Simultaneous Action of Electric Fields and Nonelectric Forces on a Polyelectrolyte: Motion and Deformation

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We describe the deformation and drift of a charged polymer in solution under the simultaneous action of an electric field and a nonelectric force. This should be of interest for current micromanipulation experiments on DNA fragments and for electrophoretic separation methods. Our description is qualitatively different from existing theories. The main results are (i) that the force to hold a polyelectrolyte immobile in an electric field $\mathbf{E}_\infty$ is proportional to its 3D size (and not to its curvilinear length or total charge), and (ii) that its deformation is then essentially identical to that in a purely hydrodynamic uniform flow of velocity $\mathbf{V} = \mu_{\mathrm{el}}\mathbf{E}_\infty$ (μ_{el} is the electrophoretic mobility of the polyelectrolyte). [S0031-9007(96)00185-8]

Micromanipulation of "soft" objects (DNA, vesicles, filaments, motor-coated beads) in aqueous buffers is a very trendy theme in current condensed matter physics [1–5]. It has been prompted by the development of experimental techniques, allowing the manipulation (by optical tweezers, micropipettes, etc.) and the direct visualization of single objects in various situations (fluorescence, phase contrast, etc.). DNA fragments have been the subject of considerable attention as, in addition to their biological importance, they are individually observable model polymers [1,2,5].

Electric fields constitute an interesting way to induce motion and deformation of such polyelectrolytes (charged polymers) to probe their structure and properties. Electrophoresis (i.e., the motion under the sole action of an electric field) in various media is furthermore the leading separation technique of these charged macromolecules [6,7]. Its theoretical analysis even in solution is on a theoretical standpoint quite difficult, as it combines features specific of polymer physics to the intrinsic complexity of electrokinetic phenomena [8].

In this Letter we consider an even more general situation: a polyelectrolyte under the *simultaneous* effect of an electric field $\mathbf{E}_\infty$ and a nonelectric force $\mathbf{F}$. Not only is this a theoretically challenging problem, but it is of direct relevance for recent electrophoretic DNA separation methods and for micromanipulation experiments where a polyelectrolyte is moved or held immobile in an electric field: The presence of the counterions generically induces a hydrodynamic flow *that may or not be visible depending on the visualization technique*, but induces shear forces, drag, and deformation of the visible polyelectrolyte anyway. Although the problem at hand is complex and very nonlinear [9], we propose for a given conformation of the chain to linearize the coupled electrohydrodynamic equations (CEHE), so that by an appropriate superposition of situations in which only the force or only the electric field acts, we are able to make quantitative predictions that should be experimentally testable and that disagree with

the formalism used in earlier analysis [10–12]: (i) The stall force $\mathbf{F}_0$ to immobilize a coily polyelectrolyte under an electric field is proportional to its spatial size (and not to its curvilinear length); (ii) a hydrodynamic-electric (HE) equivalence that, in particular, predicts that an end-anchored polyelectrolyte deforms in a similar way in an electric field $\mathbf{E}_\infty$ and in a hydrodynamic flow at velocity $\mathbf{V}_\infty = \mu_{\mathrm{el}}\mathbf{E}_\infty$ (where μ_{el} is the electrophoretic mobility of the polyelectrolyte). We stress that these predictions require linearization of the CEHE, but not that the deformation of the chain remains in its linear elasticity domain.

The outline of this Letter is as follows. We first recall the behavior of a polyelectrolyte under the sole force $\mathbf{F}$ or the sole electric field $\mathbf{E}_\infty$, and stress the differences between the two cases. We then describe the result of their simultaneous action, in the regime when linearization of the CEHE holds, successively for low and high deformation of the polyelectrolyte. Eventually, in a brief discussion we point out the differences between our predictions and earlier ones, the relevance of our results for different practical situations and for other deformable soft objects.

Take a linear polyelectrolyte of uniform linear charge density λ, local radius a, persistence length L_p (characterizing its rigidity), and overall curvilinear length L (proportional to its polymerization index). L and L_p are taken much larger than the thickness κ^{-1} of the sheath of counterions that surrounds the backbone. We will consider here long polyelectrolytes ($L \gg L_p$) so that their average unperturbed morphology is coil-like of radius $R \simeq L_p(L/L_p)^\nu$, with $\nu = 1/2$ for ideal chains and $\nu \simeq 3/5$ if excluded volume effects are important [13]. The description of dynamical properties of polyelectrolytes is difficult on many grounds (for a recent review see [14]), but a few generic features are presented below.

A weak nonelectric force $\mathbf{F}$ uniformly applied to the chain will induce its motion at a velocity $\mathbf{U_F}$ proportional to $\mathbf{F}$. In many cases the deformation of the counterion cloud can be neglected so that the resulting electric

"retardation effect" can be neglected [8,14]. Therefore the polyelectrolyte behaves as a neutral polymer would: Hydrodynamic interactions between monomers separated by a distance r decay as $\simeq a/r$, so that a collective response builds up [13]. The polyelectrolyte is opaque to flow, and its friction coefficient $\xi = \mathbf{F}/\mathbf{U_F}$ is given by a Stokes formula with a hydrodynamic radius roughly similar to R so that $\xi \simeq 6\pi\eta R$ up to a prefactor of order unity (η is the solvent viscosity).

Note that the force $\mathbf{F}$ can be distributed inhomogeneously between the monomers. An extreme case of practical interest corresponds to a force $\mathbf{F}$ applied at only one extremity. One then expects the chain to deform, with tension increasing from zero at the free end to $F = |\mathbf{F}|$ at the pulled one [15,16]. When $F > k_B T/R$, the chain elongates in a quantitative manner (in a "trumpet" shape in this force geometry) to reach a length l. The conformation, and thus the effective friction coefficient, will then depend on F, with typically $\xi \simeq 6\pi\eta l$. Note that this problem is identical to the extension of an end-anchored chain in a uniform flow, which has recently been the object of both theoretical and experimental studies [1,12,16].

Let us now consider pure electrophoresis of polyelectrolytes. It is a difficult problem from a colloid physicist point of view as one of their dimensions (L) is usually much larger than the Debye length κ^{-1}, while a is typically comparable to it. This prevents the use of results available in the literature for surfaces almost flat at the κ^{-1} length scale (see, e.g., [17]). Furthermore, the electrostatic energies are typically (e.g., for DNA) comparable to the thermal energy $k_B T$ so that the use of the Debye-Huckel approximation is questionable [14].

However, from a polymer physicist point of view, clear-cut statements can be made [14]. When a field $\mathbf{E}_\infty$ is applied, electric forces act on the counterions and are transmitted to the chain by viscous shearing. Thus, during the drift of the polyelectrolyte at a velocity $\mathbf{U}_E$, most of the dissipation occurs in the double layer around the backbone, and the hydrodynamic interactions between monomers are *screened*. Papers that describe the polyelectrolyte as an infinitely thin line conclude in a $\simeq\exp(-\kappa r)$ decay of the interaction [14,18], whereas taking into account the finite radius leads to a $\simeq(a/r)^3$ decay [19]. In both cases, the decrease is fast enough to induce the breakdown of the collective response. This is in agreement with the experimental observation [14,20] that the electrophoretic mobility $\mu_{\mathrm{el}} = \mathbf{U}_E/\mathbf{E}$ is independent of the total length L. The coil is transparent to the "electro-osmotic" flow in this so-called free-draining picture. The chain experiences an electric force and a viscous friction that *locally* cancel each other. Thus no deformation of the coil in pure electrophoresis is expected, and the electrophoretic mobility is independent of the instantaneous conformation.

The fact that (contrary to a nonelectric force) the electric field acts on the counterions explains the failure

of the too simple guess mobility = charge/friction, i.e., $\mu_{\mathrm{el}} = \lambda L/\xi$. To recover from this drawback, polyelectrolyte electrophoresis is often described in terms of a *local picture* in which the dynamics of the polyelectrolyte in an electric field is well represented by a local "effective" or "electrophoretic" charge density λ_{eff} [10,11] and a local friction coefficient per unit length f_{eff}, so that $\mu_{\mathrm{el}} = \lambda_{\mathrm{eff}}/f_{\mathrm{eff}}$, independently of length or configuration. Although of some use to describe pure electrophoresis, this picture is dangerous whenever nonelectrical forces are applied, the situation which we address now.

Consider first a force $\mathbf{F}$ and an electric field $\mathbf{E}_\infty$ weak enough so that their effects do not lead to appreciable deformation of the coil, but induce its motion at a velocity $\mathbf{U}$. To deal with their combined effect, we linearize the set of CEHE describing the motion of the solvent, the ionic fluxes, and electrostatics, in the vicinity of their equilibrium solution ($\mathbf{F} = \mathbf{O}, \mathbf{E}_\infty = \mathbf{O}$, no flow). This linearization procedure is commonly used for rigid particles [8] and seems to be valid in many practical cases. Then our problem is solved by superposition of the pure force ($\mathbf{F}$ active, $\mathbf{E}_\infty = \mathbf{O}$), and the pure electrophoresis problem ($\mathbf{F} = \mathbf{O}, \mathbf{E}_\infty$ active). The solvent flow is the superposition of a Stokes-like flow around the coil proportional to $\mathbf{F}$ and an almost uniform flow penetrating freely the coil proportional to $\mathbf{E}_\infty$. The velocity of the object is the sum of that in the two problems, as can be extracted, for example, from the global force balance on the object:

$$\mathbf{F} - \xi \cdot (\mathbf{U} - \mu_{\mathrm{el}} \cdot \mathbf{E}_\infty) = \mathbf{O}. \qquad (1)$$

This equation actually holds for any object, if the scalars ξ and μ_{el} are replaced by the friction and electrophoretic mobility *tensors* of the object. As the coil is here undeformed and thus symmetric, these tensors are actually scalars. Formula (1) can be of interest, e.g., to determine, in the linear regime of the CEHE, the *stall force* $\mathbf{F}_0$ required to maintain the coil immobile ($\mathbf{U} = \mathbf{O}$) in an electric field:

$$\mathbf{F}_0 = -\xi \cdot \mu_{\mathrm{el}} \cdot \mathbf{E}_\infty. \qquad (2)$$

As the electrophoretic mobility does not depend on the size of the coil, the stall force is thus proportional to ξ and thus to R. In particular, this force is not $-\lambda_{\mathrm{eff}} L \mathbf{E}_\infty$ as a local force picture would suggest, but scales as L^ν.

If the combined effect of $\mathbf{F}$ and $\mathbf{E}_\infty$ induces tensions larger than kT/R, significant deformation of the chain will occur. However, this does not preclude the linearization of the electrohydrodynamics equations for the solvent and the small ions around the polyelectrolyte *in its eventual deformed conformation*. So Eq. (1) is still valid in this regime even though the polyelectrolyte is very deformed, if ξ and μ_{el} are replaced by the friction tensor and the electrophoretic mobility tensor in this deformed conformation. Let us recall now that, in the simple description of polyelectrolytes presented above, (a) the mobility is conformation independent, and (b) in a pure electrophoresis

situation, electric and hydrodynamic forces on the polyelectrolyte balance locally, so that no stress results on the backbone whatever its conformation.

We can then make profit of our superposition scheme. Take first the purely nonelectric problem: $\mathbf{F}$ distributed in a given way, $\mathbf{E}_\infty = \mathbf{O}$. The coil then adopts a deformed average conformation, say, C and moves at a velocity $\mathbf{U}_F$. Consider now the electrophoresis of the polyelectrolyte "stuck" in the conformation C. As stated previously, the polyelectrolyte moves at $\mathbf{U}_E = \mu_{\mathrm{el}}\mathbf{E}_\infty$, and stresses exerted on the backbone balance locally. So, superimposing the two problems does not lead to any further deformation: Local force balance is satisfied in the conformation C, and the coil moves at a velocity $\mathbf{U} = \mathbf{U}_F + \mathbf{U}_E$, which coincides with Eq. (1) if ξ is now the friction coefficient of the chain in the conformation C (along its extended direction, i.e., parallel to $\mathbf{F}$). The flow is still the sum of a Stokes-like part avoiding the interior of the deformed coily object and of a homogeneous electro-osmotic one. The former still has to be calculated, but we have on our way proven what we call a hydrodynamic-electric equivalence: As long as statements (a) and (b) in the preceding paragraph hold, the polyelectrolyte adopts the same conformation if (i) moved at a velocity $\mathbf{U}$ in the electric field $\mathbf{E}_\infty$ or (ii) moved at $\mathbf{U} - \mu_{\mathrm{el}}\mathbf{E}_\infty$ in the absence of electric field. In particular, we predict that an end-anchored polymer should deform in the same way in an electric field $\mathbf{E}_\infty$ and in a uniform hydrodynamic flow of velocity $\mathbf{V}_\infty = \mu_{\mathrm{el}}\mathbf{E}_\infty$, a result at odds with previous propositions [10,12].

Let us now discuss the interest, limitations, and domain of application of our results. First, our two main results (stall force and HE equivalence) are in opposition to both previous estimates drawn from a local force picture that would predict a stall force proportional to the length and a deformation in an electric field qualitatively different from that in a flow (e.g., Rouse trumpet and not Zimm trumpet in the language of [15]). Second, our predictions should be easily checked with current micromanipulation techniques [1,2,5].

To reach these simple propositions we, however, made a few hypothesis.

First, we linearized the electrohydrodynamic equations. This is a common procedure in electrophoresis textbooks for rigid colloids [8]. Let us stress again that the deformability threshold of the polyelectrolyte (kT/R) has nothing to do with the description of small ions, and, furthermore, this threshold decreases with L. Thus, for long polyelectrolytes, there will be a regime where forces and fields weak from the point of view of electrohydrodynamics are still strong enough to stretch the chain considerably. Our HE analogy should then fully apply. Considering the actual value of the rigidity of a DNA chain, one can also argue that it should apply even for rather short (i.e., rodlike) segments.

To discuss a second approximation, we remark that electrophoretic mobility should, in fact, be weakly dependent on the conformation due to the anisotropy of the electrophoretic mobility tensor for rodlike molecules [21]. This local anisotropy could, in principle, induce deformation of very long chains undergoing electrophoresis as can be inferred from the formal analysis of [22], although available experimental results do not support the existence of a strong effect [23]. This weak breakdown of statements (a) and (b) may induce a slight departure from our (HE) equivalence, and should be taken into account in a more elaborate theory. Note also that for higher fields one should take into account form and intrinsic birefringence of the flexible objects [13,23], whereas we focused on the electrohydrodynamics and the sole polarization of the counterionic cloud.

As to their relevance, our novel predictions for polyelectrolytes suggest the reconsideration of earlier experimental results aimed at determining elastic or electric properties of DNA chains [24]. Furthermore, electrically induced DNA motion in the presence of obstacles underlies most of their current separation methods [6,11,25–27], and the analysis of such situations should benefit from our approach. Another situation of practical interest where forces and field act on a charged chain is the recently proposed electrophoresis of composite objects obtained by attaching a buoy (protein or polymer) to the DNA fragments to be separated. Our predictions indeed allow one to compute the electrophoretic mobility of such complexes [28], correcting estimates based on a local picture. Eventually, the arguments in this Letter of course do not hold for DNA chains in gels [6], where hydrodynamic flows are screened on a scale comparable to the pore size [9], so that the forces exerted by the gel do not give rise to collective effects. A local picture (at the pore scale) is thus relevant, and the extensive theoretical corpus developed for gel electrophoresis [29] remains valid.

In conclusion, we have analyzed the motion and deformation of polyelectrolytes under both forces and electric fields, obtained results in disagreement with previous theories, and proposed experimentally testable checks. A similar approach could also be undertaken for the analysis of the micromanipulation of other flexible objects under electric fields. In particular, the statement that the stall force is *not* the total charge times the field is rather general, and useful to keep in mind. The linearization procedure leading to Eqs. (1) and (2) is also broadly applicable, but, in general, does not allow one to derive the eventual conformation of the deformed object. Only features specific to polyelectrolytes allowed us to go further here.

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