THEORY OF POLYEOLECTROLYTE SOLUTIONS

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1. Introduction

Polyelectrolytes are polymers bearing ionizable groups, which, in polar solvents, can dissociate into charged polymer chains (macro-ions) and small "counter-ions". Well known examples of such systems are proteins, nucleic acids or synthetic systems such as sulfonated polystyrene or polyacrylic acid. Very often, the polar solvent is water. Because of their fundamental importance in biology and biochemistry, and because of their hydrosolubility, ionizable polymers have been the object of a continued interest since the early days of polymer science (see e.g. [1,2] and references therein). It is however, a widely acknowledged fact [3] that they remain among the least understood systems in macromolecular science. This situation is in sharp contrast with the case of neutral polymers. In fact, even the properties that are now routinely used to characterize neutral polymers (e.g. light scattering, osmometry, viscosity..) are still very poorly understood in polyelectrolyte solutions.

Briefly speaking, the origin of this difference with neutral polymers can be traced back to the difficulty to apply renormalization group theories and scaling ideas to systems in which long range (coulomb) forces are present. The success of the modern theories (and, although this was not always realized as they were developed, of many older approaches) of neutral polymer solutions is based on the fact that the range of the interactions between molecules is much smaller than the scale determining the physical properties of the solution, which is the size of the polymer chain or the correlation length. If, as it is in general the case in polymer physics, the main issue is the variation of solution properties with molecular weight, the interactions only affect prefactors that can be adjusted to experimental results. The theories [4,5,6] developed in this spirit have proven extremely powerful for the interpretation of experimental data on neutral polymer solutions. Polyelectrolyte solutions are more complex, both short range (excluded volume) and long range (coulombic) interactions are simultaneously present. The screening of the electrostatic in-
teractions introduces an intermediate length scale in the problem, that can be comparable to the chain size or to the correlation length. Moreover, the details of the local chain structure are important and control the phenomenon of counterion condensation [7] (see section 3). This condensation in turn modifies the long range part of the interaction. The long range interactions actually also has have a nontrivial influence on the local structure [8,9,10] (stiffness) of the polymer chains (section 4). The implication of this complicated coupling between small and large length scales is that the theoretical results for polyelectrolytes can be expected to be more "model-dependent" than for neutral polymers. In particular, the functional dependence of several physical properties on molecular weight or concentration depends in some cases on the local description that is used for the polymer chain. Such situations never occur in neutral polymers.

Intrinsically related to this theoretical problem, is the more practical difficulty in comparing experiments and theory for polyelectrolyte solutions. In neutral polymers, the comparison is made possible by adjusting interaction dependent prefactors and fitting experimental results to the theoretically predicted dependence on, e.g. molecular weight. In polyelectrolytes, "microscopic" parameters can have bigger influence, and a much more precise modelling might be necessary in order to interpret experimental results. This often involves the introduction of more adjustable parameters in the interpretation, which sometimes becomes inconclusive.

In spite of these considerations, the modern approach to neutral polymers physics has inspired a number of contributions to the polyelectrolyte problem in the last two decades. By "modern", we mean here those theoretical approaches that attempt to use as much as possible "coarse grained" models, with a minimal number of microscopic parameters. The goal of this review is to summarize these approaches, with the hope that they could provide a useful conceptual framework for further development. The review is organized as follows. Sections 2 to 4 are concerned with single chain properties. Section 2 deals with
the academic problem of a charged chain in the absence of counterions. The phenomenon of screening, and the influence of the small ions on the interaction between monomers, is discussed in section 3. The influence of long range interaction on the local stiffness (electrostatic rigidity) is described in section 4. In sections 5 and 6, the properties of interacting polyelectrolyte chains are considered. The simpler case of gels and brushes-in which the structure is controlled by the preparation of the system- is described first. Semidilute and concentrated solutions are the subject of section 6. Finally, some results on dynamical properties (diffusion, electrophoretic mobility and viscosity) are presented in section 7.

Some important subjects have been left out of the scope of this review, either because they have been reviewed recently elsewhere or because our understanding is too fragmentary. Among those are the dielectric properties of polyelectrolyte solutions [11], their rheological properties, computer simulation results [12], and all the problems related to polyelectrolyte adsorption [13]. Finally, we systematically refer the reader to the original papers for detailed comparison with the experimental results. The reason, mentioned above, is that such comparisons are, in general, not simple, and involve the determination of several parameters.

2. Charged chains at infinite dilution - asymptotic properties

2.1 Definition of the Model and Flory-like calculation

In the theoretical limit of infinite dilution and zero salt concentration, a polyelectrolyte chain can be modelled as a connected sequence of charged and uncharged monomers in a "dielectric vacuum" that represents the solvent. This model is not very realistic to describe actual polyelectrolyte solutions, as will become clear in our discussion of ion condensation and screening but it serves here to introduce some important concepts relative to charged polymer chains.
The energy for such an isolated polymer chain, made up of \( N \) monomers, is written as:

\[
H = H_0 + \frac{1}{2}k_B T \sum_{i=1}^{N} \sum_{j \neq i} \frac{\ell_B z_i z_j}{|\mathbf{r}_i - \mathbf{r}_j|}
\]  

(2.1)

where \( H_0 \) is the energy of the neutral polymer chain that would be obtained by "switching off" the electrostatic interaction, and the double summation on the left hand side includes all monomer pairs. Here \( z_i \) is the charge (in units of the electronic charge \( e \)) of monomer \( i \), \( T \) is the absolute temperature and \( \ell_B = e^2/(4\pi \epsilon_0 \epsilon_r k_B T) \) is the Bjerrum length, that characterizes the strength of electrostatic interactions in the solvent. For water at \( T = 300K \), \( \ell_B \simeq 0.7nm \).

The "neutral polymer" energy \( H_0 \) contains terms describing the chemical bonding of the monomers as well as short range excluded volume terms. In this section, we focus on the very simple case where \( H_0 \) is the free energy of a gaussian, or bead-spring, chain, i.e.

\[
H_0 = \frac{3k_B T}{2b^2} \sum_{i=1}^{N-1} (\mathbf{r}_i - \mathbf{r}_{i+1})^2 .
\]  

(2.2)

The "monomer size" \( b \) is such that the mean squared averaged end-to-end distance for the neutral chain is \( R_0^2 = Nb^2 \). The physical situation described by this model is that of a very weakly charged, flexible chain. In that case, each "spring" actually represents a flexible subchain of several neutral monomers. Moreover, the absence of excluded volume interactions implies theta conditions for the neutral backbone. Although these conditions are rather unlikely to be achieved in experiments, the model contains the two key ingredients that monitor the asymptotic behavior of charged polymers in the absence of screening, namely long range interactions and monomer connectivity. These are the only relevant contributions as can be seen from the form of the Flory free energy for a chain of \( N \) monomers, carrying a total charge \( fNe \) (i.e. \( f \) is the fraction of charged monomers, \((1 - f)N \) monomers are neutral). The Flory energy [14] for a chain of size \( R \) is the sum

\footnote{The Flory free energy ignores numerical prefactors of order unity; the prefactor of the electrostatic energy depends on the actual distribution of the charges in the sphere of radius \( R \), it is equal to \( 3/5 \) if the charges are uniformly distributed.}
of an elastic energy $k_B TR^2/Nb^2$ and of a Coulombic energy $k_B T (Nf)^2 \ell_B/R$,

$$E_{Flory} = k_B T \left( \frac{R^2}{Nb^2} + \frac{(Nf)^2 \ell_B}{R} \right),$$

which upon minimization with respect to $R$ gives an equilibrium size

$$R \sim N f^{2/3}(\ell_B b^2)^{1/3}.$$  \hspace{1cm} (2.3)

This establishes the well known result, that the chain size is proportional to the number of monomers and to a $1/3$ power of the charge fraction $f$. This result was first obtained by Katchalsky and coworkers [15] using a distribution function approach, shortly before Flory published an equivalent calculation for chains with short range excluded volume.

The electrostatic interactions tend to swell the chain, therefore the equilibrium radius of a weakly charged polyelectrolyte chain must be larger than the gaussian radius $R_0$. This condition defines a minimum charge fraction $f_G \simeq N^{-3/4} (b/lb)^{1/2}$ above which the electrostatic interactions are relevant and the radius is given by (2.4). If the fraction of charges $f$ is smaller than $f_G$ the polyelectrolyte chain essentially behaves as a neutral chain and has a gaussian radius $R_0$. In the following we always implicitly assume that $f > f_G$.

In contrast to Flory’s calculation, whose success is known [5] to arise from an uncontrolled cancellation of errors, Katchalsky’s approach is now believed to yield an essentially exact scaling result, as will become clear in the next sections. A more refined calculation of the electrostatic energy, accounting for the fact that the shape of the chain is rodlike rather than spherical, only yields a logarithmic correction to (2.4)

$$R \sim N f^{2/3}(\ell_B b^2 \ln(N))^{1/3}.$$  \hspace{1cm} (2.5)

Because of this rodlike character, the polyelectrolyte chain is often described as being a "fully extended" object. This statement, however, somewhat overinterprets the actual meaning of relation (2.4). Short range molecular flexibility does not have to be frozen in a locally stretched configuration to obtain such relations.
To understand this point, and to get a deeper insight into the meaning of Katchalsky’s calculation, it is useful to introduce the concept of electrostatic blob [14]. An electrostatic blob is a chain subunit within which the electrostatic interactions can be considered as a weak perturbation. The size $\xi_e$ and the number of monomers $g$ in such a subunit are thus related by

$$\frac{(fg)^2\ell_B}{\xi_e} \simeq 1 \quad \text{(2.6)}$$

Another relation between $\xi_e$ and $g$ is obtained from the gaussian statistics of the chains on the scale $\xi_e$, $\xi_e^2 \simeq gb^2$. This gives

$$\xi_e \sim b(f^2\ell_B/b)^{-1/3} \quad \text{and} \quad g \sim (f^2\ell_B/b)^{-2/3} \quad \text{(2.7)}$$

The size of the chain (equation (2.4)) is therefore $(N/g)\xi_e$, so that the chain can be thought of as a linear (in the sense that its lateral dimensions are vanishingly small compared to its length) string of ”electrostatic blobs” (figure 1).

The blob picture is particularly useful to discuss the structure of a charged chain in a good or poor solvent. In a good solvent, the only modification compared to the theta solvent case is the good solvent statistics characterized by a swelling exponent $\nu \neq 1/2$ must be used in the relation that relates the blob size to the number of monomers in a blob, $\xi_e \sim g^\nu$. The result is still a linear string of blobs, $R \sim Nf^y$, but the exponent $y$ that describes the variation with the charge fraction is now $(2 - 2\nu)/(2 - \nu)$. In a poor solvent, the problem is more subtle, and has been analysed in detail by Khokhlov [16]. In that case, the chain would be completely collapsed into a globular state in the absence of electrostatic interactions. The effect of these interactions is to break up the globular structure into a string of ”globular blobs”. The criterion that determines the blob size is now that the electrostatic energy within the blob is sufficient to overcome the interfacial energy that must be paid when monomers are exposed to the solvent, i.e.

$$\frac{(fg)^2\ell_B}{\xi_e} \sim \Gamma \xi_e^2/(k_BT) \quad \text{(2.8)}$$
where $\Gamma$ is the interfacial tension between the collapsed phase and the pure solvent. A second relation is obtained by expressing that the blob has the same structure as a small section of collapsed polymer,

$$g \sim n\xi_e^3.$$  \hspace{1cm} (2.9)

Here $n$ is the density of the collapsed chain. In the simple case where the second and third virial coefficients between monomers are, respectively, $b^3(T - \theta)/T = -b^3\tau$ and $b^6$, $n \sim \tau b^{-3}$ and $\Gamma = k_B T \tau^2 b^{-2}$. Equations (2.7) and (2.4) are replaced by

$$\xi_e \sim b(f^2\ell_B/b)^{-1/3}$$

$$g \sim \tau(f^2\ell_B/b)^{-1}$$

$$R \sim (N/g)\xi_e \sim N\tau^{-1}(f^2\ell_B/b)^{2/3}. $$ \hspace{1cm} (2.10)

### 2.2 Variational approaches

The Flory-type calculation discussed above is a typical mean-field approach. Similar approaches which have been successfully applied to the charged bead spring model of section 2.1. include the ”chain under tension” model [14,17] and the ”gaussian variational method” [5,17,18,19]. Both methods are mean-field approaches, formulated in a variational fashion. The chain is approximated by a simpler system described by a trial Hamiltonian $H_t$, and the ”best” trial Hamiltonian is obtained by minimizing the variational free energy

$$F_{var} = < H >_t - TS_t $$ \hspace{1cm} (2.11)

where $< H >_t$ is the average value of the energy for the true system, taken with a statistical weight $\exp(-H_t/k_B T)$, and $S_t$ is the entropy of the trial system.

In the ”chain under tension” model, the trial Hamiltonian is that of a noninteracting gaussian chain subject to an external tension $\mathbf{F}$,

$$H_t (\mathbf{F}) = \frac{3k_B T}{2b^2} \sum_{i=1}^{N-1} (r_{i+1} - r_i)^2 + \mathbf{F}.(r_N - r_1).$$ \hspace{1cm} (2.12)
This model is simple enough to allow explicit calculations of many properties of the chain. In particular, it can be shown that the minimization of the corresponding variational free energy yields a force

$$F \sim (f^2 \ell_B/b)^{1/3} \ln(FN^{1/2})^{1/3}$$

(2.13)

and a chain size

$$R \sim N(f^2 \ell_B/b)^{1/3} \left[ \ln \left( N(f^2 \ell_B/b)^{2/3} \right) \right]^{1/3}$$

(2.14)

The results for the chain size and chain structure factor were shown to agree quantitatively with Monte-Carlo calculations [17]. This model can also be used to give a quantitative meaning to the "electrostatic blob size" introduced above. This is done by noting that in the chain under tension, the mean squared distance between two monomers separated by $n$ monomers along the chain is

$$R(n)^2 = nb^2 + n^2(b^2F/3k_BT)^2$$

The blob size can be obtained by identifying the second term with $((n/g)\xi_e)^2$, $\xi_e = 3k_BT/F$, in agreement with (2.7). The blob size is therefore directly related to the prefactor of $n^2$ in the expression of $R(n)^2$.

In the gaussian variational approach, the trial Hamiltonian is a general quadratic form of all monomers coordinates. This method, which is tractable for cyclic chains only, was first introduced by des Cloizeaux [5] as an alternative to Flory’s theory for chains with short range excluded volume. In that case, however, the method gives a swelling exponent $\nu = 2/3$ in three dimensions, and is therefore inferior to Flory’s approach. For long range interactions. It was shown [18] that the variational gaussian approach predicts the same asymptotic behaviour as Flory’s theory and as the "chain under tension" method. As for the chain under tension model, the quantitative agreement with numerical simulation results is good [17].

2.3 Renormalisation group calculations

The coincidence of the predictions from the Flory approach and the variational gaussian
method suggests that the predicted asymptotic behaviour is indeed exact, except may be for logarithmic corrections. Exact renormalisation group calculations were performed for space dimensions \( d > 4 \) [20,21], showing that for \( 4 < d < 6 \) the swelling exponent of the chain is \( \nu = 2/(d-2) \) (as does the variational calculation of reference [18]). No such calculation is available for \( d = 3 \), but the result for \( d = 4 \) suggests that the maximum value \( \nu = 1 \) is obtained for \( d < 4 \), while gaussian behaviour is recovered for \( d > 6 \). Moreover, a "naive" real space renormalisation argument [4] also predicts \( \nu = 1 \). Note that a naive extension of the Flory theory to \( d \) dimensions predicts an upper critical dimension where the chains are gaussian equal to 6 but a lower critical dimension where \( \nu = 1 \) equal to 3 in disagreement with the renormalisation group results.

The success of variational and mean-field methods for chains with long range interactions is not unexpected. As pointed out in [18], these methods usually fail because a poor approximation of the monomer-monomer correlation function is used in the calculation of the potential energy. A gaussian correlation function will be maximum when two monomers are in contact, whereas the true correlation function vanishes in that case. For long range forces, most of the potential energy comes from configurations in which the monomers are far apart, so that the gaussian approximation becomes much better.

2.4 Screening of electrostatic interactions

When a finite concentration of salt is present in the solution - which is always the case in experiments, at least because of water dissociation-, the solution becomes a conducting, rather than dielectric, medium. The fundamental implication is that the Coulomb interaction between charged monomers is screened by the salt solution, i.e. the electrostatic potential created by a monomer, or a group of monomers, falls off exponentially rather than algebraically with distance. Thus distant parts of the chain do not interact, and the chain can be expected to behave, in the asymptotic limit \( N \to \infty \), as a random walk with short-ranged repulsive interactions.
It is a general result from the theory of charged solutions that charge fluctuations become uncorrelated (or, equivalently, that an external charge distribution is screened) over a typical distance $\kappa_s^{-1}$, where $\kappa_s$ is related to the thermodynamic properties of the solution [22]. The screened interaction between monomers, mediated by the salt solution, can formally be obtained by integrating out the degrees of freedom associated to the salt ions in the partition function as shown in Appendix A. The resulting interaction is in general a complex function of the monomer coordinates, involving many body interactions. In the case of dilute salt solutions and sufficiently weak perturbations, however, the linear response (or Debye-Hückel) theory can be used, and the salt can be treated as an ideal gas. The screening length $\kappa^{-1}$ is then given by

$$\kappa^2 = 4\pi \ell_B I, \quad (2.15)$$

where $I$ is the ionic strength of the solution defined as $I = \sum_{\text{ionic species}} Z_i^2 c_i$, $Z_i$ being the valence and $c_i$ the concentration of species $i$.

The effective interaction can in this limit be written as a sum of pairwise additive interactions between the monomers. The effective pair potential is given by the Debye-Hückel formula [23]

$$v_{D\!H}(r) = k_B T \frac{\ell_B}{r} \exp(-\kappa r). \quad (2.16)$$

This short range interaction potential is the starting point of many theoretical studies of polyelectrolyte solutions. The definition of an effective pair potential requires however two conditions. The first condition, that the ionic solution is dilute, is usually satisfied in polyelectrolyte solutions. The second condition of a weak external perturbation introduced by the polymer on the small ion solution must be considered more carefully, and is addressed in the next section.

Although the potential (2.16) is short-ranged, its range $\kappa^{-1}$ can be much larger than the monomer size, which is the typical interaction range in neutral polymers. Depending
on the ionic strength, $\kappa^{-1}$ can vary typically from less than 1 nm to more than 100 nm. At distances smaller than $\kappa^{-1}$, the screened potential (2.16) is close to the unscreened Coulomb potential discussed in section (2.1). The behaviour and properties of polyelectrolyte chains can therefore be markedly different from those of neutral chains over rather large length scales. In fact, section 4 will show that in some cases the effect of electrostatic interactions extends over length scales much larger than $\kappa^{-1}$.

Finally, it should be noted that the concept of effective interaction between monomers, obtained by integrating out the degrees of freedom of the small ions, is useful only for the calculation of static properties. Dynamical properties such as diffusion constants or viscosities do not have to be identical to those of an hypothetical polymer solution in which the monomer-monomer interaction would be given by (2.16). The ionic degrees of freedom can play a nontrivial role in the dynamics, as they do in suspensions of charged colloids [24].

2.5 Annealed and quenched polyelectrolytes

An important degree of freedom of polyelectrolyte chains is the distribution of the charges along the chemical sequence. This distribution can be either quenched or annealed [25]. When a weakly charged polyelectrolyte is obtained by copolymerisation of a neutral and of a charged monomer, the number of charges on each chain and the positions of the charges along the chain are fixed, the distribution is quenched. If the charges are sufficiently regularly distributed along the chain and do not have a tendency to form long blocks, the precise distribution of the charges does not seem to be a relevant variable for the chain statistics. At the level of scaling laws that we use, one can expect that only the numerical prefactors are different when polyelectrolytes with a random or a periodic distribution of charges are compared.

Polyacids or polybases are polymers where the monomers can dissociate depending on
the pH of the solution and acquire a charge. The dissociation of an $H^+$ ion from a polyacid gives rise to the apparition of a COO$^-$ group and thus of a negative charge. This is an annealed process, the total number of charges on a given chain is not fixed but the chemical potential of the $H^+$ ions and thus the chemical potential of the charges is imposed (by the pH of the solution). The positions of the charges along the chain are also not fixed; the charges can move by recombination and redissociation of an $H^+$. The chemical potential of the charges $\mu$ depends on the fraction $f$ of dissociated acid groups and is related to the pH of the solution by [2]

$$\text{pH} = pK_0 + \mu(f).$$  \hspace{1cm} (2.17)

The charge chemical potential has two contributions, an entropic contribution related to the mixing of charged and non charged groups along the chains $k_B T \ln[f/(1-f)]$ and an electrostatic contribution $\mu_{el}(f) = N^{-1} \partial F_{el}/\partial f$ which is the derivative of the electrostatic free energy of the chain. In a good or $\theta$ solvent, the electrostatic contribution $\mu_{el}$ is an increasing monotonic function of $f$ and for a given pH the fraction of charges $f$ is well defined, the properties of the chains are very similar to those of a quenched chain with a charge fraction $f$. In a poor solvent, the blob model introduced by Khokhlov and discussed above leads to a non monotonic variation of $\mu_{el}$ and thus of $\mu$ with $f$. This non monotonic variation indicates a conformational transition of the chain between a collapsed weakly charged conformation and a stretched strongly charged conformation. The collapse transition of a polyelectrolyte with varying $f$ is thus predicted to be a first order transition [25]. The discontinuous collapse of the chains could explain titration curves of polyacids or polybases in a poor solvent (polymethacrylicacid for example) which show a plateau in the $pH - f$ curve [26].

3. Local aspects of screening

The Flory-like model presented in the previous section considers only the interactions...
between charged monomers along the polyelectrolyte chain and ignores the role of the small counterions that neutralize the polyelectrolyte charge. When the polyelectrolyte is strongly charged, the electrostatic potential on the chain is large and some of the counterions remain bound to the chain. This phenomenon is known as counterion condensation, or Manning condensation [7]. For many purposes one must then consider that the chain has an effective charge due to the charged monomers and to the sheath of bound, or condensed, counterions. The effective charge is lower than the nominal charge of the monomers. Counterion condensation can be effective even at infinite dilution and reduces the electrostatic interactions between monomers. We first give here the more qualitative description of the condensation due to Manning [7] and then present an earlier discussion based on the Poisson-Boltzmann equation due to Fuoss et al. [27]. The condensed counterion sheath around a polyelectrolyte chain is electrically polarizable; this can induce attractive interactions between polyelectrolyte chains. We discuss in section 3.2. possible mechanisms for attractive electrostatic interactions in polyelectrolyte solutions.

3.1 Counterion condensation

For simplicity, we consider a negatively charged polyelectrolyte chain, in a salt-free solution, which has locally a rodlike conformation and can thus be considered as a rod over a distance $L$ much larger than the monomer size $b$. The distance between charges along the chain is $A$ and the fraction of charged monomers is $f = b/A$. If we ignore the contribution of the counterions, the electrostatic potential at a distance $r << L$ from the chain is obtained from Gauss theorem as $\psi(r) = 2\ell_B/A \ln(r)$ (we use here as unit of the electrostatic potential $k_B T/e$ where $e$ is the elementary charge). The distribution of the counterions around the chain is given by Boltzmann statistics, for monovalent counterions, $n(r) = n_0 \exp -\psi(r) \simeq r^{-(2\ell_B/A)}$ where $n_0$ is a constant. The total number of counterions
per unit length within a distance $r$ from the chain is then

$$p(r) = \int_0^r 2\pi r' dr' n(r') = \int_0^r 2\pi n_0 r'(1-2\ell_B/A) dr'$$

When the charge parameter $u = \ell_B/A$ is smaller than one, the integral giving $p(r)$ is dominated by its upper bound and $p(r)$ decreases to zero as the distance $r$ gets small. In this case where the charge fraction is small $f < b/\ell_B$ there is no counterion condensation on the polyelectrolyte chain. In the opposite limite where the charge is large $u = \ell_B/A > 1$, the integral giving $p(r)$ diverges at its lower bound indicating a strong condensation of the counterions on the polyelectrolyte chains. As the condensation proceeds, the effective value of the charge parameter decreases. The counterion condensation stops when the effective charge parameter is equal to one. The polyelectrolyte chain and the condensed counterion sheath are then equivalent to a polyelectrolyte with a distance between charges $A = \ell_B$ or to a fraction of charged monomers $f = b/\ell_B$. The remaining monomeric charges are neutralized by the condensed counterions.

One of the directly measurable quantities that strongly depends on the condensation of the counterions is the osmotic pressure of the polyelectrolyte solution. As shown below, in many cases the osmotic pressure of a polyelectrolyte solution is dominated by the counterions, the contribution of the polyelectrolyte chains being only a very small correction. Below the Manning condensation threshold, the counterions are not condensed and are essentially free. At leading order, the solution can be considered as an ideal gas of counterions of concentration $fc$ where $c$ is the total monomer concentration and the osmotic pressure is [28]

$$\pi = k_B T f c$$

The first correction to the ideal gas behavior is due to the polarisation of the counterion gas by the polyelectrolyte chains. The polarisation energy is estimated using the Debye-Hückel approximation for the gas of counterions [29]. The screening is due to the counterions and
\[ \kappa^2 = 4\pi\ell_B f_c. \] The polarisation free energy per unit volume reads

\[ F_{pol} = -k_BT fc u \ln(\kappa) = -\frac{k_BT}{2} c\left(\frac{b\ell_B}{A^2}\right) \ln(4\pi\ell_B cb/A) \] (3.3)

The osmotic pressure of the solution is directly calculated from this relation

\[ \pi = k_BT fc (1 - u/2) \] (3.4)

In many cases, for weakly charged polyelectrolytes, \( \ell_B \approx b \), so that \( u \approx f \), and the polarisation correction is small. In most of the following, we use the ideal gas expression for the osmotic pressure of the counterions in a weakly charged polyelectrolyte solution.

Above Manning condensation threshold \( u > 1 \), the bound counterions do not contribute to the osmotic pressure. The remaining counterions, at a concentration \( cb/\ell_B = fc/u \), behave as a Debye-Hückel gas, polarized by a chain which has an effective charge parameter equal to unity. The osmotic pressure is given by equation (3.4), where \( fc \) is replaced by \( cb/\ell_B \) and \( u \) by 1,

\[ \pi = k_BT cb/(2\ell_B) = k_BT fc/(2u) . \] (3.5)

Several other physical quantities such as the electrical conductivity of the solution or the electrophoretic mobility of the chains [30] strongly depend on the condensation of the counterions and are dominated by the free counterions. Their determination is, in general, in good agreement with Manning condensation theory.

### 3.2 Poisson-Boltzmann approach

Fuoss, Katchalsky, and Lifson [27] have studied the interaction between the polyelectrolyte chains and their counterion clouds using the so-called Poisson-Boltzmann equation. They consider a solution of infinite rodlike molecules, which are all parallel. The number of molecules per unit area is \( \Gamma \). Around each of these molecules, there exists an equipotential surface where the electric field vanishes. On average, this surface can be approximated by a
cylinder parallel to the polyelectrolyte chains with a radius \( R \) defined such that \( \Gamma \pi R^2 = 1 \). The average density of counterions in the cylinder is \( c_i = f_c = 1/(\pi R^2 A) \) where \( A \) is the distance between charges along the chain. From an electrostatic point of view, each chain with its counterions in the cylinder of radius \( R \) is independent of all the other chains. The electrostatic problem that must be solved is therefore that of a single infinite chain with its counterions embedded in a cylinder of radius \( R \) with the boundary condition that the electric field vanishes on the surface of the cylinder.

The electrostatic potential in this cell satisfies the Poisson equation \( \Delta \psi = -4\pi \ell_B c_i(r) \) where \( c_i(r) \) is the local counterion concentration at a distance \( r \) from the chain. The local counterion concentration is obtained from Boltzmann statistics \( c_i(r) = c_i \exp (-\psi(r)) \). This leads to the Poisson Boltzmann equation

\[
\Delta \psi(r) = -\kappa^2 \exp (-\psi(r)) \tag{3.6}
\]

The Debye screening length is defined here as \( \kappa^2 = 4\pi \ell_B c_i \); it is such that \( \kappa^2 R^2 = 4u \) where \( u \) is the charge parameter defined above. The Poisson Boltzmann equation has been solved exactly in this geometry in reference [27]. The expression of the potential critically depends on the value of the charge parameter. Below the Manning condensation threshold where \( u < 1 \) the electrostatic potential is given by

\[
\psi = \ln \left[ \frac{\kappa^2 r^2}{2\beta^2} \sinh^2 (-\arctanh \beta + \beta \ln(r/R)) \right] \tag{3.7}
\]

where \( \beta \) is an integration constant related to \( u \) by \( u = (1 - \beta^2)(1 - \beta / \tan(\beta \ln(b/R)))^{-1} \).

Above the Manning condensation threshold the electrostatic potential reads

\[
\psi = \ln \left[ \frac{\kappa^2 r^2}{2\beta^2} \sin^2 (-\arctan \beta + \beta \ln(r/R)) \right] \tag{3.8}
\]

and \( \beta \) is given by \( u = (1 - \beta^2)(1 - \beta / \tan(\beta \ln(b/R)))^{-1} \). The distribution of counterions around each polyion can then be determined using Boltzmann’s statistics.
At each point of the solution, the pressure has two contributions, an ideal gas contribution and an electrostatic contribution proportional to the square of the local electric field. At the edge of the cell \((r = R)\), the electric field vanishes and there is only an ideal gas contribution. The pressure being uniform throughout the solution can be calculated at this point \(\pi = k_B T c_i(r = R) = k_B T c_i \exp - (\psi(r = R))\). Both above the Manning condensation threshold (3.4) and below the threshold (3.5) the calculated pressure is in agreement with that calculated from Manning theory.

Manning theory describes the condensation of the counterions as a transition between two states, a bound state and a free state. In the Poisson Boltzmann approach, the distribution of the counterions is continuous and there is no bound state. However, close to the polyelectrolyte chain, the interaction energy between one counterion and the polyelectrolyte chain becomes much larger than \(k_B T\) (in the region where \(\psi >> 1\)). One could then divide space into two regions, a region close to the chain where the interaction energy is larger than \(k_B T\) (with a size of the order of a few times the monomer size \(b\)) and where the counterions can be considered as bound and a region further away from the chain where the interaction between a counterion and the chain is smaller than \(k_B T\) and where the counterions can be considered as unbound.

### 3.3 Attractive electrostatic interactions

The counterions condensed on a polyelectrolyte chain move essentially freely along the chain; they more or less form a one dimensional gas of average density \(g/b\) where \(g = f - b/\ell_B\) is the fraction of condensed counterions. The charge density along the chain is therefore not a frozen variable and shows thermal fluctuations due to the mobility of the counterions. When two chains are sufficiently close, the charge density fluctuations on the two chains are coupled by the electrostatic interactions; this leads to attractions between the polymers which are very similar in nature to the Van der Waals interactions between polarizable molecules. A fluctuation induced attraction can be expected for all
polyelectrolytes where the charges are mobile along the chain. This is for example the case above Manning condensation threshold but also for annealed polyelectrolytes, which are polyacids or polybases, where the charge can be monitored by tuning the pH of the solution [25?]. The ionised groups are not fixed on these chains, only the chemical potential of the charges is imposed and the charge density also has thermal fluctuations.

We first calculate the attractive interaction for two parallel rodlike molecules of length $L$ at a distance $x$ in a solution where the salt concentration is $n$, following the ideas introduced by Oosawa [31]. When a charge fluctuation $\delta c_1(z)$ occurs along the first chain it polarizes the second chain where a charge fluctuation of opposite sign $\delta c_2(z)$ appears. The attraction between the two chains is due to the Coulomb interaction between these charge fluctuations. Within a linear response approximation, the free energy of the charge fluctuations can be written in Fourier space as

$$H = \frac{k_B T}{2} \sum q \sum_{i,j} S_{ij}^{-1} \delta c_i(q) \delta c_j(-q)$$  \hspace{1cm} (3.9)

$\delta c_i(q)$ is the Fourier transform at a wave vector $q$ of the charge fluctuation $\delta c_i(z)$ ($i = 1, 2$). The charge structure factor on one of the chains is $S_{11}(q) = g/b$ and corresponds to a one-dimensional ideal gas of charges. The crossed structure factor is due to the electrostatic interactions between the two chains obtained by summing the Debye-Hückel interactions

$$S_{12}^{-1}(q) = \frac{4\pi \ell_B}{4\pi^2} \frac{e^{iqx \cos \theta}}{k^2 + q^2 + \kappa^2} = 2\ell_B K_0[x(q^2 + \kappa^2)^{1/2}]$$  \hspace{1cm} (3.10)

where $K_0[x]$ is a modified Bessel function of the second kind [32]. The fluctuation contribution to the interaction free energy between the two rods is obtained by summing the partition function $\exp -H/k_BT$ over all fluctuations. We obtain

$$F_{att}(x) = L \frac{k_B T}{2} \int \frac{dq}{2\pi} \ln \left( 1 - \frac{g^2 \ell_B^2}{b^2} K_0[x(q^2 + \kappa^2)^{1/2}] \right)$$  \hspace{1cm} (3.11)

This expression can be simplified by assuming that the fraction $g$ of recondensed counterions is smaller than one and by looking for the asymptotic limits where the distance $x$...
between the rods is smaller or larger than the screening length $\kappa^{-1}$. For short distances between the rods, the interaction energy is

$$F_{\text{att}}(x) = -\alpha k_B T \frac{g^2 \ell_B^2}{b^2} \frac{L}{x^3}$$

where $\alpha$ is a numerical constant. For large distances, the attractive interaction decays as

$$F_{\text{att}}(x) = -\beta k_B T \frac{g^2 \ell_B^2}{b^2} \frac{L}{x^{3/2} \kappa^{1/2}} \exp(-2\kappa x)$$

$\beta$ being another numerical constant. As expected the interaction is attractive. It is proportional to the square of the Bjerrum length indicating that this is a second order electrostatic effect: the fluctuation on the first rod creates an electric field that polarises the second rod; the charge fluctuation on the second rod then creates an electric field which interacts with the charge fluctuation of the first rod. For parallel rods, the interaction is also proportional to the length of the rod, each segment interacts mainly with the segment of the other rod which is directly facing it. For the same reason, the attractive interaction is screened over a length $\kappa^{-1}/2$, i.e. over half the screening length of the repulsive coulombic interaction.

When the two rods make an angle $\theta$ ($0 < \theta < \pi/2$), the attractive electrostatic interaction cannot be calculated from the fluctuation free energy (3.10). Instead, we directly discuss it in terms of the polarisability of the two polyelectrolytes. If a charge fluctuation $\delta c_1(q)$ is created on the first rod, it creates an electrostatic potential on the second rod $\delta\psi(q') = K(q, q')\delta c_1(q)$ where the kernel is defined as $K(q, q') = \frac{2\pi\ell_B}{\sin\theta} \exp(-px) p$ with a wavevector $p$ related to $q$ and $q'$ by $p^2 = \kappa^2 + q^2 + q'^2 - \frac{2qq'\cos\theta}{\sin^2\theta}$. The response function of the one dimensional gas of recondensed counterions on the second rod is $\frac{q}{\theta}$ and the induced charge fluctuation on the second rod is $\delta c_2(q') = -\frac{q}{\theta} K(q, q')\delta c_1(q)$. This charge fluctuation creates a potential on the first rod $\delta\psi'(q) = K(q, q')\delta c_2(q')$. The attractive interaction

---

2 This is equivalent to performing a perturbation expansion to second order in the crossed term that appears in equation (3.10).
energy between the two rods forming an angle $\theta$ at a distance $x$ is then estimated as

$$F_{\text{att}}(x) = -k_B T \frac{g}{b} \int \frac{dq dq'}{4\pi^2} K^2(q, q') <\delta c_1^2(q)>$$

(3.14)

The average value of the charge fluctuation is given by the ideal gas statistics $<\delta c_1^2(q)> = g/b$. This leads to an attractive interaction between non parallel rods

$$F_{\text{att}}(x) = -k_B T \frac{g^2 \ell_\theta^2}{b^2 \sin \theta} (\pi - \theta) \text{Ei}(2\kappa x)$$

(3.15)

where $\text{Ei}(u)$ is the exponential integral function [32]. As for parallel rods, the attractive interaction is a second order electrostatic effect, it is proportional to $\ell_\theta^2$ and it decays at large distances as $\exp -2\kappa x$. When the angle between the two rods is not very small, the attractive force is independent of the length of the rods. In this geometry only the chain segments in the vicinity of the crossing point interact. If the distance between the rods is smaller than the screening length, the crossover to the parallel rod behavior occurs when the angle $\theta$ is smaller than $x/L$. At short distances $x < \kappa^{-1}$, $\text{Ei}(u) = \ln u$ and the attractive interaction energy varies logarithmically. As the attraction is independent of the chain length, the attractive interaction between two polymers which are rodlike over a distance larger than the screening length is also given by equation (3.14).

The fluctuation attractive interaction must be compared to the repulsive coulombic interaction between the chains. For two rods at a distance $x$ that make a finite angle, the repulsive Coulomb interaction is of order $F_{\text{el}} \simeq k_B T 2\pi \ell_B f^2/(\kappa b^2) \exp -\kappa x$ where $f$ is the effective fraction of charged monomers (equal to $b/\ell_B$ above the condensation threshold). At large distances, as already mentionned, the screening of the attractive interaction is stronger and the repulsive interaction is dominant. At small distances the attractive interaction is dominant. The distance at which the attractive force is larger than the repulsive force is of order $x \simeq \ell_B (g/f)^2$. In general this corresponds to very short distances of the order of the Bjerrum length. The attractive fluctuation interaction is thus expected to be important only in strong coupling situations where the Bjerrum length
is large (for example in the presence of multivalent ions) or if some external constraint imposes very small distances between chains.

The attractive interaction can also be considered within the framework of the Poisson-Boltzmann approach. The Poisson-Boltzmann equation is derived from a mean field theory that considers only the average concentration profile of the counterions around each polyelectrolyte chain. A more refined theory should take into account the thermal fluctuations around this concentration profile. Such a theory has been built to study the interactions between charged colloidal particles and also leads to attractive interactions [33,34]. Qualitatively, the conclusions are the same as the one presented here, the attractive interactions are dominant at short distances and becomes relevant only in the limit of strong electrostatic coupling.

Experimentally, the addition of multivalent ions to polyelectrolyte solutions often provokes a precipitation. This can be explained by attractive electrostatic interactions [35] or by complexation of the polymer by the multivalent ions [36].

The interaction between charge fluctuations is not the only mechanism that leads to attractive interactions between polyelectrolyte chains. Recently, Ray and Manning [37] have presented a model for attractive interactions based on the overlap between the condensed counterions sheaths around the two interacting polymers. In the simple version of Manning condensation theory presented here, the polyelectrolyte chains are infinitely thin lines and the pointlike counterions condense directly on the line. A more refined version allows for a finite condensation volume that can be determined by minimization of the free energy of the condensed counterions. When two parallel rods come close to one another, the condensation volume around each rod expands in the space between the two rods and the two condensation volumes overlap. This leads to the formation of a polyelectrolyte dimer with a single condensation sheath. The expansion of the condensation volume leads to an increase in translational entropy of the counterions and thus to an
attractive interaction. The model shares thus some analogy with the capillary condensation between thin films wetting parallel cylinders [38]. An attractive interaction is predicted at intermediate distances much larger than the polyelectrolyte diameter but much smaller than the electrostatic screening length. This interaction has been calculated only for parallel polyelectrolyte rods, it has not been calculated for rods intersecting at a finite angle.

4. Electrostatic rigidity

In this section, we assume that the interaction between charged monomers can be described by the Debye-Hückel potential, (2.16). Within this approximation, we discuss the structure of the polymer chain at length scales intermediate between the short length scales discussed in section 3. and the chain size. It has already been mentioned in section 2.4 that at very large scales, a charged chain has the same structure as a neutral polymer chain in a good solvent, since the potential (2.16) is short ranged. The radius increases with molecular weight as $R \simeq N^{3/5}$ (in the Flory approximation). At short scales ($L < \kappa^{-1}$), on the other hand, screening is inoperant, so that the chain is expected to take the rodlike structure described in section 1. The simplest assumption concerning the chain structure at intermediate length scales, which was made in all early work in the field [39], is that the crossover from rodlike to Flory-like behaviour takes place above a length scale $\kappa^{-1}$, equal to the range of the interactions. This simple assumption was challenged by the works of Odijk [8,10] and Skolnick and Fixman [9], who showed how the Debye-Hückel interaction can induce a rodlike conformation at length scales much larger than the interaction range. Their theory, and its limitations, are presented here.

4.1 The Odijk-Skolnick-Fixman theory

In their calculations, Odijk-Skolnick and Fixman (OSF) consider a semi-flexible chain with total contour length $L$ characterized by its ”bare” persistence length $\ell_0$, and that
carries charges separated by a distance $A$ along its contour. The interaction between the charged monomers is given by (2.16), and only electrostatic interactions are taken into account (the polymer backbone is in a theta solvent). For strongly charged chains with $A < \ell_B$ Manning condensation can in a first approximation be accounted for by replacing $A$ with $\ell_B$. In the limit $\ell_0 << A$ of a weakly charged chain, this model is equivalent to the gaussian chain model discussed in section (2.1), with $N = L/A$, $b^2 = A\ell_0$ and $f = 1$. We consider here the general case, where $\ell_0/A$ is not small [40].

The total energy of the chain is the sum of the intrinsic curvature energy and of the (screened) electrostatic energy. If the polymer is described as a planar curve of curvilinear length $L$, a chain configuration is specified by the function $\theta(s)$ defined for $-L/2 < s < L/2$ by $\cos(\theta(s)) = t(s) \cdot t(0)$ where $t(s)$ is the unit vector tangent to the chain at the point of curvilinear abscissa $s$. Assuming that $\theta(s)$ remains small, the electrostatic potential between two charges located at $s_1$ and $s_2$ on the chain may be expanded around the value obtained for a rodlike configuration, $v_{DH}(|s_2 - s_1|)$. The following expression is then obtained for the total energy $H[\theta]$ of a given configuration $\{\theta(s)\}$:

$$H[\theta] = H_0 + \frac{1}{2}k_BT \int_{-L/2}^{L/2} ds \int_{-L/2}^{L/2} ds' \frac{d\theta(s)}{ds} \left[ \ell_0 \delta(s - s') + K(s, s') \right] \frac{d\theta(s')}{ds}.$$  \hspace{1cm} (4.1)

Here $H_0$ is the electrostatic energy of a rod, the term proportional to $\ell_0$ is the "bare" curvature energy of a noninteracting semiflexible chain, and the contribution of the electrostatic interactions is described by the kernel $K(s, s')$ which reads (for $s > s'$):

$$K(s, s') = \frac{1}{A^2} \int_{-L/2}^{s'} ds_1 \int_{s}^{L/2} ds_2 \frac{dv_{DH}(s_2 - s_1)}{ds} \frac{v_{DH}(s_2 - s_1)(s_2 - s)(s' - s_1)}{(s_2 - s_1)}.$$  \hspace{1cm} (4.2)

with $v_{DH}'(s) = \frac{dv_{DH}}{ds}$. The only assumption made in obtaining this result is that, within the range $\kappa^{-1}$ of the interaction potential, the chain remains in an almost rodlike configuration, i.e. $|s_2 - s_1| - |R(s_1) - R| << |s_2 - s_1|$ for $|s_2 - s_1| < \kappa^{-1}$. For long chains, the integration in (4.2) can be extended to infinity, and $K(s, s')$ becomes a function of $s - s'$,

$$K(s) = \frac{1}{6A^2} \int_0^\infty dx \frac{x^3}{x + s} v_{DH}'(x + s).$$  \hspace{1cm} (4.3)
The statistical properties of the chain are obtained by integrating the Boltzmann factor \( \exp(-H[\theta]/k_BT) \) over all possible configurations, i.e. over all functions \( \theta(s) \). The integration can be carried out analytically, since the energy is a quadratic function of \( \theta \). The calculation is simplified by introducing the Fourier transform of the kernel (4.3),

\[
\tilde{K}(q) = \int_0^\infty ds \exp(iqs)K(s) = \ell_{OSF} \frac{2\kappa^2}{q^2} \left( \frac{\kappa^2 + q^2}{q^2} \ln \left( \frac{\kappa^2 + q^2}{\kappa^2} \right) - 1 \right),
\]

(4.4)

where

\[
\ell_{OSF} = \ell_B/(4A^2\kappa^2)
\]

(4.5)

has the dimension of a length, and is known as the Odijk-Skolnick-Fixman length. The local flexibility of the chain can be characterized by the mean squared angle \( <\theta(s)^2> \) between the chain direction at the origin and after a contour length \( s \). For a neutral semiflexible chain, \( <\theta(s)^2> = s/\ell_0 \) varies linearly with \( s \). The chain configuration can be described as resulting from an ”angular diffusion” process, with a diffusion constant \( \ell_0^{-1} \).

For the charged chain, with the approximate energy (4.1), one gets

\[
<\theta(s)^2> = 4\pi \int_0^\infty dq \frac{\sin^2(qs/2)}{q^2} \frac{1}{\ell_0 + \tilde{K}(q)},
\]

(4.6)

This expression simplifies in the limits of small \( s \) and large \( s \). For large \( s \),

\[
<\theta(s)^2> = \frac{s}{\ell_0 + \ell_{OSF}}
\]

(4.7)

which expresses the fact that at large scales, the chain conformation can be described by an effective persistence length \( \ell_0 + \ell_{OSF} \), which is the sum of a ”bare” and of an electrostatic contribution. This is the well known result first obtained in references [8] and [9]. It indicates that the influence of the screened electrostatic interactions can extend much beyond their range \( \kappa^{-1} \), since \( \ell_{OSF} \) is, for weakly screened solutions, much larger than \( \kappa^{-1} \). The persistence length also decreases with the salt concentration as \( \ell_{OSF} \simeq n^{-1} \) whereas the Debye screening length has a slower decay \( \kappa^{-1} \simeq n^{-1/2} \).
For small values of $s$, (4.6) reduces to

$$<\theta(s)^2> = \frac{s}{\ell_0},$$  

(4.8)

The chain statistics at short scales are not modified by electrostatic interactions. The crossover between the "intrinsic" regime described by (4.8) and the "electrostatic" regime described by (4.7) takes place when the electrostatic interactions become strong enough to perturb the statistics of the neutral flexible chain. The crossover length $s_c$ can be obtained qualitatively from the following argument\(^3\). If a small chain section, of length $s < \kappa^{-1}$, is bent to form an angle $\theta$, the cost in "bare" curvature energy is $k_B T \ell_0 \theta^2 / s$, while the cost in electrostatic energy is $k_B T \ell_B (s/A)^2 (\theta^2 / s)$. The two energies are comparable for $s \approx s_c$, which gives $s_c \approx A (\ell_0 / \ell_B)^{1/2}$.

A more detailed treatment of the crossover regime is possible by ignoring logarithmic factors and replacing the exact Kernel (4.4) by the approximate expression, $\tilde{K}(q) = \ell_{OSF} \kappa^2 / (\kappa^2 + 2 q^2)$. The integral (4.6) can then be computed analytically, and yields,

$$<\theta(s)^2> = \frac{s}{\ell_{OSF} + \ell_0} + \frac{\ell_{OSF}}{\kappa \ell_0^{1/2} (\ell_0 + \ell_{OSF})^{3/2}} (1 - \exp(-\frac{s}{s_c}))$$  

(4.9)

with $s_c = \kappa^{-1} (\ell_{OSF} + \ell_0)^{-1/2} \ell_0^{1/2}$. This formula crosses over from the "intrinsic" regime towards the electrostatic regime for $s \sim s_c$. In the weak screening limit, $\ell_0 \ll \ell_{OSF}$ and the simple result $s_c \sim A (\ell_0 / \ell_B)^{1/2}$ is recovered.

The picture that emerges from this calculation is that the chain flexibility depends on the length scale. At short scales, $s < s_c$, the chain structure is determined by its bare rigidity $\ell_0$, while the electrostatic rigidity (4.5) dominates at large scales. Large scale properties, such as the giration radius or the structure factor at small wavevector, can be determined by applying the standard formula for semi-flexible chains of persistence length $\ell_{OSF}$. Excluded volume effects between Kuhn segments of length $2 \ell_{OSF}$ are accounted
for by assigning a diameter $\kappa^{-1}$ to each segment. The excluded volume between Kuhn segments is $\ell_{OSF}^2 \kappa^{-1}$ [10].

The only approximation required to obtain the Odijk-Skolnick-Fixman length is the expansion that yields equation (4.1). The calculation is therefore consistent if the angle $<\theta(\kappa^{-1})^2>$ is small compared to unity. It is easily checked that for $s \sim \kappa^{-1}$, the second term dominates in the r.h.s. of (4.9). The requirement $<\theta(\kappa^{-1})^2> << 1$ is then equivalent to $s \ell_{OSF}/(\ell_0(\ell_0 + \ell_{OSF})) \simeq s_c/\ell_0 << 1$. i.e. the angular deflection of the chain must be small when the crossover region is reached. In other words, the angular fluctuations that take place before the electrostatic interactions can come into play and rigidify the chain should not be too strong. If these fluctuations are too large, i.e. if the chain is too flexible, the perturbation expansion that underlies the OSF calculation breaks down. The criterion for the validity of the calculation can be simply written, in the limit of weak screening, as $\ell_0 > A^2/\ell_B$. This implies that the OSF calculation should be directly applicable to stiff chains such as DNA ($\ell_0 \sim 50\text{nm}$), but has to be reconsidered for flexible chains such as polystyrene sulfonate ($\ell_0 \sim 1\text{nm}$). Indeed, numerical simulations clearly confirm the behaviour described by equations (4.4) and (4.6) for values of $s_c/\ell_0$ smaller than 0.2 [40]. Deviations from this behaviour appear for larger values of $s_c/\ell_0$.

Before closing this section, it is worth mentioning that the electrostatic rigidity of a charged chain was computed numerically by Le Bret and Fiman [41,42] using the Poisson-Boltzmann equation, rather than the Debye-Hückel approximation. At high ionic strength, the results deviate significantly from the OSF prediction, and the electrostatic rigidity tends to behave as $\kappa^{-1}$ rather than $\kappa^{-2}$.

4.2 Alternative calculations for flexible chains

The calculation presented in the previous section shows that the Odijk-Skolnick-Fixman theory in its original form is not applicable to flexible or weakly charged chains as such. A generalization of this theory was nevertheless used by Khokhlov and Katchaturian [43].
These authors propose that the expression (4.5) can be used for flexible chains, with the only modification that the distance between charges $A$ had to be replaced by $\xi_e/(fg)$ (see equation (2.7). The bare persistence length $\ell_0$ is also replaced by the blob size $\xi_e$ (A recent calculation of Li and Witten, including the thermal fluctuations of the chain gives a more quantitative basis to this approach [44]). As a result, the total persistence length of the chain reads

$$\ell_{KK} = \xi_e + \frac{1}{4\kappa^2 \xi_e}. \quad (4.10)$$

The arguments of section (4.3) show, however, that the extension of the OSF formula is rather speculative, since the condition that was derived for the validity of the OSF theory is not met for a chain characterized by the parameters $\ell_0 = \xi_e$ and $A = \xi_e/fg$. When the persistence length is dominated by the electrostatic interactions, the radius of the chain is given by the Flory statistics

$$R_{KK} = N^{3/5} \xi_e^{-4/5} \kappa^{-3/5} b^{6/5}. \quad (4.11)$$

This generalisation of the Odijk theory is consistent if the Debye screening length is larger than the electrostatic blob size $\xi_e$. At higher ionic strength, in the weak coupling limit there is no electrostatic rigidity and the polyelectrolyte chain behaves as a flexible chain with short range interactions given by the Debye-Hückel formula. Its radius is given by equation (4.12) below.

A number of approximate theories, based on different variational ansatz, have been proposed to describe the structure of flexible chains [45,40,46,47]. These calculations differ at the technical level. The basic idea is to describe a flexible charged chain (with screened interactions) by some model of noninteracting semiflexible chain, and to variationally optimize the persistence length of the noninteracting system. All these variational calculations produce for flexible chains a persistence length that scales as $\kappa^{-1}$, i.e. the ”naive” result of Katchalsky and Pfeuty. An exemple of such a variational calculation can be given for
the particularly simple case of a freely jointed charged chain, with $\ell_0 = A$. The variational ansatz used to represent the system is that of a noninteracting chain in which the angle between neighboring segments is bounded by a maximum value $\theta_{\text{max}}$, so that the persistence length is $\ell_p = 2A/\theta_{\text{max}}^2$. The variational entropy per segment is then $-\ln(\theta_{\text{max}})$.

The variational energy can be expressed as a function of the structure factor of a chain with a persistence length $\ell_p$, $S_{ni}(q)$ as $\int d^3 q S_{ni}(q)v_{DH}(q)$. Using the expression of the structure factor obtained by desCloizeaux [48], the energy is the sum of the electrostatic energy of a rod and of a correction due to the bending that can be approximated by $k_BT(\ell_B/A)(1/\kappa\ell_p)$. Minimizing the sum of these two terms with respect to $\theta_{\text{max}}$, one finds $\ell_p \sim \kappa^{-1}$. This approach can be straightforwardly generalized to the case where each rod in the freely jointed chain represents an electrostatic blob [40], in which case it applies to the charged gaussian chain considered in section 2. The variational model is then that of a of a ”semiflexible chain of electrostatic blobs”, analogous to the ”chain under tension” model (section 2), except for the fact that the direction of the tension is now fluctuating, and becomes uncorrelated over a persistence length $\kappa^{-1}$. In that case, it must be realized that the ”persistence length” $\kappa^{-1}$ is defined in reference to the distance in space, rather than the contour length along the chain. The radius of the chain scales in this case as

$$R_P = N^{3/5}\xi^{-3/5}\kappa^{-2/5}b^{6/5}.$$  \hfill (4.12)

Variational calculations have the obvious drawback that the result crucially depends on the variational ansatz. An ansatz too far from the actual structure can yield incorrect results. Also, their range of validity is difficult to assess. The variational calculation for gaussian chains briefly described above is consistent only as long as the ”electrostatic blob” concept can be used. This gives an upper limit for the charge density of the chain for which its description by a ”semiflexible chain of electrostatic blobs” is possible, $A^{-1} < (\ell_0\ell_B)^{-1/2}$ (this corresponds to $g > 1$ in 2.7). This upper limit corresponds to the lower charge
density for which the OSF calculation is expected to be consistent. The coincidence, however, might be only fortunate. A complete calculation that would crossover from the \( \kappa^{-2} \) behaviour of the electrostatic stiffness which is well understood for rigid chains, to the \( \kappa^{-1} \) behaviour that is suspected for flexible chains on the basis of variational calculations, is still missing.

4.3 The case of poor solvents

The above discussion focuses on the case where the neutral chain backbone is in a good or theta solvent. A rather different result is obtained for the case of a flexible, weakly charged chain in a poor solvent. This case was considered in the absence of screening in section (2.1), where the chain was described as a linear string of "poor solvent blobs", each of size \( \xi = b(f^2 \ell_b/b)^{-1/3} \) and containing \( \tau f(f^2 \ell_b/b)^{-1} \) charged monomers (cf. equation (2.10)). Following the procedure of [43], one can attempt to apply the OSF theory to the chain of blobs. The theory is valid if the linear charge density along the chain of blobs, \( fg/\xi \), is larger than the critical value \( (\xi \ell_B)^{-1/2} \). This condition can be rewritten as \( \tau > (f^2 \ell_B/b)^{1/3} \). For weakly charged chains \( (f \ll 1) \), it is thus satisfied even for moderately poor solvents. The electrostatic persistence length that results from applying the OSF theory is

\[
\ell_p = \xi e + \frac{f^2 g^2 \ell_B}{\kappa^2 \xi^2} = \xi e + \left( \frac{\tau^2}{b \kappa^2} \right) \left( \frac{f^2 \ell_B}{b} \right)^{-1/3} \quad (4.13)
\]

The surprising implication of this result is that the persistence length, (and therefore the radius of gyration of the chain), increases as the solvent quality decreases. This increase is the consequence of an increase in the linear charge density, which is itself induced by the collapse of the monomers into dense blobs. This effect, however, exists only as long as the charge density exceeds the value \( \ell_B^{-1} \) at which Manning condensation takes place. This gives an upper limit for \( \tau \), \( \tau < f(f^2 \ell_B/b)^{-1/3} \). The conclusion is that an increase in the persistence length as \( \tau \) increases should occur in the temperature range...
\( f^{1/3}(b/\ell_B)^{1/3} > \tau > f^{2/3}(\ell_B/b)^{2/3}. \)

5. Charged Gels and Brushes

Many properties of polyelectrolyte solutions are dominated not by the chain conformation, but by the counterions. We discuss below two examples of this situation, the polyelectrolyte gel and the polyelectrolyte brush. In both problems, the polyelectrolyte chains occupy a small region of space (close to the grafting surface for the brush), surrounded by pure solvent. The small ions in the solution are free to diffuse in and out the polyelectrolyte region, and the external solvent region acts as a reservoir that imposes the small ion chemical potential. A Donnan equilibrium \([49,50]\) is reached, that relates the concentrations of the small ions inside the polyelectrolyte region to their imposed concentration in the reservoir. If the monomer concentration in the polyelectrolyte region is \(c\), the charge density due to the polymer is \(fc\). The reservoir contains salt at a density \(n\), and the Debye-Hückel screening length \(\kappa^{-1}\) is given by \(\kappa^2 = 8\pi n\ell_B\). For simplicity we assume in the following that the counterion of the polymer is identical to the positive ion of the salt, we call \(n_+\) and \(n_-\) the concentration of positive and negative ions respectively in the polyelectrolyte region.

The polyelectrolyte charge creates an electrostatic potential difference between the polyelectrolyte region and the reservoir \(U\). The chemical potentials of the small ions in the polyelectrolyte region are \(\mu_+ = k_B T \ln n_+ + U\) and \(\mu_- = k_B T \ln n_- - U\). At equilibrium these chemical potentials are equal to the salt chemical potential in the reservoir \(\mu = k_B T \ln n\). This leads to a chemical equilibrium law for the small ions

\[
n_+ n_- = n^2 \tag{5.1}\]

A second relation between the concentrations \(n_+\) and \(n_-\) is provided by the electroneutrality condition \(n_+ = n_- + fc\). The salt concentration inside the polyelectrolyte region
(given by \(n_-\)) is smaller than that of the reservoir. The difference in osmotic pressure between the two regions is \(\pi = k_B T(n_+ + n_- - 2n) = [(fc)^2 + 4n^2]^{1/2} - 2n\). When the salt concentration \(n\) is smaller than the counterion concentration \(fc\), the difference in salt concentration is small and the osmotic pressure is that of the ideal gas of counterions discussed in section (3.1), \(\pi = k_B T fc\). In the limit where the salt concentration is larger than the counterion concentration, the osmotic pressure is given by

\[
\pi = k_B T \frac{(fc)^2}{4n} = k_B T \frac{c^2 4\pi\ell_B f^2}{2 \kappa^2}
\]

This osmotic pressure defines an effective virial coefficient between monomers \(v_{cl} = f^2/2n = 4\pi\ell_B f^2 \kappa^{-2}\). This is identical to the excluded volume that can be calculated from the Debye-Hückel interaction (2.16) between monomers.

The major assumption made here is that the ion densities are uniform. This is the case when regions of size \(\kappa^{-1}\) around each polyelectrolyte, where the counterion concentration is increased, overlap, i.e. when the Debye-Hückel screening length is larger than the distance between chains. This is always true in the absence of salt. The osmotic pressure calculated from the Donnan equilibrium is of purely entropic origin. If the ion densities are uniform the electrostatic contribution to the osmotic pressure is small compared to the translational entropy of the small ions as checked below for a gel. The osmotic pressure is thus independent of the strength of the electrostatic interaction characterised by the Bjerrum length \(\ell_B\). The only role of the electrostatic interaction is to enforce electrical neutrality.

### 5.1 Grafted polyelectrolyte layers

Grafted polymer layers (polymer brushes) [51] are obtained by attaching one of the polymer end points on a planar solid surface. If the distance between chains is smaller than their natural size, a thick layer with a size proportional to the chain molecular weight is formed. The chains are stretched by the repulsive interactions between monomers.
Polymer brushes are often very efficient to enhance colloidal stabilisation [52]. Grafted polyelectrolyte layers have been described theoretically by several authors [53,54,55,56], we follow here the lines of the original work of Pincus which assumes that the polymer concentration is uniform throughout the thickness \( h \) of the brush. A similar approximation for neutral polymer brushes was introduced by Alexander [57] and de Gennes [58]. We also assume in this section that the local electrostatic screening length is larger than the distance between chains imposed by the distance \( D \) between grafting points so that the counterion concentration is roughly constant in the layer.

The electrostatic field and the distribution of counterions in the vicinity of a charged solid surface with a surface charge density \( \rho \) can be determined from the Poisson-Boltzmann equation. In the absence of added salt, the counterion density decays as a power law of the distance from the surface, and the counterions are confined in the vicinity of the surface over the Gouy-Chapman length \( \lambda = (2\pi \rho \ell_B)^{-1} \). If the grafting surface is neutral, the charge density of a grafted polyelectrolyte with \( \sigma = D^{-2} \) grafted chains per unit area layer is due to the monomer charges \( \rho = \sigma N f \), the Gouy-Chapman length [23] of the polymer brush is

\[
\lambda \simeq \frac{1}{\sigma f N \ell_B} \tag{5.3}
\]

Two cases must then be considered. When the Gouy-Chapman length is larger than the brush size \( h \), most of the counterions are outside the brush, and the brush is charged. When \( \lambda \) is smaller than the brush height, the counterions are confined in the grafted layer and the brush is neutral.

In the neutral limit, the brush is swollen by the osmotic pressure of the counterions \( \pi = k_B T f c \). This pressure is balanced by the elasticity of the polymer chains. For a gaussian chain, the elastic pressure is \( \pi_{el} = \sigma h/(N b^2) \). The monomer concentration in the brush being \( c = \sigma N/h \) the thickness of the brush is given by

\[
h = N b f^{1/2} \tag{5.4}
\]
The thickness of the brush is in this regime independent of the strength of the electrostatic interactions since the stretching of the chains is due only to entropic effects. The thickness given by equation (5.4) is larger than the size of an individual chain in a dilute solution given by (2.5). This result has been obtained by assuming that the monomer concentration is constant inside the adsorbed polymer layer. Similar scaling results are obtained if this constraint is released. Using a self-consistent field method, Zhulina et al. [54] have shown that the concentration profile has then a Gaussian decay.

In the charged limit, one can in a first approximation assume that the counterion concentration is constant up to the Gouy-Chapman length, it is equal to \( c_i = (fch)/\lambda \). The counterion pressure that stretches the chain is therefore \( \pi = k_B T fch/\lambda \). The thickness of the brush is then

\[
 h = N^3 \ell_B b^2 \sigma f^2
\]

In this regime the electrostatic interactions have a contribution of the same order as the entropic contribution and the thickness depends on their strength. The thickness of the layer grows faster than linearly with molecular weight, however one should keep in mind that the layer thickness remains smaller than the Gouy-Chapman length and thus that this thickness remains smaller than the thickness in the neutral regime (5.4). A precise determination of the counterion profile in this regime has been done by Pincus [53], the same scaling laws are obtained when this profile is taken into account.

When salt is added to the layer, the polyelectrolyte brush behaves as a neutral polymer brush with an effective excluded volume \( v_{el} = f^2/(2n) \); the thickness of the brush is then

\[
 h = Nb(\sigma b^2)^{1/3} f^{2/3}(nb^3)^{-1/3}
\]

The monomer concentration profile has also been calculated in this limit by Zhulina et al. [54] The important result is that the cross-over to the neutral brush regime (5.4) occurs when the salt concentration is larger than the counterion concentration in the brush. This
leads in general to a high ionic strength and the thickness of a grafted polymer layer is rather insensitive to ionic strength over a broad range of ionic strength. This makes grafted polyelectrolyte layers particularly interesting to promote colloidal stabilisation.

If the polyelectrolyte is annealed, the pH inside the grafted layer can be significantly different from outside. This could induce a non monotonic variation of the thickness with grafting density [59].

5.2 Polyelectrolyte gels

A model based on the Donnan equilibrium, very similar to that of polymer brushes, can be made for charged polymeric gels [60]. The polymer gel is at equilibrium with a reservoir of solvent if the osmotic pressure in the gel is equal to the osmotic pressure of the salt in the reservoir, i.e. if the swelling osmotic pressure due to the entropy of the counterions is balanced by the pressure due to the elasticity of the polymer chains. If the chains between the crosslinks of the gel are gaussian chains and have N monomers and an end to end distance (mesh size) $R$, the elastic pressure is of order $\pi \simeq k_B T (c/N)(R^2/Nb^2)$. If we now make the $c^*$ assumption proposed by de Gennes [4] that, in the swollen gel at equilibrium, the chains are just at the overlap concentration, the mesh size of the gel is such that $c = N/R^3$. In the absence of salt, the mesh size is then given by equation (5.4)

$$R = Nbf^{1/2} \quad (5.7)$$

In the presence of salt, the mesh size is given by

$$R = N^{3/5}b(\frac{f^2}{2n})^{1/5} \quad (5.8)$$

The important point to notice is that, in contrast to neutral gels, the mesh size of the gel is different from the radius of an isolated polymer chain in a dilute solution. As explained above, these results are valid when the salt concentration is small enough that the Debye-Hückel screening length is larger than the gel mesh size i.e. when the mesh size
is larger than the radius of an isolated chain in solution given by (2.4). The chains in this case should be viewed as chains under strong tension. The small ions osmotic pressure is exerted at the surface of the gel and the force is transmitted to the internal chains via the crosslinks.

The mesh size and thus the equilibrium swelling of the gel do not depend on the strength of the electrostatic interaction \(\ell_B\). When the monomer concentration in the gel is uniform, the electrostatic energy of the gel vanishes. The actual concentration in the gel is not homogeneous and the inhomogeneity can be characterised by the structure factor \(S(q)\). The electrostatic energy per unit volume of the gel can then be expressed as

\[
E_{el} = c \frac{f^2}{2} \int dq S(q) \frac{4\pi \ell_B}{q^2 + \kappa^2} \tag{5.9}
\]

The structure factor of the charged gel is not known exactly but one can expect it to have a sharp peak at a position \(q^* \approx R^{-1}\) the height of the peak being of order \(N\). The integral giving the electrostatic energy of the gel is dominated by the peak of the structure factor and can be estimated up to numerical prefactors

\[
E_{el} = c k_B T \frac{f^2 N^2 \ell_B}{R} \frac{1}{1 + \kappa^2 R^2} \tag{5.10}
\]

It can then be directly checked that, in the weak screening limit where \(\kappa R \ll 1\), the electrostatic energy is smaller than the translational entropy of the counterions.

In the strong screening limit \(\kappa R >> 1\), the electrostatic interactions are dominant. The charged monomers in the gel interact via a Debye-Hückel potential and the electrostatic interactions contribute to the rigidity of the chains between crosslinks as discussed in the previous section. At very high ionic strength the electrostatic persistence length is small, and the chains behave as neutral chains with an electrostatic excluded volume \(v_{el} = \frac{f^2}{2n}\). The same scaling result as equation (5.8) is then found for the mesh size.

The elastic shear modulus of the gel can be calculated by imposing a uniform deformation \(\gamma\) to the crosslinks. The increase of the square of the mesh size imposed by the
deformation is of order \((\gamma R)^2\) and if the chains are gaussian, the elastic energy stored in the gel is

\[ F_{el} = k_B T \frac{c \gamma^2 R^2}{N b^2} \]  

(5.11)

This leads to a shear modulus

\[ G = k_B T \frac{c R^2}{N Nb^2} \simeq k_B T f c \quad \text{(salt free case)} \]  
\[ \simeq k_B T f^2 c^2 \frac{n}{N} \quad \text{(with added salt)} \]  

(5.11)

In all cases, the shear modulus of the gel is thus of the order of the osmotic pressure of the small ions (counterions and salt).

The last property of the gel that we discuss is the cooperative diffusion constant, that can be obtained from a two-fluid model [61]. The displacement field of the gel \(u(\mathbf{r}, t)\) results from a balance between the elastic restoring force and a viscous force due to the solvent drag. The elastic force per unit volume of the gel is \(G\nabla^2 u\). The viscous force exerted by a solvent flowing through a porous medium of pore size \(R\) is given by the Brinkman equation [62] and is of order \(\eta R^{-2} \frac{\partial u}{\partial t}\) where \(\eta\) is the solvent viscosity. The force balance on the gel is then written as

\[ \eta R^{-2} \frac{\partial u}{\partial t} = G\nabla^2 u \]  

(5.12)

The relaxation of the gel deformation is diffusive with a cooperative diffusion constant

\[ D = \frac{GR^2}{\eta} \]  

(5.13)

The cooperative diffusion constant is independent of the molecular weight in the absence of salt \((D \simeq f^{1/2})\). It decreases with \(N\) in the presence of salt \((D \simeq N^{-2/5}(f^2/n)^{1/5})\).

Experimentally, the properties of charged gels, as well as the properties of neutral gels, strongly depend on the preparation condition of the gels. The simple results presented here (based on the so-called \(c^*\) theorem) implicitly assume that the gel was prepared by crosslinking chains in the vicinity of their overlap concentration. A more refined theory
based on an affine deformation hypothesis first proposed by Flory [64] and then developed by Panyukov [65] has recently been constructed. It provides an explanation for the experiments of Candau and coworkers [66] which show that the elastic shear modulus of polyelectrolyte gels with a fixed concentration smaller than the equilibrium swelling concentration decreases with the fraction of charged monomers.

6. Semidilute solutions

The overlap concentration of polyelectrolyte solutions in the absence of salt is very low; the chain radius given by equation (2.4) increases linearly with molecular weight and the overlap concentration decreases as $c^* \simeq b^4/(\ell_B N^2 f^2)$. Most of the experiments with long chains are thus performed in the semidilute range where the electrostatic interactions between different chains are strong. Our understanding of the conformation of polyelectrolyte chains in semidilute solutions is however rather poor and no general view is available. We discuss in this section a few aspects of the static properties of interacting polyelectrolyte chains.

6.1 Ordering transitions in polyelectrolyte solutions

The models presented in section 2 to describe the conformation of polyelectrolytes in salt free dilute solutions consider only a single chain and ignore the screening due to the counterions. If the polymer concentration is finite, the counterion concentration is finite and the screening length due to the counterions $\kappa^{-1}$ is given by $\kappa^2 = 4\pi \ell_B f c$. In a dilute solution the screening length is always larger than the average distance between chains $d \simeq (N/c)^{1/3}$. Different chains thus interact via a long range pure Coulomb potential. The polyelectrolyte chains are strongly charged objects and this long range interaction can lead to the formation of Wigner crystals, very similar to the colloidal crystals observed in solutions of charged spherical particles [67] or charged elongated particles (viruses) with a mesoscopic size. The centers of mass of the particles are then regularly distributed on a
periodic lattice. The solution has a tendency to crystallise when the interaction between neighboring chains \( k_B T N^2 f^2 \ell_B / d \) is larger than the thermal excitation \( k_B T \). This naive estimate predicts crystal formation at a very low concentration, way in the dilute range \( c \simeq 1/(N^5 f^6 \ell_B^3) \). The crystal is expected to melt when screening is important, in the vicinity of the overlap concentration. There is no clear experimental evidence for this crystallisation in flexible polyelectrolyte solutions. This may be due to the weak elastic resistance of this crystal that could be destroyed by any kind of perturbation (mechanical perturbation). In any case we expect strong interactions in dilute polyelectrolyte solutions that lead to a structuration of the solution and thus to the appearance of a peak in the structure factor \( S(q) \) of the solution corresponding either to liquidlike or to solidlike order. The wavevector \( q^* \) at the peak is of the order of the inverse distance between chains \( q^* \simeq 2\pi / d \simeq (c/N)^{1/3} \) [68]. The peak is observed experimentally and the variation of its position with concentration is in good agreement with this prediction. It can be suppressed by adding salt to the solution, so that the screening length \( \kappa^{-1} \) becomes smaller than the distance between chains.

As in dilute solutions, polyelectrolytes have, in a semidilute solution, a locally rodlike conformation that can be characterized by a persistence length \( \ell_p \). Quite similarly to rodlike molecules, semiflexible macromolecules undergo an Onsager transition [69,70] between an isotropic liquid phase and a nematic ordered phase where the molecules are parallel. The Onsager concentration where this transition takes place has been calculated by Semenov and Khokhlov [71,72], for neutral molecules of diameter \( d \) it scales as \( c_o \simeq 1/(\ell_p db) \). For charged molecules, the diameter of the molecule must be replaced by an effective diameter equal to the range of the electrostatic interaction \( \kappa^{-1} \) [70] and the Onsager concentration is of order \( c_o \simeq 1/(\ell_p \kappa^{-1} b) \). All the models for polyelectrolyte conformation based on the Odijk-Skolnick-Fixman approach predict an isotropic-nematic transition for polyelectrolyte solutions in the presence of salt. Experimentally, the transition is only observed
for very rigid polymers (such as DNA where a cholesteric phase is observed) where the intrinsic persistence length is very large and dominates the electrostatic persistence length. There is no definite evidence for an Onsager transition in flexible polyelectrolyte solutions. This is an unresolved issue. Possible explanations are based on the idea that the scaling theories ignore some prefactors that may be large and shift the transition to an unobservable value. The isotropic-nematic transition is also expected only for anisotropic enough objects, the ratio between the persistence length and effective diameter $\kappa^{-1}$ must be larger than a finite number $\simeq 5$ [73]. This criterion is not always met experimentally. A thorough theoretical study of possible isotropic-nematic transition in polyelectrolyte solutions has been made by Nyrkova [74]. In the following we will ignore this possibility and consider that a semidilute polyelectrolyte solution remains isotropic at any concentration.

6.2 Correlation length and osmotic pressure of semi-dilute polyelectrolyte solutions

In a dilute solution, polyelectrolyte chains have a rodlike conformation at a local scale smaller than the persistence length $\ell_p$ and the persistence length is always larger (or of the same order of magnitude) than the screening length of the electrostatic interactions. In a semidilute solution, the polymer chains overlap and, if we assume that they do not form ordered phases, they form a temporary network with a mesh size $\xi$. In the absence of salt, the chains also have a rodlike conformation at the scale $\xi$ and their persistence length is, as shown below, larger than the mesh size. The mesh size can then be calculated from a scaling argument by imposing that it is equal to the isolated chain radius (2.4) at the overlap concentration $c^\ast$. (For simplicity, we suppose here that locally the polymer shows local gaussian statistics, the other cases can be treated in a similar way). Equivalently, a pure geometrical argument can be used, by imposing a close packing condition for chain subunits of size $\xi$, $c = (\xi/\xi_c)g/\xi^3$. In any case, $\xi$ is given by [14,39]

$$\xi \simeq b^{-1}c^{-1/2}\xi_c^{1/2}$$

(6.1)
The number of monomers within a volume of size $\xi^3$, or correlation blob, is then $G_\xi = c^{-1/2} \xi_c^{3/2} b^{-3}$.

For weakly charged polyelectrolytes, the counterions are free and behave roughly as an ideal gas. The screening length due to the counterions is then $\kappa_i^{-1} = (4\pi \ell_B f c)^{-1/2}$. This screening length is of the order of the mesh size for strongly charged polyelectrolytes ($f \approx 1$) but it is larger than $\xi$ for weakly charged polyelectrolytes. The polymer itself, however, contributes to the screening of the electrostatic interactions and the actual screening length is smaller than the counterion screening length. From a purely electrostatic point of view each cell of size $\xi$ containing $G_\xi$ monomers is neutral and can be considered as independent of all the others. It is thus reasonable to assume that the effective screening length is of the order of the mesh size $\xi$ [43,75].

As salt is added to the solution, the screening length decreases and becomes dominated by salt ($\kappa^2 = 8\pi n\ell_B$) when the Debye-Hückel screening length of the salt $\kappa^{-1}$ is smaller than the mesh size $\xi$. When the screening is dominated by the salt, the electrostatic persistence length of the chains decreases with the salt concentration. As long as the persistence length is larger than the mesh size $\xi$, the mesh size is still given by equation (6.1). If the persistence length is smaller than the mesh size, the polyelectrolyte solution behaves as a neutral semi-flexible polymer solution and the mesh size or correlation length can be calculated from the radius in a dilute solution using scaling arguments. If the Odijk-Skolnick-Fixman statistics is assumed [76,43]

$$\xi \approx b \xi_c c^{-3/4} \kappa^{3/4} b^{-3/2},$$

(6.2)

while if the persistence length is assumed equal to the screening length [14,39]

$$\xi \approx \xi_c^{3/4} c^{-3/4} \kappa^{1/2} b^{-3/2}$$

(6.3)

This is somewhat similar to the assumption that, in neutral polymers, the hydrodynamic screening length is equal to the static correlation length.

4
Experimentally, the important feature of semidilute polyelectrolyte solutions is the fact that, if the salt concentration is low enough, the structure factor $S(q)$ has a peak at a finite wavevector $q^*$. At small wavevectors, the structure factor, because of the electroneutrality of the solution, is dominated by the small ions, that behave as an ideal gas. In the absence of salt, $S(q = 0) = 1/f$. If the salt concentration $n$ is larger than the counterion concentration, $S(q = 0) = 2n/(f^2c)$. At large wavevectors, corresponding to distances smaller than the mesh size $\xi$, the polyelectrolyte has a rodlike behavior and the structure factor is given by $S(q) = \xi_e/(qb^2)$. When the wavelength $q^{-1}$ is equal to the mesh size, the value of the structure factor is $S^* = G_\xi = c^{-1/2}\xi_e^{3/2}b^{-3}$. It can be checked explicitly that this value is larger than the thermodynamic value $S(q = 0)$ and the structure factor must thus have a peak at a finite wavevector $q^*$. The existence of the peak is therefore related to the very small compressibility of the small ion gas which gives $S(q = 0)$ due to the electroneutrality constraint. This discussion is valid as long as the counterions and the salt ions are uniformly distributed throughout the solution, i.e. as long as the screening length is larger than the mesh size of the solution. In the salt dominated regime, where the salt screening length is smaller than the mesh size of the solution, the counterions are confined in a sheath of size $\kappa^{-1}$ around each polymer and the solution essentially behaves as a neutral polymer solution where the structure factor decays monotonically. The peak thus disappears in the salt dominated regime. At the crossover between the two regimes, the $q = 0$ value of the structure factor increases very sharply. When the effect of salt is not dominant, the peak position $q^*$ defines the correlation length of the solution and one expects that it is of the order of the inverse of the mesh size $q^* \simeq 1/\xi$. The position of the peak of the structure factor increases thus as $c^{1/2}$ in a semidilute solution (and as $c^{1/3}$ in a dilute solution as explained above). It is also important to note that the correlation length $\xi$ and thus the peak position are roughly independent of the salt concentration as long as the Debye-Hückel screening length is smaller than $\xi$. These results are in rather
good agreement with experiments.

In the osmotic regime where the Debye-Hückel screening length is smaller than the mesh size, the small ions are uniformly distributed and the osmotic pressure of the solution is the same as that of a gel as discussed in section 5, it is dominated by the counterions. It is equal to \( \pi = k_B T f c \) if the counterion concentration is smaller than the salt concentration, \((f c > n)\) and to \( \pi = k_B T f^2 c^2 / (4 n) \) if \( f c < n \). In the salt dominated regime \( \kappa^{-1} < \xi \), the polyelectrolyte chains behave as neutral semiflexible chains with a persistence length \( \ell_p \) and an effective diameter equal to the screening length \( \kappa^{-1} \) (up to logarithmic corrections). The excluded volume between Kuhn segments of size \( \ell_p \) is of order \( \ell_p^2 \kappa^{-1} \). If the persistence length is larger than the mesh size (or of the same order), the osmotic pressure varies as

\[
\pi / k_B T = c^2 \kappa^{-1} \xi_e^{-2} b^4
\] (6.4)

At the crossover between the osmotic and the salt dominated regime, the osmotic pressure varies very rapidly and the crossover is not smooth. When the persistence length becomes small enough compared to the mesh size, the excluded volume correlations are relevant and the osmotic pressure increases as \( \pi \simeq c^{9/4} \). At very high ionic strength, the electrostatic interaction is very weak and cannot be approximated by an excluded volume between Kuhn segments. In this weak coupling regime there no longer is an electrostatic persistence length (it is shorter than the screening length) and the polyelectrolyte chains should be considered as flexible chains where the monomers interact via the short range Debye-Hückel potential with an effective excluded volume \( v_{el} = f^2 / 2 n \). The smooth crossover between the salt dominated and the weak coupling regimes occur when \( \kappa \xi_e \simeq 1 \) i.e. when the screening length becomes equal to the electrostatic blob size.

6.3 Electrostatic rigidity in semidilute solutions

In this section we discuss the conformation of polyelectrolyte chains in a semidilute solution and the effect of the interactions between different chains on the persistence length
of a polyelectrolyte. For simplicity we consider only a strongly charged polyelectrolyte for which the bare persistence length $\ell_0$ and the distance between charges $A$ are such that $A^2 > \ell_0 \ell_B$ so that the Odijk-Skolnick-Fixman theory can be applied in a dilute solution. We also assume that the bare persistence length is much smaller than the mesh size of the semidilute solution. The results can easily be extended to weakly charged polyelectrolytes if necessary by renormalising the bare persistence length to the blob size.

Two types of theories have been proposed to describe chain conformation in a semidilute solution. The early work of Odijk [76,77] makes the assumption that the interchain interactions have a negligible influence on the persistence length so that the persistence length is given by the usual Odijk-Skolnick-Fixman theory with the relevant screening length. A scaling theory for the chain conformation has been built on this assumption. It was however later pointed out by Witten and Pincus [78] that if a polyelectrolyte solution is isotropic, the electrostatic interaction energy between two chains can be reduced by a bending of the chains to avoid each other and thus that the interaction energy between different chains reduces the persistence length. A persistence length equal to the mesh size of the solution is obtained in the osmotic regime where the Debye-Hückel screening length of the salt is larger than the solution mesh size. In a revised version of this theory, in the salt dominated regime, the corrections to the persistence length due to the interactions between chains are found to be small.

The simplest approach [79] to the persistence length of a polymer chain in a semidilute solution is to use linear response theory. Within the framework of linear response, an effective pair interaction between monomers can be introduced. The Fourier transform of the effective interaction is related to the structure factor $S(q)$ of the solution by $\hat{v}_{eff}(q) = \hat{v}_{DH}(q) (1 - cS(q)\hat{v}_{DH}(q))$. Following the lines of Odijk argument, the effective persistence
length can then be calculated as
\[ \ell_p = \ell_0 + \frac{\hat{v}_{DH}(q = 0)}{16\pi k_B T A^2} (1 - cS(q = 0)\hat{v}_{DH}(q = 0)). \] (6.5)

This relation gives the persistence length as a function of the \( q = 0 \) value of the structure factor which is a thermodynamic quantity. If the explicit form of the Debye-Hückel potential is substituted, the persistence length is
\[ \ell_p = \ell_0 + \ell_{OSF}(1 - 4\pi \ell_B cS(q = 0)/\kappa^2). \]

A reduction of the persistence length from the single chain value induced by interchain interactions is therefore predicted. However this result can be used only in the limit of linear response, i.e. if the interaction between chains is smaller than \( k_B T \). The interaction between two rods crossing at perpendicular angle is
\[ \beta = \frac{2\pi \ell_B}{\kappa A^2}; \] (6.6)

The linear response result is thus valid if \( \beta << 1 \) which corresponds to the weak coupling regime for rigid polyelectrolytes.

No direct calculation of the effect of interchains interactions on the persistence length seems available in the strong coupling regime \( \beta >> 1 \). Some insight into the problem can however be gained by looking at the following simpler two dimensional problem: one semiflexible test chain lies in a plane, and interacts with all the other chains replaced by infinite rods perpendicular to this plane with a concentration per unit area \( \Gamma \). It is a good approximation to replace the other chains by infinite rods as long as their persistence length is larger than the screening length. In the limit where the Debye screening length is smaller than the distance between the chains, the solution can be considered as a quasi ideal gas of rods. When the test chain bends, the distribution of the rods around the test chain is changed and this contributes to the bending energy. The persistence length can be calculated following the lines of the work of Odijk in a dilute solution, the result is
\[ \ell_p = \ell_{OSF} - \Gamma\kappa^{-3} f(\beta). \] (6.7)
where the function \( f(\beta) \) is defined as

\[
f(\beta) = \frac{\beta}{2} \int_0^{+\infty} dz \exp(-\beta \exp(-z)) \left[ -\beta z^2 \exp(-2z) + \exp(-z)(-z^2 + z + 1) \right]
\] (6.8)

The correction to the Odijk value is always negative which corresponds also to a reduction of the persistence length from the isolated chain value. In the weak coupling limit, \( f(\beta) = 3\beta^2/8 \) in agreement with the linear response theory. In the strong coupling limit, the interaction is very similar to a hard sphere interaction and \( f(\beta) = (\ln \beta)^2 \) varies only logarithmically with the interaction strength. The correction to the single chain persistence length due to interchain interactions is small.

These results obtained in two dimensions find a simple interpretation in terms of individual deflections of the test chain by the perpendicular rod. When the test chain interacts with one rod at a distance \( r \), it bends and its orientation changes over a distance \( \kappa^{-1} \) by a finite angle that can be shown to be equal to

\[
\theta \simeq \kappa r \exp(-\kappa r).
\] (6.9)

The persistence length can then be obtained by summing the individual deflections weighed by the Boltzmann factor related to the direct electrostatic interactions between the chains. The persistence length given by equation (6.7) is then found up to a numerical prefactor. The independent deflection model is easily generalisable to real three dimensional chains. The chains do not always cross at a finite angle, but the conformations where two chains are almost parallel are energetically costly, since the electrostatic interaction is very high in this case (it increases linearly with chain length). This leads to a persistence length

\[
\ell_p^{-1} = \ell_{OSF}^{-1} \left[ 1 + \ln^2(\beta) \left( \frac{\alpha c A^3}{\kappa \ell_B} \right) \right],
\] (6.10)

where \( \alpha \) is a numerical constant of order unity. The important result is that the correction is small and thus that in the salt dominated regime, the reduction of the persistence length due to the interactions between different chains can be neglected.
The situation is very different in the osmotic regime, the chains interact very strongly and the distance between interacting chains is always of the order of the mesh size $\xi \simeq (cb)^{-1/2}$; the screening length $\kappa^{-1}$ is also of order $\xi$. There is no precise theory of the persistence length in the osmotic regime, the two following qualitative arguments suggest however that the persistence length is of the order of the mesh size $\xi$. As the distance $r$ between interacting chains is of order $\kappa^{-1}$, the deflection angle given by equation (6.9) is always of order one. Whenever two chains cross they bend by an angle of order unity and loose the memory of their orientation. The persistence length is thus of the order of the distance between crossings i.e. of the order of the mesh size $\xi$. The second argument is based on the strong structuration of the solution in the osmotic regime. The structure factor has a strong peak and with a very rough approximation the chains can be thought of as lying on a lattice with a lattice constant of order $\xi$. The total electrostatic energy of this lattice does not depend of the bending of the chains over distances larger than $\xi$. When the chains are bent on a scale $\xi$, entropy is gained but at the expense of bending energy associated with the bare persistence length $\ell_0$. The entropy is clearly dominant when $\ell_0 < \xi$ which leads to a persistence length of order $\xi$. An important consequence is that in saltfree semidilute solutions, both flexible and rigid polyelectrolytes have a persistence length of the order of the correlation length. It is also important to notice that the persistence length of rigid polyelectrolytes is predicted to vary non-monotonically with ionic strength. In the osmotic regime, it is dominated by interchain interactions and increases with ionic strength. In the salt-dominated regime, it is dominated by intrachain interactions and decreases with ionic strength. There is no clearcut experimental evidence of this non-monotonic variation of the persistence length with ionic strength [80].

6.4 Concentrated solutions of flexible polyelectrolytes

The semidilute regime discussed in the two previous subsections corresponds to chains which are rodlike at intermediate length scales and that can be described locally by the
electrostatic blob model of section 2. At a higher concentration however, the mesh size of the solution is smaller than the electrostatic blob size. Electrostatic interactions only play a minor role in this regime and the polyelectrolyte chains remain gaussian at all length scales. The electrostatic blob size $\xi_e$ is equal to the correlation length $\xi$ when the electrostatic blobs are close packed. If the local structure of the blobs is gaussian, this occurs at a concentration

$$c^{**} = b^{-3}f^{2/3}(\ell_B/b)^{1/3}$$

(6.11)

In the concentrated regime $c > c^{**}$, the electrostatic interactions are weak and the correlations in the solution can be studied within the framework of the so-called random phase approximation, as first suggested by Borue and Erukhimovich [81,82]. This leads to a structure factor (monomer-monomer concentration correlation function)

$$\frac{1}{S(q)} = \frac{1}{S_0(q)} + v + w^2c + \frac{4\pi \ell_B f^2}{q^2 + \kappa^2}.$$  

(6.12)

Here $S_0(q)$ is the structure factor of gaussian chains, given by the Debye function, and in the following it is written as $S_0(q)^{-1} = (Nc)^{-1}[1 + g(Nq^2b^2/6)]$. The second and third virial coefficients that describe the interactions between neutral monomers (i.e. that would describe the interactions for $f = 0$) are, respectively, $v$ and $w$. The second virial coefficient $v$ is the excluded volume $v$ and vanishes at the $\theta$ temperature. The third virial coefficient $w^2$ is assumed here to be positive. The last term comes from the screened electrostatic interactions. The screening is due to all the small ions and the Debye-Hückel screening length is defined here by $\kappa^2 = 4\pi \ell_B (fc + 2n)$. The statistics of the electrostatic blobs remain gaussian if the excluded volume is small enough, namely if the electrostatic blob size $\xi_e$ is smaller than the so-called thermal blob size $\xi_t \simeq b^4/v$.

Within the RPA approximation (6.12), the inverse osmotic compressibility of the neutral solution is $1/(Nc) + v + w^2c$. That of the charged solution is $1/(Nc) + v + w^2c + 4\pi \ell_B f^2/\kappa^2$. Hence, in the small wavevector limit, the electrostatic interactions give rise to an additional excluded volume $v_{el} = 4\pi \ell_B f^2/\kappa^2$. 

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At high wavevectors, the chains are gaussian and the structure factor decays as \( S(q) \approx \frac{12}{q^2 b^2} \). At small salt concentrations, the structure factor given by (6.12) has a peak at a wavevector \( q^* \) given by

\[
(q^*^2 + \kappa^2)^2 = \frac{24 \pi \ell_B f^2 c}{g'b^2}
\]

where \( g' \) is the derivative of \( g \) with respect to \((Nq^2 b^2/6)\), equal to \(1/2\) when \((Nq^2 b^2/6)\) is large and to \(1/3\) when it is small. The peak position is independent of the solvent quality. In the absence of salt, it scales as \( q^* \approx f^{1/2} c^{1/4} \) and crosses over smoothly to the peak position in the semidilute range \( q^* \approx 1/\xi \) given by equation (6.1) at the concentration \( c^{**} \). As the salt concentration is increased, the peak shifts towards zero wavevector and disappears when \( \kappa^4 > (24 \pi \ell_B f^2 c)/(g'b^2) \). At higher ionic strength the polymer solution behaves as a neutral polymer solution and the structure factor decreases monotonically with the wavevector. The structure factor given by equation (6.12) is in good agreement with neutron scattering experiments on weakly charged polyacrylic acid or polymethacrylic acid solutions in water \[83\].

The osmotic pressure of the solution can also be calculated from the RPA (one loop) approximation. In the absence of salt it is equal to

\[
\frac{\pi}{k_B T} = f c + \frac{1}{2} v c^2 + \frac{1}{3} w^2 c^3 - A f^{3/2} c^{3/4} \ell_B^{3/4} b^{-3/2}
\]

where \( A \) is a numerical constant of order unity \[81\]. The first term is the osmotic pressure of the counterions discussed extensively above; the two following terms are due to the non electrostatic interactions between monomers. The last term is due to the charge fluctuations and is very similar to the so-called polarisation pressure of simple electrolytes.

Finally, the cooperative diffusion constant of the solution can be calculated from the structure factor using linear response theory and describing the hydrodynamic interactions by the so-called Oseen tensor \[84\]. When the electrostatic interactions dominate over the
excluded volume interactions, the cooperative diffusion constant is given by

\[ D = \frac{k_B T \alpha^3}{6\pi \eta \kappa^2} (1 + \frac{\kappa^2}{\alpha^2}) (2 + \frac{\kappa^2}{\alpha^2})^{-1/2} \]  \hspace{1cm} (6.15)

where \( \eta \) is the solvent viscosity and where the wave vector \( \alpha \) is defined as \( \alpha^4 = (q^*\kappa^2) \). In a first approximation, the cooperative diffusion constant varies as \( D \sim f^{3/2} c^{3/4} (fc + 2n)^{-1} \). It is thus a non monotonic function of the monomer concentration \( c \). It increases at low concentration, reaches a maximum when the counterion concentration is of the order of the salt concentration and decreases at higher concentration. The unusual decrease at high concentration is due to the coupling to the counterion gas which dominates the compressibility of the solution. This might explain the unusual variation of the diffusion constant observed on polyacrylic acid solutions and gels.

A summary of the various regimes expected for polyelectrolyte solutions in the semidilute and concentrated ranges is given in figure 2.

6.5 Mesophase formation in poor solvents

In a poor solvent below the \( \theta \) temperature, the polyelectrolyte chains are subject to two antagonist forces, the attractive (Van der Waals like) interaction and the repulsive Coulombic interaction. As explained for isolated chains in section 2, the attractive interaction is dominant at short length scales and induces a local collapse of the solution. If the salt concentration is not too high, phase separation is not expected at a macroscopic scale but at a mesoscopic scale. The polymer solution is expected to form mesophases where the polyelectrolyte concentration is not homogeneous and where polymer dense and polymer dilute regions are periodically arranged. These phases are very similar to the mesophases observed in surfactant or block copolymer systems and various symmetries are possible (lamellar, cubic and hexagonal phases) [85,86]. Qualitatively, the mesophases are stabilised by the translational entropy of the counterions. If a macroscopic phase separation occurs, the separated phases must be electrically neutral and the translational entropy
of the counterions is low. When a mesophase is formed, the electroneutrality can be locally violated, this is associated to a cost in electrostatic energy but the translational entropy of the counterions is tremendously increased compared to a neutral dense state.

In the vicinity of the \( \theta \) temperature, mesophase formation can be investigated using the same random phase approximation as in the previous section. The structure factor is given by equation (6.12) where the excluded volume \( v = -b^3 \tau \) is now negative, \( \tau \) being the temperature shift from the \( \theta \) point. The structure factor has a strong peak at a wavevector \( q^* \) and this peak diverges as the temperature is lowered (\( v \) becoming more negative) indicating the formation of a periodic structure with a period \( 2\pi/q^* \). In the absence of salt, the spinodal for mesophase formation obtained from the divergence of the peak of the structure factor occurs when

\[
\frac{1}{N} + vc + w^2c^2 + \frac{1}{N} g(Nq^*b^2/6) + \frac{g' b^2}{6b^2} \left( \frac{24\pi \ell_B f^2 c}{g' b^2} \right)^{1/2} = 0 \quad (6.16)
\]

The qualitative shape of this spinodal line in a temperature \( \tau \)-concentration \( c \) plane is shown in figure 3. The temperature and the concentration at the maximum of the spinodal line are given by \( \tau_m \simeq f^{2/3}(\ell_B/b)^{1/3} \) and \( c_m \simeq b^{-3} f^{2/3}(\ell_B/b)^{1/3} \). Upon addition of salt, the period of the mesophase increases and when \( q^* = 0 \) (\( \kappa^4 = (24\pi \ell_B f^2 c)/(g' b^2) \)), the mesophase transition becomes a macroscopic phase separation very similar to the demixing transition of a polymer in a poor solvent.

In this weak segregation limit the symmetry of the phases and the topology of the phase diagram have been calculated by the Moscow group [87] by studying the non-linear fluctuations of the solution.

At a temperature much smaller than the \( \theta \) temperature, in the strong segregation regime, the interface between the dilute and dense polymer regions is sharp and can be described in terms of a surface tension. In a very dilute solution micelles are expected to form and their characteristics have been studied in references [82,88]. At higher concentra-
tions periodic phases are predicted. A partial phase diagram considering only the lamellar ordering has been determined by Nyrkova et al. [89] by a direct minimisation of the mean field free energy.

Most experimental results seem to be obtained outside the region of the phase diagram where mesophases form. To our knowledge, mesophase formation has been reported only in one case [90] and no detailed study of the mesophase structure seems to exist.

7. Dynamical properties

In this section, we briefly discuss some dynamic properties of polyelectrolyte solutions. Only two quantities are considered: the mobility and the electrophoretic mobility of a chain in a very dilute solution and the viscosity of the solution. In an electrophoresis experiment, the hydrodynamic interactions are screened and the electrophoretic mobility is independent of the molecular weight. The separation of molecules of different size (such as DNA) is thus not possible by simple electrophoresis. The concentration variation of the viscosity of a polyelectrolyte solution is very different from that of an organic neutral polymer solution. This effect has been known experimentally for a long time (it is sometimes referred to as the polyelectrolyte effect) but it remains poorly understood.

7.1 Mobility and electrophoretic mobility of a single charged chain

The theory of transport properties in dilute electrolyte solution has been worked out long ago by Debye, Onsager and Falkenhagen (see [91],[92], and historical references therein). The existence of long range Coulomb interactions between the species in solution results in a deviation of the transport coefficients from the pure solvent values (ionic mobility, conductivity, electrophoretic mobility and viscosity) that increases as the square root of the concentration, rather than the linear increase which is the rule for neutral species. The origin of this anomalous behaviour can be traced back to two effects known as the relaxation effect and the electrophoretic effects. Although these effects have different phys-
ical origins, they both produce a variation of the transport coefficients as the square root of the ionic concentration.

The relaxation effect can be described as follows. A test charge placed in an ionic solution is surrounded by a spherically symmetric polarisation cloud where charges of opposite sign are predominant, that can be described by the standard Debye-Hückel theory. If the test charge moves at a constant velocity \( U \) with respect to the solvent, the polarisation cloud is slightly distorted, and the charge experiences an additional electric field that tends to slow down its motion. The resulting force therefore appears as an electrostatic friction on the test charge. More generally, the moving charge \( Q \) (position \( R \), velocity \( U \)) in an electrolyte solution can be shown (see Appendix B) to produce an electric field inside the solution of the form

\[
E(r) = -T(r - R)U
\]

where the \( \alpha \beta \) component of the matrix \( T \) is

\[
T_{\alpha\beta}(R) = \frac{1}{(2\pi)^3} \int d^3k \exp(ik\cdot R) \frac{k_{\alpha}k_{\beta}}{k^2} \frac{Q\kappa^2}{k_BT(k^2 + \kappa^2)^2}
\]

The ionic mobility \( \zeta_0^{-1} \) is for simplicity assumed to be identical for all small ions.

The electrophoretic effect is important only for the description of ionic motion driven by an external electric field (electrophoresis). In that case, the force that drives a charge motion also acts on the surrounding polarisation cloud. The solvent velocity field that results from this body force acting on the polarisation cloud modifies the relative velocity of the charge with respect to the solvent creating an increased dissipation. In other words, the volume of solvent within a distance \( \kappa^{-1} \) of the moving charge is dragged along as the charge moves, with a friction coefficient of order \( \eta\kappa^{-1} \), where \( \eta \) is the solvent viscosity. In the language used to study polymer dynamics, the electrophoretic effect can be described as a screening of the hydrodynamic interactions when the motion is created by an electric
field. The hydrodynamic interactions are usually described in terms of the Oseen tensor $H(r)$ [6], which gives the velocity field that results from the application of a local force $F_0\delta(r)$ localized at the origin. When the force results from an electric field $E_0$ applied to a charge $Q$ located at the origin, it is easily shown (see Appendix B) that, if the polarization cloud is described within the Debye-Hückel approximation, the velocity field is given by

$$\exp(-\kappa r)H(r)Q E_0$$

(7.3)

This velocity field is screened in a similar way as the electrostatic interaction and decays as $\exp(-\kappa r)/r$. The hydrodynamic interaction with neighboring particles is also screened over a distance $\kappa^{-1}$.

The extension of these concepts to macroions has been the subject of numerous contributions. Much of this work however is concerned with spherical ([24], and references therein) or rodlike [93] particles. The case of flexible polymers has been considered by Hermans [94] Manning [92] and Muthukumar [95]. In reference [92], the relaxation and electrophoretic effects are treated on a different footing. In reference [95], the relaxation effect is ignored. In the following, we present a simplified description that allows for a simultaneous treatment of the two effects at a microscopic level. Our conclusions are essentially similar $^5$ of [92]. They differ from those of reference [95], which we believe to be in error.

We consider here two types of experiments. In a sedimentation experiment, the external force is the same on all monomers and has no effects on the small ions. The chain mobility $\mu$ relates the velocity of the center of mass of the molecule $v_G$ to the total force acting on the molecule $F$: $v_G = \mu F$. In the electrophoresis experiment, the external force is due

$^5$ The result that is arrived at in [92] can be obtained within our analysis by ignoring the second term in the r.h.s. of equation (7.6). The result that is obtained for the electrophoretic mobility is then $\mu_e = f e\langle H_{s0}\rangle/(1 + f e\langle H_{s0}\rangle T_0)$, which is only slightly different from (7.9), since $\langle H_{s0}\rangle$ is independent of molecular weight. A problem would arise, however, if the same approximation were made in the calculation of the mobility.
to the applied electric field $\mathbf{E}$ acting both on the charged monomers and on the free small ions. The electrophoretic mobility is defined by $v_G = \mu_e E$.

The model that we use to describe the dynamics of the charged polymer is a simple extension of the standard Zimm model of neutral polymers [6]. The velocity and position of monomer $i$ are denoted respectively by $\mathbf{R}_i$ and $\mathbf{v}_i$, the velocity field of the solvent is $\mathbf{u}(r)$. The equation of motion of monomer $i$, bearing a charge $fe$ results from a balance between a friction force and all the other forces acting on the monomer:

$$\zeta(\mathbf{v}_i - \mathbf{u}(\mathbf{R}_i)) = \mathbf{F}_i + fe\mathbf{E}_r(\mathbf{R}_i) \quad (7.4)$$

The monomer solvent friction coefficient is $\zeta$. The force $\mathbf{F}_i$ is the sum of an external force $F_{ext}$ (the sedimentation force or the applied electric field), a Langevin random force $\theta_i$ and of an intramolecular force $\mathbf{F}_{pol,i}$. The last term $\mathbf{E}_r$ is the electric relaxation field.

The velocity field of the solvent is given by an Oseen-type relation

$$\mathbf{u}(\mathbf{R}_i) = \sum_j \mathbf{H}(\mathbf{R}_i - \mathbf{R}_j)\left[s(\mathbf{R}_i - \mathbf{R}_j)\mathbf{F}_{ext} + \mathbf{F}_{pol,j} + \theta_j\right] + \mathbf{H}_s(\mathbf{R}_i - \mathbf{R}_j)fe\mathbf{E}_r(\mathbf{R}_j) \quad (7.5)$$

the screening factor $s(r)$ is equal to $\exp(-\kappa r)$ in the case of electrophoresis and to unity otherwise. If we assume that the solvent velocity field varies slowly over a scale $\kappa^{-1}$, the relaxation field $\mathbf{E}_r(\mathbf{R}_i)$ on monomer $i$ is obtained from (7.1) as

$$\mathbf{E}_r(\mathbf{R}_i) = -\sum_j \mathbf{T}(\mathbf{R}_i - \mathbf{R}_j)(\mathbf{v}_j - \mathbf{u}(\mathbf{R}_j)). \quad (7.6)$$

These equations can be treated in the spirit of the Kirkwood-Rieseman preaveraging approximation, by replacing the tensors $\mathbf{H}(\mathbf{R}_i - \mathbf{R}_j)$, $s(\mathbf{R}_i - \mathbf{R}_j)\mathbf{H}(\mathbf{R}_i - \mathbf{R}_j)$ and $\mathbf{T}(\mathbf{R}_i - \mathbf{R}_j)$ by their equilibrium average values. Introducing

$$H_0 = N^{-1} < \sum_{ij} \mathbf{H}(\mathbf{R}_i - \mathbf{R}_j) >$$

$$H_{s0} = N^{-1} < \sum_{ij} \exp(-\kappa|\mathbf{R}_i - \mathbf{R}_j|)\mathbf{H}(\mathbf{R}_i - \mathbf{R}_j) > \quad (7.7)$$

$$T_0 = N^{-1} < \sum_{ij} \mathbf{T}(\mathbf{R}_i - \mathbf{R}_j) >$$
the mobility $\mu$ and electrophoretic mobility $\mu_e$ are expressed as:

$$\mu = \frac{1}{N} \left[ H_0 - H_{s0} f e \frac{T_0}{\zeta} (1 + f e \frac{T_0}{\zeta})^{-1} \right] \quad (7.8)$$

$$\mu_e = f e H_{s0} (1 + f e \frac{T_0}{\zeta})^{-1} \quad (7.9)$$

The mobility is given by the usual Kirkwood-Riseman result [6], with a correction that arises from the relaxation effect. This relaxation correction reduces the mobility. Using equation (7.2), $T_0$ can be computed as

$$f e \frac{T_0}{\zeta} = f^2 \ell_B \frac{\zeta_0}{3\zeta} \int \frac{d^3q}{(2\pi)^3} S(q) \frac{\kappa^2}{q^2 + \kappa^2}$$

$$= f^2 \kappa \ell_B \frac{\zeta_0}{3\zeta} N^{-1} < \sum_{ij} \exp(-\kappa |\mathbf{R}_i - \mathbf{R}_j|) > \quad (7.10)$$

where $S(q)$ is the structure factor of the chain (normalized so that $S(q = 0) = N$). From the second line of (7.10) it is seen that the effect of the relaxation field is independent of molecular weight whatever the chain conformation and is small when the charge fraction $f$ is small.

For example, if the polymer is rodlike over a distance $\kappa^{-1}$, $f e T_0 / \zeta = f^2 \ell_B / (3b)(\zeta_0 / \zeta)$. The averaged screened Oseen tensor, $H_{s0}$, is also independent of molecular weight and proportional to $-\ln(\kappa b)$. The mobility is thus dominated by the Kirkwood Riseman contribution, and is essentially the same as for a neutral chain with the same conformation. The relaxation correction becomes important for strongly charged rodlike chains in the vicinity of Manning condensation threshold. In this case, the mobility is reduced by a factor of order unity from the Kirkwood Riseman value. The approximations that we have made are only valid for long chains, $R >> \kappa^{-1}$. In view of the complex form of equation (7.8), it is not surprising that experimental results for polyelectrolyte diffusion constants are often intermediate between the "non-draining" and "free draining" limits [96].

The electrophoretic mobility $\mu_e$, on the other hand, is in any case independent of molecular weight because of the screening of hydrodynamic interactions. For weakly charged
polyelectrolytes, the relaxation correction is small and the electrophoretic mobility can be rewritten in terms of the structure factor of the chains as

$$\mu_e = \frac{f_e}{3\eta \pi^2} \int dk S(k) \frac{k^2}{k^2 + \kappa^2}$$  \hspace{1cm} (7.11)

For a rodlike molecule, the electrophoretic mobility decreases logarithmically as the ionic strength is increased $\mu_e = -\frac{f_e}{3\eta \pi^2 b} \ln \kappa b$. For a flexible chain, using the stretched chain model of section 2 to describe the local conformation of the chains, we obtain $\mu_e = -(f b/\ell_B)^{1/3} (e/\eta b) \ln \kappa \xi_e$, the increase with the charge fraction is weaker and the electrophoretic mobility also decreases logarithmically with ionic strength. The general features of these theoretical predictions are in reasonable agreement with experimental observations. A detailed comparison between theoretical and experimental results is given in [92].

7.2 Viscosity of polyelectrolyte solutions

The viscosity of polyelectrolyte solutions has been known very early to exhibit a behaviour qualitatively different from that of neutral polymer solutions (see [1], and references therein). This behaviour was first described by Fuoss [97] using an empirical law, which gives the reduced viscosity $\eta_r = (\eta(c) - \eta_s)/\eta_s c$ as a function of the polymer concentration $c$

$$\eta_r = \frac{A}{1 + B c^{1/2}}.$$  \hspace{1cm} (7.12)

Detailed studies [98] show that the constant $A$, obtained by extrapolating the results to vanishing concentration, is proportional to $N^2 f^2$, while the ratio $A/B$ is proportional to $N f$.

It was later realized that this law is satisfactory only for high enough concentrations and in saltfree solutions, in which case it reduces to $\eta_r \sim c^{-1/2}$. At low concentration, the behaviour of $\eta_r$ is actually nonmonotonic [99]. The reduced viscosity $\eta_r$ presents a peak at a finite concentration, of the order of the salt concentration. This peak disappears

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when enough salt is added to the solution. A phenomenological law, recently proposed by Cohen, Priel and Rabin [100], seems to account well for the experimental observations. According to these authors, the intrinsic viscosity is given by

$$\eta_r = \frac{A_1 c}{\kappa^3}$$

(7.13)

where $\kappa$ is the Debye screening parameter, and $A_1$ is proportional to the molecular weight.

Finally, it is important to note that this anomalous behaviour of polyelectrolyte solutions can be rationalized at low concentrations by using the method of isoionic dilution [1,101]. In this method, the viscosity is studied as a function of polymer concentration for a given value of the ionic strength (i.e. as the solution is diluted, salt is added in order to keep the ionic strength constant). The increase of the reduced viscosity at low $c$ is then linear, as for neutral polymers. In neutral polymer solutions, this linear behaviour is usually represented in the form $\eta_r = [\eta] + k_H[\eta]^2 c$, where $[\eta]$ is the intrinsic viscosity and $k_H$ is the Huggins constant. In polyelectrolyte solutions, $[\eta]$ is large and varies strongly with the ionic strength $I$. The data of [101], for example, can be represented in the form $[\eta] = [\eta](I = \infty) + CI^{-1/2}$ [102]. The slope of the linear term, $k_H[\eta]^2$, is also much larger than the corresponding quantity in neutral polymers. The Huggins constant $k_H$ varies as $I^{-1/2}$ [102]. This indicates the importance of interactions between chains, and also shows that, as $c$ is increased a crossover to the ”interaction dominated” behaviour described by (7.13) rapidly takes place.

In short, three different concentration regimes can be distinguished in the behaviour of the reduced viscosity as a function of $c$ (figure 4) \(^6\). In the low concentration region (left side of the peak), $\eta_r$ is an increasing function of $c$. This region is most usefully

\(^6\) In fact, the Huggins constant is not a particularly useful concept in a system where interactions that are not of hydrodynamic origin are expected to be important.

\(^7\) This distinction is a simplification of the description proposed by Wolff [102], and seems valid at all but the highest concentrations.
characterized by isoionic dilution curves. The peak region corresponds to comparable salt and counterions concentrations \( fc \approx n \). Finally, in the more concentrated region, \( \eta_r \) is a decreasing function of \( c \), \( \eta_r \sim c^{-y} \) with \( y < 1 \). Obviously, this description is valid only in solutions where the salt concentration is small enough, since if \( n \) is large the behaviour of usual neutral polymers must be recovered.

At present, a comprehensive theory of polyelectrolyte viscosity is lacking. A number of interpretations, however, have been put forward to explain the unusual behaviour of these solutions. We will distinguish here two types of models based either on the conformation of the polymers or on the interactions between different chains.

In conformation based models [14,103,104,105] (which have been formulated for flexible polyelectrolytes), it is assumed that the viscosity of the polyelectrolyte solution is only a consequence of the structural properties of the solution. The calculation proceeds by analogy with the well understood case of neutral polymers. For semidilute solutions, the viscosity can be computed by applying the Rouse or reptation theories to a chain of correlation blobs of size \( \xi \), containing \( G_\xi \) monomers. The correlation length of polyelectrolyte solutions has a variation with concentration very different from that of neutral polymer solutions, so that the behaviour of the viscosity is also qualitatively different. This idea was first applied by de Gennes and coworkers [14]. These authors interpreted the \( \eta \sim N c^{-1/2} \) behaviour in saltfree semidilute solutions given by Fuoss law as corresponding to Rouse dynamics for a chain of correlation blobs of size \( \xi \sim \kappa^{-1} \) (equation (6.1)) with \( G_\xi = g(\xi/\xi_e) \) monomers. The viscosity is then given by

\[
\eta = \eta_s \frac{c}{N} \left( \frac{N}{G_\xi} \right)^2 \xi^3
\]

(7.14)

This analysis was extended by Dobrynin et al to the case where salt is added to the solution
In that case, $\xi$ is given by (6.3), $G_\xi = c\xi^3$ and the viscosity is

$$\eta = N\eta_s c^{5/4} \kappa^{-3/2} \xi^{-9/4} b^{9/2}.$$  \hfill (7.15)

The crossover between (7.14) and (7.15) takes place when the mesh size is equal to $\kappa^{-1}$, like the crossover between (6.1) and (6.3). Note that equation (7.15) predicts a maximum in the reduced viscosity $\eta_r(c)$ for $fc = n$.

Rubinstein and coworkers [75] also give an empirical justification for the observation that semidilute polyelectrolyte solutions obey Rouse dynamics over a broader range of concentrations above the overlap concentration than neutral polymer solutions. In neutral polymers, it is observed that entanglements become important when each chain interacts with about 10 other chains [106]. If this criterion is applied to polyelectrolytes, the concentration $c_{\text{rept}}$ for the onset of reptation behaviour is given by

$$\frac{c_{\text{rept}}}{N} \left( \frac{N}{G_\xi} \xi(c_{\text{rept}}) \right)^{3/2} \simeq 10.$$  \hfill (7.16)

This can be rewritten as $c_{\text{rept}} \xi(c_{\text{rept}})^3 \simeq N/100$. The overlap concentration $c^*$, on the other hand, is given by $c^* \xi(c^*)^3 \simeq N$. In polyelectrolyte solutions, $c\xi^3(c)$ decreases much more slowly with increasing concentration $c$ than in neutral polymer solutions, so that the onset of reptation is expected at higher concentrations. If equation (6.1) is used, the ratio $c_{\text{rept}}/c^*$ is of order $10^4$, while for neutral polymers it is of order $10^2$.

Another useful way of computing the viscosity of neutral polymer solutions, which allows a description of the dilute/semidilute crossover, is to write it in a scaling form

$$\eta = \eta_s F \left( \frac{c}{c^*} \right)$$  \hfill (7.17)

where $\eta_s$ is the solvent viscosity, $F$ is a scaling function and $c^*$ is the overlap concentration. The function $F$ can be expanded as a power series ($F(x) = 1 + a_1 x + a_2 x^2..$) for small values of its argument, i.e. in dilute solutions. In the semi-dilute regime, the functional
form of $F$ depends on the mechanism (Rouse or reptation) that governs stress relaxation. In this formulation, the specificity of polyelectrolyte solutions is related to the fact that the interactions between monomers depend on the polymer concentration. Therefore $c^*$ in (7.17) must now be interpreted as the overlap concentration corresponding to a polymer having the same interactions as the charged polymer at concentration $c$. For example, when the mesh size is larger than $\kappa^{-1}$, we can write

$$c^*(c) = N/R(c)^3.$$  \hspace{1cm} (7.18)

Where $R(c) = \kappa^{-1}(N/g)\xi_c^3/\kappa^{3/5}$, given by equation (4.12), is the radius of an isolated chain with this interaction. The viscosity is obtained by writing $\eta = \eta_s F(c/c^*(c))$, and assuming Rouse behaviour $\eta \sim N$. This gives

$$\eta = \eta_s \left(\frac{c}{c^*(c)}\right)^{5/4} = N\eta_s c^{5/4} \kappa^{-3/2} (\xi_c)^{9/4} b^{-9/2}$$  \hspace{1cm} (7.19)

which is identical to (7.15).

Another ”conformational” interpretation of polyelectrolyte viscosity was given by Reed [104], using similar arguments. His calculation assumes that $c$ is in the vicinity of $c^*(c)$, so that the $x^2$ contribution in the function $F(x)$ dominates. The formula used for $c^*$ is appropriate for short chains or large $\kappa^{-1}$. It corresponds to an ideal behaviour for a chain with a persistence length $\kappa^{-1}$

$$R(c)^2 = 2(N/g)\xi_c\kappa^{-1}.$$  \hspace{1cm} (7.20)

This leads to a viscosity

$$\eta \sim \eta_s (c/c^*)^2 \sim \eta_s N c^2 (\xi_c/g)^3.$$  \hspace{1cm} (7.21)

(Note that the same result would be obtained by requiring Rouse behaviour for the viscosity, i.e. $F(c/c^*) \sim N$) Again, the behaviour $\eta_r \sim f N c^{-1/2}$ is obtained in the absence of salt. With added salt, the experimentally observed behaviour (7.13) is reproduced. The
main difference between the interpretations of Reed and of Dobrynin et al. is the expression used for $R(c)$. The crossover from (7.21) to (7.15) can be expected to take place as $c$ increases and $R(c)$ crosses over from the ideal expression (7.20) to the Flory expression (2.5).

Finally, we note that in all conformation based models the $c^{-1/2}$ behaviour of $\eta_r$, corresponds to situations where the role of added salt is negligible. It is interesting that the value of the constant $A$ in Fuoss law (7.12), which corresponds to a (generally incorrect) extrapolation of this behaviour to $c = 0$, yields a value $A \sim N/R^3 \sim N^2 f^2$ that corresponds to the intrinsic viscosity for a saltfree, dilute solution of polyelectrolytes ($R \sim N f^{2/3}$). This coincidence, however, is not explained theoretically. At high concentrations, entanglements become important, and the reduced viscosity increases with concentration [102,75]

The conformation based models appear to provide a qualitatively correct description of flexible polyelectrolyte viscosity (see [104,75] for a comparison with experimental data). They only apply, however, to sufficiently concentrated solutions, near or above overlap concentration. The ”polyelectrolyte behaviour” described by equations (7.12) or (7.13) is also observed in solutions of short chains, or even for charged spherical particles [107]. In [108], it was suggested that this behaviour could be described on the basis of the liquid state ”mode-coupling” theories developped for the study of spherical charged colloïds [109]. Unfortunately, these theories are analytically tractable only in the limit of weak electrostatic coupling between the particles, which is certainly not realized in dilute polyelectrolyte solutions (see section 6.1). In this weak coupling regime, it was shown that the viscosity of a suspension of spherical charged particles (charge $Z$, concentration $c_0$, hydrodynamic radius $R$) is given by

$$\eta \sim \eta_s R c_0^2 Z^4 \ell_B^2 \kappa^{-3}$$

(7.22)

The authors of reference [108] noticed that this behaviour is similar to the experimentally observed one (7.13), if the polymer chain is assumed to bear an effective charge $Z^\ast =$
The particle concentration is replaced by $c/N$, and the hydrodynamic radius is proportional to $N$. The physical origin of the effective charge $Z^*$, however, is unclear.

This discussion indicates that a full theoretical understanding of the viscosity of poly-electrolyte solutions is far from being achieved. The main results can be summarized as follows. In all models, a maximum in $\eta_r$ is predicted when the salt and the counterion concentration are of the same order of magnitude, $fc \simeq n$. The maximum can occur, depending on chain length and salt concentrations, either in the dilute or in the semi-dilute region. For short chains or small salt concentrations, it thus takes place in dilute solution. The appropriate theory to describe the peak should be similar to that of references [109,108]. At concentration higher than the peak concentration, the reduced viscosity behaves as $fNc^{-1/2}$. Although the behaviour is similar above and below the overlap concentration, the interpretations that have been proposed are very different. For longer chains, or higher salt concentrations, $fc \simeq n$ corresponds to a semidilute solution. In that case, the viscosity can be described using equations (7.15) (for $c$ larger than $c^*$) or (7.21) (for $c$ near $c^*$). Below $c^*$, the appropriate description is again that of [109,108].

8. Conclusions

In this review we have presented the recent theories that describe the conformational and dynamical properties of charged polymer chains. Much of the focus has been put on the long range character of the electrostatic interactions and on the role of the small counterions that insure the electrical neutrality. Little attention has been paid to interactions of non electrostatic origin [110] which have only been introduced at some places in terms of virial coefficients. Most experiments on polyelectrolyte solutions are made in water that is not a good solvent for polyelectrolytes which are organic polymers. The non electrostatic interactions between molecules dissolved in water are not simple Van der Waals interactions and have components due to hydrogen bonding or to the hydrophobic effect [23]. It is not obvious that these very specific interactions can be modelled simply in terms of virial
coefficients. Experimentally these strong attractive interactions lead in some cases to the formation of aggregates which can be responsible for the slow modes [111,96,112] sometimes observed when measuring the relaxation of concentration fluctuations via quasielastic light scattering. The simple theoretical models that we have described do not take into account these complicated effects which are in many cases dominant. This makes a direct comparison between the theory and the experimental results rather difficult and we have not attempted here any quantitative comparison.

Despite this difficulty, some experimental features seem to be rather general in poly-electrolyte solutions. The structure factor of a polyelectrolyte solution always shows a peak at low ionic strength. The position of the peak has been discussed in section 6, both in dilute and semidilute solutions. Most experiments are also consistent with a rodlike behavior of the polyelectrolyte chains at small length scales. The rigidity of the chain is then characterized by an electrostatic persistence length. The variation of the persistence length with ionic strength or with the polymer concentration is however still a matter of controversy as seen in section 4, and more complete theories are certainly needed. The effect of heterogeneities of the charge distribution or of non electrostatic interactions on the persistence length do not seem to have been discussed. A good agreement between theory and experiment seems to exist only for rigid polymers where the theory of Odijk or Skolnick and Fixman [113,114] gives a quantitative description when counterion condensation is properly taken into account. Fuoss law and the variation of the viscosity of polyelectrolyte solutions with the concentration have also been extensively confirmed experimentally. The theoretical results presented in section 7 remain at the level of scaling laws and are not based on very systematic arguments. It should be also noted that the derivation of Fuoss law in semidilute solution based on the Rouse model implicitly assumes that there is only one length scale and therefore that the chain persistence length is of the order of the correlation length $\xi$ as suggested by some of the theoretical models.
An alternative way to study the properties of polyelectrolyte solutions is numerical simulations [12]. All the parameters are well controlled in the simulations and they should allow to sort out the respective roles of the electrostatic and non electrostatic interactions and thus to provide quantitative tests of the theoretical models. Many simulations have been performed on isolated polyelectrolyte chains in a salt free solution. There is in general quantitative agreement between the results and the electrostatic blob model. The simulations in the presence of salt often performed by using the Debye-Hückel potential are less conclusive. For rigid polyelectrolytes, the agreement with the Odijk-Skolnick and Fixman theory is good; for flexible weakly charged polyelectrolytes, there is no good separation of length scales between the screening length and the persistence length and a quantitative test of the theories is difficult. Recently, Kremer and Stevens [115] have performed simulations on semidilute polyelectrolyte solutions, taking into account explicitly the discrete counterions. The polymers are strongly charged flexible chains in the vicinity of Manning condensation threshold. This is a very heavy numerical work but it should allow a very detailed description of the influence of electrostatic interactions in polyelectrolyte solutions. The extension of these simulations to weakly charged or more rigid polyelectrolytes for which the analytical theories have been constructed would provide strong tests of these theories.

The review has also been limited to simple polyelectrolyte chains comprising only monomers with the same charge and neutral monomers. There are several other polymeric sytems where electrostatic interactions play an important role. Polyampholytes [116,117] are polymers that carry charges of both signs. Due to the attractions between opposite charges, they are often insoluble in salt free water and can only be dissolved at a finite ionic strength. They also show an antipolyelectrolyte effect, the reduced viscosity increasing with ionic strength. Polysoaps are comblike polymers, often polyelectrolytes, where hydrophobic side chains are grafted on the backbone [1,118]. They have properties combining those of
polyelectrolyte chains and of small ionic surfactants and form for example intramolecular micelles. Another system of interest is mixtures between neutral and charged polymers [119,120] which have been studied both experimentally and theoretically. The addition of a charged polymers can increase the solubility of a neutral polymer in water. The formation of mesophases is also expected in these systems.

Throughout this review we also have implicitly assumed that the solvent (essentially water) is a continuous dielectric medium with a uniform dielectric constant. At high polymer concentration the dielectric constant crosses over from that of the polar solvent to that of an organic medium (essentially polymer) [121]. If the dielectric constant is low, charges of opposite signs are not dissociated and the polymer has an ionomer behavior dominated by attractive interactions between dipoles. Even in a more dilute solution, it is not clear that locally, the dielectric constant has the solvent value; this could turn out important in Manning condensation theory for example. There seems to be little theoretical work on these issues. Also, the small ions have been considered as pointlike, all specific interactions due to hydration or to the finite size of the ions have been neglected. Small differences between ions due to these effects are usually observed.

One of the essential conclusions of this review is that polyelectrolytes remain a poorly understood state of matter and that much work is still needed both from the experimental and from the theoretical point of view to reach a degree of understanding equivalent to that of neutral polymers. From a theoretical viewpoint, polyelectrolytes are in most cases strongly coupled systems, involving many different length scales. It might well be that in such situations, an appropriate description of the system can only be obtained by the use of sophisticated liquid state theories, such as those recently developped for dense neutral polymers [122]. Experimentally, it is surprising that relatively few systematic studies on charged polymers, using modern investigation tools, in particular neutron scattering, are available. Such studies were initiated in the late seventies (see e.g [123]), but have not been
as conclusive as the equivalent studies on neutral polymers. Finally, it is obvious that the area of polyelectrolyte solutions offers a number of problems that can be approached by simulation. Simulations that explicitly include counterions can be used to assess the accuracy of the Debye-Hückel or Poisson-Boltzmann approximations [124]. Density functional based simulation methods [125] for classical charged systems can be used to go beyond such approximations, even in the presence of added salt. Finally, the dynamical properties of charged polymers have not, up to now, been investigated in numerical studies.
Effective interaction between charged monomers

In this appendix, it is shown that the effective interaction between charged monomers can, within the linear response approximation, rigorously be written as a sum of pairwise additive interactions (equation (2.16). As a byproduct of the calculation, the various structure factors (ion-ion, polymer-polymer and polymer-ion) are linked within this approximation, by simple relations.

The system is a polymer solution with a concentration $c$ of (positively) charged monomers, and a concentration $n$ of monovalent added salt. For simplicity we assume that the counterions are identical to the salt cations. The densities of charged monomers, charged positive and negative ions are denoted by $\rho_P(r)$, $n_+(r)$ and $n_-(r)$, respectively. By integrating out the coordinates of the small ions, the partition function of the system can formally be written as

$$Z = \text{Tr}_P \exp\left(-\left(H_P + F_i[\psi]\right)/k_B T\right)$$

(A.1)

where $\text{Tr}_P$ denotes an integration over monomer coordinates, and $H_P$ is the energy of the polymer (2.1). $F_i[\psi]$ is the free energy of the small ions in a potential that is the sum of the external potential and of the electrostatic potential $\psi(r)$ created by the polymer

$$\psi(r) = k_B T \ell_B \int dr' \frac{\rho_P(r')}{|r-r'|}.$$  

(A.2)

The free energy $F_i$ is obtained by minimizing with respect to the ionic densities $n_+(r)$ and $n_-(r)$ a free energy functional, which in the mean field or Poisson-Boltzmann approximation reads

$$k_B T \int dr (n_+(r) \ln(n_+(r)) + n_-(r) \ln(n_-(r)))$$

$$+ \frac{1}{2} \ell_B k_B T \int dr dr' \frac{(n_+(r) - n_-(r))(n_+(r') - n_-(r'))}{|r-r'|} + \int dr (n_+(r) - n_-(r)) \psi(r)$$

(A.3)
The linear response, or Debye-Hückel, approximation, involves a further simplification of equation (A.3), by expanding the first two terms to second order in the deviations of $n_+$ and $n_-$ from their average values. The minimisation is easily carried out, and the resulting expression for $F_i$ is

$$F_i[\psi] = -\int d^3k \frac{1}{2} \frac{4\pi \ell_B}{k^2} \kappa^2 \rho_P(k) \rho_P(-k) .$$

(A.4)

with $\kappa^2 = 4\pi \ell_B (2c+n)$. The interaction that results from adding this contribution from the ionic free energy to the electrostatic repulsion between the monomers, $\int d^3k \frac{4\pi \ell_B}{k^2} \rho_P(k) \rho_P(-k)$, gives the screened pair potential (2.16).

The Debye-Hückel calculation can easily be extended to compute the response of various densities to external fields, or equivalently the partial structure factors. The results are simple in the case of a salt concentration much larger than the counterion concentration ($n >> c$). Defining the ionic charge density as $\rho_Z = n_+ - n_-$, the following relationships are obtained between the Fourier transforms of the polymer-polymer, polymer-charge and charge-charge correlation functions (denoted by $S_{PP}$, $S_{PZ}$ and $S_{ZZ}$, respectively)

$$S_{PZ}(k) = -\frac{\kappa^2}{k^2 + \kappa^2} S_{PP}(k)$$

$$S_{ZZ}(k) = 2n \frac{k^2}{k^2 + \kappa^2} + \left( \frac{\kappa^2}{k^2 + \kappa^2} \right)^2 S_{PP}(k) .$$

(A.5)

The total charge structure factor, $S_{PP} + S_{ZZ} - 2S_{PZ}$, vanishes as $2nk^2/\kappa^2$ in the small $k$ limit, as implied by the Stillinger and Lovett sum rules [22].
APPENDIX B

Relaxation and electrophoretic effects

In this appendix, we derive equations (7.1) and (7.3), describing respectively the relaxation and electrophoretic effects. As usual, the two effects are considered independently [91], since the coupling between them is relevant only at a level that goes beyond the limits of the Debye-Hückel linearized theory.

B.1 Relaxation field

The relaxation field is the electric field created by a charged particle (charge $Qe$) moving in a monovalent salt solution (concentration $n$) with a constant velocity $V$. As explained in section 7.1, this relaxation field arises from the deformation of the Debye-Hückel polarisation cloud when the charge is set into motion. At equilibrium, the densities $n_+(r)$ of positive and $n_-(r)$ of negative ions that surround the charged particle (placed at the origin) are

$$n_\pm^{(eq)}(r) = n(1 \mp Q\ell_B r \exp(-\kappa r)).$$  

(B.1)

In a time dependent situation, however, the Boltzmann statistics that is used to obtain these densities must be replaced with a diffusion equation

$$\zeta_0 \frac{\partial n_\pm(r,t)}{\partial t} = \nabla \cdot (k_B T \nabla n_\pm(r,t) \mp n_\pm(r,t) E(r,t)).$$  

(B.2)

where $\zeta_0$ is the ionic mobility. The electric field $E$ is the sum of the field $E_P(r - Vt)$ created by the moving particle and of the electric field created by the ionic charge density, $E_i$, which verifies Poisson equation

$$\nabla \cdot E_i(r,t) = 4\pi \ell_B (n_+(r,t) - n_-(r,t)).$$  

(B.3)

The solution of (B.2) in the stationary state is of the form $n_\pm(r,t) = n_\pm^{(eq)}(r - Vt) + \delta n_\pm(r - Vt)$. Inserting this form into (B.2) and (B.3), and linearizing with respect to $V$
and $Q$, the following equation for $\delta n_+ - \delta n_-$ is obtained.

$$(\nabla^2 + \kappa^2)(\delta n_+(\mathbf{r}) - \delta n_-(\mathbf{r})) = \frac{\zeta_0}{k_B T} \mathbf{V} \cdot \nabla \left[ (2nQ\ell_B^2) \exp(-\kappa r) \right].$$  \hfill (B.4)

The resulting ionic charge density can be expressed as

$$(\delta n_+(\mathbf{r}) - \delta n_-(\mathbf{r})(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d^3\mathbf{k} \left( \frac{\zeta_0 Q \kappa^2}{k_B T} \right) \frac{i\mathbf{k} \cdot \mathbf{V}}{(k^2 + \kappa^2)^2} \exp(-i\mathbf{k} \cdot \mathbf{r})$$ \hfill (B.5)

and the resulting electric field is given by equation (7.1).

\subsection*{B.2 Electrophoretic effect}

We now consider the calculation of the hydrodynamic velocity field around a charge $Q$ at the origin, when the charge experiences a force $QE_{\text{ext}}$ created by an external electric field $E_{\text{ext}}$. The solvent experiences a force $QE_{\text{ext}}\delta(\mathbf{r})$ created by the charge at the origin, and a body force $e(n_+(\mathbf{r}) - n_-(\mathbf{r}))E_{\text{ext}}$. The equation that determines the hydrodynamic velocity field $\mathbf{U}(\mathbf{r})$ in the solvent is

$$-\eta_s \nabla^2 \mathbf{U} + \nabla P = Q\mathbf{E}_{\text{ext}}\delta(\mathbf{r}) + e(n_+(\mathbf{r}) - n_-(\mathbf{r}))\mathbf{E}_{\text{ext}},$$ \hfill (B.6)

where $\eta_s$ is the viscosity and $P$ the pressure. $(n_+(\mathbf{r}) - n_-(\mathbf{r}))$ is the charge density within the \textit{equilibrium} Debye-Hückel polarisation cloud. In Fourier space, the velocity field is given by a generalization of Oseen’s formula,

$$U_i(\mathbf{k}) = \frac{1}{\eta_s(k^2 + \kappa^2)}(\delta_{ij} - k_ik_j/k^2)(Q\mathbf{E}_j).$$ \hfill (B.7)

Which gives in real space,

$$\mathbf{U}(\mathbf{r}) = \mathbf{H}_s(\mathbf{r})(Q\mathbf{E}_{\text{ext}})$$ \hfill (B.8)

with the screened Oseen tensor $H_s$ being

$$H_{s,ij} = \frac{\exp(-\kappa r)}{8\pi\eta_s r}(\delta_{ij} + r_ir_j/r^2).$$ \hfill (B.9)
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**FIGURE CAPTIONS**

**figure 1**: schematic representation of the blob structure of a charged polymer chain. The chain is gaussian up to the scale $\xi_e$, stretched on larger length scales.

**figure 2**: schematic ”state diagram” for a polyelectrolyte solution, in the plane $c$ (polymer concentration), $n$ (concentration of monovalent added salt). The boundaries between the different regions of the plane indicate crossovers, not sharp transitions. Region I (dilute) is discussed in sections 2, 3 and 6.1. Regions II,III and IV (semidilute) are discussed in section 6.2 and 6.3. Region V (concentrated) is discussed in section 6.5.

**figure 3**: Phase diagram of a dense polyelectrolyte solution in a bad solvent. Upper part: phase diagram in the concentration, temperature plane for a fixed salt concentration. Lower part: phase diagram as a function of salt concentration and temperature for a given polymer concentration.

**figure 4**: schematic representation of the reduced viscosity as a function of polymer concentration $c$ at a fixed salt concentration $n$. 