Electrophoresis of polyampholytes

Didier Long
Laboratoire de Physico-Chimie Théorique, U.R.A. CNRS 1382, ESPCI, 10 rue Vauquelin F-75231 Paris Cedex 05, France

Andrey V. Dobrynin and Michael Rubinstein
Department of Chemistry, Venable Hall, University of North Carolina, Chapel Hill, North Carolina 27599-3290

Armand Ajdari
Laboratoire de Physico-Chimie Théorique, U.R.A. CNRS 1382, ESPCI, 10 rue Vauquelin F-75231 Paris Cedex 05, France

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We consider the motion and the deformation of Gaussian polyampholytes in free flow electrophoresis, i.e., in an applied external electric field. The electrophoretic mobility and the deformation of the chains are calculated in the linear regime, as functions of the charge distribution along the backbone and of the salt concentration. The results in salt-free solutions differ from those in solutions with a high concentration of salt even at the level of scaling laws. It is shown that in solutions with a high salt concentration, the electrophoretic mobility of a given polyampholyte strongly depends not only on its total charge but also on the details of the charge distribution along the chain. The very direction of motion can also depend on it. Indeed, even “neutral” polyampholytes, i.e., chains with equal number of positive and negative charges can move in an applied electric field. To demonstrate further these effects, we systematically compare the behavior of the linear and circular chains. © 1998 American Institute of Physics. [S0021-9606(98)50703-9]

I. INTRODUCTION

Charged polymers have attracted much attention due to their unique properties and their technological importance.1 If the charges on the polymers are all positive or all negative they are called polyelectrolytes.2,3 Common polyelectrolytes include polyacrylic and methacrylic acids and their salts, cellulose derivatives, sulfonated polystyrene, DNA and other strong polycids and polybases. Another class of charged polymers (polyampholytes) are amphoteric in nature carrying both positive and negative charges. Examples in the biological realm are proteins or protein-DNA complexes. Synthetic polyampholytes are typically macromolecules obtained by random copolymerization reactions,3 made of different kinds of monomers, some of which can acquire a positive charge in solutions and others a negative charge. The net charge of a given polyampholyte in an aqueous solution is usually determined by the pH of this solution.

In this article we consider the electrophoresis of such chains, i.e., their behavior in an applied electric field. Electrophoresis is a common separation technique, used, e.g., to separate various surfactants or polyelectrolytes.4,5 We will focus here on the linear regime of small applied fields so that the chains almost retain their equilibrium conformational statistics.

In salt free solutions, the equilibrium conformation of polyampholytes is controlled by the long range electrostatic interactions between charged monomers.6–16 A polyampholyte with an equal number of positively \( N_+ \) and negatively \( N_- \) charged monomers may collapse into a globule (microelectrolyte) due to Debye–Huckel’s fluctuation-induced attraction between charges. If salt is added to the solution, it “screens” the attraction between charges and causes the swelling of the globally neutral polyampholyte chain. On the other hand, polyampholyte chains with charge imbalance \( |N_+ - N_-| \) larger than \( (N_+ + N_-)^{1/2} \) do stretch in salt-free solutions, into a necklace-like configuration, rather than collapse at low temperatures into a spherical globule.16 This is the consequence of the long-range Coulomb repulsion between excess charges. However, if the electrostatic forces are too weak to induce a significant deformation of the chain, the polyampholyte adopts a Gaussian conformation.7,16 In the present paper we will be interested only in the case of polyampholyte chains with almost Gaussian equilibrium statistics. We will also consider the charge distribution along the chain to be quenched.

Let us sketch briefly the mechanisms at work when an electric field is applied. For dilute solutions of polyelectrolytes with no salt, counterions are far away from the chains. In an applied electric field \( \mathbf{E} \) each charged monomer of charge \( q \) is subjected to an electric force \( q \mathbf{E} \), which is partly transmitted to the fluid and generates long-range hydrodynamic interactions between the monomers. These hydrodynamic interactions build up collective effects so that the hydrodynamic friction coefficient of polyelectrolytes is proportional to the 3D size of the chains.17–19 As a result, electric and hydrodynamic forces need not balance locally, which results in the build up of tension and the deformation of the coils in free flow electrophoresis.
In solutions with a high salt concentration, the situation is very different, due to the existence of a sheath of counterions around the chain. It is, for example, well established experimentally\textsuperscript{20–22} that the electrophoretic mobility of uniformly charged polyelectrolytes (e.g., DNA) is size-independent and that such polyelectrolytes move without significant deformation in free-flow electrophoresis. The theoretical explanation of this effect (see, e.g., Ref. 23 for a review) is that the electric force on the counter-ions, of same amplitude but opposite sign than the one acting on the backbone, leads to a cancelation of the long-range hydrodynamic interactions between the monomers,\textsuperscript{23–25} and imposes a local balance of the electric and hydrodynamic forces.\textsuperscript{26,27} Nevertheless, hydrodynamic interactions can play an important role in the electrophoresis of nonuniformly charged chains in solutions with a high concentration of salt. This can be demonstrated by considering a diblock copolyelectrolyte with one block positively charged and the other block negatively charged.\textsuperscript{28} In free flow electrophoresis conditions, each block exerts a tension on the other. This tension is a nonelectric force and thus is transmitted to the fluid without any screening effect by the counter-ions, generating long-range hydrodynamic interactions. Another consequence of the hydrodynamic interactions, is that not all the monomers play the same role. Monomers located, on average, closer to the outer part of the coil, such as end monomers in linear chains, are subject, on average, to higher hydrodynamic friction than the monomers located inside the coil. This difference can contribute to the deformation of the coil and results in a charge-distribution-dependent electrophoretic mobility.

Electrophoresis could thus be used to separate polyelectrolytes according to their size and to the charge distribution along the polymer backbones. The influence of an external electric field on the conformation and drift of a polyelectrolyte chain in a salt-free solution was considered in a recent series of works.\textsuperscript{29–31} The electric field pulls the oppositely charged monomers in opposite directions, stretching the chain. Unfortunately, these considerations\textsuperscript{29–31} were limited to a Rouse model description of the polyelectrolytes and did not include hydrodynamic interactions. The latter were taken into account in Ref. 32 but only to calculate the deformation in the nonlinear regime of very high electric fields using a description in terms of Pincus blobs. In an earlier paper, Anderson and Solomontsev had discussed some aspects of the problem we address but neglected hydrodynamic interactions in the case of coily polymers and focused on slender objects with very specific frozen configurations: either rod like or toroidal.\textsuperscript{33}

In the present paper we calculate the electrophoretic mobility of polyelectrolyte chains within the framework of the Zimm model, thus taking into account both the hydrodynamic interactions and the elasticity of the chain. We describe both salt-free and high-salt solutions. In Sec. II we give a general description of the dynamics of a charged chain in an external electric field. To account for the importance of end-effects we compare the behavior of the circular and linear chains. In Sec. III, we derive the electrophoretic mobility and the deformation of polyelectrolytes in salt-free solutions and apply these general results to various types of charge distributions along the chain (uniform, periodic and random). Following the same scheme, Sec. IV deals with polyelectrolytes in solutions with a high concentration of salt. Section V summarizes our results and discusses the possible applications of our approach.

II. MODELS FOR POLYAMPHOLYTEs IN AN EXTERNAL ELECTRIC FIELD

A. Adapting the Zimm model

We want in this section to describe the dynamics of a polyelectrolyte chain under an external electric field, in the spirit of the presentation of the Zimm model\textsuperscript{17} given by Doi and Edwards in Ref. 18. The polyelectrolyte chain is thus modeled as \( N \) beads connected by springs of average length \( b \). The position and conformation of the chain is given by the set of position vectors of its beads \( \mathbf{R}(n) \). The distribution of the charges along the polymer chain is described by a set of variables \( z(n) \): \( e_z(n) \) is the charge of the \( n \)th monomer, which can be positive, zero, or negative. We now want to account properly for the hydrodynamic interactions.

The main difference with the usual description of, e.g., the sedimentation of a neutral polymer is that here the electric field acts not only on the monomers, but also on the charged ions joins in the solution. The corresponding forces also generate hydrodynamic interactions. To address the problem, we propose here to consider first a single given bead (say the \( m \)th), independently from the rest of the chain, together with the corresponding "cloud" of ions (counter- and coions) in an electric field \( \mathbf{E} \). We want to characterize the own velocity of the bead, and the resulting velocity field \( \mathbf{v}_m(\mathbf{r}) \) around it, so as to calculate how it contributes to the motion of the other monomers. In the linear regime the bead moves at a velocity \( \mu_b(m)\mathbf{E} \), which defines its "bare" electrophoretic mobility \( \mu_b \), and there is around it a flow field which has the form

\[
\mathbf{v}_m(\mathbf{r}) = \mathbf{H}_0^e (\mathbf{r} - \mathbf{R}(m))(e_z(\mathbf{r})\mathbf{E}),
\]

where \( \mathbf{H}_0^e \) is a tensor which has been analyzed at length in the electrophoresis literature\textsuperscript{34–37} Its structure is rather simple in two limits. If the Debye length \( r_D \) is very large, the counterions are far away, so \( \mathbf{H}_0^e \) is equal to the Oseen tensor up to distances of order \( r_D \) [and \( \mu_b(m) = \text{simple } e_z(m)/\xi \), where \( \xi \) is the bead’s friction coefficient]. In the opposite limit where the Debye length is small compared to the distances \( |\mathbf{r} - \mathbf{R}(m)| \) of interest, \( \mathbf{H}_0^e \) decays faster: It is the sum of a term decaying exponentially over the Debye length and of a "potential" term slower than the Oseen tensor, i.e., scaling as \( 1/r^3 \) instead of the usual \( 1/r \). This last point is a consequence of the fact that the bead and its double layer together constitute as neutral ensemble: Thus the applied electric field exerts no net force on it and thus no net momentum is transmitted to the fluid. Consider now the own velocity of the bead. The model we propose here is a generalization to polyelectrolytes of that of Barrat and Joanny for polyelectrolytes in salty solutions.\textsuperscript{23} It allowed them to give an expression of the mobility as a function of the charge...
density along the backbone, the persistence length of the chain and the salt concentration, which we could use in principle to calculate \( \mu_\mu(m) \). But it was for infinitely thin chains, which is a specific case. Thus we keep here the bare electrophoretic mobility \( \mu_\mu(m) \) of the individual monomers as an input, which incorporates all the effects of the smaller scales details. The former can indeed be a complicated function of the latter as has been shown in the context of the electrophoresis of colloidal particles. These forces of nonelectrical nature acting on the monomer. These forces of nonelectrical nature acting on the monomer will produce an additional flow field, classically described by the Oseen tensor \( \mathbf{H}^0(r) \) with the above mentioned \( 1/r \) decay

\[
[\mathbf{H}^0(r)]_{ij} = \frac{1}{8 \pi \eta r} \left( \delta_{ij} + \frac{r_i r_j}{r^2} \right).
\]

So, summing up the electrical and nonelectrical contributions to the hydrodynamic interactions, we arrive at the equation of motion of the \( n \)th bead in the external electric field \( \mathbf{E} \)

\[
\frac{\partial \mathbf{R}(n)}{\partial t} = \frac{1}{\xi} \left[ \mathbf{T}(n) + \mathbf{g}(n) \right] + \mu_\mu(n) \mathbf{E} + \mathbf{u}(\mathbf{R}(n)),
\]

where \( \xi \) is the friction coefficient of the bead, and \( \mathbf{u}(\mathbf{R}(n)) \) is the flow field created at the location of the \( n \)th monomer by all the other monomers. Note that we have omitted the description of retardation effects which do not modify the picture and are usually negligible. The flow \( \mathbf{u}(\mathbf{R}(n)) \) is from the above analysis

\[
\mathbf{u}(\mathbf{R}(n)) = \sum_{m \neq n} \left[ \mathbf{H}^0(\mathbf{R}(n) - \mathbf{R}(m)) (\mathbf{T}(m) + \mathbf{g}(m)) \right. \\
+ \mathbf{H}^0_{el}(\mathbf{R}(n) - \mathbf{R}(m)) (\varepsilon z(m) \mathbf{E}) \left].
\]

We then take the usual convention that \( \mathbf{H}^0(n,n) = I/\xi \) and \( \mathbf{H}^0(n,m) = \mathbf{H}^0(\mathbf{R}(n) - \mathbf{R}(m)) \), and adapt it for the electric part \( \mathbf{H}^0_{el}(n,n) = (\mu_\mu(n)\varepsilon z(n) I) \) and \( \mathbf{H}^0_{el}(n,m) = \mathbf{H}^0_{el}(\mathbf{R}(n) - \mathbf{R}(m)) \), to rewrite (3) in a more explicit form

\[
\frac{\partial \mathbf{R}(n)}{\partial t} = \int_0^N \! dm \mathbf{H}^0_{el}(n,m) \varepsilon z(m) \mathbf{E} + \int_0^N \! dm \mathbf{H}^0(n,m) \\
 \times \left( k \frac{\partial^2 \mathbf{R}(m)}{\partial m^2} + \mathbf{g}(m) \right).
\]

As we want to describe the linear response of the chains, we will use the Kirkwood–Riseman approximation, which consists in replacing both tensors \( \mathbf{H}^0_{el}(n,m) \) and \( \mathbf{H}^0(n,m) \) by their average equilibrium values \( \mathbf{H}^0_{el}(n,m) \) and \( \mathbf{H}^0(n,m) \). These averages are actually scalar tensors which will allow us to simplify notations: \( \mathbf{H}^0_{el}(n,m) = \mathbf{H}^0_{el}(\mathbf{R}(n) - \mathbf{R}(m)) \) and \( \mathbf{H}^0(n,m) = \mathbf{H}^0(n,m) \). respectively. After this preaveraging the equations of motion (5) become

\[
\frac{\partial \mathbf{R}(n)}{\partial t} = \int_0^N \! dm \mathbf{H}^0_{el}(n,m) \varepsilon z(m) \mathbf{E} + \int_0^N \! dm \mathbf{H}^0(n,m) \\
 \times \left( k \frac{\partial^2 \mathbf{R}(m)}{\partial m^2} + \mathbf{g}(m) \right).
\]

Note that for pointlike beads the tensor \( \mathbf{H}^0_{el}(n,m) \) has a rather simple form (see, e.g., Ref. 23)

\[
\mathbf{H}^0_{el}(n,m) = \frac{1}{8 \pi \eta r_D^2} \left( \mathbf{I} + \mathbf{n} \mathbf{n} \right) \exp \left( - \frac{r_D^2}{N} \right),
\]

where \( n \) is the unit vector pointing from \( \mathbf{R}(n) \) to \( \mathbf{R}(m) \) and \( r_D \) is again the Debye length. In this form the above mentioned notion of electrohydrodynamic screening becomes clear: The counterions “screen” the flow created by the electric force on the monomer, but only at distances larger than the Debye radius. At smaller distances, the exponential is roughly 1, and we recover the Oseen tensor \( \mathbf{H}^0_{el} = \mathbf{H}^{av} \). The \( 1/r^3 \) term has disappeared due to the averaging with a spherical symmetry. A rather simple analysis of the complex dynamics of the chain can thus be presented in two opposite limits: (1) the Debye length is much larger than the typical size of the chain \( R_0 \sim Nb \) (low-salt solution) and (2) the Debye length is much smaller than the size of the chain.

In solutions with low concentration of salt the hydrodynamic interaction is unscreened on length scales of the order of the chain size \( r \approx R_0 \leq r_D \), so we can substitute \( \mathbf{H}^{av} \) for \( \mathbf{H}^0_{el} \) in Eq. (6) which becomes

\[
\frac{\partial \mathbf{R}(n)}{\partial t} = \int_0^N \! dm \mathbf{H}^{av}(n,m) \left( k \frac{\partial^2 \mathbf{R}(m)}{\partial m^2} + \varepsilon z(m) \mathbf{E} + \mathbf{g}(m) \right)
\]

with, for a linear chain,

\[
\mathbf{H}^{av}(n,m) = \frac{1}{(6 \pi \eta r_D^2 N^{1/2})^2 \eta b},
\]

whereas for a circular chain

\[
\mathbf{H}^{av}(n,m) = \frac{N^{1/2}}{(6 \pi \eta r_D^2 N^{1/2} (N^{1/2} - 1)^{1/2} \eta b}).
\]

This is the classical Zimm model. If we consider now a polypeptide in a solution with a high content of salt, the hydrodynamic interaction described by \( \mathbf{H}^{av} \) is screened at distances larger than the Debye screening length, \( r_D \), and can thus be effectively reduced to a local contribution. Therefore, Eq. (6) takes the form

\[
\frac{\partial \mathbf{R}(n)}{\partial t} = \int_0^N \! dm \mathbf{H}^{av}(n,m) \varepsilon z(m) \mathbf{E} + \int_0^N \! dm \mathbf{H}^{av}(n,m) \\
 \times \left( k \frac{\partial^2 \mathbf{R}(m)}{\partial m^2} + \mathbf{g}(m) \right).
\]
The Fourier transform $\hat{G}$ of the matrix $G(n,m)$ can be defined the same way as $\hat{H}$ for the matrix $H^{av}(n,m)$ Eq. (15), and is also diagonal $\hat{G}(p,q) = \delta_{p,q} \hat{G}(p)$. Note that $N^{2}\hat{G}(0)\hat{H}(p) = 1$. Using Eq. (10) and definition (15), it is easy to calculate the diagonal elements of the tensor $\hat{H}$

$$\hat{H}(0) = \frac{1}{(6\pi N)^{1/2}} \eta b,$$

and $\hat{H}(p) = \frac{1}{(6\pi N p)^{1/2}} \eta b \delta_{p,q}$.

In particular, $N^{2}\hat{G}(0) = (6\pi)^{1/2} \eta bN^{1/2}$ is the hydrodynamic friction coefficient of a circular chain in the Zimm model.

Using the normal modes we can rewrite Eq. (8) for salt-free solutions

$$\frac{\partial \hat{X}(p)}{\partial t} = -k_{p}^{e} \hat{X}(p) + e \hat{\varepsilon}(p) \hat{E} + \hat{g}(p),$$

and Eq. (11) for high salt solutions

$$\frac{\partial \hat{X}(p)}{\partial t} = \mu(p) \hat{E} + N \hat{H}(p)(-k_{p}^{e} \hat{X}(p) + \hat{g}(p)).$$

In Eqs. (19) and (20) we have introduced

$$k_{p}^{e} = \frac{12\pi^{2} k_{B} T}{N^{2} b^{2}} p^{2}.$$

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$$k_{p}^{e} = \frac{12\pi^{2} k_{B} T}{N^{2} b^{2}} p^{2}.$$
\[ 2N^2 \sum_{q=p}^{+\infty} \hat{G}(p,q) \hat{H}(q,p') = \delta_{p,p'} + \delta_{p,-p'}, \]  

where \( \delta_{p,p'} \) is the usual Kroneker symbol. For a linear chain Eqs. (8) and (11) read in terms of normal mode amplitudes

\[ \frac{\partial \hat{X}(q)}{\partial t} = N \sum_{p=-\infty}^{\infty} \hat{H}(q,p)(-k_p^l \hat{X}(p) + e \hat{z}(p) \mathbf{E}) + \hat{g}(p), \]  

with \( k_p^l = (3 \pi^2 q^2 k_B T)/(N^2 b^2) \). Below, we refer implicitly to definitions and relations (13)–(20) for circular chains and to (21)–(26) for linear chains.

### III. ELECTROPHORESIS OF A POLYAMPHOLYTE IN A SALT-FREE SOLUTION

#### A. General results

Let us establish general results for the electrophoretic motion of a polyampholyte in a salt-free solution for an arbitrary distribution \( z(n) \).

First we consider the case of a circular chain moving with a steady-state average velocity \( \mathbf{V} \). It is easy to see that \( \mathbf{V} \) is the average of \( \partial \hat{X}(0)/\partial t \), whereas for \( p \neq 0 \), the average of \( \partial \hat{X}(p)/\partial t \) is zero as all monomers move, on average, with the same velocity \( \mathbf{V} \). Thus after time averaging, Eq. (19) reads

\[ \mathbf{V} \partial \hat{X}(0)/\partial t = N \hat{H}(0)(-k_p^l \hat{X}(0) + e \hat{z}(0) \mathbf{E}). \]  

The electrophoretic mobility \( \mu \) of the polyampholyte, defined by \( \mathbf{V} = \mu \mathbf{E} \), is obtained from (27) by taking \( p = 0 \)

\[ \mu = \frac{N e \hat{z}(0)}{N^2 \hat{G}(0)} = \frac{Q}{(6 \pi)^{1/2} \eta R_0}. \]  

It is thus the total charge \( e N \hat{z}(0) = Q \) divided by the Zimm hydrodynamic friction coefficient \( N^2 \hat{G}(0) \). The amplitudes of the deformation modes are

\[ \hat{X}(p) = \frac{\hat{z}(p) e \mathbf{E}}{k_p^l}, \quad \text{for} \quad p \neq 0. \]  

The last equation allows us to calculate the deformation of the chain as a function of the charge distribution.

For a linear chain, Eq. (25) reads

\[ N \hat{G}(p,0) \mathbf{V} = -k_p^l \hat{X}(p) + e \hat{z}(p) \mathbf{E}. \]  

The electrophoretic mobility \( \mu \) of the chain is still the ratio of the total charge \( e N \hat{z}(0) = Q \) to the Zimm hydrodynamic friction coefficient \( N^2 \hat{G}(0,0) \)

\[ \mu = \frac{N e \hat{z}(0)}{N^2 \hat{G}(0,0)} = \frac{Q}{\eta R_0}. \]  

The amplitude of the deformation in this case is characterized by

\[ \hat{X}(p) = \frac{\hat{z}(p) e \mathbf{E}}{k_p^l}, \quad \text{for} \quad p \neq 0. \]  

\[ \hat{X}(0) = e \hat{z}(0) \mathbf{E}/k_p^l. \]  

### B. Specific charge distributions

For both circular and linear chains, we consider chains with uniform, periodic and random charge distributions. The uniform and periodic distributions are defined by \( z(n) = z_0 \) and \( z(n) = z_0 \cos \pi n q/N \), respectively. The random distribution of charges \( z(n) \) is characterized by the mean value \( z_0 \) of the charge of a given monomer, its variance \( \sigma^2 \), and a correlation length \( g \) along the backbone which is (expressed in monomers units) given by

\[ \langle z(n) \rangle = z_0. \]  

\[ \langle z(n) z(n') \rangle = \sigma^2 \exp \left( -|n-n'|/g \right). \]

In all cases the electrophoretic mobility \( \mu \) is simply the ratio of the total charge to the friction coefficient. For randomly charged chains it is thus a random variable with mean value \( \langle Q \rangle/(6 \pi \eta R_0) \), where \( \langle Q \rangle = N z_0 \) is the mean value of the total charge of the chains. Using Eqs. (29) and (32), one can characterize in the linear regime the amplitude of the deformation by estimating \( \delta \mathbf{R} = \mathbf{R}(0) - \mathbf{R}(N/2) \) which is the mean value of the algebraic distance between the first and the \( (N/2) \)th monomer. The results are presented in Table I (for more details, see Appendix B).

<table>
<thead>
<tr>
<th>Uniform</th>
<th>Periodic</th>
<th>Random</th>
</tr>
</thead>
<tbody>
<tr>
<td>Circular chain</td>
<td>- ( \frac{e z_0 E}{k_B T} N^2 b^2 )</td>
<td>0</td>
</tr>
<tr>
<td>Linear chain</td>
<td>- ( \frac{e z_0 E}{k_B T} N^2 b^2 )</td>
<td>( \frac{e z_0 E}{k_B T} N^2 b^2 )</td>
</tr>
</tbody>
</table>

\[ k_p^l \hat{X}(p) = \left( -\frac{\hat{z}(0) \hat{G}(p,0)}{\hat{G}(0,0)} + \hat{z}(p) \right) e \mathbf{E}. \]  

The mobility, \( \mu \), in the linear regime considered here, depends only on the total charge of the chain. However, the deformation of the chain depends on the details of the charge distribution. Note that the off-diagonal elements \( \hat{G}(p,0) \) couple the first mode of the charge distribution to all the other modes of deformation. The behavior of this term is crucial for the deformation of the chains in free flow electrophoresis. One can show numerically (see Appendix A and Fig. 3) that for \( p \) even, \( \hat{G}(p,0) \sim \hat{G}(0,0) p^{-\alpha} \), with \( \alpha = 0.75 \), and is positive [for \( p \) odd \( \hat{G}(p,0) = 0 \) for symmetry reasons]. Let us apply now the results of this section to different charge distributions.

### Uniformly charged chain. (Polyelectrolyte)

The deformation of a uniform circular chain in free flow electrophoresis is zero. This result is a direct consequence of the Kirkwood–Riseman approximation: Every monomer plays exactly the same role, and the conformation of the chain
cannot change. In the case of a linear chain, the amplitude of the deformation modes is non-zero, due to the off diagonal elements of the inverse tensor $\hat{G}(p,q)$: In free flow electrophoresis the hydrodynamic and electric forces do not balance locally but on the scale of the coil size. This results in the deformation of the chain. Note that $\delta \mathbf{R}$ points in the direction opposite to $\mathbf{Q}E$, which means that the ends of the chain, on average, lay behind the middle of the chain as they are subject to higher hydrodynamic friction than the rest of the chain. Moreover this deformation has the maximal expected value of the order of the deformation of an attached Gaussian chain of elastic constant $k_{ch} = (3k_BT)/(Nb^2)$ pulled by the total electric force $\mathbf{Q}E$.

**Chain with a periodic distribution of charged monomers.** The amplitude of the deformation of this chain is proportional to the electric force $(N/p_0)\varepsilon_0 E$ acting on a strand of $N/p_0$ consecutive monomers divided by the elastic constant $(k_BT)/(Nb^2)$ of this section. This contribution diminishes with $p_0$ as $p_0^{-2}$, as weaker electric forces are equilibrated on smaller scales. The amplitude of deformation is the same for linear and circular chains. It is the consequence of the vanishing mobility: No hydrodynamic effect is present for these chains of zero total charge.

**Randomly charged chain.** The average deformation of randomly charged circular chains is zero. The charge inhomogeneities induce deformations better characterized by the mean square end-to-middle distance $\langle (\mathbf{R}(0) - \mathbf{R}(N/2))^2 \rangle^{1/2} = (\delta \mathbf{Q})/(k_{ch}E)$, where $\delta \mathbf{Q} = e(N/g)^{1/2} \sigma$ is the typical excess of charge due to the statistical fluctuations and $k_{ch} = (3k_BT)/(Nb^2)$ is the elastic constant of the chain. Note that the quantity $(\delta \mathbf{Q})/(k_{ch}E)$ adds to the thermal noise contribution $Nb^2$. In the case of linear chains, the contribution of the charge inhomogeneities to $\langle (\mathbf{R}(0) - \mathbf{R}(N/2))^2 \rangle^{1/2}$ is negligible compared to the contribution of the mean average charge $Q = Ne\varepsilon_0$ unless the mean charge per monomer $\varepsilon_0$ is very small [cf. Eq. (B8) in Appendix B].

**IV. ELECTROPHORESIS OF A POLYAMPHOLYTE AT HIGH SALT CONCENTRATIONS**

**A. General results**

The steady-state velocity $V$ of a circular chain in a solution with a high concentration of salt can be obtained by time averaging Eq. (20) which leads to

$$V \delta_{p,0} = \hat{\mu}(p)e - N\kappa_p \hat{H}(p) \hat{X}(p)$$

(35)

from which we deduce the electrophoretic mobility $\mu$ of the chain

$$\mu = \hat{\mu}(0) = \frac{1}{N} \int_0^N \mu(n) dn.$$  (36)

Thus within a linear response theory, the mobility of a circular polyampholyte at high salt concentration does not depend on the details of its charge distribution: It is the average value of the local electrophoretic mobility of its individual monomers. Note that this is no more true in the limit of high electric fields, when the chain is strongly deformed. 28,38 The amplitude of the deformation of a circular chain can be obtained in the linear response analysis from Eq. (35)

$$\hat{X}(p) = \frac{NG(p)}{\kappa_p} \hat{\mu}(p)E = (24\pi)^{-1/2} \left( \frac{N}{p} \right)^{3/2} \frac{\eta b_3}{k_BT} \hat{\mu}(p)E.$$  (37)

The motion of a linear chain at high salt concentration is described by Eq. (26), which after averaging reduces at steady state to

$$V \delta_{p,0} = \hat{\mu}(p)e - N \sum_{q=-\infty}^{\infty} \hat{H}(p,q)k_q \hat{X}(q).$$  (38)

The electrophoretic mobility of this linear chain is then

$$\mu = \frac{\sum_{n=0}^{\infty} \hat{G}(0,p) \hat{\mu}(p)}{\hat{G}(0,0)} = \frac{\int_0^N \int_0^N \hat{G}(n,m) \mu(n) dn dm}{\int_0^N \int_0^N \hat{G}(n,m) dn dm}$$

(39)

which we can rewrite

$$\mu = \int_0^N \psi(n) \mu(n) dn,$$  (40)

with the definition

$$\psi(n) = \frac{\int_0^N \hat{G}(n,m) dm}{\int_0^N \int_0^N \hat{G}(n,m) dn dm}$$

(41)

$\psi(n) \mu(n)$ is the contribution of the $n$th monomer to the electrostatic mobility of the chain. As in Sec. III, we see that the behavior of $\hat{G}(0,p)$ or that of $\psi$, which is the inverse Fourier transform of $\hat{G}(0,p)/\hat{G}(0,0)$, are crucial to describe electrophoresis in solutions with a high concentration of salt. The function $\psi$ has a strong $n$-dependence, in particular, $\psi(n) \approx 1/(n\langle N/n \rangle)^B$ with $B=0.25$ for $n\ll N$ (see Appendix A and Fig. 3). This quantifies end-effects, which make Eq. (39) different from Eq. (36) for circular chains. However, this difference between Eqs. (39) and (36) becomes smaller when the chain is heterogeneous only at small length scales as $\hat{G}(0,p) = \hat{G}(0,0)p^{-\alpha}$ with $\alpha \approx 0.75$. Let us now calculate the deformation of the chain. The amplitudes of the deformation modes are

$$\hat{X}(p) = \frac{NG(p)}{\kappa_p} \hat{\mu}(p)e - \hat{G}(0,p)\hat{G}(0,q) \hat{\mu}(q)e,$$

(42)

for $p \neq 0$

which is also different from Eq. (37). Now we can apply the results of this section to different charge distributions.

**B. Specific charge distributions**

As in the case of salt-free solutions, we will consider uniform, periodic and random charge distributions, resulting in a local electrophoretic mobility $\mu(n)$. The uniform and periodic distributions are defined by $\mu(n) = \mu_0$ and $

= \mu_0 \cos(\pi pn/N)$, respectively. The local electrophoretic mobility $\mu(n)$ of the randomly charged chains is a sequence of random variables of average value $\mu_0$ and standard devia-
TABLE II. Electrophoretic mobility of the chains. For linear and periodically charged chains, the result in the table corresponds to even values of $p_0$. For odd values, the mobility is zero by symmetry.

<table>
<thead>
<tr>
<th></th>
<th>Uniform</th>
<th>Periodic</th>
<th>Random</th>
</tr>
</thead>
<tbody>
<tr>
<td>Circular chain</td>
<td>$\mu_0$</td>
<td>0</td>
<td>$\mu_0$</td>
</tr>
<tr>
<td>Linear chain</td>
<td>$\mu_0$</td>
<td>$\approx \mu_0 p_0^{-a}$</td>
<td>$\mu_0$</td>
</tr>
</tbody>
</table>

FIG. 1. High salt concentrations: The circular chain with a periodic mobility distribution $\mu(n) = \mu_0 \cos(2\pi n/N)$ has a zero electrophoretic mobility. If cut at monomer 0 (or $N$), it becomes a linear chain with a nonzero electrophoretic mobility, of the same sign than $\mu_0$, the local electrophoretic mobility of the ends. The figure depicts, e.g., positively charged regions with thick lines.

Periodically charged chain. For linear chains the mobility $\mu$ is nonzero whereas it vanishes for circular chains. This clearly shows that otherwise identical chains can have different electrophoretic mobilities, depending on whether they are circular or linear (Fig. 1). For the present case of a linear periodic chain and for even values of $p_0$, the mobility $\mu$ has the sign of the electrophoretic mobility of the end monomers. Thus we have an example of an object globally neutral which has a non-zero electrophoretic mobility due to geometrical effects. This electrophoretic mobility is entirely due to end-effects. Monomers located close to the ends of the chain are “hydrodynamically” more efficient than monomers in the middle of the chain as they are on average closer to the “surface” of the coil. Note that $\mu$ decreases with increasing $p_0$: End-effects become less important for periodic chains which are heterogeneous only on small length scales.

Consider now the deformation of periodically charged chains. Both linear and circular chains are deformed. The deformation of circular chains can be written as

$$\delta \mathbf{R} = 6\pi \frac{\eta b^3}{k_B T} \frac{N}{p_0} \mu_0 \mathbf{E}.$$

This relation shows that the deformation takes place at the scale of the mobility variation period $N/p_0$, as it can be understood in terms of a force balance between the typical hydrodynamic force exerted on a strand of $N/p_0$ consecutive monomers $6\pi \eta b (N/p_0)^{1/2} \mu_0 \mathbf{E}$ and the elastic restoring force of this section of elastic constant $(p_0 k_B T)/(N b^2)$. For linear chains, $\delta \mathbf{R}$ is proportional to $(6\pi \eta R_0)/(k_B \mu_0 \mathbf{E})$ where $6\pi \eta R_0$ is roughly the hydrodynamic friction coefficient of the coil, $k_B \mu_0$ its elastic constant and $\mu \mathbf{E}$ the velocity of the chain. This deformation is thus similar to that of an attached homogeneous chain with the same electrophoretic mobility $\mu$ pulled by an electric field $\mathbf{E}$. Note that $\delta \mathbf{R} = \mathbf{R}(0) - \mathbf{R}(N/2)$ points in the direction of electrophoretic motion—the chain is pulled by its extremities. As the chain here moves as a whole, hydrodynamic effects at the coil scale are recovered, i.e., the deformation depends on $N/p_0$ and $N$, whereas it depends only on the former for linear chains which have no net electrophoretic mobility. The deformation is actually larger by a factor $p_0^{3/2-a}$ for linear chain.

Randomly charged chain. The electrophoretic mobility of the polyampholyte chain is here a random variable with mean value $\mu_0$ and with variance $\langle \delta \mu^2 \rangle = \sigma^2 (2g/N)$ for both circular and linear chains. The deformation of the chain, as in Sec. III, is better characterized by the mean square end-to-middle distance

$$\langle (\mathbf{R}(0) - \mathbf{R}(N/2))^2 \rangle^{1/2} = \frac{N^2 \langle \hat{G}(0,0) \rangle}{k_{ch}} \frac{g}{N} \sigma \mathbf{E},$$

where $\langle \hat{G}(0,0) \rangle$ is the mean square end-to-end distance of the chain.
which is \((6\pi\eta R_0)/(k_{\text{cb}})(\delta\mu^2)^{1/2}E\). This quantity of course adds up to the thermal noise contribution. In contrast to the case of the salt-free solutions, the deformation of the chain is determined by the charge inhomogenities, as a uniform charge distribution does not contribute to any deformation in electrophoresis in high salt concentration solutions. One can indeed verify that the deformations of a linear and circular chains are similar in this context.

V. DISCUSSION

We have derived general relations that allowed us to calculate in the linear response regime the electrophoretic mobility and the deformation of chains in both salt-free and high salt concentration solutions, as a function of the charge distribution (see Tables I–III). It was demonstrated that hydrodynamic interactions generally play a major role in both type of solutions, and end-effects were emphasized by a systematic comparison between linear and circular chains. The importance of the two points is most clearly illustrated by the two following results: (i) In salt-free conditions a linear uniformly charged chain deforms, contrarily to what a model without hydrodynamic interactions or end-effects would predict, (ii) In the high salt concentration regime, a given sequence of monomers will have a different mobility (even the sign can change) depending on whether it is closed in a circular chain or not. Both effects result from the fact that monomers in the middle of the chain are on average hydrodynamically less exposed to the outside of the coil.

We have assumed (i) that the chain equilibrium conformations are almost Gaussian, which means that the intrachain electrostatic interactions are negligible (either because the chains are weakly charged in salt-free solutions, or because the counter-ions screen these interactions in high salt concentration solutions) and (ii) that chains are only slightly deformed by the external electric field, i.e., we analyzed the linear response regime. Let us now find the range of the parameters (strength of the electric field and fraction of the charged monomers on the polymer chain) for which our approximations are valid.

Salt-free solutions. As mentioned in the introduction, the equilibrium conformational statistics of a polynampholyte is determined by the balance between its entropy and the electrostatic interaction between its charged monomers. The condition for which the latter is negligible compared to the former have been analyzed in the literature (see, e.g., Ref. 16) so we here only sketch the results:

— for almost neutral chains \((N^+ \approx N^-)\) the fluctuation induced attraction is negligible if the fraction \(f = (N^+ + N^-)/N\) of charged monomers verifies \(f \leq (b/l_B)N^{-1/2}\), where \(l_B = e^2/(\varepsilon k_B T)\) is the Bjerrum length (about 7A for water at room temperature).

— for a chain with a larger charge unbalance \(\Delta f = |N^+ - N^-|/N\), the electrostatic repulsion can be safely neglected if

\[\Delta f \leq \Delta f_c = (b/l_B)^{1/2}N^{-3/4}.\]

Note that for long chains this is very restrictive: for a Kuhn length of order \(b = 5\)A, and a degree of polymerization \(N = 10^4\), this leads to \(\Delta f_c = 10^{-3}\).

We have seen in Sec. III that we expect the deformation to be dominated by the effect of the total charge \(Q = N\Delta f\). The deformation \(\delta R\) of an asymmetric polynampholyte chain with a charge asymmetry \(\Delta f \approx \Delta f_c\) in an external electric field is proportional to

\[\delta R = \frac{N b^2}{k_B T} Q E = \left(\frac{b l_B}{N}\right)^{1/2} \frac{e b^2}{k_B T} E.\]

For this deformation to be smaller than the Gaussian size of the chain \(R_0 = N^{1/2}b\), the electric field has to be smaller than

\[E < E_c = (b l_B)^{1/2} \frac{N^{-3/4} k_B T}{e b}.\]

For a chain with bond length \(b = 5\)A, degree of polymerization \(N = 10^4\), and a charge unbalance \(\Delta f \approx 10^{-3}\) the critical field \(E_c\) is of the order of \(10^3 \text{V/cm}\) which is a quite high value. So our formalism seems to apply quite safely in salt-free conditions for (very) weakly charged chains.

Solutions with a high concentration of salt. From Sec. IV, the largest deformation is obtained for an alternating polynampholyte made of monomers with local electrophoretic mobility \(\mu(n) = \mu_0 \cos(\pi \nu n/N)\) with \(\mu_0\) small. The amplitude of the deformation is given in Table III. For this deformation to be smaller than the equilibrium coil radius \(R_0\), one must have (for \(p_0\) of order 1)

\[E < E_c = \frac{k_B T}{6\pi \eta \mu_0 Nb}.\]

Note that \(\mu_0\) is typically at most of the same order than the mobility of small ions, i.e., \(\mu_0 \approx 10^{-7} - 10^{-8} \text{ms}^{-1}/(\text{V/m})\). Taking again \(b = 5\)A and \(N = 10^4\), this leads to a critical field of order \(E_c \approx 10^{-1} - 1 \text{V/cm}\). This value is quite high although within the range of field amplitudes used in capillary electrophoresis. Note, however, that the threshold \(E_c\) decreases as chain rigidity increases, and that there are many examples of quite rigid chains in solutions of high ionic strength. A well studied case is DNA, for which \(b\) is of order 100 nm. Thus a DNA fragment of about a 100 kilobase-pairs \((N = 300\) Kuhn lengths\) attached to a neutral object\(^{28}\) would start to deform appreciably for fields as low as \(E_c \approx 10^{-1} - 1 \text{V/cm}\). So the range of validity of the linear response theory crucially depends on the chain flexibility.

Our approach could be extended to chains with non-Gaussian equilibrium conformations. An obvious possibility is chains with excluded volume interactions. An other direction would be to consider chains strongly deformed by electrostatic interactions, such as extended chains in salt-free solutions, with an end-to-end distance proportional to the degree of polymerization of the chain. For all these situations, the basic formalism is the same, and only the actual calculation of the tensors \(H^{av}\), \(H_{0}^{av}\), and of their inverses and Fourier transforms would have to be adapted to the situation at hand.
APPENDIX A: END EFFECTS

Let us describe in some more detail the structure of \( \hat{H}(p,q) \), the Fourier transform of the preaveraged Oseen tensor \( H^{nm}(n,m) \), for a linear chain. From Eqs. (9) and (23),

\[
\hat{H}(p,q) = \int_0^N \int_0^N \cos(p \pi n/N) \cos(q \pi m/N) \frac{dn}{n-m}^{1/2}
\]

which can be rewritten

\[
\hat{H}(p,q) = \int_0^1 dx \int_0^1 dy \frac{\cos(p \pi x) \cos(q \pi y)}{|x-y|^{1/2}}
\]

From this one can get information on the diagonal components, \( \hat{H}(0,0) \), and for large values of \( p \), asymptotically,

\[
\hat{H}(0,0) = \frac{8N^{-1/2}}{3(6 \pi)^{1/2} \eta b}
\]

and for large values of \( p \), asymptotically,

\[
\hat{H}(p,0) \approx \frac{p^{-1/2}N^{-1/2}}{(12 \pi)^{1/2} \eta b}
\]

But one can also derive the asymptotic behavior of some nondiagonal components, responsible for the end-effects described in the article; for example, for large values of \( p \),

\[
\hat{H}(p,0) \approx -\frac{1+(-1)^p}{(12 \pi)^{1/2} \eta b} N^{-1/2} p^{-3/2}
\]

as can be seen from (A2) and

\[
\int_0^1 dx \int_0^1 dy \frac{\cos(p \pi x)\cos(q \pi y)}{|x-y|^{1/2}}
\]

\[
= 2 \int_0^1 dx \cos(p \pi x) (x^{1/2} + (1-x)^{1/2})
\]

\[
= -\frac{1+(-1)^p}{\pi bp^{3/2}} \int_0^p du \sin(\pi u)u^{1/2}
\]

with the last integral converging to \( 2^{-1/2} \) as \( p \to \infty \).

Let us now consider \( \psi(n) \) which describes the weight of monomer \( n \) to the electrophoretic mobility in very salty solutions. From its definition (41) (and the structure of \( G(n,m) \)), \( \psi \) must be self-similar in the sense that

\[
\psi(n) = \frac{1}{N} \Psi(n/N),
\]

where \( \Psi \) is a universal function on [0,1]. It is indeed what we obtained by numerically inverting \( H^{nm}(n,m) \) for various large values of \( N \) (see Fig. 2). Note that \( \Psi \) is obviously not constant. End effects are clearly visible and can be quantified numerically: \( \Psi(x) \sim x^{-\beta} \) as \( x \to 0 \), with \( \beta = 0.25 \) (Fig. 3).

Eventually, we turn to \( \hat{G}(p,q) \). In scaling form, we can write from (23) and (24) that \( \hat{G}(p,q) = \eta b N^{-3/2} f(p,q) \), but it is difficult to go further. However, by Fourier transforming the (numerically) calculated \( \psi(n) \) we obtain \( \hat{G}(0,p) \). It is clearly zero for odd values of \( p \) and for even values it scales as

\[
\hat{G}(0,p) \approx \hat{G}(0,0)p^{-\alpha}
\]

with \( \alpha = 1 - \beta = 0.75 \). These terms are all positive.

APPENDIX B: SALT-FREE SOLUTIONS

Let us calculate the deformation of a uniformly charged linear chain. The amplitude of the normal modes quantifying
this deformation are given by Eq. (32) with \( \dot{z}(p) = 0 \) for \( p \neq 0 \). From the scaling behavior of \( G(0,p) \) and the inversion formula (22), one obtains

\[
\delta R = - \left( \sum_{p=1}^{\infty} p^{-2} a(1 - \cos(p \pi/2)) \right) \frac{N b^2}{3 \pi^2 k_B T} \frac{Q E.}{(B1)}
\]

Now we turn to a linear chain with a periodic charge distribution \( z(n) = z_0 \cos(p_0 n \pi/N) \) with \( p_0 \neq 0 \). This chain is globally neutral and has a zero mobility. It however deforms according to (32) so that

\[
\hat{X}(p) = \frac{z_0 N^2 b^2}{3 \pi^2 k_B T N_p^2} \frac{1}{2} \left( \delta_{p,p_0} + \delta_{p,-p_0} \right) e E.
\]

Using again the inversion formula (22) this leads to

\[
R(N) - R(0) = \frac{z_0 N^2 b^2}{3 \pi^2 k_B T} \frac{1 - (-1)^{p_0}}{N_p} e E.
\]

Eventually we take the random charge distribution defined by (33) and (34). Its Fourier modes \( \hat{z}(p) \) are then also Gaussian random variables with

\[
\langle \hat{z}(p) \rangle = z_0 \delta_{p,0}, \quad (B4)
\]

\[
\langle \hat{z}(p) \hat{z}(p') \rangle = \langle \hat{z}(p) \rangle \langle \hat{z}(p') \rangle = \frac{\sigma^2 g N}{N^2 + \pi p^2 g} \left( \delta_{p,p'} + \delta_{p,-p'} \right)
\]

\[
= \frac{\sigma^2 g}{N} \left( \delta_{p,p'} + \delta_{p,-p'} \right). \quad (B5)
\]

The last relation is valid for small values of \( p \), which are the most important ones. In particular, the total charge of the chain \( Q = N \hat{z}(0) \) is also a Gaussian variable of mean value \( \langle Q \rangle = N z_0 \) and standard deviation \( \delta Q = (2 g N)^{1/2} \sigma \). From (32) the mean value of the deformation modes are given by

\[
\langle \hat{X}(p) \rangle = \frac{\hat{G}(p,0)}{N k_p G(0,0)} \langle Q \rangle E. \quad (B6)
\]

with \( k_p = k_p^0 \) or \( k_p^c \) depending on the situation. The deformation is thus the same than that of a uniformly charged chain of total charge \( \langle Q \rangle \). Let us now look at the effects of the inhomogeneities of the charge distribution along the backbone. An easy variable to characterize them is their contribution to the mean square distance between two monomers. For example,

\[
\langle (R(N/2) - R(0))^2 \rangle = \sum_{p=1}^{\infty} \langle \hat{X}(p) \hat{X}(p) \rangle = \langle \hat{X}(p) \hat{X}(p) \rangle.
\]

Then from (32),

\[
\langle (R(N/2) - R(0))^2 \rangle = \left( \sum_{p=1}^{\infty} p^{-4} \frac{\sigma g^{1/2} N^{3/2} b^2}{k_B T} \right) \frac{(R(0))^2}{k_p G(0,0)} \frac{1}{N} \mu_0. \quad (B7)
\]

\[
\sim \sum_{p=1}^{\infty} p^{-4} \frac{\sigma g^{1/2} N^{3/2} b^2}{k_B T} \frac{1}{k_p G(0,0)} \frac{1}{N} \mu_0. \quad (B8)
\]

The first term of the right-hand side is the only term contributing for circular chains, whereas the second one usually dominates for linear chains (i.e., unless the mean charge per monomer is very small).

**APPENDIX C: HIGH SALT CONCENTRATION**

We will deal here with charged chains in solutions of high ionic strength, using the general formulas of Sec. IV A.

Let us take first a circular chain with a periodic charge distribution: The mobility of the \( n \)th monomer is \( \mu(n) = \mu_0 \cos(2 p_0 n \pi/N) \) with \( p_0 \neq 0 \) (note the 2 introduced for convenience). Then \( \hat{\mu}(p) = \delta_{p,p_0} + \delta_{p,-p_0} \mu_0/2 \) and according to (36) the mobility of the chain is zero. Using (37) and the inversion formula (14) we obtain

\[
R(0) - R(N/2) = 2 \hat{X}(p_0)(1 - (-1)^{p_0})
\]

\[
= (1 - (-1)^{p_0}) \frac{\eta b^3}{(24 \pi)^{1/2} k_B T} \times \left( \frac{N}{p_0} \right)^{3/2} \mu_0 E. \quad (C1)
\]

Let us now consider a linear chain with a periodic mobility distribution: \( \mu(n) = \mu_0 \cos(p_0 n \pi/N) \). Due to end-effects it will have a non zero average mobility (for even values of \( p_0 \) given by

\[
\mu = \mu_0 \frac{\hat{G}(0,p_0)}{G(0,0)}
\]

\[
= \mu_0 \frac{\hat{G}(0,p_0)}{G(0,0)} \quad (C2)
\]

which for large \( p_0 \) scales according to Eq. (A6) in Appendix A as \( \mu \propto \mu_0 p_0^{-a} \).

From (42), the distortion of the chain is described by

\[
\hat{X}(p) = \frac{N k_p}{k_p^c} \frac{\hat{G}(p,0) - \hat{G}(p,0)}{G(0,0)} \mu_0. \quad (C3)
\]

Take large values of \( p_0 \). Then, for \( p < p_0 \), we expect \( \hat{G}(p,p_0) \) to be of the same order than \( \hat{G}(0,p_0) \), and thus that the second term in the parenthesis of Eq. (63) above is at most of the same order of magnitude. This leads to a result of the form

\[
\hat{X}(p) \sim \frac{N^2}{k_p^c} \hat{G}(0,0) p_0^{-a} \mu_0 E.
\]

The typical extension of the chain is then

\[
R(0) - R(N/2) \sim \frac{N^2}{k_p^c} \hat{G}(0,0) p_0^{-a} \mu_0 E. \quad (C5)
\]
We now address the case of a random polyampholyte: \( \hat{\mu}(p) \) are then random variables which satisfy equations analogous to (B4) and (B5). The mobility of the chain is thus a random variable described by (39), of mean value \( \langle \mu \rangle \equiv \mu_0 \) and of variance
\[
\langle \delta \mu^2 \rangle = \frac{1}{G^2(0,0)} \sum_{p=-\infty}^{+\infty} \sum_{p'}^{-\infty} \hat{G}(0,p)\hat{G}(p',0) \times \langle (\hat{\mu}(p)\hat{\mu}(p')) - \langle \hat{\mu}(p) \rangle \langle \hat{\mu}(p') \rangle \rangle
\]
so that \( \langle \delta \mu^2 \rangle \approx 2g\sigma^2/N \).

The deformation is described by Eq. (42). Note that the electrophoretic mobility component \( \hat{\mu}(0) \) does not contribute to any deformation mode \( \hat{X}(p) \): We recover the fact that uniformly charged chains do not deform at high salt concentrations. Note also that the algebraic end-to-end distance has a zero average as \( \langle \hat{X}(p) \rangle = 0 \). The deformation is thus better characterized by its mean quadratic value, which in scaling form is roughly
\[
\langle (R(N) - R(0))^2 \rangle \approx \frac{N^2 g\sigma^2 \hat{G}^2(0,0)}{k_{ch}} E^2.
\]