Instabilities of polyampholytes in external electrical fields

H. Schiessel and A. Blumen
Theoretical Polymer Physics, Freiburg University, Rheinstrasse 12, 79104 Freiburg, Germany

(Received 15 March 1996; accepted 7 June 1996)

We consider the behavior of polyampholytes (PAs; heteropolymers carrying quenched positive and negative charges along the backbone) in external electrical fields. Whereas our previous treatments were devoted to the regime of a weak coupling of the charges, we consider here the regime where the electrostatic interactions between the charged monomers play the dominant role. Starting from a fluid drop picture we estimate the critical value of the external field that induces a breakup of the structure. As we proceed to show by scaling arguments, in strong fields the PA stretches out to a highly extended form, for which only a small fraction of the material is still organized in mesoscopic condensates along the rodlike configuration. *© 1996 American Institute of Physics.* [S0021-9606(96)52834-5]

I. INTRODUCTION

Polyampholytes (PAs), i.e., polymers with positively and negatively charged monomers, have received much attention in recent years, and the investigation of their conformational and dynamical properties is of much current interest. A prominent feature of PAs are the competing interactions between the charged monomers. PAs resemble in a certain way proteins, whose structure is determined by the specific sequence of their monomers.[1,2] From a more general point of view PAs may be seen as soft matter counterparts to random systems with competing interactions, such as spin glasses.[3]

The main emphasis of the recent work is devoted to the investigation of the influence of the charge distribution on the PAs' conformational properties.[4–15] Especially for random PAs, i.e., PAs where the charges $\pm q$ are distributed randomly along the chain, the determination of the conformation is a difficult task. The most important parameter here is the excess charge: Whereas a neutral PA forms a spherical globule, a highly charged PA behaves similarly to a polyelectrolyte, i.e., it is highly expanded. As theoretical and numerical investigations indicate, there is a critical excess charge Q_c, namely $Q_c \approx q\sqrt{N}$, which marks the borderline between the compact and the expanded states.[9,12]

Another question that can be asked in this context is the following: Assume one has a neutral PA in a globular state; what is the influence of an external electrical field on this object? Using a droplike model we show that there exists a critical value E_c for the external field E, so that only above E_c a breakup of the structure may occur. At E_c the external force overcomes the surface tension; above E_c the PA becomes highly extended. Using scaling arguments we will show that for $E \gg E_c$ only a small fraction of the monomers remains in a ''condensed,'' globular state; we recover in this regime our previous results for weak coupling concerning the conformational properties of PAs in external electrical fields.[16–18]

II. THE DROP ANALOGY

We consider in the following neutral PAs of polymerization degree N. A fraction $2f$ of the monomers is charged so that one has fN positive charges $+q$ and fN negative charges $-q$. The charges are distributed randomly along the chain and form a quenched pattern. It is well known that such neutral PAs collapse to spherical globules. Higgs and Joanny[6] assumed that the charged monomers arrange themselves in a way similar to a (micro)electrolyte. The electrostatic free energy F_e is estimated in the Debye–Hückel approximation as being[19]

$$\frac{F_e}{T} \approx -\frac{fNl_B}{r_D} = -\frac{(fNl_B)^{3/2}}{V^{1/2}}. \tag{1}$$

Here T denotes the temperature in units of the Boltzmann constant k_B, $l_B = q^2/(\epsilon T)$ is the Bjerrum length (with ϵ being the dielectric constant of the solvent), V is the volume of the PA globule, and $r_D = \sqrt{V/(fNl_B)}$ the screening length. [In Eq. (1) and in other expressions we omit dimensionless constants of order unity.]

The electrostatic part of the free energy, Eq. (1), induces a collapse of the PA; the excluded volume effect counteracts these attractive forces.[6] The virial expansion of the excluded volume interaction between the monomers takes the form

$$\frac{F_1}{T} \approx \frac{vb^3N^2}{V} + \frac{wb^6N^3}{V^2} + \cdots , \tag{2}$$

where b is the monomer size and v and w are the dimensionless second and third virial coefficients. Depending on the solvent quality v may be either positive or negative, whereas w is, in general, positive and of order unity.

Let us first consider a chain in a θ solvent, where $v = 0$; then one obtains for the excluded volume interaction $F_1 \approx b^6N^3/V^2$. Minimizing $F = F_e + F_1$ with respect to V, one finds

$$V \approx b^3N\,\frac{b}{fl_B}, \tag{3}$$

i.e., this Flory-type argument predicts a collapsed PA globule with a monomer density of $\rho \approx fl_B/b^4$. Note, however, that the above given argument is only valid as long as the PA volume, Eq. (3), is larger than the volume b^3N of the packed

0021-9606/96/105(10)/4250/7/$10.00

monomers and smaller than the volume of a Gaussian coil $b^3N^{3/2}$. This leads to the following condition:

$$fl_B < b < \sqrt{N} fl_B. \tag{4}$$

The first inequality is necessary for the applicability of the Debye–Hückel approximation,[19] the second one is the condition that the electrostatic interaction dominates the thermal agitation. In the opposite case, $b > \sqrt{N} fl_B$, the charges are coupled only weakly, so that the PA takes a Gaussian conformation. Since then the interaction between the charges can be neglected, the behavior of such a chain in external electrical fields can be treated analytically by modeling the PA as a Gaussian chain[16,17] or—in the case of strong external fields—as a freely jointed chain.[18]

Here we consider the opposite regime, where one has a strong coupling of the charges, i.e., $b \ll \sqrt{N} fl_B$. It was shown by Higgs and Joanny[6] that the PA can then be interpreted in terms of the following blob picture: Consider a subchain containing g_D monomers, with

$$g_D \approx \left(\frac{b}{fl_B}\right)^2. \tag{5}$$

Subchains of this length obey the Gaussian statistics, i.e., the volume given in Eq. (3) (with $N=g_D$) equals the volume $b^3 g_D^{3/2}$ of a Gaussian chain. The electrostatic free energy of these blobs is of order T [cf. Eq. (1)] and their size $r=b\sqrt{g_D}$ coincides with the Debye–Hückel length r_D, i.e., $r \cong r_D$. Assuming further that these Debye blobs form a closely packed arrangement, one has for the volume of the whole PA, $V \approx (N/g_D) b^3 g_D^{3/2} \approx b^3 N(b/fl_B)$, by which we recover Eq. (3).

The volume of the PA in a good solvent can be estimated along the same lines.[6] In a Flory-type approach one has to minimize $F=F_e+F_1$ with respect to V. The excluded volume part of the free energy, Eq. (2), has to be modified by a suitable resummation of the mean-field-like virial expansion. Scaling arguments[20,21] predict that the excluded volume contribution to the free energy for a polymer confined to a volume V is given by

$$\frac{F_1}{T} \approx \frac{b^{3/(3\nu-1)} N^{3\nu/(3\nu-1)}}{V^{1/(3\nu-1)}}, \tag{6}$$

in which ν, the Flory exponent, explicitly appears. Setting $\nu=\frac{3}{5}$ and minimizing $F=F_e+F_1$ with respect to V, one finds for the volume of the PA

$$V \approx b^3 N \left(\frac{b}{fl_B}\right)^2. \tag{7}$$

This result can be interpreted through a picture in which the Debye blobs are swollen.[6] Note that the electrostatic free energy is of order T for subchains of size $r \approx r_D$ [cf. Eq. (1)]. Because of the swelling exponent $\nu=\frac{3}{5}$, one now has $r \approx r_D \approx b g_D^{3/5}$, where g_D is the number of monomers in a blob. This, together with $r_D \approx f g_D l_B$, gives $g_D \approx (b/fl_B)^{5/2}$. By assuming that the whole PA is densely packed with swollen blobs, the volume of the PA is estimated as being $V \approx (N/g_D) r^3$, from which Eq. (7) again follows.

The above arguments lead to fixed volume conditions, namely Eq. (3) for the θ case and Eq. (7) for a good solvent. Thus, we are concerned with incompressible PAs. Their shapes, however, are controlled by other mechanisms: the competition between the surface tension and the external perturbations. The free energy of the surface is of the form

$$F_S = \gamma S, \tag{8}$$

where S denotes the surface of the PA and γ is the surface tension. Following Dobrynin and Rubinstein,[11] γ can be estimated by noting that each thermal blob at the surface has (because of missing neighboring blobs) an additional energy of order T. Since the radius of these blobs is of the order of the screening length r_D, one finds, for the surface tension,

$$\gamma \approx T/r_D^2. \tag{9}$$

In the absence of an external electrical field the PA takes a spherical shape to minimize its surface energy, Eq. (8)—a situation that is reminiscent of a fluid drop. Note that the overall neutrality is required for the spherical geometry to hold: charged PAs are deformed and a sufficiently large net charge $Q > Q_c \approx q\sqrt{N}$ causes a breakup of the drop, as was discussed by Kantor and Kardar.[12]

Here we consider the case of a neutral PA in an external electrical field. Related situations are given when one applies external electrical fields to dielectric or conducting drops (see Ref. 22 and references therein). Especially, a conducting, fluid drop of conductivity σ_1 suspended in a fluid of conductivity σ_2 (with $\sigma_2 < \sigma_1$) behaves as follows: Under small external fields the drop undergoes only a smooth deformation, under larger fields it takes a dumbbell-like shape. Under a further increase of the field the drop lengthens rapidly and divides itself into two blobs connected by a thin thread, before the final breakup occurs. For $\sigma_1 \gg \sigma_2$ the response to the external field is different: both ends of the drop become pointed and from them charged droplets are ejected. The ratio of conductivities dividing these two mechanisms lies around $\sigma_1/\sigma_2 \approx 30$.

The situation of a neutral PA in an external field is related to the above. If the charges could move freely along the chain (the annealed case) and follow the field, a response similar to the tip-formation mechanism would occur. Due to the connectivity of the PA it is not possible for the system to eject droplets, but it can lower its energy by extruding charges along fingers at the two ends. A similar situation may occur for a charged annealed PA, where the polymer may lower its energy by forming charged, protruding fingers.[12]

Here we are, however, interested in the usual case of *quenched* charge distributions. Due to the connectivity of the chain, the positive and the negative charges cannot be arbitrarily separated. The situation can be envisaged as follows: Consider that the neutral PA chain is divided into two halves; on the average they have excess charges of opposite sign, which are typically of the order $q\sqrt{fN}$. When a sufficiently large external field is applied we expect that these halves will rearrange themselves in a way that minimizes the free energy. A way to achieve this is through a deformation

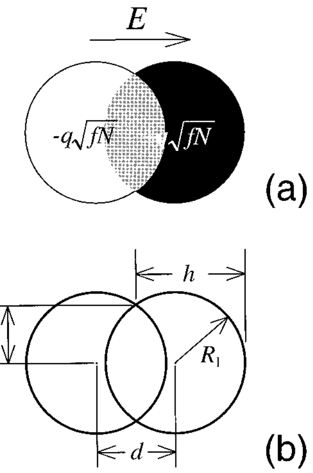

FIG. 1. Neck formation of a polyampholyte globule in an external electrical field: charge distribution (a) and geometrical parameters (b). The pictures display a cross section of a cylindrically symmetric dumbbell.

of the—incompressible—PA volume, similarly to the dumbbell previously mentioned. Note that the fixed volume (incompressibility) condition is not affected by the presence of a (not-too-strong) external field: The major part of the monomers is still organized in blobs according to the Debye–Hückel prescription.

Here we follow a simple liquidlike model for the PA that fulfills the fixed volume condition, Eq. (3) or Eq. (7). Furthermore, we have to restrict the whole spectrum of possible shapes to a reasonably small subclass. Since we expect that for increasing external fields the PA follows similar deformations as conducting drops (especially the formation of a neck), we start from a dumbbell-like structure, as shown in Fig. 1(a). It consists of two spheres of equal size that overlap each other. We let one of them carry as total charge $q\sqrt{fN}$, and the other one $-q\sqrt{fN}$. This takes implicitly into account that the charges are connected via the PA backbone. This picture leads to an effective dipole, and to a one-parameter family of shapes that depend—for a fixed total volume V—only on the distance d between the centers of the spheres [see Fig. 1(b)]. Due to its simple geometrical form this model has the advantage of being analytically tractable (the surface energy and the electrical potential energy of the effective dipole can be expressed analytically; see below). We speculate that this class of shapes represents a good approximation to the equilibrium shapes of the real PA under moderate external fields; this holds good up to a critical electric field E_c at which the whole structure breaks down; see below.

To be more quantitative, we calculate now the potential (free) energy F_{ext} of the effective dipole and the surface free energy F_S, Eq. (8), as a function of the distance d between the centers. Then we have to minimize $F'=F_{\text{ext}}+F_S$ with respect to d. Now F_{ext} in the external field E is of the form

$$F_{\text{ext}}(d)=-q\sqrt{fN}Ed, \tag{10}$$

where we set, for simplicity, the dielectric constant ϵ of the medium to be unity.

Now, to evaluate F_S we need to know the surface of the dumbbell as a function of d, i.e., $S=S(d)$. The surface is simply given by the surface of the two intersecting spherical portions. We find by simple integration

$$S=4\pi hR_1=4\pi h(h-d/2), \tag{11}$$

with R_1 being the radius of the spheres and $h=R_1+d/2$ the height of the portions [see Fig. 1(b)]. Furthermore, d has to be confined to the interval

$$0\leqslant d\leqslant 2^{2/3}R, \tag{12}$$

the lower limit corresponding to one (neutral) sphere, with radius $R=[3V/(4\pi)]^{1/3}$, the upper limit to two smaller (oppositely charged) spheres attached at one point. Now h has to be chosen such that the fixed volume condition is fulfilled. Hence, again through integration, we have

$$\frac{2\pi}{3}h^2(3R_1-h)=V, \tag{13}$$

with V being given by Eq. (3) (θ case) or Eq. (7) (good solvent), respectively. Thus we arrive at a cubic equation for h, namely at $h^3-3dh^2/4-R^3=0$, whose solution is

$$h=h(d)=\frac{R}{2^{2/3}}\left[\left(1+\sqrt{1+\frac{d^3}{16R^3}}\right)^{2/3}+\left(1-\sqrt{1+\frac{d^3}{16R^3}}\right)^{2/3}\right]+\frac{d}{4}. \tag{14}$$

Series expansion of Eq. (14) to order $(d/R)^3$ yields

$$h(d)\cong R\left(1+\frac{1}{4}\frac{d}{R}+\frac{1}{16}\frac{d^2}{R^2}+\frac{1}{96}\frac{d^3}{R^3}\right). \tag{15}$$

Now Eq. (15) agrees with Eq. (14) within a relative error of 0.5% over the whole range of d values, and is hence a reasonable approximation for us. From Eqs. (11) and (15) we obtain S as a function of d

$$S(d)\cong 4\pi R^2\left(1+\frac{1}{16}\frac{d^2}{R^2}+\frac{1}{48}\frac{d^3}{R^3}\right), \tag{16}$$

where again terms of the order $(d/R)^4$ were neglected. Now, minimizing $F'=F_{\text{ext}}+F_S$ with respect to d [cf. Eqs. (8), (10), and (16)], we find that

$$d(E)\cong R\left[\left(\frac{4\sqrt{fN}qE}{\pi\gamma R}+1\right)^{1/2}-1\right]. \tag{17}$$

The properties of the solvent are implicitly included in Eq. (17) through R and γ. Note that Eq. (17) characterizes the equilibrium shape of the PA when one restricts all possible shapes (with a given volume V) and charge distributions (under the constraint of overall neutrality) to the special class of dumbbell-like objects depicted in Fig. 1(a).

Inserting Eq. (17) into Eq. (15) we find that L, the PA length in the direction of the field, grows with E as

$$L(E)=2h[d(E)]$$
$$\cong R\left(\tfrac{5}{3}+\tfrac{5}{16}(1+\alpha E)^{1/2}+\tfrac{1}{16}\alpha E+\tfrac{1}{48}(1+\alpha E)^{3/2}\right), \tag{18}$$

with $\alpha=4\sqrt{fN}q/(\pi\gamma R)$. Especially for $E\alpha\ll 1$ the PA globule shows a linear response of the extension $\Delta L=L(E)-L(0)$ to the external field, namely,

$$\Delta L\cong\frac{\sqrt{fN}qE}{\pi\gamma}. \tag{19}$$

The dumbbell shape is, however, stable only for external fields E up to a critical value E_c. At $E=E_c$ the neck has become so narrow that the PA lengthens rapidly by forming a bridge between the two blobs. The critical value can be estimated as follows: The radius a of the neck is given by $a^2=h(2R_1-h)=h(h-d)$ [cf. Fig. 1(b)]. Thus we find from Eq. (15)

$$a^2\cong R^2\left(1-\frac{1}{2}\frac{d}{R}-\frac{1}{16}\frac{d^2}{R^2}-\frac{1}{96}\frac{d^3}{R^3}\right), \tag{20}$$

where terms of order $(d/R)^4$ were neglected. The dumbbell becomes unstable when the external electrical field is so large that there exists an infinitesimal deformation where the increase of the surface energy equals the decrease in the electrical potential. The ''weak point'' of the dumbbell is located at the neck. When at the neck a cylindrical bridge of radius a and (infinitesimal) height dL is formed, the change in surface energy is given by $dF_S=2\pi\gamma a\ dL$, whereas we find for the electrical potential $dF_{\mathrm{ext}}=-\sqrt{fN}qE\ dL$. Thus the dumbbell becomes unstable at $E=E_c$ with E_c given by

$$2\pi\gamma a[d(E_c)]=\sqrt{fN}qE_c. \tag{21}$$

Inserting Eqs. (17) and (20) into Eq. (21) results in the quartic equation $x^4+2x^3/3+26x-\frac{275}{3}=0$ for $x=\sqrt{1+\alpha E_c}$, which determines the critical value E_c. Thus $x\cong 2.25$, and we obtain finally

$$E_c\cong 4.06\alpha^{-1}\cong 3.19\frac{\gamma R}{\sqrt{fN}q}. \tag{22}$$

With this result we obtain for $E=E_c$ the geometrical parameters that characterize the dumbbell: they are $d\cong 1.25R$, $a\cong 0.51R$, $h\cong 1.43R$, and $R_1\cong 0.81R$.

At $E\cong E_c$ the surface tension cannot counterbalance the electrical force anymore and the PA lengthens rapidly. The PA takes an extended configuration that we discuss in the next section.

III. THE EXTENDED STATE

The conformational properties of the extended state for $E\geqslant E_c$ can be derived by using scaling arguments. We have to modify an approach going back to Pincus[23] (cf. also Ref. 21), which we shortly recall here. Pincus considered a single chain under traction where the forces $\mathbf{F}$ and $-\mathbf{F}$ are applied to the ends. Then the elongation ΔL of the chain may be written as

$$\Delta L=L(F)-L=L\varphi\left(\frac{L}{\xi}\right), \tag{23}$$

with a dimensionless function φ. Here $L=L(0)$ denotes the end-to-end distance of the unperturbed chain $L=bN^{\nu}$ (with $\nu=\frac{3}{5}$ in a good solvent and $\nu=\frac{1}{2}$ in a θ solvent), and $\xi=T/F$. Now ξ is a characteristic length of the problem: For small F, $L/\xi\ll 1$, the response is linear in F, i.e., $\varphi(x)\propto x$, and thus $\Delta L\propto L^2F/T$; for large F, $L/\xi\gg 1$, the chain breaks up into a string of independent blobs, each of size ξ. Inside the blob the external force induces only a small perturbation so that one has a swollen (ideal) subchain consisting of $g=(\xi/b)^{1/\nu}$ monomers. The elongation of the whole chain is then given as

$$\Delta L\cong\frac{N}{g}\,\xi\cong\begin{cases} Nb\,\dfrac{bF}{T}, & \text{in a }\theta\text{ solvent},\\[2ex] Nb\left(\dfrac{bF}{T}\right)^{2/3}, & \text{in a good solvent.}\end{cases} \tag{24}$$

Note that in this regime the response of the excluded volume chain is nonlinear in the applied force.

In the following we use similar arguments to analyze the extended state of the PA in strong fields. First, let us mentally switch off the electrostatic interaction between the charges; as we will see later, this interaction can be incorporated easily *a posteriori*. We note further that the discussion of PAs without interactions between the charges is interesting for its own sake, since it describes the regime $b>\sqrt{N}fl_{\mathrm{B}}$ (weak coupling limit).[16–18]

We consider here neutral PAs, built out of N monomers ($n=1,2,\ldots,N$), carrying the charges q_n. Let us introduce the cumulative charge variable $Q_n=\Sigma_{i=1}^{n}q_i$, which denotes the net charge of the subchain consisting of the n first monomers. Due to the overall charge neutrality of the PA the remaining $N-n$ monomers carry the net charge $-Q_n$. Consider now the force acting on the segment between the monomers n and $n+1$: In an external field E it is given by $F_n=Q_nE$. Therefore, contrary to the original Pincus problem we have here the situation of a nonuniform, n-dependent force that stretches the chain. Thus we need in the following a generalization of Eq. (24) (strong field) for nonuniform stretching. We follow here an argument given by Brochard–Wyart, who considered the nonuniform deformation of tethered chains in strong external flows.[26] We denote by $\xi_n=T/F_n$ the (n-dependent) blob sizes, by $g_n=(\xi_n/b)^{1/\nu}$ the number of monomers of the blob to which n belongs, and by l_n the position of the nth monomer in the direction of the field. Then we find from Eq. (24) for the local deformation of the chain at n

$$dl_n\cong\frac{\xi_n}{g_n}\,dn. \tag{25}$$

In order to simplify the calculations and to get a clearer picture we use in the following a preaveraged charge distribution. For a homogeneous random distribution of charges along the chain the correlation between sites is given by[17]

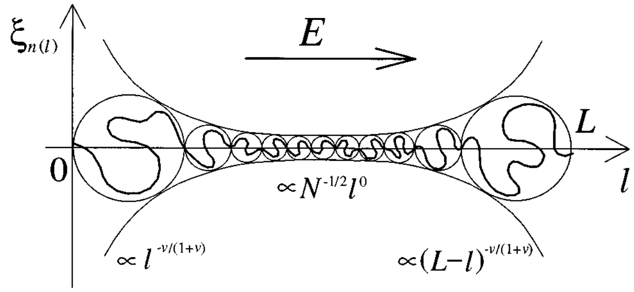

FIG. 2. Equilibrium conformation of polyampholytes in an external field for a weak coupling between the charges. The PA shape for a preaveraged charge distribution is depicted (see the text for details).

$$\langle q_i q_j\rangle = \begin{cases} q^2 f, & \text{for } i=j, \\ -\dfrac{q^2 f}{N-1}, & \text{for } i\neq j, \end{cases} \tag{26}$$

where the brackets denote averages with respect to the realizations of the q_n. From Eq. (26) we find for the mean squared cumulative charge variable $\langle Q_n^2\rangle \cong q^2 fn(1-n/N)$. We use in the following $Q_n=\sqrt{\langle Q_n^2\rangle}$ instead of Q_n. Now, in this preaveraged picture the sizes of the Pincus blobs obey

$$\xi_n \cong \frac{T}{\sqrt{fn(1-n/N)}qE}, \tag{27}$$

i.e., we have a series of blobs whose sizes increase toward both ends (cf. Fig. 2). Inserting the n dependence of the blob size, Eq. (27) into Eq. (25), and integrating from 0 to n, we find for the position of the nth monomer

$$l_n \cong \beta \int_0^{n/N} dx [x(1-x)]^{(1-\nu)/(2\nu)}$$
$$= \beta B\left(\frac{1+\nu}{2\nu};\frac{1+\nu}{2\nu};\frac{n}{N}\right), \tag{28}$$

with $\beta = b^{1/\nu}(\sqrt{f}qE/T)^{(1-\nu)/\nu}N^{(1+\nu)/(2\nu)}$ and B being the incomplete beta function [cf. Eq. (58.3.1) of Ref. 27]. Consider now the deformation around one of the chain's ends. Since the situation is symmetric with respect to the middle of the chain it is sufficient to consider the end that contains the monomer $k=1$. From Eq. (28) follows that $l_n \propto n^{(1+\nu)/(2\nu)}$ for $n \ll N$, a result that can also be found analytically for the Gaussian chain ($\nu=1/2$).[24] Note that here the deformation is independent of N since only the local charge distribution q_k (or Q_k) with $k=1,\ldots,n$ affects the deformation at the chain's end. Thus, to the left of Fig. 2 the blob sizes increase with decreasing l as $\xi_{n(l)} \propto n(l)^{-1/2} \propto l^{-\nu/(1+\nu)}$, as indicated in the figure; the exponent equals $-\frac{3}{8}$ for a swollen chain and $-\frac{1}{3}$ for an ideal chain. The scaling behavior in the middle of the chain is different: From Eq. (28) one finds for a subchain comprising m monomers ($m \ll N$)

$$l_{N/2} - l_{N/2-m} \propto mN^{(1-\nu)/2\nu}, \tag{29}$$

which is due to the typical charge fluctuations of both halves of the chain, a result that also follows from more general considerations.[25] Hence, in the central part of the chain the Pincus blobs have nearly the same size, namely $\xi_{n(l)} \propto N^{-1/2}l^0$ [cf. Eq. (27) and Fig. 2]. The shape in Fig. 2 can now be compared with the typical conformation of a tethered chain in a strong flow.[26] There the forces (blob sizes) decrease (increase) from the grafted site to the free end, so that the chain attains a trumpetlike shape. Our preaveraged PA shape is similar, having, however, two trumpetlike ends.

To obtain the end-to-end distance we have to set in Eq. (28) $n=N$ and find

$$L \cong \beta \int_0^1 dx [x(1-x)]^{(1-\nu)/(2\nu)}$$
$$= \beta \frac{\Gamma^2[(1+\nu)/(2\nu)]}{\Gamma[(1+\nu)/\nu]} \approx \beta, \tag{30}$$

[cf. (43.13.1) of Ref. 27 for the evaluation of the integral]; i.e., explicitly

$$L \approx \begin{cases} bN\dfrac{\sqrt{fN}qEb}{T}, & \text{in a } \theta \text{ solvent}, \\ bN\left(\dfrac{\sqrt{fN}qEb}{T}\right)^{2/3}, & \text{in a good solvent}. \end{cases} \tag{31}$$

For the θ case we hence recover with Eq. (31) (up to a numerical constant) an exact result for Gaussian chains that we have calculated recently.[16,17] The excluded volume chain shows a similar nonlinear response, as in the case of a uniform deformation, Eq. (24); one has simply to replace F by an effective force of the order $\sqrt{fN}qE$. The deformation under strong stretching in the middle part of the chain already determines the overall size of the PA: Setting in Eq. (29) $m=N$ one finds the same N dependence as for L in Eq. (31). Clearly, all the results given above are only valid in the case of strong deformations, i.e., when the sizes of most Pincus blobs become smaller than the unperturbed size of the PA, i.e., using the smallest blob as reference, when $\xi_{N/2} \ll bN^\nu$. This translates into the following condition for E:

$$E \gg E_1 = \frac{T}{\sqrt{fN}qbN^\nu}. \tag{32}$$

Let us now consider the role of the electrostatic interactions between the charges. The critical electrical field E_c [cf. Eq. (22)], which is necessary to induce a breakup of the globule, is strong enough to fulfill condition (32), since $E_c/E_1 \approx (R/r_{\mathrm{D}})(bN^\nu/r_{\mathrm{D}})$ is obviously much larger than unity. The blob picture given above remains unchanged for Pincus blobs with $\xi_n < r_{\mathrm{D}}$. For such blobs the electrostatic energy, Eq. (1), is smaller than T so that the interaction between the charged monomers is only a small perturbation. For $\xi_n > r_{\mathrm{D}}$ each Debye blob inside the Pincus blob contributes an electrostatic free energy of the order T, so that one has roughly $T(\xi_n/r_{\mathrm{D}})^3$ for the electrostatic energy of the whole Pincus blob. The Pincus blob of size ξ_n consists of a condensed set of closely packed Debye blobs (condensate) similar to the unperturbed situation discussed in Sec. II).

In the preaveraged picture where the blob sizes are given by Eq. (27) the larger Pincus blobs are located at the ends of the chain. These are now candidates to become condensates of Debye blobs. Consider the half-chain containing the bead with $n=1$. Here any given monomer n may belong to a condensate as long as $\xi_n > r_D$, i.e., as long as $n < n_1$ with $n_1(E) = [T/(\sqrt{f}qEr_D)]^2$. This means, however, that already after the breakup of the PA for $E=E_c$ only a very small amount of the material is still found in such condensates, since $2n_1(E_c)/N \approx r_D^2/R^2 \ll 1$ holds. Thus, Eq. (31) is also in the case of a strong coupling of charges a good approximation for L.

For a given realization $\{q_n\}$ of the charge distribution the extended conformation may deviate from this ''typical'' picture. Instead of the preaveraged equation (27), the size of the Pincus blob around the nth monomer is given by $\xi_n \cong T/(Q_nE)$. Thus, there may occur condensates of blobs along the chain at the positions n for which $\xi_n > r_D$. Especially, if the cumulative charge variable Q_n changes its sign at the monomer position n_0 then one has around $n=n_0$ a condensate. A further effect that occurs at such changes of sign is that the external force acting on the segments before and beyond n_0 changes its direction so that the PA may become folded.

We note here that there are other systems in which strings and globules coexist: Especially polymers that are charged as a whole may take the form of necklaces; these may be ordered for uniformly charged polyelectrolytes[28] or disordered for random PAs with an excess charge $Q > Q_c$.[12] A coil–globule coexistence may also occur when a collapsed polymer in a poor solvent is deformed (*vide infra* and Ref. 29).

Note that due to Eq. (31) one has a rather pronounced stretching of the PA with $L \propto N^{(1+\nu)/(2\nu)}$. Due to their finite extensibility real PAs will show a crossover from this regime to stretched configurations where the bonds are directed parallel or antiparallel to the external field. In the preaveraged picture the onset of this effect is predicted to occur in the middle of the chain when $\xi_{N/2} \approx b$, so that there the Pincus-blob picture breaks down. This means that the field strength E_2 with

$$E_2 = \frac{T}{\sqrt{fN}qb} \tag{33}$$

marks the border between the Pincus regime, Eq. (31) $(E < E_2)$ and the regime of stretched chain configurations $(E \gg E_2)$. In Ref. 18 we have modeled the PA as a freely jointed chain and found

$$L^2 = \frac{b^2N^2}{3}, \tag{34}$$

for the mean-squared end-to-end distance of the stretched chain configuration. Note that L^2 is a third of the length of the fully stretched rodlike chain, $L^2 = b^2N^2$. This is due to random, zig–zag configurations that occur for certain charge configurations, as discussed above. In our problem the Pincus regime, Eq. (31), occurs only when $E_c < E_2$, i.e., when $b > N^\delta f l_B$ with $\delta = \frac{1}{7}$ (good solvent) or $\delta = \frac{1}{5}$ (θ solvent). Together with condition (4) this means that $N^\delta f l_B < b < \sqrt{N} f l_B$. On the other hand, in the strong coupling case, $f l_B < b < N^\delta f l_B$, the forces necessary to induce a breakup of the structure are so strong that one is for $E=E_c$ already beyond the Pincus regime.

The instability at $E \cong E_c$ may be first order. Here we want to discuss similarities and differences of our problem to a related situation where such a transition may be found: the deformation of a collapsed polymer in a poor solvent, which was studied by Halperin and Zhulina.[29] Similar to our case the response of the polymer for weak deformations ΔL is controlled by the surface tension so that the restoring force f depends linearly on ΔL: $f \propto \Delta L$; this parallels Eq. (19) in the PA problem. On the other hand, for strong deformations the chain breaks up in a series of equally sized (ideal) Pincus blobs resulting again in a linear relationship $f \propto \Delta L$; this corresponds in our problem to Eq. (31) (θ solvent). For intermediate deformations Halperin and Zhulina find from a scaling analysis of a hypothetical cylindrical phase a $(\Delta L)^{-1/2}$ dependence of f, i.e., they have a van der Waals loop in the $(f, \Delta L)$ diagram, which is reminiscent of a first-order transition. Using the Maxwell equal area construction[19] they postulate that in this regime $f \propto (\Delta L)^0$ and interpret this as a region where strings and globules coexist (for instance, a tadpole configuration).

In our case, however, a PA globule behaves differently under a slowly increasing field; this is due to the fact that the field strength E_D that is necessary to unravel the PA globule (by pulling a Debye blob out of the condensate in order to generate a string) is *much* higher than the critical value E_c [cf. Eq. (22)]: E_D is given by $\sqrt{fg_D}qE_Dr_D \approx T$, and thus $E_D/E_c \approx (N/g_D)^{1/2} r_D/R \gg 1$. Here the globule does not increase its size through discharging Debye blobs, but by a sudden breakup at $E \cong E_c \ll E_D$. This is different from the situation in Ref. 29 and it is due to the characteristic way in which the PA is coupled to the external field: The force acting on a portion of the chain containing g monomers scales typically with $g^{1/2}$ so that small parts of the chain prefer to remain in the condensate. Thus the surface tension controls the scenario (necklace forming) until a relatively high field $E \cong E_c$ is reached, at which the PA changes abruptly its state. We note that the surface-controlled scenario may be circumvented when the procedure is inverted, i.e., when one starts from the highly extended state and then decreases the field strength moderately. Then the PA may pass through coil–globule states (hysteresis effect). Being beyond the scope of this paper this effect deserves further investigation.

IV. CONCLUSION

In summary, we have considered the deformation of neutral polyampholytes in external electrical fields in the case of a strong coupling of the charges. Without external perturbations a neutral PA forms a spherical globule. In small external fields the surface free energy dominates the PA's response and the PA assumes a dumbbell-like shape. When the field strength exceeds a critical value the external perturbation overcomes the surface tension so that the PA becomes unstable and reaches rapidly a highly extended stable state. In such configurations only a small amount of the material is still bound in a few condensates, which are connected by an inhomogeneous string of Pincus blobs.

ACKNOWLEDGMENTS

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

[1] T. E. Creighton, *Proteins: Their Structure and Molecular Properties* (Freeman, San Francisco, 1984).
[2] E. I. Shakhnovich and A. M. Gutin, J. Phys. A **22**, 1647 (1989).
[3] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).
[4] S. F. Edwards, P. R. King, and P. Pincus, Ferroelectr. **30**, 3 (1980).
[5] C. Qian and A. L. Kholodenko, J. Chem. Phys. **89**, 5273 (1988).
[6] P. G. Higgs and J. F. Joanny, J. Chem. Phys. **94**, 1543 (1991).
[7] J. M. Victor and J. B. Imbert, Europhys. Lett. **24**, 189 (1993).
[8] J. Wittmer, A. Johner, and J. F. Joanny, Europhys. Lett. **24**, 263 (1993).
[9] Y. Kantor, M. Kardar, and H. Li, Phys. Rev. E **49**, 1383 (1994).
[10] A. M. Gutin and E. I. Shakhnovich, Phys. Rev. E **50**, R3322 (1994).
[11] A. V. Dobrynin and M. Rubinstein, J. Phys. II France **5**, 677 (1995).
[12] Y. Kantor and M. Kardar, Phys. Rev. E **51**, 1299 (1995).
[13] Y. Kantor and M. Kardar, Phys. Rev. E **52**, 835 (1995).
[14] Y. Levin and M. C. Barbosa, Europhys. Lett. **31**, 513 (1995).
[15] D. Ertas and Y. Kantor, Phys. Rev. E **53**, 846 (1996).
[16] H. Schiessel, G. Oshanin, and A. Blumen, J. Chem. Phys. **103**, 5070 (1995).
[17] H. Schiessel, G. Oshanin, and A. Blumen, Macromol. Theory Simul. **5**, 45 (1996).
[18] H. Schiessel and A. Blumen, J. Chem. Phys. **104**, 6036 (1996).
[19] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1981).
[20] J. des Cloizeaux, J. Phys. Paris **36**, 281 (1975).
[21] P. G. de Gennes, Scaling *Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
[22] J. D. Sherwood, J. Fluid Mech. **188**, 133 (1988).
[23] P. Pincus, Macromolecules **9**, 386 (1976).
[24] H. Schiessel and A. Blumen, Macromol. Theory Simul. (in press).
[25] J. F. Joanny (private communication).
[26] F. Brochard-Wyart, Europhys. Lett. **23**, 105 (1993).
[27] J. Spanier and K. B. Oldham, *An Atlas of Functions* (Hemisphere, Washington, 1987).
[28] A. V. Dobrynin, M. Rubinstein, and S. P. Obukhov, Macromolecules **29**, 2974 (1996).
[29] A. Halperin and E. B. Zhulina, Europhys. Lett. **15**, 417 (1991).