

## Dynamics of a polyampholyte hooked around an obstacle

H. Schiessel,\* I. M. Sokolov,† and A. Blumen

*Theoretical Polymer Physics, Freiburg University, Rheinstrasse 12, 79104 Freiburg, Germany*

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We consider polyampholytes (PAs), which are polymers carrying positive and negative charges. The PAs are submitted to electric fields and collide with single obstacles. Field separation of PAs depends drastically on  $\tau_u$ , the time to unhook. Our analysis shows  $\tau_u$  to be very sensitive to the charge distribution of the chains: Unhooking is diffusional for regular, multiblock PAs, with  $\tau_u$  depending on the length of the blocks; for random charge distributions  $\tau_u$  increases exponentially with the PAs' length and unhooking is subdiffusive. [S1063-651X(97)51409-7]

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Gel-electrophoresis (GE) is a widely used technique for size separation of polyelectrolytes (PEs) of different length such as DNA fragments [1]. During GE the polymer gets temporarily hooked around gel fibers, and the release time determines the overall process. In a more general fashion one investigates the time  $\tau_u$  needed by polymers to disentangle from single obstacles (say posts) [2–7].

A related problem is the behavior of polyampholytes (PAs), which are heteropolymers that carry both positive and negative charges, in gels under external electrical fields. In a series of works [8–12] we have investigated the behavior of PAs in dilute solutions and found that the charge distribution (CD) leads to a great variety of static and dynamical laws [9,12] which furthermore depend on the intramolecular electrostatic coupling [11,12], on the solvent's quality [11,12], on the chain's extensibility [10] (cf. also the paper of Winkler and Reineker [13]), and on the hydrodynamically mediated monomer interactions [12]. A study of the PAs' motion using the biased reptation framework [14] revealed the paramount role played by the detailed distribution of positive and negative charges along the chain on the overall PA's mobility in a network. We hence focus here on how  $\tau_u$ , the time to unhook from a single obstacle, depends on the PA's particular CD. As we proceed to show, we indeed find  $\tau_u$  to depend drastically on the CD.

Before discussing PAs we recall the findings for PEs entangled to a fiber. Just after the collision the PE coil gets unraveled by the external field and shows in the simplest case only two arms, left and right of the fiber, consisting of monomers 1 to  $m$  and  $m+1$  to  $N$ , respectively. In general, we denote by  $q_n$  the charge on the  $n$ th monomer, so that for PE, evidently,  $q_n = q$  for all  $n$ . The total charge on the left arm is  $Q_m = mq$ , and on the right arm  $Q_{\text{tot}} - Q_m = (N-m)q$ , where  $Q_{\text{tot}} = Q_N$  is the total charge of the PE. Hence, the tangential force  $F(m)$  acting along the chain from right to left is  $F(m) = Q_m E - (Q_{\text{tot}} - Q_m) E = 2qEm - qEN$ . Assuming the chain to be free-draining (i.e., the friction to be proportional to  $N$ ) and to be inextensible and neglecting the Brown-

ian motion and the friction between PE and fiber, one has

$$N\zeta b \dot{m}(t) = 2qEm(t) - qEN. \quad (1)$$

In Eq. (1)  $m(t)$  denotes the number of the monomer which is in contact with the fiber at time  $t$ ,  $b$  is the monomer length, and  $\zeta$  the friction constant per monomer. The solution of Eq. (1) with initial condition  $m(0) = m$  is

$$m(t) = \left( m - \frac{N}{2} \right) \exp \left[ \frac{2qE}{N\zeta b} t \right] + \frac{N}{2}. \quad (2)$$

From Eq. (2) the time  $\tau_u$  is given implicitly by  $m(\tau_u) = 0$  for  $m < N/2$  and by  $m(\tau_u) = N$  for  $m > N/2$ . Thus, say for  $m < N/2$ , one has  $\tau_u = (N\zeta b/2qE) \ln[N/(N-2m)]$ . Hence, assuming  $m = m(0)$  to be equally distributed we find by averaging over  $m$

$$\tau_u = \frac{\zeta b}{2qE} N. \quad (3)$$

We note that other models, as long as the chain is inextensible, lead to the same dependence on the parameters [3–7]. For Gaussian chains, however, one has  $\tau_u \propto N^2$  [5,6]. Consider, namely, a bead-spring model, whose harmonic springs have equal spring constants  $K$ . The tension acting on each arm increases from the free end to the hook, where the force is of the order of  $qEN$ . Thus the extension  $\Delta l$  of the springs near the hook is of the order  $\Delta l \approx qEN/K$ ; taking  $\Delta l$  as the typical segment length, i.e., assuming  $b \approx \Delta l$ , Eq. (3) takes now the form  $\tau_u \approx \zeta N^2/K$  which is independent of  $E$  [5,6]. Furthermore, the same power-law dependences of  $\tau_u$  on  $N$  also hold in the non-draining case, despite the complex PE behavior discussed in Ref. [15]. Hence, for PEs  $\tau_u$  is a power law of  $N$ ; now, since the standard deviation  $\sigma_\tau$  of  $\tau_u$  is of the same order than  $\tau_u$  itself (for the inextensible case, discussed above, one has  $\sigma_\tau = \sqrt{2}\tau_u$ ), collisions with individual obstacles are not a powerful means to separate different PE according to length (see the discussion in Ref. [4]).

As shown, a PE gets unhooked due to the difference in the forces acting on its two arms. As we proceed to show, the unhooking scenario of PAs is generally different, since in many cases a PA requires thermal activations to disentangle from a fiber. This leads to an exponential  $N$  dependence of

\*Present address: Materials Department, University of California at Santa Barbara, Santa Barbara, CA 93106.

†Also at P. N. Lebedev Physical Institute of the Academy of Sciences of Russia, Leninski Prospect 53, Moscow 117924, Russia.

$\tau_u$  (and, indeed, to a standard deviation  $\sigma_\tau$  of a similar form). Note that due to the exponential  $N$ -dependence long chains stick for very long times to the hook, times in which most of the shorter chains unhook.

Let us first calculate the deformation of a free PA with the charge distribution  $\{q_n\}$  having a vanishing total charge  $Q_{\text{tot}} = \sum_{k=1}^N q_k = 0$ . We use the Gaussian, bead-spring model, in which the monomers are connected by harmonic springs to a chain; the (entropic) spring constant is  $K = 3T/b^2$ , where  $T$  denotes the temperature in units of the Boltzmann constant  $k_B$ . We take the external field to point in the  $Y$ -direction and denote by  $Y(n)$  the time-averaged position of the  $n$ th monomer in the  $Y$ -direction relative to the first, i.e.,  $Y(1) = 0$ . Thus,  $Y(n)$  is the sum of all the elongations of the first  $n-1$  bonds. For the free PA the mean distance between the monomers  $k$  and  $k+1$  in the direction of the field, i.e.,  $Y(k+1) - Y(k)$ , can be calculated as follows: The bond connecting the beads  $k$  and  $k+1$  subdivides the chain in two parts, one consisting of the monomers  $n=1, \dots, k$  with the charge  $Q_k = \sum_{i=1}^k q_i$ , and the other consisting of the monomers  $n=k+1, \dots, N$  with the charge  $-Q_k$ . Hence,  $Y(k+1) - Y(k) = -Q_k E/K$  and thus

$$Y(n) = -\frac{b^2 E}{3T} \sum_{k=1}^{n-1} Q_k \quad (4)$$

(cf. also Eq. (16) of Ref. [12] with  $i=0$  and  $j=n-1$ ). In Eq. (4) we neglect the intramolecular electrostatic interaction of the charged monomers. This may be realized experimentally for weakly charged PA chains: For randomly charged PAs with  $Q_{\text{tot}} = 0$  in a  $\Theta$  solvent, the coupling between the charges can be neglected as long as  $N < (b/fl_B)^2$  holds (*weak coupling limit*) [12,16]. Here  $f$  denotes the fraction of charged monomers and  $l_B = q^2/(\epsilon T)$  is the Bjerrum-length ( $\epsilon$  is the dielectric constant); in water at room temperature one has  $l_B \cong 7 \text{ \AA}$ . These arguments remain valid for non-neutral chains as long as the charge asymmetry is small enough:  $Q_{\text{tot}} < qN^{1/2}$  [12,17]. Note that neutral and/or weakly charged PA solutions can be prepared without counterions [18].

We assume now that the *free* PA drifts *moderately* with a constant velocity  $v_0$ ; this may be due to a uniform flow field acting on the PA or due to a small excess charge  $Q_{\text{tot}}$  which is added uniformly to the PA (so that each monomer carries the additional charge  $\Delta q = Q_{\text{tot}}/N$  which is small compared to the characteristic charge per monomer). We denote by  $F_{\text{tot}} = Q_{\text{tot}} E$  the overall external force which induces this drift. Note that the additional excess charge  $\Delta q$  per monomer does not influence the internal deformation of the PA, i.e., Eq. (4) remains valid (cf. Ref. [12] for a rigorous discussion).

Let us now consider the potential energy of a PA in contact with a fiber; such a situation may arise when the PA drifts through the gel (due to a flow or to a small additional charge). Let the contact occur at the  $m$ th monomer; the situation is shown in Fig. 1. Assume, for instance, that  $Q_m > 0$ . Then  $Y(m+1) - Y(m)$  as well as  $Y(m) - Y(m-1)$  have, in general, the same sign, as depicted in Fig. 1. This is different from the PE problem where a hairpin situation develops, with two arms directed parallel to the field; here, it is even not clear that the PA will stay in contact with the fiber during the whole unhooking process.

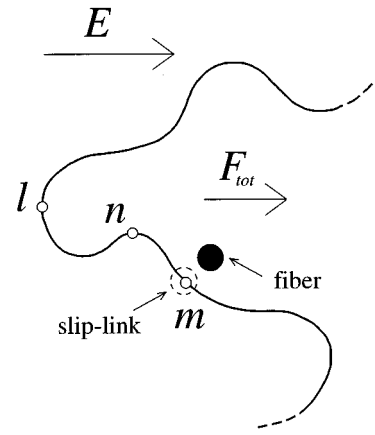


FIG. 1. PA hooked around a fiber. Depicted is a small part of the chain with a minimum at  $l$ .

A simplification of the model can be achieved by assuming the PA to be restricted through a slip-link [19,20] located at the point of impact. The motion is then one-dimensional and the potential energy of a chain hooked at  $n$  is given by

$$U(n) = F_{\text{tot}} Y(n) = -\frac{b^2 F_{\text{tot}} E}{3T} \sum_{k=1}^{n-1} Q_k, \quad (5)$$

where we set  $U(1) = 0$ . We expect the introduction of the slip-link to capture the main physical aspects in the determination of  $\tau_u$  and we relegate towards the end of the letter the discussion of the additional degrees of freedom which are involved for a PA colliding with a fiber. In Eq. (5) we assume further that the external force is small enough so that the perturbation of  $Y(n)$  caused by the hook-chain interaction can be neglected; this perturbation is of second order in  $U(n)$ , which restricts our theory to moderate values of  $\Delta q$  independent of the field strength (see below). Furthermore in the linear regime [assumed in Eq. (4)] one has no lever action since the dynamics in the directions perpendicular to the field direction is decoupled from the dynamics in field direction [8,12], i.e., we have here no rotation of the whole chain around its anchor point.

As we will show, the dynamics of the PA through the slip-link depends strongly on its CD which enters Eq. (5). We consider two cases: periodic CDs (multiblock PAs) as well as completely random patterns. As we proceed to show, the first case leads to diffusive behavior whereas the second case is highly subdiffusive.

Consider first multiblock PAs consisting of regular patterns of positively and negatively charged blocks. For mathematical convenience we take the CD  $\{q_n\}$  to be periodic,

$$q_n = q \cos\left(\frac{2\pi p n}{N}\right) + \Delta q, \quad (6)$$

with  $0 \leq n \leq N$ . In Eq. (6)  $p$  is the number of repeat units, each consisting of  $N/p$  monomers. We have  $Q_n = (qN/2\pi p) \sin(2\pi p n/N) + n\Delta q$  and thus  $Q_{\text{tot}} = Q_N = N\Delta q$ . Now it follows from  $Q_n$  that for  $qN/p \gg N\Delta q$ , i.e.,  $\Delta q \ll q/p$  the interaction with the hook affects only slightly the conformation of the free chain, Eq. (4) (this is independent

of  $E$ ). Inserting  $Q_n$  (without the small  $\Delta q$ -correction term) into Eq. (5) leads to  $U(n) = A_p [\cos(2\pi pn/N) - 1]$  with  $A_p = qEF_{\text{tot}} b^2 N^2 / (12\pi^2 p^2 T)$ .

Let us now calculate the time  $\tau_u$  needed by the PA to free itself from the slip-link, by having one of its end-monomers pass through it. We make use of arguments from activation theory. If the potential barrier  $\Delta U$  is much larger than the thermal energy  $T$ , i.e. if  $p \ll p_0 = bN \sqrt{qEF_{\text{tot}} / (6\pi^2 T^2)}$  the chain will be trapped in one of the  $p$  minima, situated at the monomer positions  $n_k = (k - 1/2)N/p$  with  $k = 1, \dots, p$ . The escape time  $\tau_p$  from each of these minima is the same and can be estimated from the Arrhenius-Kramers argument to be  $\tau_p \cong (6\pi N \zeta T / F_{\text{tot}} qE) \exp(2A_p/T)$  (the preexponential factor follows from Eq. (XIII.2.2) of Ref. [21]). Thus the dynamics of the multiblock PA through the slip-link may be viewed as being a hopping process from one minimum to one of the two neighboring minima; this is effectively a one-dimensional random walk. Typically one of the PAs ends is reached when the number of steps is of the order  $p^2$  so that  $\tau_u$  follows,

$$\tau_u \cong p^2 \tau_p \cong \frac{6\pi N \zeta T}{qEF_{\text{tot}}} p^2 \exp\left[\frac{b^2 qEF_{\text{tot}} N^2}{6\pi^2 T^2 p^2}\right], \quad (7)$$

for  $p < p_0$ . Now  $\tau_u$  grows with decreasing  $p$  and attains its maximal value  $\tau_u \propto NF_{\text{tot}}^{-1} \exp[cF_{\text{tot}} N^2]$  for  $p = 1$  ( $c$  is a numerical constant). The limit of validity of the Arrhenius argument is reached when  $p$  approaches  $p_0$ ; then

$$\tau_u \cong \frac{b^2 N^2 N \zeta}{T} = \frac{b^2 N^2}{D}, \quad (8)$$

where  $D = T/(N\zeta)$  is the diffusion constant of the free chain. Evidently, Eq. (8) holds also for  $p > p_0$ , since then the thermal energy  $T$  is larger than the amplitude of the potential so that the Brownian motion given by Eq. (8) is not affected by the external potential. The two limiting cases, Eqs. (7) and (8) also follow from the solution of the corresponding one-dimensional diffusion problem, leading to  $\tau_u \cong (b^2 N^2 / D) [I_0(A_p/T)]$  [where  $I_0(x)$  denotes the hyperbolic Bessel function of order zero].

Let us now consider PAs whose charges are randomly distributed along the chain, so that each monomer carries either the charge  $+q$  or  $-q$ . For an uncorrelated distribution of charges one has  $\langle q_i q_j \rangle = q^2 \delta_{ij}$  where the brackets denote the average with respect of different realizations of  $\{q_n\}$ . Such PAs, however, have typically total charges  $Q_N$  of the order of  $\pm q\sqrt{N}$ , whereas we require  $Q_N = N\Delta q$  with  $\Delta q \ll q/\sqrt{N}$  (this ensures that the collision perturbs the PA's conformation only slightly). This is achieved by distributing (in addition to the excess charge  $\Delta q$  per monomer)  $N/2$  positive and  $N/2$  negative charges along the chain, resulting in a small negative correlation [9]

$$\langle q_i q_j \rangle \cong \begin{cases} q^2 & \text{for } i = j \\ -q^2/(N-1) & \text{for } i \neq j. \end{cases} \quad (9)$$

This leads to  $\langle (\sum_{k=1}^N Q_k)^2 \rangle = q^2 N^3 / 12$  from which the typical fluctuations  $\Delta U$  of the potential, Eq. (5), follow,

$$\Delta U \cong \sqrt{\langle U^2 \rangle} \cong \frac{b^2 F_{\text{tot}} qE}{T} N^{3/2}. \quad (10)$$

$\Delta U$  is also a measure for the typical depth of the largest minimum of  $U(x)$ . The typical  $\tau_u$  for random PAs follows then as an Arrhenius-type law:

$$\tau_u \propto \tau_0 N \exp\left[\frac{b^2 F_{\text{tot}} qE}{T^2} N^{3/2}\right], \quad (11)$$

where the preexponential factor  $\tau_0$  depends only weakly on  $N$ .

Let us draw now comparison to a similar, classical example for diffusion in disordered media, namely, *Sinai diffusion* [22–26]. In this case one has diffusion in a random-walk-like potential, which means that the local bias fields are uncorrelated. Sinai showed that in this case the mean-squared displacement  $\overline{x^2}$  of the random walker displays a logarithmic time-dependence, namely,  $\overline{x^2} \propto \ln^4 t$  [22]. Thus the random external potential leads to a drastically slowed-down, subdiffusive process. In our case we have also a random potential, being however, the integral of a random walk, since  $U(n)$  is proportional to the sum of the  $Q_k$  [cf. Eq. (5)], which itself is a random walk. Due to the correlations of the potential the scaling argument given above indicates that then the mean-squared displacement is even slower than in the Sinai case, namely,  $\overline{x^2} \propto \ln^{4/3} t$  [cf. Eq. (11)]. This is consistent with the results of Refs. [23, 24], where it is shown that correlations of the potential of the form  $(\Delta U)^2 \propto N^{1+\lambda}$  (with  $\lambda > -1$ ) lead to a mean-square displacement of the form  $\overline{x^2} \propto (\ln t)^{4/(1+\lambda)}$ ; our case corresponds to  $\lambda = 2$ . Thus we find that long PAs with random CDs will practically not become disentangled.

Up to now we have tacitly assumed that the hindrance (fiber, post) scans the potential, Eq. (5), sequentially along the arclength of the chain. There may be, however, overhangs as depicted in Fig. 1: In the reference frame of the chain the hook may drift directly from the position of the  $n$ th monomer to the position of the  $l$ th one. Nevertheless, such a situation will not lead to a significant perturbation of the dynamics of the hooked chain since in any case the PA will become trapped in the minimum at  $l$ . In three dimensions (3D), however, rotations of parts of the chain around the fiber during such noncontact periods may allow the fiber to bypass one or several neighboring minima or may even release the whole chain from the entanglement. Nevertheless, despite these effects the trapping in the deepest minimum of  $U(n)$  controls the dependence of the unhook time, i.e., Eqs. (7) and (11) are good estimates for  $\tau_u$ .

In 2D, which may be achieved by confining the polymer between two parallel plates, such disentanglement mechanisms can be avoided. Let the chain be confined between  $Z = 0$  and  $Z = h$  with  $h$  being much smaller than the radius of gyration of the chain. Assume that the PA is initially ordered in the  $X$  direction (i.e.,  $X_{n+1} > X_n$ ) and is not allowed to cross itself. Then the fiber will practically see all minima along the PA's contour; we expect  $\tau_u$  to be larger in 2D than in 3D. Especially in the case of multiblock PAs one has  $\tau_u^{(3D)} < \tau_u^{(2D)}$ , with  $\tau_u^{(2D)}$  given by Eq. (7); assuming in the

3D-case that the chain's conformation in the  $XZ$  plane (perpendicular to the electrical field) is Gaussian, one has typically  $\sqrt{p}$  minima which are effectively accessible for the hook instead of  $p$  ones in 2D. Thus we predict  $\tau_u^{(3D)} \approx \tau_u^{(2D)}/p$ .

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