$), macromolecule is described as a line charge of infinite length.

- No polyion-polyion interaction takes place.

- Bjerrum length is calculated using the dielectric constant of the solvent.

4.2 Combining Coupled Mode and Counterion Condensation Theory

Many polyelectrolytes, including DNA, are highly charged. This means that the linearized Poisson-Boltzmann equation is not valid, because the condition of low potential $Z_p e_0 \phi \ll k_B T$ is not fullfilled. However, we can use the counterion condensation theory to calculate a reduced charge on the polyion. This reduced charge may then be used in conjunction with the linearized Poisson-Boltzmann equation to give the equations of coupled mode theory.

5 Experimental Verification

Liu et al. [2] used a 20 base pair oligonucleotide for studying polyelectrolyte solution dynamics. It can serve well as a model for solution dynamics of highly charged polyelectrolytes: DNA is one of the most highly charged polymers known (2 charges per 0.34 nm) and it can be prepared as a monodisperse sample of well-defined rigid rod molecules, albeit short.

5.1 The Molecule

The oligonucleotide used was a 20 base pair synthetic DNA, with the primary structure: 5'-CGT ACT AGT TAA CTA GTA CG-3' [2], with diameter of 2.0 nm and of length 6.8 nm. It was in double helical form. With 20 negatively charged phosphate groups, the double helix has 42 negative charges in neutral or basic pH solutions. Dynamic light scattering experiments were performed on various samples. Experiment at different scattering vector lengths, temperatures, DNA concentrations and added salt (NaCl) concentrations were performed. With data analysis, diffusion coefficients were obtained.

5.2 Effective Charge

The diffusion coefficients were obtained theoretically, as well as experimentally. In experiments, they varied polyion concentration and performed measurements with three different concentrations of added salt. In figure (8), theoretical calculations, together
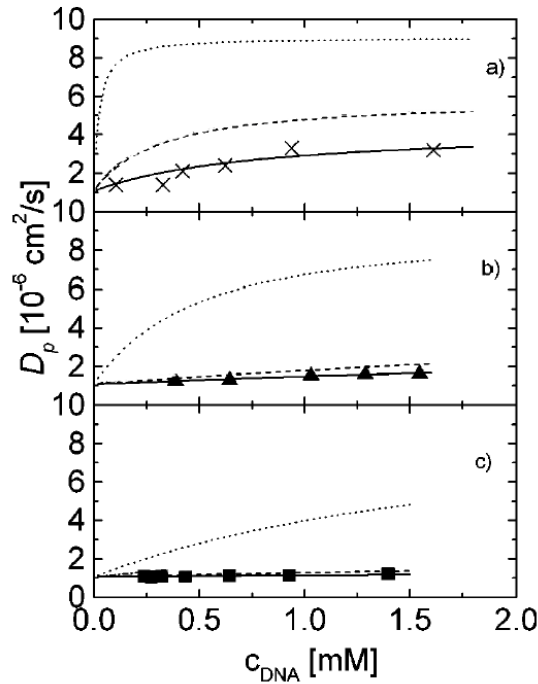
Figure 8: *Determination of best fit charge. It is a fit of coupled mode theory to the experimental results with different concentrations of added salt: a) 3mM NaCl b) 53 mM NaCl c) 203 mM NaCl. Symbols represent the experimental data, the lines are the theoretical predictions for different effective charges: dotted line is for $Z_{eff} = -42$ (complete dissociation); dashed line is for $Z_{eff} = -9.6$ (Manning theory); solid line is a fit to the experimental data. For comparison, in human cells, the concentration of salt (NaCl) is 154 mM.*
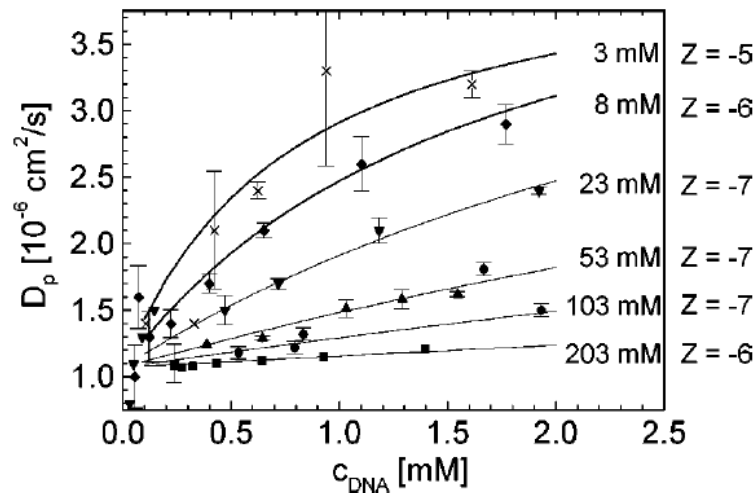

Figure 9: *Concentration dependence of apparent diffusion coefficient and best fit effective charges from coupled mode theory for different concentrations of added salt NaCl.*

with experimental results, are presented. Dotted line corresponds to coupled mode theory prediction, obtained numerically by MATLAB, for effective charge $Z_p = -42$ and
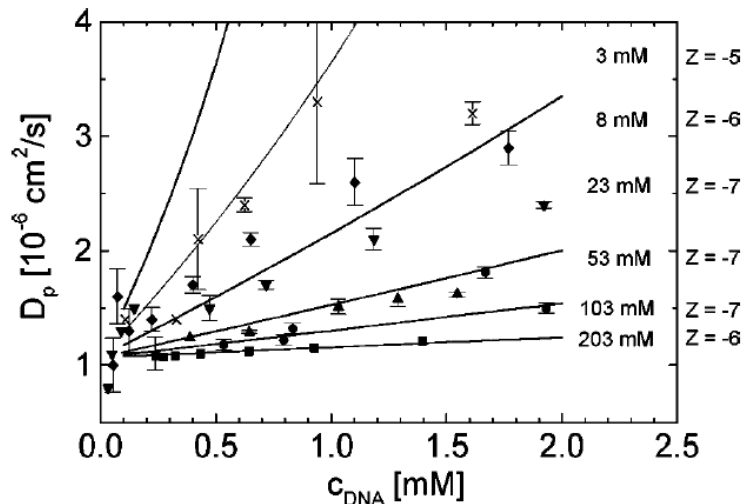
Figure 10: *Comparison of experimental results for the polyion diffusion coefficient with Lin-Lee-Schurr analytical solution of the coupled mode theory equations.*

the dashed line corresponds to coupled mode prediction for effective charge $Z_{eff} = -9.6$, which was calculated from Manning condensation theory (L/λ_B). Manning theory predicts a charge that fits the experimental data at high added salt concentration conditions but is too high at low salt concentration conditions.

5.3 Numerical and Lin-Lee-Schurr Diffusion Coefficients

In a similar experiment, Liu et al. tested theoretically obtained diffusion coefficients. Again, they measured diffusion coefficient at different polyion concentrations and different added salt concentrations (figures 9 and 10). Experimental results were compared to diffusion coefficients, that were numerically obtained from coupled mode theory matrix using MATLAB and to analytical solution by Lin, Lee and Schurr.

The results show that numerically obtained eigenvalues give a good fit to the experimental results, while calculations with Lin-Lee-Schurr analytical equations overestimate the polyion diffusion coefficient for both high polyion and low salt concentration conditions.

6 Limits of Validity

If the dynamics of polyelectrolytes was indeed as simple as to be described only by the coupled mode theory with accounting for counterion condensation, then it would not be an area of science where extensive theoretical, as well as experimental studies were still needed. All or at least some of the assumptions made on the way in developing a theory may also be untrue.

- The electrostatic forces between the polyions themselves can be far from negligible.

- The size and shape of the macromolecules are important. Coupled mode theory treats ions as point charges, but there are hydrodynamic interactions. Hard core repulsion forces prevent ions from taking any position thus affecting the diffusion coefficient.

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- Hydration. The molecules of water tend to surround a polyelectrolyte thus changing its effective charge, as well as size.

- Very often, macromolecules are not much longer than the Debye-Hückel screening length, so they cannot be regarded as of infinite length. End-effects are significant, especially in conditions of low concentrations of added salt.

- Low potential approximation quickly fails. For calculating the structure of the counterion coat that surrounds a polyelectrolyte, nonlinear Poisson-Boltzmann equation has to be numerically solved.

- Most polyelectrolytes, as said in section 2.2.2 are long enough to change shape depending on the concentration of added salt and are coiled, at least to some extent. Therefore, they can hardly be regarded as rods.

Numerous examples can be found when the description with coupled mode theory fails altogether. For example, in describing the dynamics of some proteins. While in the experiments of Liu et al. the theory was shown to work well enough for the specific polyelectrolyte studied, for each particular experiment, each of the conditions of validity has to be carefully considered before applying coupled mode theory.

7 Conclusions

Synthetical polyelectrolytes are important in industrial applications as agents in water treatment and as absorbers. Natural polyelectrolyes, such as DNA and protein polymers are the fundamental constituents of life forms as we know them. Therefore, an understanding of their behaviour is desired but not yet reached, as the dynamics is rather complicated and dominated by long range Coulomb forces.

For some purposes, the dynamics can be adequately described by the coupled mode theory that is based on linearized Poisson-Boltzmann equation and the diffusion equation that includes extra terms to account for electrostatic interactions. The validity of the coupled mode theory can be extended by taking into account counterion condensation, a property characteristic of polyelectrolytes, that can be described by Manning theory, which has an extra advantage of being simple. Experimental results for 20 base DNA oligonucleotide show good agreement with theory. However, these theories are limited as they only take into account electrostatic forces and even there the problem is simplified. Many other forces play a role, like hydrodynamic forces, interactions depend on the shape of the molecules... Coupled mode theory quickly fails, but it does give some clues for understanding the dynamics of polyelectrolytes.

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