# Dynamics and conformational properties of polyampholytes in external electrical fields: influence of the charge distribution

*Helmut Schiessel** [a], *Gleb Oshanin* [b], *Alexander Blumen* [a]

[a] Theoretical Polymer Physics, Freiburg University, Rheinstr. 12, 79104 Freiburg, Germany

[b] Laboratoire de Physique Théorique des Liquides (URA 765), Université P. et M. Curie, T. 16, 4. pl. Jussieu, 75252 Paris, France

SUMMARY:
   In the present work we study 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 we obtain for PAs in the so-called weak coupling limit explicitly the mean square displacement both of the center of mass and of individual beads, and the PAs' end-to-end distance. We study both ordered and also random charge distributions along the chains; in the latter case we also consider the role of different correlation lengths.

## 1. Introduction

Heteropolymer chains can be viewed as prototypes for biological macromolecules. Studying their behavior helps to understand basic biological processes such as protein-folding [1–4]. Recently, polyampholytes (PAs), i.e. polymer chains which carry both positive and negative charges, have received much attention [5–19]. 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 parameters (i.e., random or regular placements of charges, the presence of a net charge, the temperature and/or the quality of the solvent) PAs may collapse or, conversely, may stretch to extended configurations [5–19].

In this work we examine the behavior of PAs in external electrical fields. We propose a model which is valid in the weak coupling limit [18, 20, 21], i.e. roughly speaking for the regime $l_B/b \ll 1$ where $l_B = e^2/(\varepsilon T)$ denotes the Bjerrum length and $b$ is the monomer size (with $e$ being the electron charge, $\varepsilon$ 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 so that the PA has a Gaussian conformation. Using a Flory-type approach Dobrynin and Rubinstein [18] have specified this, so called unperturbed, regime more precisely. They showed that this situation is realized in a θ-solvent for

$$\tau > \sqrt{N} \tag{1}$$

Here $N$ is the number of monomers and $\tau$ is the reduced temperature defined by

$$\tau = \frac{b\varepsilon T}{e^2\rho} = \frac{b}{l_B\rho} \tag{2}$$

where $\rho$ denotes the fraction of charged monomers. The weak-coupling condition, Eq. (1), may be fulfilled experimentally when one has a solvent with a large dielectric constant (e. g. $l_B \approx 7\,\text{Å}$ in water at room temperature) and when the concentration $\rho$ of the charges along the backbone of the PA is sufficiently small. Due to the fact that in such a situation the intramolecular electrical interactions are of marginal importance we are led here to a model which, as we proceed to show, allows a rigorous analytical treatment.

Thus we study the dynamics and the conformational properties of PAs in external electrical fields. We solve the equations of motion of the PA in the conventional Rouse model[22,23], i. e. when the chain is regarded as being a collection of charged beads connected by harmonic springs, and when the hydrodynamically mediated interactions between beads are neglected. Depending on the details of the charge distributions one finds a great variety of responses to an applied external field. We calculate exactly the mean-square displacement (MSD) of the center of mass (CM) of the PA, its mean-square end-to-end distance as well as the MSD of a tagged monomer of the PA. The dynamics of a PA whose charges are placed randomly and in an uncorrelated manner along the chain has been already treated by us in ref.[24] Here we analyse the PAs behavior for different random and non-random charge distributions.

The paper is structured as follows: In section 2 we define the model and derive several general expressions for which the detailed properties of the charge distributions need not be yet specified. In section 3 we study non-random charge distributions: the situation when only one bead is charged, the case of alternating charges along the chain and also a homogeneous distribution of charges (polyelectrolytic case). Section 4 is devoted to random charge distributions: we consider the charges to be distributed (i) in an uncorrelated fashion, (ii) such that the total charge on the chain vanishes, and (iii) being strongly correlated. The latter case interpolates between the uncorrelated and the polyelectrolytic case. Finally, we give a conclusion in section 5.

## 2. Charged Rouse polymer in an external field

We view the PA as consisting of $N$ charged beads, connected by harmonic springs to a linear chain. The chain's position is given by the set of vectors $\{R_n(t)\}$, where $R_n(t) = (X_n(t), Y_n(t), Z_n(t))$ is the position vector of the $n$th bead ($n = 0, 1, \ldots, N - 1$) at time $t$. We denote the charge of the $n$th bead by $q_n$ and take it to be a variable which we will specify later.

Focusing here on the field-induced behavior of the PA we skip from our considerations the electrostatic interactions between the beads, i. e. we calculate the behavior in the weak coupling limit (cf. above and ref.[18]). In this case we have to account through the potential energy $U(\{R_n(t)\})$ of the PA chain only for the elastic contributions and for the influence of the external electric field $E$:

$$U(\{R_n(t)\}) = \frac{K}{2} \sum_{n=1}^{N-1} [R_n(t) - R_{n-1}(t)]^2 - E \sum_{n=0}^{N-1} q_n R_n(t) \tag{3}$$

In Eq. (3) $K$ is the (entropic) spring constant $K = 3\,T/b^2$, where $T$ denotes 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

$$E = (0, E, 0) \tag{4}$$

holds. Eq. (3) 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[22, 23)]

$$\zeta \frac{dR_n(t)}{dt} = - \frac{\partial U(\{R_n(t)\})}{\partial R_n(t)} + f_R(n, t) \tag{5}$$

In Eq. (5) $\zeta$ is the friction constant and $f_R(n, t)$ is the random thermal-noise force (which is due to the molecules of the surrounding solvent), acting on the $n$th bead of the PA. As usual, we take the Langevin forces to be Gaussian, with moments

$$\overline{f_i(n, t)} = 0 \tag{6a}$$

and

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

Here $i$ and $j$ denote the components of the force vector, i.e., $i,j = X, Y, Z$ and the dash stands for thermal averaging, i.e. averaging over the realizations of the Langevin forces $f_R(n, t)$.

Eq. (5) with the potential (3) describes the Rouse dynamics of a harmonic chain with charged beads in an external field. Regarding the suffix $n$ as being continuous (i.e. considering the chain as an elastic string) it follows from Eqs. (3) to (5)

$$\zeta \frac{\partial X_n(t)}{\partial t} = K \frac{\partial^2 X_n(t)}{\partial n^2} + f_X(n, t) \tag{7}$$

$$\zeta \frac{\partial Z_n(t)}{\partial t} = K \frac{\partial^2 Z_n(t)}{\partial n^2} + f_Z(n, t) \tag{8}$$

and

$$\zeta \frac{\partial Y_n(t)}{\partial t} = K \frac{\partial^2 Y_n(t)}{\partial n^2} + q_n E + f_Y(n, t) \tag{9}$$

Eqs. (7) to (9) are to be solved subject to the Rouse boundary conditions at the chain ends[22, 23)]:

$$\left. \frac{\partial X_n(t)}{\partial n} \right|_{n=0,N} = \left. \frac{\partial Y_n(t)}{\partial n} \right|_{n=0,N} = \left. \frac{\partial Z_n(t)}{\partial n} \right|_{n=0,N} = 0 \tag{10}$$

The $X$- and $Z$-components of the $R_n$ are field-independent and follow the standard Rouse behavior[22, 23]. We can hence restrict ourselves to the behavior of the $Y$-component, which is described by Eq. (9). This equation contains two types of forces: the ordinary thermal noise $f_Y(n, t)$ and a quenched force $q_n E$. We note that the case of configuration-dependent forces was considered recently in a related context, where the motion of polymers in random layered flows was investigated[25, 26].

The formal solution of Eq. (9) with the boundary conditions, Eq. (10), is given in the form of a Fourier series[23]

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

Here the $Y(p, t)$, $p = 0, 1, \ldots$, denote the normal coordinates:

$$Y(p, t) = \frac{1}{N} \int_0^N dn \cos\left(\frac{p\pi n}{N}\right) Y_n(t) \tag{12}$$

In terms of the normal coordinates Eq. (9) can be rewritten as

$$\frac{\partial Y(p, t)}{\partial t} = -\frac{p^2}{\tau_R} Y(p, t) + \frac{1}{\zeta} \tilde{q}_p E + \frac{1}{\zeta} \tilde{f}_Y(p, t) \tag{13}$$

In Eq. (13) $\tau_R$ denotes the Rouse time

$$\tau_R = \frac{\zeta b^2 N^2}{3\pi^2 T} \tag{14}$$

which is the largest internal relaxation time of the harmonic chain. The symbols $\tilde{q}_p$ and $\tilde{f}_Y(p, t)$ on the rhs of Eq. (13) denote the Fourier transforms of the charge variable,

$$\tilde{q}_p = \frac{1}{N} \int_0^N dn \cos\left(\frac{p\pi n}{N}\right) q_n \tag{15}$$

and of the thermal noises,

$$\tilde{f}_Y(p, t) = \frac{1}{N} \int_0^N dn \cos\left(\frac{p\pi n}{N}\right) f_Y(n, t) \tag{16}$$

respectively. Thus the Fourier transformed forces fulfill

$$\overline{\tilde{f}_Y(p, t)} = 0 \tag{17a}$$

and

$$\overline{\tilde{f}_Y(p, t) \tilde{f}_Y(q, t')} = \frac{\zeta T}{N} (\delta_{pq} + \delta_{p0}\delta_{q0}) \delta(t - t') \tag{17b}$$

At $t = 0$ the PA is assumed to be in thermal equilibrium, i.e. to have a Gaussian conformation. This can be accounted for automatically by stipulating the PA to have been subjected to the thermal forces since $t = -\infty$. Furthermore, switching on the electric field at $t = 0$, $Y(p, t)$ reads:

$$Y(p, t) = \frac{1}{\zeta} \int\limits_{-\infty}^{t} d\tau \tilde{f}_Y(p, \tau) \exp(-p^2(t - \tau)/\tau_R)$$

$$+ \frac{\tilde{q}_p E}{\zeta} \int\limits_{0}^{t} d\tau \exp(-p^2(t - \tau)/\tau_R)$$

(18)

From Eqs. (11) and (18) we now obtain readily the explicit time dependence of the MSD of the chain's CM, the mean square end-to-end distance and the MSD of a tagged bead. We begin the analysis with the CM's motion. The $Y$-component of the trajectory of the CM is given by the normal coordinate with $p = 0$, i.e.,

$$Y_{CM}(t) = \frac{1}{N} \int\limits_{0}^{N} dn \ Y_n(t) = Y(0, t)$$

(19)

Using Eq. (18) with $p = 0$ we obtain the following general result for the MSD of the CM in the $Y$-direction:

$$\overline{\langle (Y_{CM}(t) - Y_{CM}(0))^2 \rangle} = \frac{2T}{\zeta N} t + \frac{E^2}{\zeta^2} \langle \tilde{q}_0^2 \rangle t^2$$

(20)

In Eq. (20) $\langle \tilde{q}_0^2 \rangle$ is the pair correlation function of the charge variable and the brackets denote averages with respect to the realizations of $q_n$; furthermore use was made of the properties of $\tilde{f}_Y(p, t)$, i. e., Eqs. (17a) and (17b).

The $Y$-component of the end-to-end vector $P(t)$, $P(t) = R_N(t) - R_0(t)$, follows from the Fourier series, Eq. (11), for $Y_0(t)$ and $Y_N(t)$:

$$P_Y(t) = Y_N(t) - Y_0(t) = -2 \sum_{p=1}^{\infty} (1 - (-1)^p) Y(p, t) = -4 \hat{\sum_p} Y(p, t)$$

(21)

The hat on the rhs of Eq. (21) designates that the summation extends over odd, positive numbers only. Hence the double average of $P_Y$ obeys

$$\overline{\langle P_Y^2(t) \rangle} = 16 \hat{\sum_p} \hat{\sum_q} \overline{\langle Y(p, t) Y(q, t) \rangle}$$

(22)

Averaging the product of the normal coordinates on the rhs of Eq. (22) is straightforward. Using the explicit form of the normal coordinates, Eq. (18), and the properties of the Fourier transformed forces, Eqs. (17a) and (17b), we obtain

$$\overline{\langle P_Y^2(t) \rangle} = \frac{b^2 N}{3} + \frac{16E^2}{\zeta^2} \hat{\sum_p} \hat{\sum_q} \langle \tilde{q}_p \tilde{q}_q \rangle \int\limits_{0}^{t} d\tau_1 \int\limits_{0}^{t} d\tau_2 \exp(-p^2\tau_1/\tau_R - q^2\tau_2/\tau_R)$$

(23a)

Eq. (23a) will be used below to calculate the short-time behavior $t \ll \tau_R$. The long-time behavior $t \gg \tau_R$, when the end-to-end distance has reached its equilibrium, follows from Eq. (23a) by evaluating the integrals:

$$\overline{\langle P_Y^2(\infty) \rangle} = \frac{b^2 N}{3} + \frac{16E^2 b^4 N^4}{9\pi^4 T^2} \hat{\sum_p} \hat{\sum_q} \frac{\langle \tilde{q}_p \tilde{q}_q \rangle}{p^2 q^2}$$

(23b)

The behavior of a tagged bead, say one of the chain's ends, is more complicated. Using Eq. (11) with $n = 0$, i.e.,

$$Y_0(t) - Y_0(0) = Y(0,t) - Y(0,0) + 2 \sum_{p=1}^{\infty} (Y(p,t) - Y(p,0)) \tag{24}$$

we obtain by inserting the explicit solution Eq. (18) into Eq. (24):

$$Y_0(t) - Y_0(0) = \frac{1}{\zeta} \int_0^t d\tau \tilde{f}_Y(0,\tau) + \frac{2}{\zeta} \sum_{p=1}^{\infty} \int_0^t d\tau \tilde{f}_Y(p,\tau) \exp(-p^2(t-\tau)/\tau_R) \tag{25}$$

$$+ \frac{\tilde{q}_0 E}{\zeta} t + \frac{2E}{\zeta} \sum_{p=1}^{\infty} \tilde{q}_p \int_0^t d\tau \exp(-p^2(t-\tau)/\tau_R)$$

Hence, using the properties of the Fourier transformed Langevin forces, Eq. (17a) and (17b), we arrive at

$$\overline{\langle (Y_0(t) - Y_0(0))^2 \rangle} = \frac{4T}{\zeta N} \sum_{p=1}^{\infty} \int_0^t d\tau \, e^{-2p^2\tau/\tau_R} + \frac{2T}{\zeta N} t + \frac{4E^2}{\zeta^2} t \sum_{p=1}^{\infty} \langle \tilde{q}_0 \tilde{q}_p \rangle \int_0^t d\tau \, e^{-p^2\tau/\tau_R}$$

$$+ \frac{4E^2}{\zeta^2} \sum_{p=1}^{\infty} \sum_{q=1}^{\infty} \langle \tilde{q}_q \tilde{q}_p \rangle \int_0^t d\tau_1 \int_0^t d\tau_2 \, e^{-p^2\tau_1/\tau_R - q^2\tau_2/\tau_R} + \frac{E^2}{\zeta^2} \langle \tilde{q}_0^2 \rangle t^2 \tag{26}$$

## 3. Fixed charge patterns

This section is devoted to polymers whose charges are distributed according to a fixed pattern, say, having only a single charged bead, having alternating charges or having polyelectrolytes. We calculate explicitly the MSD of the CM, the mean-squared end-to-end distance and the MSD of a single bead.

### 3.1. A single charged bead

Let us first consider the situation in which only one bead of the polymer is charged, say one of its ends. Such a situation was realized experimentally by Perkins et al.[27,28] who dragged individual DNAs with optical tweezers at one of their ends. There are some interesting relations of such single charged polymers to other physical systems. In refs.[24,29] we have shown that the dynamics of the charged bead can be mapped on the response of mechanical spring-dashpot arrangements which we have proposed as mechanical analogues to fractional rheological constitutive equations[30,31] and as mesoscopic pictures of the sol-gel transition[32]. Another relevant situation concerns the solid-on-solid-model description of wetting phenomena discussed by Abraham et al.[33] Here the spreading of a liquid drop on a solid substrate, induced by capillary forces acting near the contact line, was examined using a Langevin equation approach similar to Eq. (9).

In the case that only the head-bead of the polymer is charged the charge distribution obeys

$$q_n = q \delta_{n0} \tag{27}$$

and the Fourier transformed $\tilde{q}_p$ has the form

$$\tilde{q}_p = q/N \tag{28}$$

for $p = 0, 1, 2, \ldots$. Inserting this into Eq. (20) leads to

$$\overline{(Y_{CM}(t) - Y_{CM}(0))^2} = \frac{2T}{\zeta N} t + \frac{q^2 E^2}{\zeta^2 N^2} t^2 \tag{29}$$

The MSD of the CM contains two independent contributions: a conventional Rouse diffusion term proportional to $t$[22, 23] and a drift term due to the external field, proportional to $t^2$. One can understand the $N^{-2}$-dependence of the drift term as follows: The electrical force acting on the chain, $qE$, does not depend on $N$, whereas the friction is proportional to $N$. Under both forces the polymer moves ballistically, with a velocity $V \sim qE/(\zeta N)$.

Using Eq. (23a) together with Eq. (28) and evaluating the sums over $p$ and $q$ by converting them to integrals, we obtain the following short-time behavior $t \ll \tau_R$ for the $Y$-component of the end-to-end distance:

$$\overline{P_Y^2(t)} = \frac{b^2 N}{3} + \frac{4 q^2 E^2 b^2}{3 \pi \zeta T} t \tag{30}$$

The rhs of Eq. (30) is a sum of two independent terms: the equilibrium end-to-end distance of a Rouse chain (without external forces)[22, 23] and a term proportional to $t$ as response to the external field.

Using Eq. (23b) we obtain for the equilibrium end-to-end distance for very large $t$, $t \gg \tau_R$:

$$\overline{P_Y^2(\infty)} = \frac{b^2 N}{3} + \frac{16 q^2 E^2 b^4 N^2}{9 \pi^4 T^2} \left( \sum_p \frac{1}{p^2} \right)^2 = \frac{b^2 N}{3} + \frac{q^2 E^2 b^4 N^2}{36 T^2} \tag{31}$$

The value of the infinite sum is given in Eq. (0.234(2.)) of ref.[34]: $\sum_p p^{-2} = \pi^2/8$.

Due to the charged bead which is pulled by the external field, the second term describes an elongation of the chain in the $Y$-direction. We note that the linear model is physically only useful as long the stretching is much smaller than the rodlike state[21], i.e. as long as

$$\frac{q^2 E^2 b^4 N^2}{36 T^2} \ll b^2 N^2 \tag{32}$$

holds, which restricts the external fields to values smaller than $6 T/(q b)$.

We now turn to the dynamics of the charged end of the chain. The short time behavior $t \ll \tau_R$ follows from Eq. (26) by converting the sums into integrals so that one obtains

$$\overline{(Y_0(t) - Y_0(0))^2} = 4 b \sqrt{\frac{T}{6 \pi \zeta}} t^{1/2} + \frac{2T}{\zeta N} t + \frac{4 q^2 E^2 b}{\zeta^{3/2} \sqrt{3 \pi T N}} t^{3/2}$$
$$+ \frac{4 q^2 E^2 b^2}{3 \pi \zeta T} t + \frac{q^2 E^2}{\zeta^2 N^2} t^2 \tag{33}$$

Neglecting the second term (which is of order $\sqrt{t/\tau_R}$ smaller than the first term) and the third and fifth term (which are of order $\sqrt{t/\tau_R}$ and $t/\tau_R$ smaller than the fourth term) we arrive at

$$\overline{(Y_0(t) - Y_0(0))^2} = 4b\sqrt{\frac{T}{6\pi\zeta}} \, t^{1/2} + \frac{4q^2E^2b^2}{3\pi\zeta T} \, t \tag{34}$$

i.e. a result mentioned previously in ref. [35] The first term in Eq. (34) shows a subdiffusive behavior (which also governs the short-time behavior of a bead in the absence of external forces) and can be interpreted as being induced by thermal processes, in which some local "defects", e.g., kinks, spread out diffusively along the length ($bN$) of the chain [36]. Since the chain's configuration in space is itself random-walk-like, so that in the absence of external forces $P_Y \sim (bN)^{1/2}$, these processes are spatially confined, which results in a subdiffusive behavior of single beads at short times.

The second term on the rhs of Eq. (34) describes the response of the charged monomer to the electrical field after switching on the field $E$. This term is equal to the corresponding term of Eq. (30) describing the short-time behavior of the end-to-end distance, since the uncharged end of the chain is not affected by the external field at short times.

In the long-time regime, $t \gg \tau_R$, the bead's motion mirrors the motion of the CM of the chain. This can be seen by evaluating the sums in Eq. (26) so that one has

$$\overline{(Y_0(t) - Y_0(0))^2} = \frac{b^2N}{9} + \frac{2T}{\zeta N} t + \frac{2q^2E^2b^2}{9\zeta T} t + \frac{q^2E^2b^4N^2}{81\,T^2} + \frac{q^2E^2}{\zeta^2N^2} t^2 \tag{35}$$

where the value of the infinite sums is given by Eq. (0.233(3.)) of ref. [34]:
$\sum_p p^{-2} = \pi^2/6$. Now, the first term is of order $\tau_R/t$ smaller than the second term and the third and fourth term are of order $\tau_R/t$ and $(\tau_R/t)^2$ smaller than the fifth term so that one finally arrives at

$$\overline{(Y_0(t) - Y_0(0))^2} = \frac{2T}{\zeta N} t + \frac{q^2E^2}{\zeta^2N^2} t^2 \tag{36}$$

## 3.2. Alternating charges

Let us now turn to PAs whose charges are distributed in alternating fashion, i.e.

$$q_n = (-1)^n q \tag{37}$$

This case is discussed theoretically in refs. [11, 12] We note that the mathematical treatment is rendered awkward by the discrete character of Eq. (37). In order to simplify the procedure, while still accounting for the basic feature of the alternating model we focus on the following continuous description for the charge distribution

$$q_n = \frac{\pi}{2} \sin(\pi n) q \tag{38}$$

where now $n$ is a real variable. Since this transformation only smears out the local charges, we expect the global properties of the chain to stay unaffected and we restrict the considerations to the long-time behavior. For the Fourier transform of the charge variable we obtain

$$\tilde{q}_0 = \begin{cases} 0 & \text{for } N \text{ even} \\ q/N & \text{for } N \text{ odd} \end{cases} \tag{39}$$

and

$$\tilde{q}_p = \frac{q}{2N} \frac{1}{1 - (p/N)^2} (1 - (-1)^{N+p}) \tag{40}$$

for $p = 1, 2, \ldots$. Inserting Eq. (39) into Eq. (20) we obtain for the MSD of the CM

$$\overline{(Y_{\text{CM}}(t) - Y_{\text{CM}}(0))^2} = \begin{cases} \dfrac{2T}{\zeta N} t & \text{for } N \text{ even} \\ \dfrac{2T}{\zeta N} t + \dfrac{q^2 E^2}{\zeta^2 N^2} t^2 & \text{for } N \text{ odd} \end{cases} \tag{41}$$

A drift occurs only when there is an excess charge, i.e. when the chain has an odd number of monomers. In this case the excess charge equals $q$, as in the case of one charged bead, resulting in the same behavior of the CM (cf. Eq. (29)). Clearly, Eq. (41) also describes the long-time behavior of a single bead.

The equilibrium end-to-end distance (i.e., $t \gg \tau_R$) can be evaluated by inserting the Fourier transformed charge variable, Eq. (40), into the general expression, Eq. (23 b). We find:

$$\overline{P_Y^2(\infty)} = \begin{cases} \dfrac{b^2 N}{3} + \dfrac{q^2 E^2 b^4 N^2}{36 T^2} & \text{for } N \text{ even} \\ \dfrac{b^2 N}{3} & \text{for } N \text{ odd} \end{cases} \tag{42}$$

If $N$ is odd $\tilde{q}_p$ vanishes for all odd p; hence the sums in Eq. (23 b) vanish, since they extend over odd $p$ only. In the case of an even number of monomers we have used the approximation

$$\sum_p^{\wedge} \frac{1}{1 - (p/N)^2} \frac{1}{p^2} \cong \sum_p^{\wedge} \frac{1}{p^2} \tag{43}$$

which is correct to order $1/N$.

Eq. (42) can be interpreted as follows: Due to the external field the chain takes for $N$ odd a zigzag configuration. Only in the case where charges of the ends have opposite signs (i.e., $N$ even), we obtain a small net effect. One may note that the value of the mean-squared end-to-end distance is identical to that of a polymer with only one charged bead (cf. Eq. (31)).

*3.3. Polyelectrolytes*

Now we turn to polyelectrolytes, i.e. homogeneously charged chains, for which

$$q_n \equiv q \tag{44}$$

holds. In this case the formulas become simple, since the Fourier transformed charge distribution fulfills

$$\tilde{q}_p = q \, \delta_{p0} \tag{45}$$

From Eq. (20) we have for the MSD of the CM

$$\overline{(Y_{CM}(t) - Y_{CM}(0))^2} = \frac{2T}{\zeta N} t + \frac{q^2 E^2}{\zeta^2} t^2 \tag{46}$$

The drift term is independent of $N$ since the overall charge of the chain is equal to $qN$ and therefore the electrical force acting on it (as well as the friction force) is proportional to $N$. A detailed discussion of the mobility of polyelectrolytes is given by Muthukumar[37] who also takes into account the hydrodynamic and electrostatic forces between the beads.

Due to the fact that the field acts on each monomer in the same way, the chain moves ballistically, without being deformed by the external field. The end-to-end distance is not affected by the external field so that one has for all times

$$\overline{P_Y^2(t)} = \frac{b^2 N}{3} \tag{47}$$

i.e. the chain's shape is Gaussian, as it is also the case in the absence of charges. However this result does not correspond to the experimental situation: due to the strong electrostatic repulsions (which we neglect here) the typical shape of a polyelectrolyte is mostly rodlike (so that $P_Y^2 \sim N^2$)[21]. Nonetheless, since the electrical field acts on all beads in the same way the chain moves as a whole, without being deformed by the external forces, regardless of its true shape. For the MSD of a single bead this fact results in an additional drift term so that one has from Eq. (26):

$$\overline{(Y_0(t) - Y_0(0))^2} = \frac{4T}{\zeta N} \sum_{p=1}^{\infty} \int_0^t d\tau \exp(-2p^2\tau/\tau_R) + \frac{2T}{\zeta N} t + \frac{q^2 E^2}{\zeta^2} t^2 \tag{48}$$

## 4. Random charge distributions

This section is devoted to PAs, whose charges are randomly distributed along the chain. Note first that a situation in which the charges are totally uncorrelated does not guarantee charge neutrality, since then the total charge is itself random (binomial). Asking for the chain to be electrically neutral as a whole poses an additional constraint. Furthermore, the distribution of charges along the chain may be strongly correlated, as was for instance attained experimentally in ref.[38] Here we examine first the uncorrelated case (section 4.1), then chains which are globally electrically neutral (section 4.2) and end with the analysis of correlated charge distributions (section 4.3). The latter case interpolates between the uncorrelated charge distribution and the polyelectrolytes (section 3.3), and displays a great variety of dynamical scaling laws.

## 4.1. Uncorrelated distribution of charges

In this section we calculate the behavior of PAs, for which the beads are either positively or negatively charged, $q_n = \pm q$; the distribution is such that different beads are uncorrelated, i.e. one has $\langle q_n q_m \rangle = q^2 \delta_{nm}$. This reads in the continuum limit:

$$\langle q_n q_m \rangle = q^2 \delta(n - m) \tag{49}$$

Eq. (49) implies automatically that the average charge equals zero, $\langle q_n \rangle = 0$. Note, however, that the latter condition does not imply that each chain is electrically neutral. For the Fourier transform of the charge variables we find now

$$\langle \tilde{q}_0^2 \rangle = \frac{q^2}{N} \tag{50a}$$

and

$$\langle \tilde{q}_p \tilde{q}_r \rangle = \frac{q^2}{2N} \delta_{pr} \tag{50b}$$

otherwise.

Inserting Eq. (50a) into Eq. (20) we obtain for the MSD of the CM in the $Y$-direction:

$$\overline{\langle (Y_{CM}(t) - Y_{CM}(0))^2 \rangle} = \frac{2T}{\zeta N} t + \frac{q^2 E^2}{\zeta^2 N} t^2 \tag{51}$$

The drift term shows here a $N^{-1}$-dependence which is by a factor of $N$ larger than in the case of one charged bead (section 3.1) and by a factor of $1/N$ smaller than in the polyelectrolyte case (section 3.3). One can understand the $N^{-1}$-dependence of the drift term in the following way: due to the randomness of 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 CM moves ballistically, with a velocity $V \sim qE/(\zeta\sqrt{N})$.

Consider now the behavior of the PA's end-to-end distance for a random placement of charges. Inserting Eqs. (50) into Eq. (23a) we obtain the following short-time behavior

$$\overline{\langle P_Y^2(t) \rangle} = \frac{b^2 N}{3} + \frac{16 b q^2 E^2 (\sqrt{2} - 1)}{3 \zeta^{3/2} \sqrt{3 \pi T}} t^{3/2} \tag{52}$$

for $t \ll \tau_R$. The response of the end-to-end distance to the electrical field follows a $t^{3/2}$ behavior which mirrors the behavior of the chain ends (see below).

Inserting Eq. (50) into Eq. (23b) we obtain for the equilibrium end-to-end distance $(t \gg \tau_R)$:

$$\overline{\langle P_Y^2(\infty) \rangle} = \frac{b^2 N}{3} + \frac{8 q^2 E^2 b^4 N^3}{9 \pi^4 T^2} \sum_p \frac{1}{p^4} = \frac{b^2 N}{3} + \frac{q^2 E^2 b^4 N^3}{108 T^2} \tag{53}$$

The value of the infinite sum is given by $\sum\limits_{p} p^{-4} = \pi^4/96$ (Eq. (0.234 (5.)) of ref. [34]. Besides the usual term proportional to $N$, we find an additional field-induced stretching characterized by a $N^3$-dependence. This scaling behavior emerges from the fact that the charge distribution shows fluctuations, whose magnitude grows with the number of beads. In ref. [24] we give also a Flory-type argument for this pronounced stretching. Note, however, that our linear model is physically only useful as long as the stretching is much smaller than the end-to-end distance of the rodlike state, i.e. as long as

$$\frac{q^2 E^2 b^4 N^3}{108\, T^2} \ll b^2 N^2 \tag{54}$$

holds, which means that the external field $E$ has to be much smaller than $10\, T/(qb\sqrt{N})$. Now we turn to the dynamics of the PA's end. Making use of Eqs. (26) and (50) we get

$$\overline{\langle (Y_0(t) - Y_0(0))^2 \rangle} = 4b\sqrt{\frac{T}{6\pi\zeta}}\, t^{1/2} + \frac{8bq^2 E^2 (\sqrt{2}-1)}{3\zeta^{3/2}\sqrt{3\pi T}}\, t^{3/2} \tag{55}$$

for $t \ll \tau_R$. Only the first and the fourth term of Eq. (26) contribute to the short-time behavior, whereas (in a fashion similar to Eq. (33)) the other terms are much smaller. The $t^{3/2}$ subdrift-term is by a factor $1/2$ smaller than the corresponding term describing the short-time dynamics of the end-to-end distance, Eq. (52).

For $t \gg \tau_R$, similarly to Eq. (35), the second and the fifth term dominate, and thus

$$\overline{\langle (Y_0(t) - Y_0(0))^2 \rangle} = \frac{2T}{\zeta N}\, t + \frac{q^2 E^2}{\zeta^2 N}\, t^2 \tag{56}$$

i.e., for long times the beads follow the motion of the CM (cf. Eq. (51)).

The field-induced motion of a single bead, Eqs. (55) and (56), can be also understood by the following scaling argument. Consider a single bead at $t = 0$. In the Rouse dynamics the total number $g$ of neighboring monomers which are involved in a collective motion with this tagged bead grows as $g(t) = Ct^{1/2}$ for short times ($t \ll \tau_R$). When the Rouse time $\tau_R$ is reached, the PA moves as a whole, i.e., $g(\tau_R) \cong N$, so that $C \cong \sqrt{T}/(\sqrt{\zeta}b)$. Thus for short times, $t \ll \tau_R$, one finds

$$g(t) \cong \frac{\sqrt{T}}{\sqrt{\zeta}b}\, t^{1/2} \tag{57a}$$

whereas at longer times, $t \gg \tau_R$, one has

$$g(t) \cong N \tag{57b}$$

The excess charge $Q$ of the collectively moving set of beads grows with time; one has $\langle Q^2 \rangle \cong q^2 g(t) \cong q^2 \sqrt{T/\zeta}\, b^{-1} t^{1/2}$. The mobility of the set of beads decreases as $\mu \cong (\zeta g(t))^{-1} \cong (b/\sqrt{\zeta T})\, t^{-1/2}$. The average velocity of the tagged monomer in $Y$-direction, $v_Y$, is then given by the velocity of the collectively moving set around it. Thus it obeys $\langle v_Y^2(g) \rangle \cong \mu^2 \langle Q^2 \rangle E^2 \cong q^2 E^2 \zeta^{-2} g^{-1}$ where $g$ is given by Eq. (57a) for $t \ll \tau_R$ and by Eq. (57b) for $t \gg \tau_R$. The average displacement of a single bead can be

estimated from the average displacement of the corresponding blob of $g$ monomers, i.e. $\langle Y^2(t)\rangle \cong \langle v_Y^2(g)\rangle t^2 \cong q^2 E^2 \zeta^{-2} g^{-1} t^2$. For $t \ll \tau_R$ one finds from Eq. (57a) $\langle Y^2(t)\rangle \cong (bq^2 E^2/(\zeta^{3/2} T^{1/2})) t^{3/2}$ which reproduces (up to a numerical constant of order 1) the field induced short-time behavior of our model, i.e. Eq. (55). For longer times the PA drifts as a whole and one finds from Eq. (57b) $\langle Y^2(t)\rangle \cong (q^2 E^2/(\zeta^2 N)) t^2$ which corresponds to Eq. (56). Clearly the scaling argument, Eq. (57), holds also for other charge distributions and can be used to determine the time-dependence of the dynamics of a tagged monomer. However, for the precise determination of the numerical coefficients in our model one has to carry out the exact calculations.

### 4.2. Neutral chains

We now consider globally neutral PAs. For these each bead is still positively or negatively charged, $q_n = \pm q$, but the total charge of the chain is zero. Such PAs were discussed in refs.[7,9,13]. To have a vanishing net charge the number of charged monomers, $N$, must be even and one has exactly $N/2$ positively charged and $N/2$ negatively charged beads. A random placement of charges under this restriction can be realized by picking randomly $N/2$ monomers (the positive ones) out of $N$, and taking the remaining monomers to be negative. Then the charge correlations obey

$$\langle q_n^2\rangle = q^2 \tag{58a}$$

and

$$\langle q_n q_m\rangle = -\frac{q^2}{N-1} \qquad \text{for } n \neq m \tag{58b}$$

Eq. (58b) can be obtained as follows: Assume first that the $n$th bead may have the charge $+q\,(-q)$. Due to the condition that the whole chain is neutral, the remaining $N-1$ beads have a total charge of $-q(+q)$. Hence averaging over all realization leads to Eq. (58b).

In the continuum limit Eqs. (58a) and (58b) can be combined as follows

$$\langle q_n q_m\rangle = -\frac{q^2}{N} + q^2 \delta(n-m) \tag{59}$$

Using Eq. (59) we find for the Fourier transformed quantities

$$\langle \tilde{q}_0^2\rangle = 0 \tag{60a}$$

and

$$\langle \tilde{q}_p \tilde{q}_r\rangle = \frac{q^2}{2N}\,\delta_{pr} \tag{60b}$$

otherwise.

Eq. (60b) parallels Eq. (50b) for an uncorrelated distribution of charges, whereas due to the vanishing total charge Eq. (60a) differs from Eq. (50a). Therefore, except for the drift term, which vanishes for globally neutral chains, the behavior of the neutral chain mirrors the behavior of PA with uncorrelated charge distributions.

Especially, Eqs. (52), (53) and (55) hold without any changes. The CM shows only a diffusive behavior (it obeys Eq. (51) without the drift term); the diffusive term also governs the long-time behavior of a single bead, i.e. one has Eq. (56) without the drift term.

### 4.3. Correlated distribution of charges

Let us now turn to the case of a PA, for which the distribution of charges along the chain displays correlations. This situation is realized when during polymerization the reaction rates for the addition of different types of monomers depend on the monomers already present at the chain ends. Such correlations were investigated by McCormick and Johnson[38] for suitably prepared polyampholytes. Here we assume correlations which decay exponentially along the length of the chain[7], i.e. which obey:

$$\langle q_n q_m \rangle = q^2 c_\eta \exp(-\eta \mid n - m \mid) \tag{61}$$

In Eq. (61) $\eta^{-1}$ is the correlation length and $c_\eta$ is chosen in such a way that $\int_{n-1/2}^{n+1/2} dn' \langle q_n q_{n'} \rangle = q^2$ holds. Hence

$$c_\eta = \frac{\eta}{2(1 - e^{-\eta/2})} = \begin{cases} \eta/2 & \text{for } 1 \ll \eta \\ 1 & \text{for } \eta \ll 1 \end{cases} \tag{62}$$

Eq. (61) interpolates between the uncorrelated case ($\eta \rightarrow \infty$), i.e. Eq. (49), and the strictly correlated case ($\eta \rightarrow 0$), resulting in $\langle q_n q_m \rangle = q^2$, which corresponds to the polyelectrolyte situation (see section 3.3).

The calculations in the presence of charge correlations are rather cumbersome and are relegated to the Appendix. The results are given in Eq. (63) (MSD of the CM), Tab. 1 (mean-square end-to-end distance) and Tab. 2 (MSD of a single bead).

Inserting Eq. (A2) into the general expression, Eq. (20) we obtain

$$\overline{\langle (Y_{CM}(t) - Y_{CM}(0))^2 \rangle} = \frac{2T}{\zeta N} t + c_\eta f(\eta N) \frac{q^2 E^2}{\zeta^2} t^2 \tag{63}$$

which for the different regimes of the correlation length yields:

$$\overline{\langle (Y_{CM}(t) - Y_{CM}(0))^2 \rangle} = \begin{cases} \dfrac{2T}{\zeta N} t + \dfrac{q^2 E^2}{\zeta^2 N} t^2 & \text{for } 1 \ll \eta \\[3mm] \dfrac{2T}{\zeta N} t + \dfrac{2}{\eta} \dfrac{q^2 E^2}{\zeta^2 N} t^2 & \text{for } N^{-1} \ll \eta \ll 1 \\[3mm] \dfrac{2T}{\zeta N} t + \dfrac{q^2 E^2}{\zeta^2} \left(1 - \dfrac{\eta N}{3}\right) t^2 & \text{for } \eta \ll N^{-1} \end{cases} \tag{64}$$

Except for negligible correction terms we obtain for $1 \ll \eta$ the same behavior as in the uncorrelated case, Eq. (51). For intermediate correlation lengths, $N^{-1} \ll \eta \ll 1$, one has typically $N/L$ homogeneously charged domains of average length $L$, where $L$ is given by

$$L = 2 \int_0^\infty dx \, x \, \eta \, e^{-\eta x} = 2/\eta \tag{65}$$

Thus, typical charge fluctuations are of the order of $qL\sqrt{N/L} \sim q\sqrt{N/\eta}$, resulting in a drift velocity of $V \sim q/(\zeta\sqrt{\eta N})$.

If the correlation length is much larger than the length of the polymer, i.e., $\eta \ll N^{-1}$, the chains carry mostly only one charge type: one has mainly polyelectrolytes, Eq. (46). The correction term in Eq. (64) can be understood as follows: Due to Eq. (65), the probability to have both types of charges on the same chain is roughly $N/L = \eta N/2$. Since $\eta N \ll 1$, such a chain is mostly composed only of two parts, one of length $N_+$ with positively charged beads and one of length $N_-$ with negatively charged beads; the total charge on the chain is then $Q = q(N_+ - N_-) = q(2N_+ - N)$. The mean square total charge $\overline{Q^2}$ for chains with both types of charges is thus given by $\overline{Q^2} = (q^2/N) \sum_{n=1}^{N} (2n - N)^2 \cong q^2N^2/3$. Hence the mean square total charge $\langle Q^2 \rangle$ is approximately given by

$$\langle Q^2 \rangle = \left(1 - \frac{\eta N}{2}\right) q^2 N^2 + \frac{\eta N}{2} \overline{Q^2} = \left(1 - \frac{\eta N}{3}\right) q^2 N^2 \tag{66}$$

resulting in the drift behavior described by Eq. (64).

We now display in Tab. 1 the behavior of the end-to-end distance in the different regimes. The detailed calculations can be found in Appendix A.2. The expressions for $1 \ll \eta$ are identical to those which describe the short- and long-time behavior in the uncorrelated case, Eqs. (52) and (53), as long as $t \gg \tau_R/(\eta N)^2$. The regime of very short times $t \ll \tau_R/(\eta N)^2$ is, however, not very illuminating, since in this regime the fine details of the local structure and charge distribution matter much. Therefore we dispense with giving this very short-time behavior in Tab. 1.

For intermediate correlation lengths, $N^{-1} \ll \eta \ll 1$, one has a situation reminiscent of an uncorrelated charge distribution: The chain may be viewed as consisting of

Tab. 1. Correction terms to the mean squared end-to-end distance, given as $\overline{\langle P_Y^2(t) \rangle} - b^2N/3$, for a correlated charge distribution (see text). The coefficients are $a_1 = 8(\sqrt{2} - 1)/(3\sqrt{3\pi T})$, $a_2 = 1/(108\,T^2)$ and $a_3 = 1/(270\,T^2)$. The lower limit of the intermediate time-regime has only to be considered for $N^{-1} \ll \eta$

|  | $t \ll \tau_R/(\eta N)^2$ | $[\tau_R/(\eta N)^2 \ll] t \ll \tau_R$ | $t \gg \tau_R$ |
|---|---|---|---|
| $1 \ll \eta \leq \infty$ | see text | $2a_1 \dfrac{bq^2E^2}{\zeta^{3/2}} t^{3/2}$ | $a_2 q^2 E^2 b^4 N^3$ |
| $N^{-1} \ll \eta \ll 1$ | $\dfrac{2q^2E^2}{\zeta^2} t^2$ | $\dfrac{4}{\eta} a_1 \dfrac{bq^2E^2}{\zeta^{3/2}} t^{3/2}$ | $\dfrac{2}{\eta} a_2 q^2 E^2 b^4 N^3$ |
| $\eta \ll N^{-1}$ | — | $\left(\dfrac{\eta N}{2}\right) \dfrac{4q^2E^2}{\zeta^2} t^2$ | $\left(\dfrac{\eta N}{2}\right) a_3 q^2 E^2 b^4 N^4$ |

subchains of mean length $N/L = \eta N/2$, such that the subchains carry only one type of charge each. Because of the length fluctuations one may roughly relate this situation by rescaling to an uncorrelated charge distribution. The transformation is:

$$N \to \eta N/2 \qquad q \to 2q/\eta \qquad \zeta \to 2\zeta/\eta \qquad b \to \sqrt{2/\eta}\,b \tag{67}$$

One may verify easily that this procedure leads from the expressions for $1 \ll \eta$ (first line of Tab. 1) to the results for $N^{-1} \ll \eta \ll 1$ (second line of Tab. 1). For $t \ll \tau_R/(\eta N)^2$ the correction term is proportional to $t^2$, a term which arises from a drift-type relative motion of oppositely charged segments.

In the case $\eta \ll N^{-1}$ the chains carry mostly only one type of charge. Only a small fraction of polymer (around $\eta N/2$) carries both types of charges, a fact which leads for short-times, $t \ll \tau_R$, to the appearance of a correction term proportional to $t^2$ (cf. Tab. 1). For $t \gg \tau_R$ the correction term to the usual $b^2N/3$ expression for the equilibrium end-to-end distance stems from the fraction of polymers of order $\eta N/2$ which is highly stretched (cf. Tab. 1). For $\eta \to 0$ this fraction vanishes and one is led to the polyelectrolyte case (cf. Eq. (47)).

Finally, we discuss the motion of a single bead (see Appendix A.3 for the derivation and Tab. 2 for the results). The $Y$-component of the MSD of an end-bead is for $1 \ll \eta$ and $\tau_R/(\eta N)^2 \ll t \ll \tau_R$ the sum of a subdiffusive and a subdrift term, similar to the results for an uncorrelated charge distribution, cf. Eq. (55) and Tab. 2. For long times the bead follows, as usual, the motion of the CM (cf. Eq. (64) and Tab. 2).

Rescaling following Eq. (67) we shift from the case $1 \ll \eta$ to the case $N^{-1} \ll \eta \ll 1$, as may be easily seen by comparing the first line of Tab. 2 with the second line. The behavior for very short times, $t \ll \tau_R/(\eta N)^2$, is the sum of a subdiffusive behavior and a drift term, which may be visualized as being due to the collective motion of $\eta^{-1}$ equally charged beads located at the end of the chain. For $\eta \ll N^{-1}$ this behavior extends to times $t \ll \tau_R$. Here again the long-time behavior is governed by the motion of the CM.

## 5. Conclusion

In conclusion, we have studied the influence of electrical fields on the dynamics of PAs both for non-randomly and for randomly placed charges, and we have obtained a series of analytical, closed-form results. At long times both the chain's CM and the individual beads move ballistically; here the average velocity depends on the net charge on the PA. On the other hand, for $t \ll \tau_R$ the motion of the individual beads shows a subdrift $t^\alpha$ behavior; the exponent equals $\alpha = 1$ if only one bead is charged, $\alpha = 3/2$ if the charges are distributed in an uncorrelated fashion, and $\alpha = 2$ if the correlation length is large or if the charges have all the same sign (polyelectrolytes). Furthermore the PAs stretch in an external field: The equilibrium mean square end-to-end distance shows an additional elongation, which goes as $N^\beta$; the exponent equals $\beta = 2$ if only one bead is charged or if the charges are distributed in an alternating fashion, $\beta = 3$ if the charges are distributed in an uncorrelated fashion, and $\beta = 4$ if the correlation length of the charge distribution is large. We close by noticing that the Rouse model used in the present work is simplified due to the neglect of

Tab. 2. MSD of a single bead, $\langle \overline{(Y_0(t) - Y_0(0))^2} \rangle$, for a correlated charge distribution (see text). The coefficients are $a_1 = 8(\sqrt{2} - 1)/(3\sqrt{3\pi T})$, $a_4 = 4\sqrt{T/(6\pi)}$ and $a_5 = 2T$. For the expression in square brackets see Tab. 1

| | $t \ll \tau_R/(\eta N)^2$ | $[\tau_R/(\eta N)^2 \ll] t \ll \tau_R$ | $t \gg \tau_R$ |
|---|---|---|---|
| $1 \ll \eta \leq 8$ | see text | $a_4 \dfrac{b}{\zeta^{1/2}} t^{1/2} + a_1 \dfrac{bq^2E^2}{\zeta^{3/2}} t^{3/2}$ | $a_5 \dfrac{1}{\zeta N} t + \dfrac{q^2E^2}{\zeta^2 N} t^2$ |
| $N^{-1} \ll \eta \ll 1$ | $a_4 \dfrac{b}{\zeta^{1/2}} t^{1/2} + \dfrac{q^2E^2}{\zeta^2} t^2$ | $a_4 \dfrac{b}{\zeta^{1/2}} t^{1/2} + \dfrac{2}{\eta} a_1 \dfrac{bq^2E^2}{\zeta^{3/2}} t^{3/2}$ | $a_5 \dfrac{1}{\zeta N} t + \dfrac{2}{\eta} \dfrac{q^2E^2}{\zeta^2 N} t^2$ |
| $\eta \ll N^{-1}$ | — | $a_4 \dfrac{b}{\zeta^{1/2}} t^{1/2} + \dfrac{q^2E^2}{\zeta^2} t^2$ | $a_5 \dfrac{1}{\zeta N} t + \dfrac{q^2E^2}{\zeta^2} \left(1 - \dfrac{\eta N}{3}\right) t^2$ |

hydrodynamic interactions. A way to introduce such interactions is to use the correspondence between the equations of motion in the Rouse and in the standard Zimm model with a preaveraged Oseen tensor. In the problem discussed here, however, much care has to be exercised, since the polymer shape changes much in even moderately strong external fields; this effect influences the PAs motion strongly and we defer its study to a further work.

## Appendix. Calculations for a correlated charge distribution

### A.1. Fourier transformed charge distribution

We determine first $\langle \tilde{q}_p \tilde{q}_r \rangle$, the average of the Fourier transformed charges. Using Eq. (61) the calculation of $\langle \tilde{q}_0^2 \rangle$ is straightforward

$$
\begin{aligned}
\langle \tilde{q}_0^2 \rangle &= \frac{q^2 c_\eta}{N^2} \int_0^N dn \int_0^N dn' \, \exp(-\eta \, | \, n - n' \, |) \\
&= \frac{2 q^2 c_\eta}{N^2} \int_0^N dn \int_0^n dn' \, \exp(-\eta(n - n'))
\end{aligned}
\tag{A1}
$$

where on the rhs of Eq. (A1) we have made use of the symmetry of the correlation function.

Hence we obtain

$$
\langle \tilde{q}_0^2 \rangle = q^2 c_\eta \frac{2}{\eta^2 N^2} (e^{-\eta N} - 1 + \eta N) = q^2 c_\eta f(\eta N)
\tag{A2}
$$

where $f(x)$ denotes the Debye function [23] defined by

$$
f(x) = \frac{2}{x^2} (e^{-x} - 1 + x)
\tag{A3}
$$

The correlation $\langle \tilde{q}_0 \tilde{q}_p \rangle$ for $p = 1, 2, \ldots$ can be determined as follows:

$$
\begin{aligned}
\langle \tilde{q}_0 \tilde{q}_p \rangle &= \frac{q^2 c_\eta}{N^2} \left[ \int_0^N dn \int_n^N dn' \, e^{-\eta(n-n')} \cos\left( \frac{p \pi n'}{N} \right) \right. \\
&\qquad\qquad \left. + \int_0^N dn \int_0^n dn' \, e^{-\eta(n'-n)} \cos\left( \frac{p \pi n'}{N} \right) \right] \\
&= (1 + (-1)^p) \frac{q^2 c_\eta}{N^2} \int_0^N dn \, e^{-\eta n} \int_0^n dn' \, e^{\eta n'} \cos\left( \frac{p \pi n'}{N} \right)
\end{aligned}
\tag{A4}
$$

where we have used the substitutions $n' \to N - n'$ and $n \to N - n$ on the rhs of Eq. (A4).

Evaluating the integral we arrive at

$$
\langle \tilde{q}_0 \tilde{q}_p \rangle = \frac{q^2 c_\eta}{\eta^2 N^2} (e^{-\eta N} - 1) \frac{1 + (-1)^p}{1 + (p \pi/(\eta N))^2}
\tag{A5}
$$

Finally, we have to determine the correlations $\langle \tilde{q}_p \tilde{q}_r \rangle$ for $p, r = 1, 2, \ldots$. Similarly to Eq. (A4) we get

$$\langle \tilde{q}_p \tilde{q}_r \rangle = (1 + (-1)^{p+q}) \frac{q^2 c_\eta}{N^2} \int_0^N dn \int_0^n dn' \, e^{-\eta(n-n')} \cos(p\pi n/N) \cos(q\pi n'/N) \qquad \text{(A6)}$$

After a few additional steps we obtain finally

$$\langle \tilde{q}_p \tilde{q}_r \rangle = \frac{q^2 c_\eta}{\eta^2 N^2} \left( \frac{\eta N}{2} \delta_{pr} + \frac{(-1)^p e^{-\eta N} - 1}{1 + (p\pi/(\eta N))^2} \right) \frac{1 + (-1)^{p+q}}{1 + (q\pi/(\eta N))^2} \qquad \text{(A7)}$$

which can be simplified for the case $\eta \ll N^{-1}$ to

$$\langle \tilde{q}_p \tilde{q}_r \rangle = \frac{\eta N}{p^2 \pi^2} \delta_{pr} \qquad \text{(A8)}$$

### A.2. End-to-end distance

To calculate the behavior of the end-to-end distance we have to insert expression Eq. (A7) into the general formulas (23). Let us first consider the case when the correlation length is much smaller than the length of the chain, i.e., $N^{-1} \ll \eta$. As usual, the short-time behavior can be calculated from Eq. (23 a) by converting the discrete sums into integrals so that one has

$$\overline{\langle P_Y^2(t) \rangle} = \frac{b^2 N}{3} + c_\eta \eta \frac{8q^2 E^2 N}{\zeta^2 \pi^2} \int_0^t d\tau \int_0^t d\tau' \int_0^\infty dp \, \frac{e^{-p^2(\tau+\tau')/\tau_R}}{(\eta N/\pi)^2 + p^2}$$
$$- c_\eta \eta^2 \frac{8q^2 E^2 N^2}{\zeta^2 \pi^4} \left( \int_0^t d\tau \int_0^\infty dp \, \frac{e^{-p^2 \tau/\tau_R}}{(\eta N/\pi)^2 + p^2} \right)^2 \qquad \text{(A9)}$$

Carrying out the integrations over $p$ (see for instance Eq. (7.4.11) of ref. [39]) one arrives at

$$\overline{\langle P_Y^2(t) \rangle} = \frac{b^2 N}{3} + c_\eta \frac{4q^2 E^2}{\zeta^2} \int_0^t d\tau \int_0^t d\tau' \exp\left( \left( \frac{\eta N}{\pi} \right)^2 \frac{\tau+\tau'}{\tau_R} \right) \text{erfc}\left( \frac{\eta N}{\pi} \sqrt{\frac{\tau+\tau'}{\tau_R}} \right)$$
$$- c_\eta \frac{2q^2 E^2}{\zeta^2} \left[ \int_0^t d\tau \exp\left( \left( \frac{\eta N}{\pi} \right)^2 \frac{\tau}{\tau_R} \right) \text{erfc}\left( \frac{\eta N}{\pi} \sqrt{\frac{\tau}{\tau_R}} \right) \right]^2 \qquad \text{(A10)}$$

This rather complex expression can be evaluated for different time regimes using the behavior of the function $\exp(x) \text{erfc}(\sqrt{x})$ for small and for large $x$. For $x \ll 1$ one has

$$\exp(x) \text{erfc}(\sqrt{x}) \cong 1 - 2\sqrt{x/\pi} \qquad \text{(A11)}$$

(see, for instance, Eq. (41.6.1) of ref. [40]), where one can find an extensive discussion of this special function). On the other hand, $x$ large, $x \gg 1$, the function obeys

$$\exp(x) \text{erfc}(\sqrt{x}) \cong 1/\sqrt{\pi x} \qquad \text{(A12)}$$

(see Eq. (41.6.4) of ref.[40]). The behavior of the end-to-end distance for very short times, $t \ll \tau_R/(\eta N)^2$, can be derived from Eq. (A10) using Eq. (A11), and the result, given in Tab. 1, is discussed in section 4.3. There one can also find the behavior for the intermediate time regime $\tau_R/(\eta N)^2 \ll t \ll \tau_R$; we have determined this behavior using the appropriate approximation, Eq. (A12).

The PA's equilibrium end-to-end distance $(t \gg \tau_R)$ for the case $N^{-1} \ll \eta$ follows directly from Eq. (23b) and the approximate expression

$$\hat{\sum_p} \frac{1}{p^k} \frac{1}{1 + (p\pi/(\eta N))^2} \cong \hat{\sum_p} \frac{1}{p^k} \tag{A13}$$

valid for $k = 2, 3, \ldots$ up to terms of order $1/(\eta N)$. Hence one has

$$\overline{\langle P_Y^2(\infty) \rangle} = \frac{b^2 N}{3} + \frac{c_\eta}{\eta} \frac{q^2 E^2 b^4 N^3}{54 T^2} \tag{A14}$$

Let us now turn to the case $\eta \ll N^{-1}$. The short-time behavior $t \ll \tau_R$ follows by inserting Eq. (A8) into Eq. (23a):

$$\overline{\langle P_Y^2(t) \rangle} = \frac{b^2 N}{3} + \frac{16\eta q^2 E^2 N}{\pi^2 \zeta^2} \hat{\sum_p} \int_0^t d\tau \int_0^t d\tau' \frac{e^{-p^2(\tau+\tau')/\tau_R}}{p^2}$$

$$= \frac{b^2 N}{3} + \frac{16\eta q^2 E^2 N}{\pi^2 \zeta^2} \int_0^t d\tau \int_0^t d\tau' \left[ \hat{\sum_p} \frac{1}{p^2} - \hat{\sum_p} \frac{1 - e^{-p^2(\tau+\tau')/\tau_R}}{p^2} \right] \tag{A15}$$

The second term in the brackets on the rhs of Eq. (A15) can be neglected so that one immediately obtains the corresponding expression in Tab. 1. The long-time behavior $t \gg \tau_R$ follows from Eq. (23b) together with Eq. (A8) by making use of $\sum_p 1/p^6 = \pi^6/960$ (see Eq. (0.233(5.)) with $n = 3$ in ref.[34]).

### A.3. Motion of a single bead

Let us now turn to the behavior of one end of the PA. Inserting the charge correlations, Eqs. (A2), (A5) and (A7), into the general expression, Eq. (26), and converting the sums into integrals we obtain similarly to the derivation of Eq. (A10) the following expression for the case $N^{-1} \ll \eta$ and $t \ll \tau_R$:

$$\overline{\langle (Y_0(t) - Y_0(0))^2 \rangle} = 4b\sqrt{\frac{T}{6\pi\zeta}} t^{1/2} - \frac{2c_\eta}{\eta} \frac{q^2 E^2}{\zeta^2 N} t \int_0^t d\tau \exp\left(\left(\frac{\eta N}{\pi}\right)^2 \frac{\tau}{\tau_R}\right) \mathrm{erfc}\left(\frac{\eta N}{\pi}\sqrt{\frac{\tau}{\tau_R}}\right)$$

$$+ 2c_\eta \frac{q^2 E^2}{\zeta^2} \int_0^t d\tau \int_0^t d\tau' \exp\left(\left(\frac{\eta N}{\pi}\right)^2 \frac{\tau+\tau'}{\tau_R}\right) \mathrm{erfc}\left(\frac{\eta N}{\pi}\sqrt{\frac{\tau+\tau'}{\tau_R}}\right) \tag{A16}$$

$$- c_\eta \frac{q^2 E^2}{\zeta^2} \left(\int_0^t d\tau \exp\left(\left(\frac{\eta N}{\pi}\right)^2 \frac{\tau}{\tau_R}\right) \mathrm{erfc}\left(\frac{\eta N}{\pi}\sqrt{\frac{\tau}{\tau_R}}\right)\right)^2 + \frac{2c_\eta}{\eta} \frac{q^2 E^2}{\zeta^2 N} t^2$$

Using the approximate forms for $\exp(x)\,\mathrm{erfc}\,(\sqrt{x})$ valid for small $x$, Eq. (A11), and for large $x$, Eq. (A12), we obtain immediately the MSD of a single bead, namely

$$\overline{\langle(Y_0(t) - Y_0(0))^2\rangle} = 4b\sqrt{\frac{T}{6\pi\zeta}}\,t^{1/2} + c_\eta\,\frac{q^2E^2}{\zeta^2}\,t^2 \tag{A17}$$

for $t \ll \tau_R/(\eta N)^2$ (here we have neglected the second and fifth term of Eq. (A16) which are of order $1/(\eta N)$ smaller than the third and fourth term) and

$$\overline{\langle(Y_0(t) - Y_0(0))^2\rangle} = 4b\sqrt{\frac{T}{6\pi\zeta}}\,t^{1/2} + \frac{2c_\eta}{\eta}\,\frac{8bq^2E^2(\sqrt{2} - 1)}{3\zeta^{3/2}\sqrt{3\pi T}}\,t^{3/2} \tag{A18}$$

for $\tau_R/(\eta N)^2 \ll t \ll \tau_R$ (here we have neglected the second, fourth and fifth terms of Eq. (A16) which are of order $1/(\eta N)$, $\sqrt{\tau_R/(\eta^2 N^2 t)}$ and $\sqrt{t/\tau_R}$ smaller than the third term), respectively. These results are discussed in section 4.3.

Inserting the corresponding charge correlations into Eq. (26) and using the approximation (A13) we obtain, as usual, that for $t \gg \tau_R$ a single bead follows the motion of the CM (cf. Tab. 2 and Eq. (64)).

Finally, we have to calculate the displacement for the case $\eta \ll N^{-1}$. For $t \ll \tau_R$ one has from Eqs. (26), (A2), (A5) and (A8):

$$\overline{\langle(Y_0(t) - Y_0(0))^2\rangle} = 4b\sqrt{\frac{T}{6\pi\zeta}}\,t^{1/2} - \eta N\frac{8q^2E^2}{\zeta^2\pi^2}\,t\sum_{p=2,4,\ldots}\frac{1}{p^2}\int_0^t d\tau\,\exp(-p^2\tau/\tau_R)$$
$$+ \eta N\frac{4q^2E^2}{\zeta^2\pi^2}\sum_{p=1}^\infty\frac{1}{p^2}\int_0^t d\tau\int_0^t d\tau'\,\exp(-p^2(\tau + \tau')/\tau_R) + \frac{q^2E^2}{\zeta^2}\left(1 - \frac{\eta N}{3}\right)t^2 \tag{A19}$$

The second and third term of the rhs of Eq. (A19) can be calculated analogously to Eq. (A15) and one obtains

$$\overline{\langle(Y_0(t) - Y_0(0))^2\rangle} = 4b\sqrt{\frac{T}{6\pi\zeta}}\,t^{1/2} - \eta N\frac{q^2E^2}{3\zeta^2}\,t^2 + \eta N\frac{2q^2E^2}{3\zeta^2}\,t^2$$
$$+ \frac{q^2E^2}{\zeta^2}\left(1 - \frac{\eta N}{3}\right)t^2 \tag{A20}$$

Thus the second and third term cancel the correction term in the expression for the drift of the CM (cf. Eq. (64)) and we obtain

$$\overline{\langle(Y_0(t) - Y_0(0))^2\rangle} = 4b\sqrt{\frac{T}{6\pi\zeta}}\,t^{1/2} + \frac{q^2E^2}{\zeta^2}\,t^2 \tag{A21}$$

For $t \gg \tau_R$ the first, third and fourth terms of Eq. (26) can be neglected, so that the bead's motion follows that of the CM, i.e., Eq. (64).

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