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## A Zimm model for polyelectrolytes in an electric field

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**Abstract.** By linearizing the electro-hydrodynamic equations and using general arguments, we have recently described the deformation and drift of a polyelectrolyte in solution under the simultaneous action of an electric field and a non-electric force, and obtained results qualitatively different from previous theories. We show here how one can adapt the Zimm model to obtain a more operational description for such problems, which allows us to recover our previous results in a simple way and could be used to describe more general situations such as transient phenomena or the electrophoresis of a polyampholyte.

We are interested here in the motion and the deformation of polyelectrolyte chains in solutions at high salt concentration. In such solutions, the Debye length (i.e. the range of the electrostatic interactions) is small. The backbone of the chain is surrounded by a thin sheath of counterions, which screen the electrostatic interactions between the monomers of the chain. Its equilibrium conformation can then be described by a random walk [1, 2]. The end-to-end distance of the chain,  $R$ , scales as  $N^\nu$ , where  $N$  is the polymerization index of the chain and  $\nu = 0.5$  in the case of a Gaussian chain which will be considered here. Under the action of neutral forces (sedimentation), the chain behaves essentially as a neutral polymer and can be described by the Zimm model [3, 4]. In this model, the chain is represented as a succession of beads linked by entropic springs. Long-range hydrodynamic interactions between the monomers are taken into account, which gives rise to collective effects. For forces small enough that the conformation of the chain is close to the equilibrium one, the hydrodynamic friction scales as the end-to-end distance or as  $N^\nu$  without any reference to a monomeric friction. In this small-force regime, the chain deforms linearly from its equilibrium conformation. At higher forces the chain deforms strongly and can even reach full extension when pulled e.g. by one end in the solvent.

The behaviour of the chain under the action of an electric field (electrophoresis) is very different. The electric field pulls the chain in one direction and the counterions in the opposite one. This effect cancels the long-range hydrodynamic interactions between the monomers, and the collective effects vanish. Electric and hydrodynamic forces balance locally, which has two consequences: the electrophoretic mobility is independent of the size and the chain is not deformed in electrophoresis conditions, even in a strong field.

When an electric field and a neutral force act simultaneously, features of sedimentation and electrophoresis are both present. By linearizing the electro-hydrodynamic equations, and using general arguments, we have proven recently [5, 6] that the deformation of an end-tethered chain submitted to an electric field  $E$  is the one it adopts when submitted to a

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uniform flow of solvent at velocity  $V = \mu E$ , and that the force exerted by the anchoring point on the chain is  $f_{ch}\mu E$ , where  $f_{ch}$  is the hydrodynamic friction of the chain in the adopted conformation. In particular, in the small-force regime, where the chain is only slightly deformed, this force is proportional to the unperturbed radius and thus scales as  $N^\nu$ .

The aim of this paper is to propose a more operational model, derived from the Zimm model, to deal with the deformation and drift of polyelectrolytes under the simultaneous action of an electric field and a non-electric force, in the small-Debye-length regime. This model allows us to obtain in a different way our previous results and provides a general frame for an analytical or numerical treatment of more complex systems. First we derive our model which is then applied to the case of a uniform polyelectrolyte. To illustrate the broader applicability of our model we then show how it allows us to describe the electrophoresis of a diblock polyelectrolyte.

Let us derive our model. Consider first a uniformly charged sphere in a solution. We assume that the sphere is an insulator, that its radius  $a$  is much larger than the Debye length of the solution, and that the surface potential  $\zeta$  is small i.e.  $e\zeta/k_B T \ll 1$ . Under the action of an electric field  $E$ , the sphere moves at a velocity  $\mu E$ , where the electrophoretic mobility  $\mu$  of the sphere is given by [7]  $\mu = \varepsilon\varepsilon_0\zeta/\eta$ , where  $\varepsilon\varepsilon_0$  and  $\eta$  are the dielectric permittivity and the viscosity of the solvent respectively. The action of the electric field induces a hydrodynamic flow in the solution, which is given, in the frame of the solution and beyond the Debye layer, by [8]

$$\begin{aligned} V_r(r, \theta) &= \mu E_0(a^3/r^3) \cos \theta \\ V_\theta(r, \theta) &= \mu E_0 \frac{1}{2}(a^3/r^3) \sin \theta \end{aligned} \quad (1)$$

and is rapidly decaying ( $r^{-3}$ ). Let us now pull the sphere by an additional neutral force  $F$ . Due to the linearity of the electrohydrodynamic equations (at first order), the particle moves at a velocity  $\mu E + F/6\pi\eta a$  while the induced hydrodynamic flow is the sum of equation (1) and of a Stokes flow:

$$\begin{aligned} V_r(r, \theta) &= \mu E_0(a^3/r^3) \cos \theta + (F/6\pi\eta a) \left[ \frac{3}{2}a/r - \frac{1}{2}a^3/r^3 \right] \cos \theta \\ V_\theta(r, \theta) &= \mu E_0 \frac{1}{2}(a^3/r^3) \sin \theta - (F/6\pi\eta a) \left[ \frac{3}{4}a/r + \frac{1}{4}a^3/r^3 \right] \sin \theta. \end{aligned} \quad (2)$$

Consider now the Zimm model for polymers in a pure sedimentation situation. The molecule is represented as a chain of  $N$  connected beads. Along the chain, there is a tension  $T(m)$  at the  $m$ th bead (algebraic convention: it is the force exerted by the  $m$ th on the  $(m-1)$ th bead). Note that  $T(1) = T(N) = 0$ . Thus the total force exerted on the  $m$ th bead by its neighbours is  $\Delta T(m) = T(m+1) - T(m)$ . Under the action of a force  $f(m)$  on the  $m$ th bead, this bead reaches a velocity equal to the force divided by the bead friction and generates a long-range flow in the solution ( $r^{-1}$  term in equations (2)). The velocity of the  $n$ th bead is then  $\partial R(n)/\partial t = \sum_m H(n, m)[\Delta T(m) + f(m) + g(m)]$  where  $H(n, m)$  is the Oseen tensor which describes the hydrodynamic interaction between the monomers [3,4],  $R(n)$  is the position of the  $n$ th monomer and  $g(m)$  is the thermal noise. Note that  $R(n)$ ,  $\Delta T(m)$ ,  $f(m)$  and  $g(m)$  are vectors. The Oseen tensor derives from the long-range component of the Stokes flow and decays like the inverse of the distance between two segments, with the convention that  $H(n, n)$  is the inverse of the friction coefficient of one bead. Consider a Gaussian chain at equilibrium. If one neglects end effects, the sum  $\sum_n H(n, m)$  is independent of  $m$  and the velocity of the chain is given by

$V \cong F(1/N)[\sum_{n,m} H(n, m)]$  where  $F$  is the total force  $\sum_m f(m)$ . One has thus

$$V \cong F \frac{1}{N} \left[ \frac{1}{\zeta} + \int_a^{aN^{1/2}} \frac{1}{\eta r} g(r) r^2 dr \right] = F \frac{1}{N} \left[ \frac{1}{\zeta} + \int_a^{aN^{1/2}} \frac{1}{\eta a^2} dr \right] \quad (3)$$

where  $g(r)$  is the correlation function between monomers in the coil which scales as  $r^{-1}$ . The term  $1/\zeta$  corresponds to the mobility of a single monomer and the integral corresponds to the collective effect due to the hydrodynamic interactions between the monomers. Due to the slow decay of the hydrodynamic interactions the contribution of the off-diagonal terms is dominant for long chains as the integral in equation (3) is diverging. Thus the hydrodynamic friction of the polymer coil  $\cong [(1/N) \sum_{n,m} H(n, m)]^{-1}$ , scales as  $N^{1/2}$  in the equilibrium conformation. For a polyelectrolyte of Gaussian conformation in pure electrophoresis conditions, one obtains in an analogous way  $V \cong \mu E + \mu E a^3 \int_a^{aN^{1/2}} dr/a^2 r^2$ . In contrast to the case of sedimentation, due to the rapid decrease of the hydrodynamic interactions under pure electrophoresis conditions ( $r^{-3}$ ) and to the tenuous nature of a polymer, the integral here is convergent at large  $N$  [9]. Thus the role of the collective terms amounts at most to a redefinition of the electrophoretic mobility, which depends on the conformation of the chain at small length scale only [1, 9]. The electrophoretic mobility of the chain is thus a local property: the hydrodynamic interactions of particles in pure electrophoresis conditions are short range in the sense that no collective effects build up. Thus, under both neutral and electric forces, the velocity of the beads is given by

$$\frac{\partial R(n)}{\partial t} = \mu(n)E + \sum_m H(n, m)[\Delta T(m) + f(m) + g(m)] \quad (4)$$

where  $\mu(n)$  is the electrophoretic mobility of the  $n$ th monomer. This equation is the central result of this paper. The main points to obtain equation (4) are that the electric field acts only locally (in the high-salt-concentration regime), and that both electric and non-electric effects superimpose linearly. Note that the mobility  $\mu(n)$  depends on the conformation of the chain at small-length scale around the  $n$ th monomer. Thus equation (4) is valid whatever the conformation of the chain, provided the chain is not deformed (or only slightly) at the small-length scale on which is defined the electrophoretic mobility. To take the thermal noise into account, we make the so-called preaveraging approximation by replacing  $H(n, m)$  by the value of this tensor in the typical average conformation of the molecule, which we will still denote by  $H(n, m)$  [4], and we put  $g(m) = 0$  in the following.

Let us first apply our model to a uniform polyelectrolyte (i.e.  $\mu(n) = \mu$ , independent of the monomer) submitted simultaneously to electric and non-electric forces. The chain can deform and acquire a new conformation. At steady state, all the velocities  $\partial R(n)/\partial t$  are equal to the velocity  $V$  of the chain. Thus equation (4) reads, for each value of  $n$ ,

$$\Delta T(n) + f(n) = \left[ \sum_m G(n, m) \right] (V - \mu E) \quad (5)$$

where  $G(n, m)$  is the inverse of the tensor  $H(n, m)$ . Formally, one could calculate the conformation by solving self-consistently the equations (5) where  $G(n, m)$  depends on the conformation, which in turn depends on the tension  $\Delta T(n)$ . This calculation is not an easy task, but some general results can be obtained. Indeed, these equations (5) depend only on the difference  $V - \mu E$ . We deduce from this that the deformation of an immobilized chain, i.e.  $V = 0$ , subjected to an electric field  $E$  and to a given distribution of neutral forces, is the same as the deformation of a chain pulled in the solvent at velocity  $-\mu E$  and subjected to the same distribution of neutral forces in the absence of the electric field, i.e.  $E = 0$  [5, 6]. When the forces are small, the conformation is the equilibrium one and one finds that

$F = [\sum_{n,m} G_{eq}(n, m)](V - \mu E)$  where  $F$  is the total neutral force acting on the molecule. The quantity  $\zeta_{eq} = \sum_{n,m} G_{eq}(n, m) \cong [(1/N) \sum_{n,m} H_{eq}(n, m)]^{-1} \cong 6\pi\eta R$  is the usual hydrodynamic friction in the chain equilibrium conformation as calculated by Zimm [3]. In particular the force  $F_h$  to hold the chain immobile in an electric field is  $-\zeta_{eq}\mu E$ , which scales as  $N^{1/2}$  [5, 6].

Let us now apply our model to a diblock copolyelectrolyte, where it will allow a more systematic description than the simple one presented in [10]. The molecule is composed of two charged chains, made up of segments of electrophoretic mobilities  $\mu_1$  and  $\mu_2$  and of polymerization indices  $N_1$  and  $N_2$  respectively ( $N = N_1 + N_2$ ). Then, under the action of an electric field and neutral forces, the motion of the chain is described by the equations (4), with  $\mu(n) = \mu_1$  if  $n \leq N_1$  and  $\mu(n) = \mu_2$  if  $n > N_1$ . We consider first the case of pure electrophoresis ( $f(n) = 0$ ) in a small electric field. Then the chain is not deformed and one can calculate the velocity using the equilibrium conformation. In the permanent regime, the velocity is given by

$$V = \frac{[\sum_{n,m \leq N_1} G_{eq}(n, m)]\mu_1 + [\sum_{n,m > N_1} G_{eq}(n, m)]\mu_2}{\sum_{n,m} G_{eq}(n, m)} E. \quad (6)$$

This quantity is not easy to calculate exactly. However, for large chains, one can neglect end effects [4]. Then  $\sum_n G_{eq}(n, m)$  is essentially independent of  $m$  and the velocity  $V$  is given by

$$V = \frac{N_1\mu_1 + N_2\mu_2}{N} E. \quad (7)$$

Consider now the case of a high electric field. We consider a field sufficiently high that the two different parts of the chain are separated due to the different mobilities, with one part pulling the other. As the two different parts of the chain are separated, we neglect hydrodynamic interactions between them. Thus equation (4) for a segment of the first block becomes  $\partial R(n)/\partial t = \mu_1 E + \sum_{m=1}^{N_1} H(n, m) \Delta T(m)$ . For each block, the situation is very similar to the case of a uniform polyelectrolyte, the only difference being the non-vanishing tension at one end of each block. One obtains for the tension at the  $N_1$ th segment

$$T(N_1) = \left[ \sum_{(n,m) \leq N_1} G(n, m) \right] (V - \mu_1 E) = - \left[ \sum_{(n,m) > N_1} G(n, m) \right] (V - \mu_2 E). \quad (8)$$

The velocity of the molecule is then given by [10]

$$V = \frac{\zeta_1\mu_1 + \zeta_2\mu_2}{\zeta_1 + \zeta_2} E \quad (9)$$

where we have denoted by  $\zeta_1$  and  $\zeta_2$  the hydrodynamic friction  $\sum_{(n,m) \leq N_1} G(n, m)$  and  $\sum_{(n,m) > N_1} G(n, m)$  of each block of the chain in their stretched conformation.

In conclusion, we have proposed a Zimm model for polyelectrolytes in an electric field, which allows us to describe their deformation and drift in a more operational way than our previous analysis. This model allows for more quantitative studies and could be used to describe more complex situations such as transient effects, or the electrophoresis of a polyampholyte chain, which we wish to address in a forthcoming publication.

## References

- [1] Barrat J L and Joanny J F 1996 *Adv. Chem. Phys.* **94** 1
- [2] De Gennes P G 1979 *Scaling Concept in Polymer Physics* (Ithaca, NY: Cornell University Press)
- [3] Zimm B H 1956 *J. Chem. Phys.* **24** 269

- [4] Doi M and Edwards S F 1986 *The Physics of Polymer Dynamics* (Oxford: Oxford University Press)
- [5] Long D 1996 *PhD Thesis* Université Paris XI
- [6] Long D, Viovy J-L and Ajdari A 1996 *Phys. Rev. Lett.* **76** 3858
- [7] Russel W B, Saville D A and Schowalter W R 1989 *Colloidal Dispersions* (Cambridge: Cambridge University Press)
- [8] Levich V G 1962 *Physicochemical Hydrodynamics* (Englewood Cliffs, NJ: Prentice-Hall)
- [9] Ajdari A 1992 *PhD Thesis* Université Paris VI
- [10] Long D and Ajdari A 1996 *Electrophoresis* **17** 1161