

# Conformations of freely jointed polyampholytes in external fields

H. Schiessel and A. Blumen

*Theoretical Polymer Physics, Freiburg University, Rheinstr. 12, 79104 Freiburg, Germany*

(Received 20 November 1995; accepted 4 January 1996)

We extend our previous treatment [J. Chem. Phys. **103**, 5070 (1995)] of polyampholytes (PAs, polymers with positively and negatively charged monomers) in an external field  $E$ , by modeling the PAs through freely jointed chains. Former works, based on Rouse-type models are linear, and hence are limited to sufficiently small values of  $E$ . The freely jointed chain model allows to consider the PAs conformations for  $E$  arbitrary. We calculate the PAs end-to-end distance for several charge distributions along the chain, which may be either ordered or random. For small  $E$  we recover previous results; large  $E$ -values lead to a crossover to stretched chain configurations, which depend crucially on the distribution of charges along the chain. © 1996 American Institute of Physics. [S0021-9606(96)50514-0]

## I. INTRODUCTION

The dynamical and conformational properties of charged heteropolymers show rich behavior patterns due to the interactions of the charges with each other and with applied electrical fields. Polyampholytes (PAs, polymers which carry positive and negative charges) are an especially interesting class of materials. The recent research focuses mainly on the role of the mutual electrical interactions on the conformational properties.<sup>1-10</sup> Depending on different physical parameters (i.e., on the charge distribution which can be random or regular, on the net charge of the whole chain, on the solvent quality and on the temperature) a PA may be in a collapsed or, conversely, in an extended configuration. In general, the collapse of random heteropolymers is very intriguing; a particularly interesting question here are the proteins, where a specific sequence of monomers induces their unique structure, a problem of much theoretical interest nowadays.<sup>11,12</sup>

Here we focus on the question how the PAs are affected by external electrical fields. We consider, for simplicity, a situation in which field-induced effects play a dominant role, whereas the intramolecular interactions between the charged monomers are unimportant. This situation (weak coupling of the charges) is achieved experimentally when at the temperature  $T$  the thermal energy (measured in units of the Boltzmann constant  $k_B$ ) is much larger than the electrical energy between neighbouring charges. With  $e$  being the electron charge,  $\epsilon$  the dielectric constant of the solvent and  $b$  the monomer size the relation is  $T \gg e^2/(\epsilon b)$ . By introducing the Bjerrum length  $l_B = e^2/(\epsilon T)$  the relation takes the form  $b \gg l_B$ . In this limit the thermal fluctuations disrupt the effect of the electrical interaction between the charges on the PAs configuration; in a  $\Theta$ -solvent and in the absence of an external field the PA is Gaussian. In Ref. 9 Dobrynin and Rubinstein have provided an even more accurate estimate of this weak-coupling regime. Using a Flory-type argument they find that the Gaussian conformation holds as long as

$$b > \rho \sqrt{N} l_B, \quad (1)$$

where  $N$  is the number of monomers and  $\rho$  denotes the fraction of charged monomers. Equation (1) can be achieved

readily by taking a solvent with a large dielectric constant; one has for water at room temperature  $l_B \cong 7 \text{ \AA}$  so that for small  $\rho$  Eq. (1) is fulfilled.

Putting PAs (in the weak coupling limit) in an external electrical field is one way of expose portions of a polymer chain to forces acting in different directions (tug of war); another way to achieve this is to consider an  $A-B$  copolymer at the interface between the two immiscible homopolymers  $A$  and  $B$ .<sup>13</sup> The concentration profile at the interface between the two phases may exhibit an extended gradient region;<sup>14,15</sup> if the  $A-B$  copolymer is located in this gradient region, its different monomers will feel forces in opposite directions, quite similar to the situation of a PA in an external electrical field.

In Refs. 16 and 17 we have calculated dynamical and conformational properties of PAs in external electrical fields in the weak coupling limit, Eq. (1). There we have used Rouse dynamics and thus assumed a linear behavior of the forces between the charges, fact which restricts the model to external fields which are sufficiently small. Thus for random PAs where each monomer carries either the charge  $+q$  or the charge  $-q$  the electrical field has to be much smaller than  $10T/(qb\sqrt{N})$ .<sup>16</sup>

In this work we examine a model for PAs which can also be used in strong external fields. We model the PA as a freely jointed chain with a fixed bond length  $b$  and calculate explicitly the end-to-end distance of the PA in equilibrium. We investigate the dependence of the PAs conformation on different random and nonrandom charge distributions along the chain. For small external fields we recover the results of the linear model of Refs. 16 and 17. For stronger external fields we find a crossover to stretched configurations.

## II. THE MODEL

Here we view the PA as consisting of  $N$  charged beads, connected into a linear chain by  $N-1$  links (bonds) of fixed length  $b$ . The PA is freely jointed,<sup>18</sup> i.e., each bond is able to point in any direction independently of the other bonds. We

represent the chain's conformation by the set  $\{\mathbf{R}_n\}$ , where  $\mathbf{R}_n = (X_n, Y_n, Z_n)$  denotes the position vector of the  $n$ th bead ( $n=0, \dots, N-1$ ). Alternatively the chain's configuration can be represented by the set  $\{\mathbf{r}_n\}$  of bond vectors  $\mathbf{r}_n = \mathbf{R}_n - \mathbf{R}_{n-1}$  ( $n=1, \dots, N-1$ ) from which the positions of the beads follow:

$$\mathbf{R}_n = \mathbf{R}_0 + \sum_{k=1}^n \mathbf{r}_k. \quad (2)$$

Furthermore we denote the charge of the  $n$ th bead by  $q_n$  and take it to be a quenched variable (i.e., the set  $\{q_n\}$  stays fixed for a given polymer).

In the following we investigate the behavior of PAs in the weak coupling limit where the interactions between the beads can be disregarded (cf. above and Ref. 9). Therefore we have to account only for the influence of the external, constant field  $\mathbf{E}$  on the beads. We also introduce an external force  $\mathbf{f}$  acting on the end-vectors and have as potential energy

$$U = -\mathbf{E} \left( \sum_{j=0}^{N-1} q_j \right) \mathbf{R}_0 - \mathbf{E} \sum_{j=1}^{N-1} q_j \sum_{k=1}^j \mathbf{r}_k - \mathbf{f} \sum_{k=1}^{N-1} \mathbf{r}_k. \quad (3)$$

In Eq. (3) the first term represents the potential of the total PA charge in the external field,  $Q_{\text{tot}} = \sum_{j=0}^{N-1} q_j$ . In the second term the length of the bond vectors is fixed,  $|\mathbf{r}_k| = b$ . The third term is introduced mainly for technical reasons; it can be used (see below) to derive readily from the partition function the average end-to-end vector.

Introducing the cumulative charge variable  $Q_k = \sum_{j=k}^{N-1} q_j$ , the potential energy can be reformulated as

$$U = -Q_{\text{tot}} \mathbf{E} \mathbf{R}_0 - \sum_{k=1}^{N-1} (Q_k \mathbf{E} + \mathbf{f}) \mathbf{r}_k. \quad (4)$$

In the following we restrict first our considerations to neutral PAs for which the total charge  $Q_{\text{tot}}$  vanishes; we implement the extension to PAs with a nonvanishing net charge afterwards. The interesting partition function is now

$$Z = \int d\Omega_1 \dots d\Omega_{N-1} \exp(-U/T) \\ = \prod_{k=1}^{N-1} \int d\Omega_k \exp[(Q_k \mathbf{E} + \mathbf{f}) \mathbf{r}_k / T] \quad (5)$$

in which the integrations run freely over the directions  $\Omega_k$  of the  $\mathbf{r}_k$ -vectors. Introducing spherical coordinates  $(\theta_k, \varphi_k)$  and taking the reference axis of the  $\theta_k$  parallel to  $\mathbf{E}$  we obtain in standard fashion,

$$Z = (4\pi)^{N-1} \prod_{k=1}^{N-1} \frac{\sinh[(Q_k E + f) b / T]}{(Q_k E + f) b / T}. \quad (6)$$

Note that the partition function in Eq. (6) is identical to the partition function of  $N-1$  independent dipoles (with charges  $Q_k$  and  $-Q_k$  at distance  $b$ ) in an external electrical field  $\mathbf{E}$  or, equivalently, to that of  $N-1$  magnetic dipoles in an external magnetic field, i.e., a classical paramagnetism problem.<sup>19</sup> This similarity can be understood as follows: Consider the bond connecting the beads  $k-1$  and  $k$  of the

PA. The bond subdivides the chain in two parts, one consisting of the beads  $n=0, \dots, k-1$  with total charge  $-Q_k$ , the other one consisting of the beads  $n=k, \dots, N-1$  with total charge  $Q_k$ . The external field  $\mathbf{E}$  acts on the net charges of this two parts, which are connected by a bond of fixed length  $b$  and hence display the effective dipole  $bQ_k$ .

We proceed further by calculating the end-to-end distance. In the following we take the  $Y$ -axis in the direction of the field  $\mathbf{E}$ ,

$$\mathbf{E} = (0, E, 0). \quad (7)$$

By setting further  $\mathbf{f} = (0, f, 0)$ , the thermally averaged  $Y$ -component of the end-to-end vector  $\mathbf{P}(t) = \mathbf{R}_{N-1}(t) - \mathbf{R}_0(t)$  can be evaluated by differentiating  $Z$  with respect to  $f$ ,<sup>18</sup> i.e.,

$$\overline{P_Y} = T \left( \frac{1}{Z} \frac{\partial Z}{\partial f} \right) \Big|_{f=0} = T \frac{\partial}{\partial f} \ln Z \Big|_{f=0}. \quad (8)$$

Here the dash denotes the thermal average. Inserting Eq. (6) into Eq. (8) we find for the end-to-end distance in the  $Y$ -direction,

$$\overline{P_Y} = b \sum_{k=1}^{N-1} \left[ \coth(Q_k E b / T) - \frac{T}{Q_k E b} \right] \\ = b \sum_{k=1}^{N-1} L(Q_k E b / T). \quad (9)$$

In Eq. (9)  $L(x) = \coth x - 1/x$  is the Langevin function;<sup>19</sup>  $L(x)$  shows the following approximate behavior:

$$L(x) \cong \begin{cases} 1 & \text{for } 1 \ll x \\ x/3 - x^3/45 & \text{for } -1 \ll x \ll 1, \\ -1 & \text{for } x \ll -1 \end{cases} \quad (10)$$

Using these limiting expressions for small and large external fields,  $\overline{P_Y}$  can be immediately given. For small fields  $E$ ,  $E \ll T/(b \max\{Q_k\})$ , one has

$$\overline{P_Y} = \frac{b^2 E}{3T} \sum_{k=1}^{N-1} Q_k, \quad (11)$$

i.e., the extension of the PA is proportional to the field strength  $E$ . For large fields, i.e.,  $E \gg T/(bq)$ , we find from Eqs. (9) and (10) for the end-to-end distance in field direction,

$$\overline{P_Y} = b(n_+ - n_-). \quad (12)$$

Here  $n_+$  denotes the number of  $Q_k$  with  $Q_k > 0$  and  $n_-$  the number of  $Q_k$  with  $Q_k < 0$ . Equation (12) results from the fact that in strong external fields all links with a nonvanishing effective dipole moment are directed parallel or antiparallel to the external field. Bonds with  $Q_k = 0$  are not affected by the external field and their contribution to  $\overline{P_Y}$  vanishes in the thermal average.

Let us introduce the susceptibility  $\chi = \overline{P_Y} / \partial E$ . It follows from Eq. (11) that  $\chi \propto T^{-1}$  for  $E \rightarrow 0$ . This dependence corresponds to the Curie law of paramagnetism, i.e., the magnetization  $M$  in a small external magnetic field  $B$  obeys

$\chi_M \equiv \partial M / \partial B \propto T^{-1}$ . This follows here directly from the physical analogy mentioned above. For  $E$  large  $P_Y$  is independent of  $E$ , i.e.,  $\chi=0$ , since one has a stretched situation [cf. Eq. (12)]; in the magnetic picture this corresponds to the saturation of dipoles in a strong external  $B$ -field.

We turn now to PAs with a nonvanishing total charge. In this case the center of mass (c.m.) moves under the influence of the field. In Refs. 16, 17 we have calculated for different charge distributions the c.m. drift motion under friction. Here we are interested in the internal deformations of the polymer and therefore we choose the c.m. as reference, whose position is  $\mathbf{R}_{\text{c.m.}} = \mathbf{R}_0 + \sum_{k=1}^{N-1} (N-k) \mathbf{r}_k / N$ . The potential energy, Eq. (4), can be rewritten as

$$U = -Q_{\text{tot}} \mathbf{E} \mathbf{R}_{\text{c.m.}}(t) - \mathbf{E} \sum_{k=1}^{N-1} (\tilde{Q}_k \mathbf{E} + \mathbf{f}) \mathbf{r}_k. \quad (13)$$

In Eq. (13)  $\tilde{Q}_k$  is a transformed charge variable defined by

$$\tilde{Q}_k = Q_k - \frac{N-k}{N} Q_{\text{tot}}. \quad (14)$$

As usual the first term in Eq. (13) represents the total external force acting on the c.m. whereas the second term describes the energy of the internal conformations (with fixed c.m.). The thermal average over the internal conformations of a PA with  $Q_{\text{tot}} \neq 0$  may be computed following the lines for a neutral PA by changing from  $Q_k$  to  $\tilde{Q}_k$ ; this change corresponds to a change in the individual charges from  $q_k$  to  $\tilde{q}_k = q_k - Q_{\text{tot}}/N$ .

### III. FIXED CHARGE DISTRIBUTIONS

In this section we discuss charge distributions with given fixed patterns. As a first example let us consider the case where only the end-beads are charged, namely  $q_0 = -q$ ,  $q_{N-1} = q$  and  $q_k = 0$  else. From this we find for the cumulative charge variable  $Q_k = q$  for  $k = 1, \dots, N-1$ . Using Eq. (9) we find for the end-to-end distance in the direction of the field

$$\begin{aligned} \overline{P_Y} &= b(N-1)L(qEb/T) \\ &\equiv \begin{cases} qEb^2(N-1)/(3T) & \text{for } E \ll T/(qb) \\ b(N-1) & \text{for } E \gg T/(qb) \end{cases}. \end{aligned} \quad (15)$$

Here the crossover from the linear regime to the fully stretched case is described by one Langevin function. This is a well-known result for the extension of a freely jointed chain when forces act on its end-beads only [see, for instance, Eq. (65) of Chap. VIII of Ref. 18].

Now we consider the case of alternating PAs where  $q_k = (-1)^{k+1}q$ . PAs with even and odd numbers of monomers have to be treated separately and, interestingly, show totally different conformations in strong external fields. For even  $N$  the PA is neutral. The cumulative charge variable fulfills

$$Q_k = \begin{cases} q & \text{for } k \text{ odd} \\ 0 & \text{for } k \text{ even.} \end{cases} \quad (16)$$

From Eq. (9) we find for the end-to-end distance

$$\begin{aligned} \overline{P_Y} &= b \sum_{k \text{ odd}} L(qEb/T) \\ &\equiv \begin{cases} (qEb^2N)/(6T) & \text{for } E \ll T/(qb) \\ bN/2 & \text{for } E \gg T/(qb) \end{cases}. \end{aligned} \quad (17)$$

In the limit of small external fields one finds a stretching term proportional to  $N$  which coincides with our previous findings [cf. Eq. (42) of Ref. 17]. For large external fields the end-to-end distance is half that of a fully stretched chain. This can be understood as follows: Due to Eq. (16) every second bond has a nonvanishing dipole moment. Only these  $N/2$  bonds orient in the  $E$ -field, each contributing to the end-to-end distance a length  $b$ . The remaining bonds may point in any direction without changing the energy of the PA, i.e., one has a highly degenerated ground state.

Now we turn to the case of alternating PAs with an odd number of monomers. Then the PA has a net charge  $Q_{\text{tot}} = -q$  and the c.m. moves in the external field. The cumulative charge is  $Q_k = 0$  for  $k$  odd and  $Q_k = -q$  for  $k$  even. Transforming according to Eq. (14) we have  $\tilde{Q}_k = Q_k + (N-k)q/N$  and thus

$$\tilde{Q}_k = \begin{cases} (N-k)q/N & \text{for } k \text{ odd} \\ -kq/N & \text{for } k \text{ even} \end{cases}. \quad (18)$$

This results in a vanishing thermal average of the end-to-end distance

$$\overline{P_Y} = b \sum_{k=2,4,\dots}^{N-1} L\left(-\frac{k}{N} \frac{qEb}{T}\right) + b \sum_{k=1,3,\dots}^{N-2} L\left(\frac{N-k}{N} \frac{qEb}{T}\right) \equiv 0. \quad (19)$$

In Eq. (19) each term of the first sum is exactly cancelled by a term of the second sum so that  $\overline{P_Y}$  is zero, regardless of the magnitude of the external field. Furthermore, due to the alternating signs of the  $\tilde{Q}_k$  [cf. Eq. (18)] the PA takes a zig-zag configuration in an external electrical field. Note that in a strong field all bonds are directed parallel to the field, pointing in alternating directions [cf. Eq. (19)], so that the PA collapses.

Summarizing, we find in our model (weak coupling limit, i.e., neglect of intrachain interactions) the following remarkable behavior for alternating PAs: In an external field the chains will stretch for  $N$  even (with a highly degenerated ground state) and will collapse for  $N$  odd to a single ground-state configuration. In other words: Even if the number of monomers is very large, the conformation of a PA with  $N$  monomers is strongly different from that of a PA with  $N+1$  monomers.

### IV. RANDOM CHARGE DISTRIBUTION

This section is devoted to PAs whose charges are randomly distributed along the chain. In such cases the calculation of the end-to-end vector is more complicated since one has to perform the average with respect to the different realizations of the charge distribution. Let us first calculate the

mean-squared end-to-end distance for a given fixed charge distribution. Using a similar procedure as in Eq. (8) we have now to differentiate  $Z$  twice, and obtain

$$\begin{aligned} \overline{P_Y^2} &= T^2 \left( \frac{1}{Z} \frac{\partial^2 Z}{\partial f^2} \right) \Big|_{f=0} \\ &= T^2 \frac{\partial^2}{\partial f^2} \ln Z \Big|_{f=0} + T^2 \left( \frac{\partial}{\partial f} \ln Z \Big|_{f=0} \right)^2. \end{aligned} \quad (20)$$

Inserting Eq. (6) renormalized according to Eq. (14) into Eq. (20) we find

$$\begin{aligned} \overline{P_Y^2} &= b^2(N-1) + b^2 \sum_{k=1}^{N-1} \sum_{l \neq k} L(\tilde{Q}_k E b / T) L(\tilde{Q}_l E b / T) \\ &\quad - 2b^2 \sum_{k=1}^{N-1} \frac{L(\tilde{Q}_k E b / T)}{\tilde{Q}_k E b / T}. \end{aligned} \quad (21)$$

Now, for random charge distributions  $\overline{P_Y^2}$  has to be averaged with respect to the realizations of  $\{q_k\}$ , and we denote this average by brackets,  $\langle \dots \rangle$ . Hence we have either to evaluate  $\langle \ln Z \rangle$  [cf. Eq. (20)] or forms such as  $\langle L(c_1 \tilde{Q}_k) L(c_2 \tilde{Q}_l) \rangle$  [cf. Eq. (21)], both of which are difficult tasks.

Using the approximate expressions for the Langevin function, Eq. (10), we can calculate  $\overline{P_Y^2}$  from Eq. (21) in the limits of weak and of strong fields. Following this strategy we find for weak fields,

$$\begin{aligned} \overline{P_Y^2} &\cong \frac{b^2(N-1)}{3} + \frac{b^4 E^2}{9T^2} \sum_{k=1}^{N-1} \sum_{l \neq k} \langle \tilde{Q}_k \tilde{Q}_l \rangle \\ &\quad + \frac{2E^2 b^4}{45T^2} \sum_{k=1}^{N-1} \langle \tilde{Q}_k^2 \rangle. \end{aligned} \quad (22)$$

For strong fields we find from Eqs. (10) and (21),

$$\overline{P_Y^2} = \frac{b^2}{3} \langle n_0 \rangle + b^2 \langle (n_+ - n_-)^2 \rangle. \quad (23)$$

Here  $n_+$ ,  $n_-$ , and  $n_0$  denote the number of  $\tilde{Q}_k$  with  $\tilde{Q}_k > 0$ ,  $\tilde{Q}_k < 0$ , and  $\tilde{Q}_k = 0$ , respectively [cf. also Eq. (12)].

In the following we consider random PAs with an uncorrelated distribution of charges. Assume that each monomer is either positively or negatively charged, i.e.,  $q_k = \pm q$  and that  $\langle q_k q_l \rangle = q^2 \delta_{kl}$ . This implies automatically that the average of the total charge vanishes, i.e.,  $\langle Q_{\text{tot}} \rangle = 0$ . A given chain, however, is not necessarily neutral so that one has to transform the charge distribution according to Eq. (14), from which we find

$$\begin{aligned} \langle \tilde{q}_k \tilde{q}_l \rangle &= \left\langle \left( q_k - \sum_{i=0}^{N-1} q_i / N \right) \left( q_l - \sum_{j=0}^{N-1} q_j / N \right) \right\rangle \\ &= q^2 \delta_{kl} - q^2 / N. \end{aligned} \quad (24)$$

In Ref. 17 we have also investigated PAs whose charges are placed randomly along the chain, under the constraint of global neutrality  $Q_{\text{tot}} = 0$ . The correlations  $\langle q_k q_l \rangle$  for this case [cf. Eq. (59) of Ref. 17] are for large  $N$  approximately

the same as the correlations  $\langle \tilde{q}_k \tilde{q}_l \rangle$  of Eq. (24). Thus the following considerations are also valid in the case of neutral PAs.

To evaluate  $\overline{P_Y^2}$  in the limit of small external fields we need the correlations of the cumulative charge variables  $\tilde{Q}_k$ . From Eq. (24) we find for  $k \geq l$ ,

$$\langle \tilde{Q}_k \tilde{Q}_l \rangle = \sum_{i=k}^{N-1} \sum_{j=l}^{N-1} \langle \tilde{q}_i \tilde{q}_j \rangle = q^2 \frac{(N-k)l}{N}. \quad (25)$$

Inserting Eq. (25) into Eq. (22) we find for  $N \gg 1$  and in the limit of small fields,  $E \ll T / (bq\sqrt{N})$ ,

$$\overline{P_Y^2} \cong \frac{b^2 N}{3} + \frac{q^2 E^2 b^4 N^3}{108 T^2}. \quad (26)$$

Besides the usual Gaussian term proportional to  $N$  we find an additional field-induced stretching proportional to  $N^3$ . This result coincides with our expression for the end-to-end distance in equilibrium, which we have calculated based on the Rouse model [cf. Eq. (20) of Ref. 16]. In Ref. 16 we also give a Flory-type argument for the  $N^3$ -dependence of the stretching term.

Let us now turn to large external perturbations. According to Eq. (23) one has to know the probability distributions of  $n_+$ ,  $n_-$ , and  $n_0$ . For  $N$  large these distributions can be deduced from results of random walk theory. Note that the set  $\{\tilde{Q}_k\}$  can be interpreted as being the path of a Brownian particle starting at  $\tilde{Q}_0 = 0$  and arriving after  $N$  elementary steps  $\tilde{q}_k$  ( $k = 0, \dots, N-1$ ) at  $\tilde{Q}_{N-1} = 0$ . It is a well-known result that for such Brownian bridges the sojourn times on the positive side, i.e.,  $n_+$ , or on the negative side, i.e.,  $n_-$ , are equally distributed (cf. the equidistribution theorem of Sec. III 9 of Ref. 20). Ignoring  $\langle n_0 \rangle$  which is of order  $\sqrt{N}$  we thus have for the probability  $p_+$  ( $p_-$ ) of having  $n_+$  ( $n_-$ ) steps on the positive (negative) side  $p_+ = p_- = N^{-1}$ . Thus we find from Eq. (23) for the end-to-end distance for large external fields,  $E \gg T / (bq)$ ,

$$\overline{P_Y^2} \cong \frac{b^2}{N} \sum_{k=0}^N (2k - N)^2 = \frac{b^2 N^2}{3}. \quad (27)$$

Thus the mean-squared end-to-end distance is a third of the squared length of a rodlike chain. This is due to the fact that typically some bonds are in the direction of the field ( $n_+$  ones) whereas  $n_-$  bonds are directed opposite to the field, resulting in a random, zig-zag configuration.

## V. CONCLUSION

In this work we have evaluated analytically the conformation of freely jointed PAs in external fields. This takes into account the finite extensibility (anharmonicity) of the chain. We calculated explicitly the end-to-end distance and find with increasing strength of the external field  $E$  a crossover from a regime linear in  $E$  to a stretched,  $E$ -independent situation. Furthermore, the end-to-end distance strongly depends on the distribution of charges along the chain. The conformation of alternating PAs in strong external fields is

highly sensitive to the number  $N$  of monomers. For  $N$  odd the PA collapses, whereas for  $N$  even the PA becomes extended.

## ACKNOWLEDGMENTS

The authors are indebted to Dr. G. Oshanin and to Dr. J.-U. Sommer for fruitful discussions. Financial support by the PROCOPE-Programme (administered by DAAD), by the Deutsche Forschungsgemeinschaft (SFB 60) and by the Fonds der Chemischen Industrie is gratefully acknowledged.

<sup>1</sup>S. F. Edwards, P. R. King, and P. Pincus, *Ferroelec.* **30**, 3 (1980).

<sup>2</sup>C. Qian and A. L. Kholodenko, *J. Chem. Phys.* **89**, 5273 (1988).

<sup>3</sup>P. G. Higgs and J. F. Joanny, *J. Chem. Phys.* **94**, 1543 (1991).

<sup>4</sup>J. M. Victor and J. B. Imbert, *Europhys. Lett.* **24**, 189 (1993).

<sup>5</sup>J. Wittmer, A. Johner, and J. F. Joanny, *Europhys. Lett.* **24**, 263 (1993).

<sup>6</sup>M. Schulz, R. G. Winkler, and P. Reineker, *Phys. Rev. Lett.* **73**, 1602 (1994).

<sup>7</sup>Y. Kantor and M. Kardar, *Europhys. Lett.* **27**, 643 (1994).

<sup>8</sup>B. Derrida and P. G. Higgs, *J. Phys. A* **27**, 5485 (1994).

<sup>9</sup>A. V. Dobrynin and M. Rubinstein, *J. Phys. II (France)* **5**, 677 (1995).

<sup>10</sup>Y. Kantor and M. Kardar, *Phys. Rev. E* **51**, 1299 (1995).

<sup>11</sup>T. E. Creighton, *Proteins: Their Structure and Molecular Properties* (Freeman, San Francisco, 1984).

<sup>12</sup>E. I. Shakhnovich and A. M. Gutin, *J. Phys. A* **22**, 1647 (1989).

<sup>13</sup>J.-U. Sommer and M. Daoud, *Phys. Rev. E* **53**, 905 (1996).

<sup>14</sup>K. Binder, *J. Chem. Phys.* **79**, 6387 (1983).

<sup>15</sup>U. K. Chaturvedi, U. Steiner, O. Zak, G. Krausch, and J. Klein, *Phys. Rev. Lett.* **63**, 616 (1989).

<sup>16</sup>H. Schiessel, G. Oshanin, and A. Blumen, *J. Chem. Phys.* **103**, 5070 (1995).

<sup>17</sup>H. Schiessel, G. Oshanin, and A. Blumen, *Macromol. Theory Simul.* **5**, 45 (1996).

<sup>18</sup>P. J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience, New York, 1969).

<sup>19</sup>R. K. Pathria, *Statistical Mechanics* (Pergamon, Oxford, 1972).

<sup>20</sup>W. Feller, *An Introduction to Probability Theory and Its Applications* (Wiley, New York, 1968), Vol. I.