EUROPHYSICS LETTERS 15 November 2001

Europhys. Lett., **56** (4), pp. 529–535 (2001)

Long-lived states in electrophoresis: Collision of a polymer chain with two or more obstacles

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(received 6 March 2001; accepted in final form 3 September 2001)

PACS. 36.20.-r – Macromolecules and polymer molecules.
PACS. 82.35.Rs – Polyelectrolytes.
PACS. 45.50.Dd – Dynamics and kinematics of a particle and a system of particles: General motion.

Abstract. – We study the long-lived states which occur when a field-driven polymer chain collides with two or more fixed obstacles. For two obstacles we show that below a critical separation distance there are two catenary states, whereas beyond this there are no such states. We further show that for the two long-lived states one is stable and the other is unstable. We introduce a simple model for the dynamics for which many exact results can be obtained. In particular we show that the long-lived states can have two very different ways of unhooking, depending sensitively on the initial conditions.

The dynamics of polymers is a well-developed field of study. However, there are still several problems of fundamental importance which have not been fully explored. Surprisingly, many of these are in the area of single-chain dynamics [1–4]. Interest in single-chain problems has been spurred in recent years by the advent of new experimental techniques that allow one to see and to manipulate individual polymer chains; namely optical/magnetic tweezers and atomic force and fluorescence microscopy. The particular problem presented in this paper is the dynamics of a polymer which collides with two or more fixed obstacles. This problem has applications in the size separation of polyelectrolytes such as DNA using electrophoresis. In electrophoresis, charged chains are driven through an array of obstacles by an applied electric field of magnitude E. These obstacles, sometimes gel fibres and sometimes "man-made" obstacles etched onto a silicon chip [5], impede the chain dynamics in a way that depends upon the degree of polymerisation or contour length, L, of the chain. The degree to which the chains are held up by these obstacles imparts size dependence to the chain mobility.

The simplest scenario involves a chain impacting against a single point frictionless obstacle. Such collisions have been created and filmed in experiment [5], simulated [6–9], and modeled analytically [10, 11]. The assumption of zero friction is apparently enough to give good agreement with the experiments. Simulation has shown that most interactions of a chain with a single obstacle or post are glancing blows, where the chain is barely slowed down by

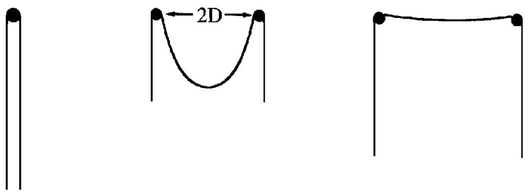

Fig. 1

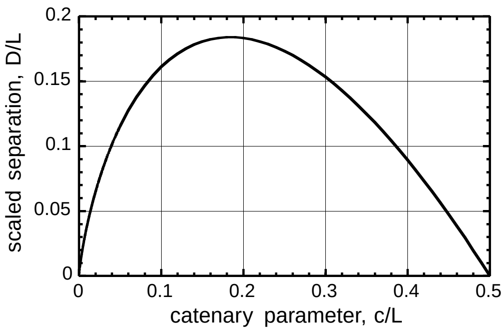

Fig. 2

Fig. 1 – Left: The long-lived hairpin state for a chain colliding with one obstacle. Middle and right: The long-lived catenary states for a chain colliding with two obstacles. The equilibrium states only exist if the obstacles are close together.

Fig. 2 – A graph of obstacle half-separation D/L against catenary parameter c/L. For $D/L > 1/(2e)$ there are no solutions, while for $D/L < 1/(2e)$ there are two solutions, one taut and one flaccid.

the obstacle. However, occasionally a chain will strongly interact with the obstacle and spend a considerable time in collision. The chain is then in a long-lived state. For a single obstacle these states are the U-shaped or hairpin states, fig. 1. These hairpin states are long-lived for two reasons. First, they are states which are at, or close to, static mechanical equilibrium for the system. In fact the equilibrium is unstable, but what is important is that close to equilibrium the potential energy surface is flat and thus the force driving the unhooking of the chain is small and the time correspondingly long. The second reason for the long collision time for these states is that the chain is stretched to perhaps half its length before the unhooking process begins.

Can we characterise the long-lived states for chains colliding with more than one obstacle and predict their dynamics? We do this here, by calculating the equilibrium states for a chain colliding with two point frictionless obstacles. This problem is mathematically more involved than the one-obstacle case; however, we are aided by some very useful results of early applied mathematics and mechanics. In particular the problem of heavy strings or ropes resting on smooth pulleys in a gravitational field is exactly analogous to our problem [12–14], at least as far as statics is concerned. We will show that the equilibrium conformation about two or more obstacles can be described by classical catenaries. Furthermore, we can describe the dynamics of the unraveling process using a simple exactly soluble model based upon the catenary solution. A description of the dynamics of a chain near obstacles is important in applications other than electrophoresis, as, for example, the flow of a dilute solution of chains through finely divided porous media. Apart from these and other applications, the interaction of a chain with fixed obstacles is a fundamental problem in polymer physics, in many ways analogous to the scattering problems encountered in atomic and nuclear physics.

The equilibrium states. – In this section we calculate the equilibrium states for a chain hanging over two frictionless point obstacles. The obstacles lie on the x-axis at $x = \pm D$ so they are a distance $2D$ apart. We consider a chain of arc length L with effective charge per unit length λ placed in a uniform electric field E in the $-y$ or downward direction. We model the chain as being inextensible and we assume that the field is sufficiently high that Brownian noise can be neglected. As far as the statics of this chain are concerned, the lowest-energy chain conformation is identical to that of a heavy inextensible rope of weight $w = \lambda E$ per unit length. The statics for this problem is dealt with extensively in the book by Routh [13, 14], from which we take some preliminary results.

The simplest equilibrium configuration consists of two vertically dangling arms and a central curved portion, fig. 1. We know that [13], irrespective of how many obstacles the chain passes over and whatever the position of the obstacles, the ends of the chain always lie at the same level, and that this level is always below (or equal to) the other parts of the chain. We also know that the local tension in the chain depends only upon the downfield distance, y. This tells us at once that the arms have equal length and that the central curved portion is symmetrical about the y-axis. In fact the central portion is in the shape of a catenary which is described by

$$y = c[\cosh(x/c) - \cosh(D/c)] . \tag{1}$$

Each catenary is specified by a catenary parameter c (a length), which is always positive. Large c's imply a very shallow or "taut" catenary, whereas small c's give a dangling or "flaccid" catenary. We should note that the physical forces involved, be they electrical or gravitational, do not enter into this equation and the shape of the catenary depends only upon geometry. The only important factor is that the force per unit arc length is constant.

It is often convenient to express the shape of the catenary in terms of the arc length, s, measured from the center of the curve,

$$s = c \sinh(x/c) . \tag{2}$$

Setting $x = D$ gives us the arc length used in the catenary dangling between the obstacles: $2P = 2c \sinh(D/c)$. Alternatively, we can find an expression for the vertical displacement y in terms of the arc length s:

$$y = c\left[\sqrt{1 + (s/c)^2} - \cosh(D/c)\right] . \tag{3}$$

The total tension in the chain at any point is $T = w(y + c\cosh(D/c))$ and in particular the tension at the obstacles is $T = wc\cosh(D/c)$. Since the total arc length of the catenary is $2P$, each arm has a length $(L - 2P)/2$. The tension at the obstacle must support the weight of each arm, $(L/2 - P)w$, hence we have $L/2 - P = c\cosh(D/c)$. This equation is the force balance equation for the catenary. Substituting $P = c\sinh(D/c)$ gives $L/2 = c\cosh(D/c) + c\sinh(D/c)$. This can also be written as

$$\frac{D}{L} = \frac{c}{L} \sinh^{-1}\left(\frac{1}{4}\frac{L}{c} - \frac{c}{L}\right) . \tag{4}$$

This equation relates the catenary shape, in terms of the catenary parameter c, to chain length L and obstacle separation $2D$. A general closed solution for c in terms of L and D cannot be found. However, a plot of the rhs of the equation *vs.* catenary parameter, fig. 2, shows the range of obstacle separations, D/L, over which catenaries can be found. First, D/L is only positive for $0 \le c/L \le 1/2$ and has a maximum value of $1/(2e)$ at $c/L = 1/(2e)$. Consequently, there are two solutions for c for $D/L < 1/(2e) \approx 0.184$, *i.e.* there exist two catenaries for obstacles which are slightly separated. Second, for larger obstacle separations, $D/L > 1/(2e)$, there are no catenaries. This means that there are no equilibrium chain configurations for obstacles whose separation $2D$ exceeds $0.378L$. The reason for this is clear: when the obstacles are too far apart there would be insufficient weight in the arms to balance the force imposed by the catenary.

The two catenaries at a given D/L correspond to two different ways of balancing the forces. The system can either have long arms and a shallow catenary, or short arms and a flaccid

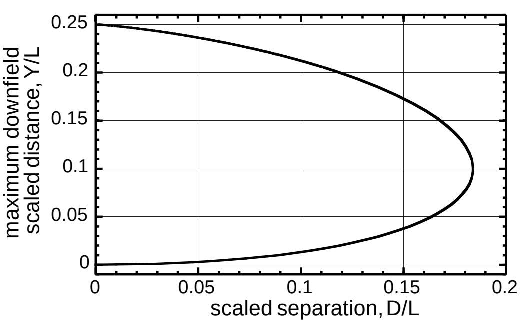

Fig. 3

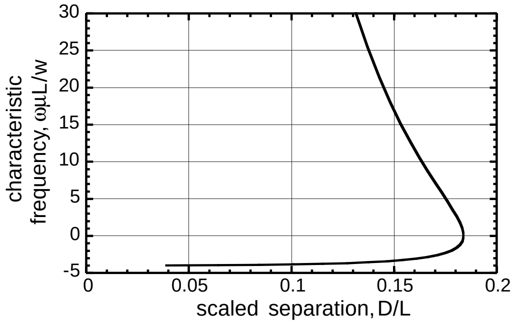

Fig. 4

Fig. 3 – The height of the catenary Y/L *vs.* half-distance between the obstacles D/L. The two different heights correspond to the flaccid and taut catenaries.

Fig. 4 – The scaled characteristic frequency for the equilibrium states $\omega\mu L/w$ *vs.* the half-distance D/L between the obstacles.

catenary. We can demonstrate this by plotting the downfield location of the catenary midpoint $Y/L = c[\cosh(D/c) - 1]L^{-1}$ for different obstacle separations, D/L, fig. 3. We should note here that the distinction between the flaccid and taut catenaries can be made quantitative by delineating them according to which part of the nose they belong to in the Y *vs.* D graph. Thus, those which have $0 < c/L < 1/(2e)$ are flaccid and always have $\alpha < Y/L < \frac{1}{4}$, where $\alpha = 1/4\,\left(\sqrt{2\,e^{-2} + 1 + e^{-4}}e^{1} - 2\right)e^{-1} \approx 0.1$. Those that have $1/(2e) < c < 1/2$ are taut and always have $0 < Y/L < \alpha$. Moreover, as we shall see when we study the dynamics, the taut configurations are stable against symmetrical perturbations, whereas the flaccid catenaries are not.

Dynamics. – We introduce the dynamics of the catenoid states by first revisiting the dynamics of the simpler hairpin states, which occur for a chain hooked over one obstacle [5, 6, 10, 11]. On these small length scales inertia plays no role and the only forces acting upon the chain are viscous drag and the electric force. We will assume that the chain is free draining so that the viscous drag on a segment of length $\mathrm{d}s$ moving with velocity $\boldsymbol{v}$ is $-\mu\boldsymbol{v}\mathrm{d}s$, where μ is a friction constant. One approach to calculating the motion of the hairpin is just to equate all the forces to zero. Here we use a different approach, which is very useful in dissipative systems. It is based on the fact that all the energy dissipated through drag must come from a change in internal energy of the system. In other words, all the heat produced by the motion must come from a change in the electrical energy. In its more sophisticated form this idea was developed by Rayleigh [15, 16] in his Rayleighian dynamics of dissipative systems, but we do not need to use the full formalism of that method here. Let us call the length of the longest arm L_1, then the length of the other arm is $L - L_1$. The electrical energy of this configuration is

$$U = -\frac{1}{2}wL_1^2 - \frac{1}{2}w(L - L_1)^2\,. \tag{5}$$

If L_1 now moves a distance $\mathrm{d}L_1$ in time $\mathrm{d}t$, then the rate of change in electrical energy is

$$\frac{\mathrm{d}U}{\mathrm{d}t} = -w(2L_1 - L)\frac{\mathrm{d}L_1}{\mathrm{d}t}\,. \tag{6}$$

The speed of each segment of the chain is $\mathrm{d}L_1/\mathrm{d}t$ so that the drag force on the whole chain is $\mu L\mathrm{d}L_1/\mathrm{d}t$ and the power dissipation is force multiplied by velocity, or

$$H = \mu L \left(\frac{\mathrm{d}L_1}{\mathrm{d}t}\right)^2 . \tag{7}$$

Equating the sum of the power dissipation and the rate of energy change to zero, $H + \frac{\mathrm{d}U}{\mathrm{d}t} = 0$ gives the equation of motion

$$\frac{\mathrm{d}L_1}{\mathrm{d}t} = \frac{w}{\mu L}(2L_1 - L)\,, \tag{8}$$

which can be integrated at once to yield $L_1 = \frac{L}{2} + (L_{10} - \frac{L}{2})\exp[\frac{2wt}{\mu L}]$, where $L_{10} = L_1(t=0)$. From this we can obtain the time taken for the hairpin to unwind $T_{\mathrm{unwind}} = \frac{\mu L}{2w}\ln(\frac{L}{2L_{10}-L})$.

We should note that the above calculation is only an approximation for many reasons, one being that only one mode of motion is allowed. Thus, we have ignored the fact that the hairpin may start off with some lateral motion and the arms may not be totally straight. However, the idea of approximating the system by one coordinate gives great simplicity, and seems to be in good agreement with experiments [5, 10].

We will now use this dissipative approach to study the motion of the catenary states. This is an intrinsically more complicated system than a simple hairpin. Once a catenary is perturbed, it is not obvious what the shape of the chain will be. We know the equilibrium states are catenaries, but all other dynamical states are at present unknown. In principle we could solve this problem by discretizing the chain into many segments and numerically integrating the equation of motion subject to appropriate constraints. Here we prefer to use a simpler approach. Rather than modeling the chain by an infinite number of coordinates we simply use a single variable. We assume that the state of the chain can always be described as a catenary and use the parameter c as our coordinate. This is clearly an approximation, but one which is very accurate close to the equilibrium states. Fortuitously, it also allows us to write down the equation of motion analytically, and hence give some "exact" results for the initial motion of perturbed equilibrium states.

We begin by calculating the energy for a catenary solution with parameter c. This consists of the energy of the catenary section itself, plus the energy of the two equal arms. If the catenary uses up a length $2P$ of chain, then each arm has length $\frac{1}{2}(L-2P)$ and the total energy of the arms is

$$-\frac{1}{4}w(L-2P)^2 = -\frac{1}{4}w(L - 2c\sinh(D/c))^2\,. \tag{9}$$

The total energy of the catenary section is

$$\begin{aligned} 2w\int_0^P \mathrm{d}s\,y(s) &= 2wc\int_0^D \mathrm{d}x\cosh(x/c)[\cosh(x/c) - \cosh(x/D)] \\ &= wc[D - c\cosh(D/c)\sinh(D/c)]\,. \end{aligned} \tag{10}$$

The total energy of the whole systems is then

$$U = -\frac{1}{4}w(L - 2c\sinh(D/c))^2 + wc(D - c\cosh(D/c)\sinh(D/c))\,. \tag{11}$$

The reader can check that this function has the properties expected from the equilibrium behaviour. Thus, for $D > L/(2e)$ it shows no maxima or minima, so there are no equilibrium states. For $D < L/(2e)$ there are two equilibrium states. That at low c (*i.e.* a flaccid catenary) gives a maximum in U and is hence unstable. That at large c (the taut catenary) gives a minimum in U and is thus stable against moving equal amounts of chain to both the arms.

We now need the dissipation of energy per unit time. A segment of length $\mathrm{d}s$ moving at velocity $\boldsymbol{v}$ dissipates a power $H = \mu\boldsymbol{v}^2\mathrm{d}s$. Integrating along the catenary gives

$$H_{\rm cat} = 2\mu \int_0^P \mathrm{d}s \left(\frac{\partial x(s,c)}{\partial t}\right)^2 + \left(\frac{\partial y(s,c)}{\partial t}\right)^2 . \tag{12}$$

The portion of the chain located at s and of length $\mathrm{d}s$ changes position only by virtue of the change in the catenary parameter c. We can thus write $\frac{\partial x}{\partial t} = \frac{\partial x}{\partial c}\dot{c}$, where $\dot{c}$ means the derivative of c with respect to time. This means we can write the rate of heat generation as

$$H_{\rm cat} = 2\mu\dot{c}^2 \int_0^P \mathrm{d}s(\frac{\partial x(s,c)}{\partial c})^2 + \left(\frac{\partial y(s,c)}{\partial c}\right)^2 . \tag{13}$$

This integral can be evaluated exactly by first carrying out the derivatives, and then converting the integral over s to one over x. The result is

$$H_{\rm cat} = 2\mu\dot{c}^2[S(3D^2c^{-1} + 6c) - 6DC + S^3(c + D^2c^{-1}) - 2DCS^2] , \tag{14}$$

where $C \equiv \cosh(D/c)$ and $S \equiv \sinh(D/c)$. The remaining dissipation arises from the straight arms on either side of the catenary. They are each of length $L_{\rm arm} = \frac{1}{2}(L - 2P) = \frac{1}{2}(L - 2c\sinh(D/c))$ and they are each moving at a speed $v = \frac{\mathrm{d}L_{\rm arm}}{\mathrm{d}c}\dot{c}$, giving a total dissipation for the two arms of $\mu(L - 2P)v^2$ or

$$H_{\rm arms} = \mu\dot{c}^2(L - 2cS)(S - DCc^{-1})^2 . \tag{15}$$

The total dissipation for the entire system is F, where $F = H_{\rm cat} + H_{\rm arms}$. The sum of the dissipation and the energy lost must be zero, $F + \frac{\mathrm{d}U}{\mathrm{d}t} = F + \dot{c}\frac{\mathrm{d}U}{\mathrm{d}c} = 0$. This yields the equation of motion for c:

$$\dot{c} = -\frac{1}{F\mu}\frac{\mathrm{d}U}{\mathrm{d}c} . \tag{16}$$

Here it is clear that $-\mathrm{d}U/\mathrm{d}c$ is a generalised force and the term $1/(\mu F)$ is a friction factor, which is a function of c. Simple numerical quadrature of this equation gives the time dependence of c. Here we look at the behaviour of the equilibrium states as they undergo small perturbations. Suppose we take an equilibrium state $c_{\rm eq}$ and perturb it slightly so that $c = c_{\rm eq} + \epsilon$. The equation of motion for the perturbation is then $\dot{\epsilon} = -\omega\epsilon$, where $\omega = (F\mu)^{-1}\frac{\mathrm{d}^2U}{\mathrm{d}c^2}$ and where everything is evaluated at $c = c_{\rm eq}$. The frequencies ω give us information about the time response of each mode. We should note that this is the characteristic time for each mode, so that, for instance, the same equation $\dot{Y} = -\omega Y$ would hold for the catenary height. If ω is positive the mode is stable and any perturbation decays back to the equilibrium state. If ω is negative the perturbation grows. Moreover, the absolute value of ω gives the rapidity of the growth or decay. A parametric plot of ω *vs.* D, fig. 4 gives several pieces of information. First, all the taut solutions are stable and in fact those at small D are very stable. Second, all the flaccid solutions are unstable, but not very unstable. It is instructive to compare this symmetric mode with the asymmetric mode for hairpin unwinding. For that mode $\omega_{hairpin} = \frac{2w}{\mu L}$ whereas for a very flaccid catenary $\omega_{\rm flaccid} = \frac{4w}{\mu L}$. This gives us two possible life histories for a chain which develops a flaccid catenary. These depend on the initial conditions:

i) If the catenary is perturbed downward it will rapidly grow at the expense of the arms. In general, one of the arms will fall off first and a hairpin will be left on one of the obstacles.

ii) If the catenary is perturbed upward it rapidly approaches the stable catenary solution. The system then behaves as a hairpin state, draped over both obstacles. It can then evolve more-or-less as a hairpin wrapped over one obstacle.

We should note that, since $\omega_{\rm flaccid} = 2\omega_{\rm hairpin}$, in general a system started in a flaccid catenary state and perturbed downward will decay first by increasing the material in the catenary, rather than through swapping length between the two hairpin arms.

In this letter we have examined the statics and dynamics of the interaction of a field-driven polymer with two obstacles. For the statics of this problem we are initially helped by some classical results. Starting from these results, we have shown that there is a critical distance between the posts above which there are no equilibrium solutions. Below this distance there are two kinds of equilibrium solutions, which act as long-lived states. We would thus expect very different dynamical behaviour for different values of the separation distance. For the dynamics we have assumed that the motion occurs through states which are close to the equilibrium solutions. This procedure has allowed us to obtain simple analytic results for the motion. There are some long-lived states we have not considered, for instance where the chain passes over each obstacle more than once. These kinds of states occur even for the single-obstacle case [6], where they are multiple hairpin configurations. Their dynamics is however analogous to those considered here. We note in passing that just as the static problem is one of heavy ropes hung over frictionless posts, the dynamic problem is one of the same system immersed in a very viscous liquid and then perturbed. Although we have described the dynamics of the long-lived states, this is only a partial solution to the problem. In fact, when a random coil collides with two obstacles the motion is obviously very complicated, and it seems likely that a full understanding can only be achieved by using a computer simulation akin to that available for a single obstacle [6].

We conclude by saying something about the case of many obstacles in the same plane. This problem is analogous to, but more complicated than the two-obstacle case. Much is known of the statics [13], and in particular all the equilibrium solutions are catenaries. If, for instance, we consider three equi-spaced obstacles, all in the same line perpendicular to the field, there are only two equilibrium states —two taut catenaries or two flaccid catenaries. The flaccid catenaries are clearly unstable and will decay rapidly. However, as with the two-obstacle case the history will depend very much on the initial conditions.

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