Dynamics and conformational properties of polyampholytes in external electrical fields

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In this work we report first analytical results on the dynamics and conformational properties of polyampholytes (PAs, polymers containing positive and negative charges) in the presence of external electrical fields. In terms of the Rouse model of polymer dynamics and in the so-called weak coupling limit we obtain for PAs explicitly the mean-square displacement both of the center of mass and of individual beads, and also determine the PAs' equilibrium end-to-end distance. For a singly charged PA we also relate the findings to a fractional differential equation. © *1995 American Institute of Physics.*

I. INTRODUCTION

Recently, the dynamics and the conformational properties of heteropolymer chains with quenched random disorder have received much attention due to their possible relevance to biological processes like protein-folding.[1–3] Therefore polyampholytes (PA), i.e., polymer chains which carry both positive and negative charges have been a subject of considerable interest within the last decade. The main emphasis of this research concerned the role of the mutual interaction of charges on the PA's conformational properties. Depending on the physical situation and on the parameters (i.e., random or regular placement of charges, the presence of a net charge, the temperature and/or the quality of the solvent) PAs may stretch to an extended configuration or, conversely, may collapse.[4–14]

This work examines the behavior of PAs in external electrical fields. We propose a model valid in the weak coupling limit,[14–16] i.e., for the regime $l_B/b \ll 1$ where $l_B = e^2/(\epsilon T)$ denotes the Bjerrum length and b is the monomer size (with e being the electron charge, ϵ the dielectric constant of the solvent, and T the temperature in units of the Boltzmann constant k_B). In this limit the thermal fluctuations dominate the electrical interaction between charged monomers and the PA has a Gaussian conformation (see below, and also Ref. 14 for a detailed discussion of this regime). The neglect of the intramolecular electrical interaction allows a rigorous analytical treatment. Our model may thus also provide a basis for more complicated cases, such as the dynamics of collapsed or extended PAs in external fields.

Here we present first analytical results on the dynamical and the conformational properties of PAs with randomly placed charges. For these PAs we derive the explicit time dependence of the mean-square displacement (MSD) of the center of mass (c.m.) and also of the position of a tagged monomer. Furthermore we determine the mean-square end-to-end distance of PAs in equilibrium. We also show that the case of a single charged monomer in the PA can be expressed in terms borrowed from fractional calculus.[17] This establishes a link between the Rouse description of the PA and a corresponding rheological constitutive equation.[18–20]

II. THE MODEL

We view the PA as consisting of N charged beads, connected into a linear chain by harmonic springs. The chain's position is given by the set $\{\mathbf{R}_n(t)\}$, where $\mathbf{R}_n(t) = [X_n(t), Y_n(t), Z_n(t)]$ is the position vector of the nth bead ($n = 0, 1, \ldots, N-1$) at time t. We denote the charge of the nth bead by q_n and take it to be a quenched random variable.

Neglecting the intramolecular electrical interactions between the charged beads the potential energy $U(\{\mathbf{R}_n(t)\})$ of the PA chain contains only elastic contributions and the interactions with the external electric field $\mathbf{E}$:

$$U(\{\mathbf{R}_n(t)\}) = \frac{K}{2}\sum_{n=1}^{N-1}[\mathbf{R}_n(t)-\mathbf{R}_{n-1}(t)]^2 - \mathbf{E}\sum_{n=0}^{N-1} q_n \mathbf{R}_n(t). \tag{1}$$

In Eq. (1) K denotes the spring constant $K = 3T/b^2$, with T being the temperature in units of the Boltzmann constant k_B and b the mean distance between beads (in the absence of an external field). The electrical field points along the Y axis, so that

$$\mathbf{E} = (0, E, 0). \tag{2}$$

In Eq. (1) we have neglected the intramolecular electrical interactions. This corresponds to the weak coupling limit where the thermal fluctuations dominate so that the electrostatic interaction is not able to deform the chain. Using a Flory-type approach Dobrynin and Rubinstein[14] have shown recently that this situation (the so-called unperturbed regime) is realized in a θ solvent for $\tau > \sqrt{N}$. Here τ is the reduced temperature so that

$$\tau = \frac{b\epsilon T}{e^2 \rho} = \frac{b}{l_B \rho}, \tag{3}$$

where ϵ is the dielectric constant of the solvent and ρ is the fraction of charged monomers. As before, l_B denotes the Bjerrum length $l_B = e^2/(\epsilon T)$. The condition $\tau > \sqrt{N}$ can be fulfilled when one has a solvent with a large dielectric con-

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stant (for instance $l_B \simeq 7$ Å in water at room temperature) and when the concentration ρ of the charges along the backbone of the PA is sufficiently small.

Equation (1) turns into the Rouse model when excluded volume effects and hydrodynamic interactions are disregarded; then the chain's dynamics is described by N coupled Langevin equations:[21,22]

$$\zeta \frac{d\mathbf{R}_n(t)}{dt} = -\frac{\partial U(\{\mathbf{R}_n(t)\})}{\partial \mathbf{R}_n(t)} + \mathbf{f}_R(n,t). \tag{4}$$

In Eq. (4) ζ is the friction constant and $\mathbf{f}_R(n,t)$ are Gaussian random forces with

$$\overline{f_i(n,t)} = 0 \tag{5}$$

and

$$\overline{f_i(n,t) f_j(n',t')} = 2\zeta T \delta_{ij} \delta_{nn'} \delta(t-t'). \tag{6}$$

Here i and j denote the components of the force vector, i.e., $i,j = X,Y,Z$ and the dash stands for the thermal averages, i.e., averages over realizations of the Langevin forces $\mathbf{f}_R(n,t)$.

Equation (4) with the potential (1) is linear and hence the dynamics of the chain decouples in the X, Y, and Z directions. The X and Z components of the $\mathbf{R}_n$ are field-independent and follow standard Rouse behavior.[21,22] We concentrate hence on the Y component. Regarding the suffix n as being continuous it follows from Eqs. (1) to (4):

$$\zeta \frac{\partial Y_n(t)}{\partial t} = K \frac{\partial^2 Y_n(t)}{\partial n^2} + q_n E + f_Y(n,t) \tag{7}$$

with the boundary condition $\partial Y_n(t)/\partial n|_{n=0,N} = 0$. Equation (7) contains two types of random forces: the ordinary thermal noise $f_Y(n,t)$ and a quenched random force $q_n E$. The case of configuration-dependent forces was considered recently when modeling polymers in random layered flows.[23,24]

Equation (7) is to solved using normal coordinates:[22]

$$Y(p,t) = \frac{1}{N} \int_0^N dn \, \cos\left(\frac{p\pi n}{N}\right) Y_n(t), \quad p = 0,1,2,\ldots \, . \tag{8}$$

These satisfy

$$\frac{\partial Y(p,t)}{\partial t} = -\frac{p^2}{\tau_R} Y(p,t) + \frac{1}{\zeta} \tilde{q}_p E + \frac{1}{\zeta} \tilde{f}_Y(p,t). \tag{9}$$

Here τ_R denotes the Rouse time $\tau_R = \zeta b^2 N^2 / 3\pi^2 T$ (the largest internal relaxation time of the harmonic chain); the symbols $\tilde{q}_p$ and $\tilde{f}_Y(p,t)$ on the right-hand side of Eq. (9) denote the Fourier transforms of the charge variable, $\tilde{q}_p = N^{-1} \int_0^N dn \, \cos(p\pi n/N) q_n$, and of the thermal noises, $\tilde{f}_Y(p,t) = N^{-1} \int_0^N dn \, \cos(p\pi n/N) f_Y(n,t)$, respectively.

Switching on the electric field at $t=0$ and assuming that the chain was initially in a Gaussian conformation, we have from Eq. (9):

$$Y(p,t) = \frac{1}{\zeta} \int_{-\infty}^{t} d\tau \, \tilde{f}_Y(p,\tau) \exp[-p^2(t-\tau)/\tau_R] + \frac{\tilde{q}_p E}{\zeta} \int_0^t d\tau \, \exp(-p^2 \tau/\tau_R). \tag{10}$$

From the $Y(p,t)$ the $Y_n(t)$ follow:

$$Y_n(t) = Y(0,t) + 2 \sum_{p=1}^{\infty} Y(p,t) \cos\left(\frac{p\pi n}{N}\right). \tag{11}$$

We obtain now readily from Eqs. (10) and (11) the explicit time dependence of the MSD of the chain's c.m. and that of a tagged bead. We begin the analysis with the c.m.'s motion. The Y component of the trajectory of the c.m. is given by the normal coordinate with $p=0$, i.e., $Y_{\text{c.m.}}(t) = Y(0,t)$. From Eq. (10) we have the following general result for the MSD of the c.m. in the Y direction:

$$\overline{\langle [Y_{\text{c.m.}}(t) - Y_{\text{c.m.}}(0)]^2 \rangle} = \frac{2T}{\zeta N} t + \frac{E^2}{\zeta^2} \langle \tilde{q}_0^2 \rangle t^2. \tag{12}$$

In Eq. (12) the brackets denote averages with respect to the realizations of q_n and use was made of the properties of $f_i(n,t)$; furthermore $\langle \tilde{q}_0^2 \rangle$ is the pair correlation function of the charge variable.

The behavior of a tagged bead, say one of the chains ends, is more complicated. Using Eq. (11) with $n=0$ we have for the Y component:

$$\begin{aligned} &\overline{\langle [Y_0(t) - Y_0(0)]^2 \rangle} \\ &= \frac{4T}{\zeta N} \sum_{p=1}^{\infty} \int_0^t d\tau \, e^{-2p^2\tau/\tau_R} + \frac{2T}{\zeta N} t + \frac{4E^2}{\zeta^2} t \sum_{p=1}^{\infty} \langle \tilde{q}_0 \tilde{q}_p \rangle \\ &\quad \times \int_0^t d\tau \, e^{-p^2\tau/\tau_R} + \frac{4E^2}{\zeta^2} \sum_{p=1}^{\infty} \sum_{q=1}^{\infty} \langle \tilde{q}_q \tilde{q}_p \rangle \\ &\quad \times \int_0^t d\tau_1 \int_0^t d\tau_2 \, e^{-p^2\tau_1/\tau_R - q^2\tau_2/\tau_R} + \frac{E^2}{\zeta^2} \langle \tilde{q}_0^2 \rangle t^2. \end{aligned} \tag{13}$$

Finally for the Y component of the end-to-end vector $\mathbf{P}(t)$, $\mathbf{P}(t) = \mathbf{R}_0(t) - \mathbf{R}_N(t)$, we obtain from Eqs. (10) and (11):

$$\begin{aligned} \overline{\langle P_Y^2(t) \rangle} &= \frac{b^2 N}{3} + \frac{16E^2}{\zeta^2} \sum_{p}^{\wedge} \sum_{q}^{\wedge} \langle \tilde{q}_p \tilde{q}_q \rangle \\ &\quad \times \int_0^t d\tau_1 \int_0^t d\tau_2 \, \exp(-p^2\tau_1/\tau_R - q^2\tau_2/\tau_R). \end{aligned} \tag{14}$$

Here the hat designates that the summation in Eq. (14) extends over odd, positive numbers only.

III. RANDOM CHARGE DISTRIBUTION

We can now specify the statistical properties of the q_n. First let each bead of the chain be either positively or negatively charged, $q_n = \pm q$. We stipulate that charges on different beads are uncorrelated, i.e.,

$$\langle q_n q_m \rangle = q^2 \delta_{nm}, \tag{15}$$

and thus that the average charge equals zero, $\langle q_n \rangle = 0$. Note, however, that the latter condition does not necessarily imply that a particular chain is electrically neutral. For the Fourier transform of the charge variables we now have

$$\langle \tilde{q}_0^2 \rangle = \frac{q^2}{N}; \quad \langle \tilde{q}_0 \tilde{q}_p \rangle = 0;$$

$$\langle \tilde{q}_p \tilde{q}_r \rangle = \frac{q^2}{2N}\,\delta_{pr} \quad \text{for } p,r = 1,2,\ldots\ . \tag{16}$$

From Eqs. (12), (13), and (14), which hold in general, we can now derive the properties of PAs with random charge distributions. Inserting Eq. (16) into Eq. (12) we obtain for the MSD of the c.m. in the Y direction:

$$\overline{\langle [Y_{\text{c.m.}}(t) - Y_{\text{c.m.}}(0)]^2 \rangle} = \frac{2T}{\zeta N}\,t + \frac{q^2E^2}{\zeta^2 N}\,t^2. \tag{17}$$

Notice that the MSD of the c.m. contains two independent contributions: a conventional Rouse diffusion term proportional to t[21,22] and a drift term due to E proportional to t^2. The N^{-1} dependence of the drift term arises as follows: due to the randomness in the q_n, the total charge of a chain is of the order of $N^{1/2}$. Hence the electric force acting on the chain goes as $N^{1/2}$, while the friction is proportional to N. Under both forces the c.m. moves ballistically, with a velocity $V \propto qE/\zeta\sqrt{N}$.

Now we turn to the dynamics of the PA's end. Making use of Eqs. (13) and (16) we get

$$\begin{aligned}\overline{\langle [Y_0(t) - Y_0(0)]^2 \rangle} = {} & \frac{2T\tau_R}{\zeta N} \sum_{p=1}^{\infty} \frac{1}{p^2}\,(1 - e^{-2p^2 t/\tau_R}) \\ & + \frac{2T}{\zeta N}\,t + \frac{2q^2E^2\tau_R^2}{\zeta^2 N} \sum_{p=1}^{\infty} \frac{1}{p^4} \\ & \times (1 - e^{-p^2 t/\tau_R})^2 + \frac{q^2E^2}{\zeta^2 N}\,t^2. \end{aligned} \tag{18}$$

The second and fourth terms on the right-hand side of Eq. (18) are identical to those for the MSD of the c.m., Eq. (17), and govern the long-time behavior, when the beads motion mirrors that of the c.m. The first and the third term are important at short times when the internal relaxation modes of the chain contribute to its dynamics. For $t \ll \tau_R$ we deduce from Eq. (18):

$$\begin{aligned}\overline{\langle [Y_0(t) - Y_0(0)]^2 \rangle} = {} & 4b\sqrt{\frac{T}{6\pi\zeta}}\,t^{1/2} + \frac{2T}{\zeta N}\,t \\ & + \frac{8bq^2E^2(\sqrt{2}-1)}{3\zeta^{3/2}\sqrt{3\pi T}}\,t^{3/2} + \frac{q^2E^2}{\zeta^2 N}\,t^2. \end{aligned} \tag{19}$$

The first term in Eq. (19) gives the conventional result for the MSD of the tagged bead of a Rouse chain in the short-time regime.[22] A new feature here is the third term, which is related to the internal relaxation of the chain and gives rise to a subdrift $t^{3/4}$ behavior. For $t \ll \tau_R$ the second and fourth term are smaller than the first and third terms, respectively.

Consider now the PA conformations for a random placement of charges. Inserting Eq. (16) into Eq. (14) we obtain for the equilibrium value of the end-to-end distance:

$$\begin{aligned}\overline{\langle P_Y^2(\infty) \rangle} &= \frac{b^2N}{3} + \frac{8q^2E^2\tau_R^2}{\zeta^2 N} \sum_{p}^{\wedge} \frac{1}{p^4} \\ &= \frac{b^2N}{3} + \frac{q^2E^2b^4N^3}{108T^2}. \end{aligned} \tag{20}$$

Besides the usual term proportional to N, we find an additional field-induced stretching characterized by a N^3 dependence. This pronounced stretching can be understood by the following Flory-type argument:[16,22] Due to the statistical properties of the charge distribution, the chain may be thought as being subdivided into two blobs, having an average charge excess around $q\sqrt{N}$ and $-q\sqrt{N}$ each. The part of the free energy of the PA which describes the averaged potential energy of this effective dipole in the external field E obeys $F_{\text{int}} \propto \sqrt{N} qEP_Y$. The penalty term (stretching in the Y direction) obeys, as usual $F_{\text{def}} \propto TP_Y^2/(b^2N)$. Hence we get

$$\frac{F(P_Y)}{T} = \frac{C_1 P_Y^2}{Nb^2} + \frac{C_2\sqrt{N}qEP_Y}{T} + C_3, \tag{21}$$

where C_1, C_2, and C_3 are constants. Now minimizing F with respect to P_Y, i.e., setting $\partial F/\partial P_Y = 0$, we have

$$P_Y^2 \propto \frac{q^2E^2b^4}{T^2}\,N^3, \tag{22}$$

which corresponds to Eq. (20). Note that this argument can be made for any subgroup (blob) of the chain. This results in a self-similar conformation of the stretched chain with a fractal dimension of $d_f = 2/3$, a value smaller than unity. However, Eq. (20) is reasonable only as long as the elongation in the Y direction is less than that of chains in a fully stretched situation, i.e., as long as

$$\frac{q^2E^2b^4N^3}{108T^2} \ll b^2N^2 \tag{23}$$

holds; this sets an upper bound on the external disturbing field E.

IV. ONE CHARGED BEAD

Finally, let us consider a situation in which only one bead of the PA is charged, say the first one, i.e.,

$$q_n = q\,\delta_{n0}. \tag{24}$$

Equations (9) to (14) generally hold, while instead of Eq. (16) one now has

$$\tilde{q}_p = qN^{-1} \tag{25}$$

for $p = 0,1,2,\ldots$. Inserting Eq. (25) into Eq. (12) leads to

$$\overline{[Y_{\text{c.m.}}(t) - Y_{\text{c.m.}}(0)]^2} = \frac{2T}{N\zeta}\,t + \frac{q^2E^2}{\zeta^2N^2}\,t^2. \tag{26}$$

Now the ballistic term in the c.m. motion is proportional to N^{-2} and is by a factor $1/N$ smaller than the previous expression, Eq. (17).

Using Eq. (14) we obtain for the Y component of the end-to-end distance:

$$\overline{P_Y^2(\infty)} = \frac{b^2N}{3} + \frac{16q^2E^2\tau_R^2}{\zeta^2N^2}\left(\sum_p^{\wedge}\ \frac{1}{p^2}\right)^2$$
$$= \frac{b^2N}{3} + \frac{q^2E^2b^4N^2}{36T^2}, \tag{27}$$

e.g., stretching is now by a factor of $1/(3N)$ smaller than previously obtained, cf. Eq. (20).

Furthermore the dependence on E of $\overline{Y_0(t)}$, the mean position of the charged bead, obeys a fractional differential equation.[17] We show this by first evaluating $\overline{Y_0(t)}$ using the explicit solution for the normal coordinates, Eq. (10), together with Eq. (11) and the initial condition $\overline{Y_0(0)} = 0$. For $t \geqslant 0$ it follows:

$$\overline{Y_0(t)} = \overline{Y(0,t)} + 2\sum_{p=1}^{\infty} \overline{Y(p,t)}$$
$$= \frac{qE}{\zeta N}\, t + \frac{2qE}{\zeta N}\sum_{p=1}^{\infty} \int_0^t d\tau\, \exp(-p^2\tau/\tau_R). \tag{28}$$

For $t \ll \tau_R$ we have in terms of the spring constant $K = 3T/b^2$ from Eq. (28):

$$\overline{Y_0(t)} = \frac{qE}{\zeta N}\, t + \frac{2}{\sqrt{\pi}}\frac{qE}{\sqrt{\zeta K}}\, t^{1/2}, \tag{29}$$

i.e., a result mentioned previously in Ref. 25. For long chains, $\tau_R \propto N^2 \gg 1$, so that $\overline{Y_0(t)} \propto t^{1/2}$ holds for a very long time. Evidently this is the PA's response to a field $E(t) = E\Theta(t)$, where Θ is the Heaviside step function. Then the position of the charged bead in the presence of an arbitrary external field $E(t)$ [with $E(t) = 0$ for $t \leqslant 0$] is well approximated by the following convolution integral:

$$\overline{Y_0(t)} = \frac{q}{\sqrt{\zeta K}}\frac{1}{\Gamma(\alpha)} \int_0^t d\tau (t-\tau)^{\alpha-1}\frac{dE(\tau)}{d\tau}$$
$$= \frac{q}{\sqrt{\zeta K}}\frac{d^{-\alpha}}{dt^{-\alpha}}\left[\frac{dE(t)}{dt}\right], \tag{30}$$

with $\alpha = 3/2$. The convolution integral of Eq. (30) is a *Riemann–Liouville integral* which for any $\alpha > 0$ defines the *fractional integral*, symbolized by the operator $d^{-\alpha}/dt^{-\alpha}$.[17] Now *fractional derivatives* d^{α}/dt^{α} for $\alpha > 0$ are obtained by applying ordinary derivatives to fractional integrals. Using the composition rule (see Ref. 17 for details) we obtain from Eq. (30) the following, so-called extraordinary, differential equation:

$$qE(t) = \sqrt{\zeta K}\,\frac{d^{1/2}\overline{Y_0(t)}}{dt^{1/2}}. \tag{31}$$

Such an expression resembles a rheological constitutive equation for a viscoelastic material; in fact, in this field fractional differentiation has recently become an important tool.[18–20] That the Rouse model may be related to a fractional differential equation was also noticed in Ref. 26. In Refs. 27 and 28 we have shown how to interpret fractional relationships in terms of sequential spring-dashpot models. For these the fractional equation

$$\sigma(t) = \eta^{\alpha}E^{1-\alpha}\,\frac{d^{\alpha}\epsilon(t)}{dt^{\alpha}} \tag{32}$$

with $0 \leqslant \alpha \leqslant 1$ holds, where σ denotes the stress, ϵ the strain, and E and η are constants. Equation (32) interpolates between solidlike ($\alpha = 0$) and fluidlike behavior ($\alpha = 1$). In the special case $\alpha = 1/2$ the model consists of equal springs and dashpots, arranged in an infinite ladderlike structure (see Ref. 27 for details).

The Rouse chain with one charged bead described above parallels this model. Due to the symmetry of the problem the mean position of any given bead lies on the Y axis, i.e., $\overline{X_n(t)} = \overline{Z_n(t)} = 0$. Therefore the beads are on the average sequentially aligned along the Y axis. The relation of the projection of the Rouse chain on the Y axis to the spring-dashpot arrangement of Ref. 27 gets to be more compelling when one recalls that the beads are connected by springs and are exposed to a velocity-dependent friction.

We close by noticing that the Rouse model used in the present work is simplified due to the neglect of hydrodynamic forces on the motion of the beads. While such effects are less important for stretched polymers, their influence on the PA's motion deserves further investigations which are now in progress.

V. CONCLUSION

We have studied in this work the influence of electrical fields on the dynamics of PAs both for randomly placed charges, and for a unique charge. At long times both the chain's c.m. and also the individual beads move ballistically, while the average velocity decreases with N. On the other hand, for $t \ll \tau_R$ the dynamics of the individual beads shows up: for randomly placed charges a subdrift behavior appears, with the MSD growing as $t^{3/2}$. The dynamics of a single charge is reminiscent of viscoelastic models which obey fractional equations.

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