Normal Modes of Stretched Polymer Chains

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ABSTRACT: We consider the normal modes and the response to a small oscillating force of one tethered polymer chain. The chain is originally stretched either by a force f applied at free end (case 1), giving a "cigar" shape, or by a uniform flow (case 2), giving a "trumpet" shape. Stretched chains can be understood as Rouse chains of impenetrable blobs: For case 1, the blobs are all identical and the long-wavelength modes are renormalized Rouse modes. A small oscillating driving force ($f + f_1 \cos \omega t$) distorts the chains up to a distance $\bar{x} = (f/\eta\omega)^{1/2}$, where η is the solvent viscosity. For case 2, the size of the blobs decreases from the free end to the attachment point. The modes are described by zero-order Bessel functions, but the dispersion relation of the p'th mode is still of the Rouse type ($1/\tau_p \sim p^2$). The penetration length of the distortion induced by a small oscillatory force applied at the free end is $\bar{x} = V/\omega$, where V is the solvent velocity. All our results hold as well for an ideal or swollen chain.

Introduction

Manipulations of single macromolecules have been performed recently using magnetic beads or optical tweezers. In a pioneer experiment,[1] DNA molecules were grafted at one end to a glass surface and at their other end to a magnetic bead. The elasticity of the DNA chain was measured by monitoring extension versus Stokes friction or magnetic forces on the bead. In the experiment, the chains are under a uniform tension and can be described as a string of blobs.[2] Pincus[3] calculated the dynamics of uniformly stretched chains and shown that they behave as Rouse chains of impenetrable blobs. For this case, we shall derive the response of the stretched chain to small oscillatory forces. As frequency increases, the portion of the chain responding to the perturbation decreases. This prediction could be tested directly by adding a small oscillating magnetic field to the flow or the static B field in the Bustamante experiment. In a second group of experiments,[4] Chu et al. observed the stretching of DNA molecules to full extension under flows, and their relaxation was measured when the flow stopped. We previously calculated the stationary state of chains stretched under flows and showed that they can be pictured as a string of blobs of decreasing size, forming a "trumpet". We calculate here the normal modes of the trumpet of one tethered chain under flow and the response of the chain to small oscillatory forces acting on the free end. For the dynamics, the chain can also be described as a Rouse chain of impenetrable blobs, but the blob size is now nonuniform. This formulation leads to a generalized diffusion equation, where the diffusion coefficient depends upon local extension.

In the first section, we review the steady state regimes of chains stretched by forces or flows. In the second section, we consider the normal modes of chains under forces or flows. In the last section, we calculate the response of the chain to a small oscillatory force, which is a direct way to investigate the dynamics of stretched chains. We use a scaling approach based on blobs, and we ignore exact numerical coefficient and logarithmic prefactors which show up in the friction of one-dimensional objects.

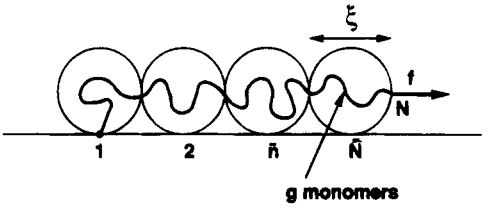

Figure 1. Polymer chain stretched under a force (case 1) pictured as a string of blobs of size ξ.

I. A Review of Steady State Regimes

The steady state deformation of one tethered chain (N monomers) deformed by an external force f applied to the free end of the chain (Figure 1) has been discussed simply by scaling arguments.[2] The chain can be described as a series of blobs of size ξ:

$$\xi = kT/f \tag{1}$$

Equation 1 expresses a balance between mechanical and thermal energy kT. Inside a blob, the force f is a weak perturbation and we expect the local correlation of a free Flory chain, but at larger scales, we have a string of independent blobs. The number of monomers (size a) per blob g is related to ξ by

$$\xi = g^{\nu}a \tag{2}$$

with

$$\nu = {}^1/_2 \quad \theta \text{ solvent} \qquad \nu = {}^3/_5 \quad \text{good solvent}$$

The chain elongation L is

$$L = (N/g)\xi = Na(fa/kT)^{(1-\nu)/\nu} \tag{3}$$

i.e., $L = Na(fa/kT)$ in θ solvent and $L = Na(fa/kT)^{2/3}$ in good solvent.

If we count the monomers 1, 2, ..., N starting from the grafted end with location x_1, ..., x_i, ..., x_N, according to eq 3, $x_n = na(fa/kT)^{(1-\nu)/\nu}$ and the deformation of the chain dx/dn is

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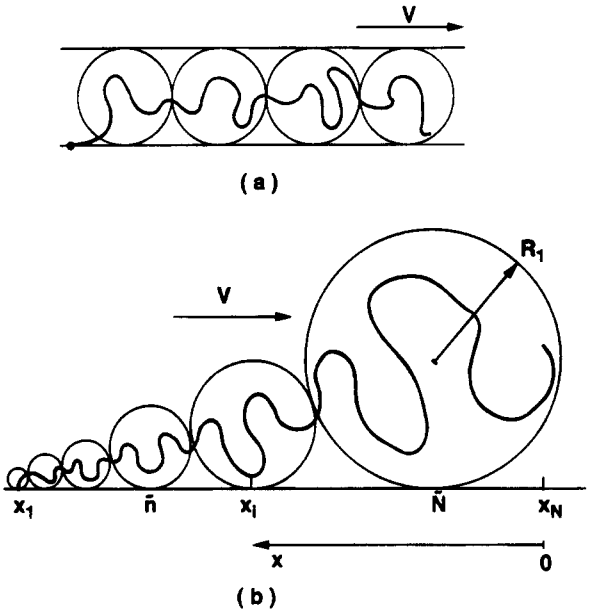

Figure 2. Polymer chain stretched under a flow (case 2): (a) monoblock approximation; (b) trumpet shape.

$$dx/dn = a(fa/kT)^{(1-\nu)/\nu} \tag{4}$$

For an ideal chain

$$dx/dn = a(fa/kT) \tag{4'}$$

For a swollen chain

$$dx/dn = a(fa/kT)^{2/3} \tag{4''}$$

This analysis has been extended to describe the nonuniform stretching of one tethered chain immersed in a good solvent moving at velocity V.[5] In strong flows, the extension L of the chain is predicted to increase quadratically with velocity. This result can be understood simply by scaling arguments. In a first approximation (Figure 2a), the chain is pictured as a cylinder of length L, diameter ξ, called the "monoblock" picture. The friction force on the N/g blobs of size ξ is

$$F_v = 6\pi\eta(N/g)\xi V \tag{5}$$

F_v is related to ξ by eq 1. In good solvent ($\nu = {}^3/_5$) it leads to

$$L = N^3(a^5/R_1^4) \tag{6}$$

where $R_1 = (kT/\eta V)^{1/2}$.

In fact, the chain has to be described as a succession of impenetrable blobs of decreasing size y called the "trumpet" picture, because the friction force increases from zero (free end) to ηLV at the attachment site (Figure 2b). The friction force $f(x)$ at distance $x = x_N - x_i$ from the free end is the sum of the friction on all blobs:

$$f(x) = \sum_i \eta V R_i = \eta V x \tag{7}$$

The size $y(x)$ of the decreasing blobs is given by eq 1:

$$y(x) = kT/f(x) \sim 1/x \tag{8}$$

Inserting $f(x)$ in eq 4 leads to

$$dx/d(N-n) = a(xa/R_1^2)^{(1-\nu)/\nu} \tag{9}$$

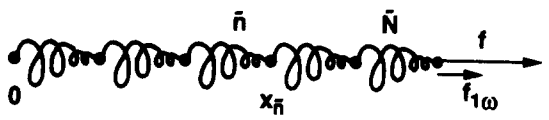

Figure 3. Renormalized Rouse model for case 1: string in series of rigidity $\kappa = kT/\xi^2$ and friction coefficient $\xi = \eta\xi$.

(i) In good solvent, the integral of eq 9 gives

$$x^{1/3} = (N-n)(a^{5/3}/R_1^{4/3}) \tag{10}$$

For the total extension L ($n = 0$ in eq 10), it leads to eq 6.

(ii) In θ solvents, or for ideal chain like DNA semiflexible polymers ($R_0 = N^{1/2}a$), the deformation is enhanced and eq 9 leads to an elongation increasing exponentially with velocity:

$$L = R_1 \exp(Na^2/R_1^2) \tag{11}$$

The ideal chain is thus fully extended above a threshold velocity $V^* = R_0/\tau_Z$, where $\tau_Z = \eta R_0^3/kT$ is the chain relaxation time, as observed in ref 4. For these reasons, experiments on *swollen* chains stretched under flows will better allow monitoring of the progressive stretching under flows. Our calculation of the stationary stretched configuration is based on the local force/deformation relationship (eq 4). As shown in the Appendix, this is strictly equivalent to the recursion method used in ref 6. Equation 4 is in fact more powerful to describe transient effects, as shown in ref 7.

II. Internal Modes of Stretched Polymer Chains

(A) Uniform Stretching (Figure 3). The internal modes of chains stretched by an external force has already been discussed in ref 3 using a different approach based on scaling concepts: it is shown that the chain behaves as a one-dimensional Rouse chain of impenetrable blobs of size ξ. We derive here the modes using the following picture: the chain is a series of springs of rigidity kT/ξ^2 and friction coefficient $z = \eta\xi$. The Rouse equation expresses the balance between (i) elastic restoring force f_{el} and (ii) friction force f_v. For f_{el}: each blob $\tilde{n}(\tilde{n} = 1, 2, ..., N/g)$ experience of force from its two neighbors. If $u_{\tilde{n}}$ is the deformation of the nth blob, around its equilibrium position ($x_{\tilde{n}} = \tilde{n}\xi + u_{\tilde{n}}$),

$$f_{el} = \frac{kT}{\xi^2}[u_{\tilde{n}+1} - u_{\tilde{n}} + u_{\tilde{n}-1} - u_{\tilde{n}}] = \frac{kT}{\xi^2}\frac{\partial^2 u}{\partial \tilde{n}^2} \tag{12}$$

where we have gone to the continuous limit. For f_v: on the nth blob, as shown in ref 3,

$$f_v = \eta\xi\,(\partial u_{\tilde{n}}/\partial t) \tag{13}$$

The balance $f_{el} = f_v$ leads to the Rouse equation:

$$\frac{kT}{\xi^2}\frac{\partial_u{}^2}{\partial \tilde{n}^2} = \eta\xi\frac{\partial^u{}_{\tilde{n}}}{\partial t} \tag{14}$$

When the relaxation time τ_b of a blob (8) $1/\tau_b = kT/\eta\xi^3$ is introduced, eq 14 becomes

$$\partial^2 u_{\tilde{n}}/\partial \tilde{n}^2 = \tau_b(\partial u_{\tilde{n}}/\partial t) \tag{14'}$$

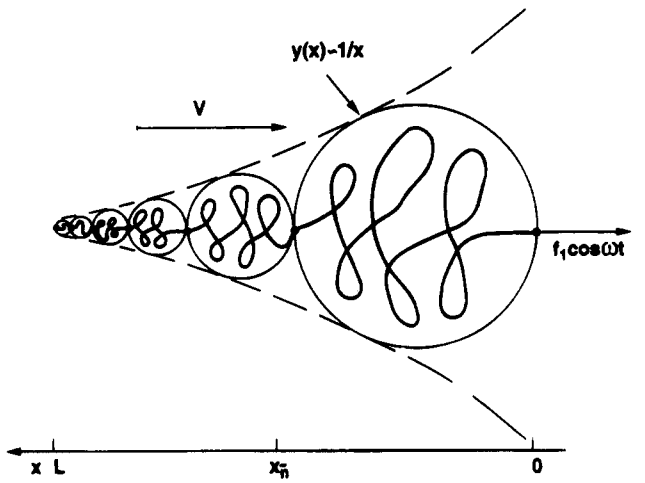

Figure 4. Rouse model extended to case 2. The rigidity of the strings ($\kappa = kT/y^2$) increases from the free end toward the grafted end.

Equation 14 must be supplemented by boundary conditions at both ends of the chain:

$$u_{\tilde{n}}|_0 = 0 \qquad \text{grafted site}$$

$$\frac{\partial u_{\tilde{n}}}{\partial \tilde{n}}\Big|_{\tilde{N}=N/g} = 0 \qquad \text{free end} \tag{15}$$

Because eq 14 is linear, it can be analyzed in terms of eigen modes:

$$u_{\tilde{n}p}(t) = \alpha_p \sin\frac{(p + {}^1/_2)\pi\tilde{n}}{\tilde{N}} e^{-t/\tau_p} \tag{16}$$

where p is an integer and the sinus is chosen to match the boundary conditions (eq 15). The time τ_p is the relaxation time of the mode p and is given by

$$\tau_b/\tau_p = (p + {}^1/_2)^2\pi^2/\tilde{N}^2 \tag{17}$$

Equation 16 is a quadratic dispersion relationship ($1/\tau_p \sim p^2$).

In conclusion, the longest relaxation time is proportional to $\tilde{N}^2$:

$$\frac{1}{\tau_{p=0}} \sim \frac{kT}{\eta\xi^3\tilde{N}^2} = \frac{f}{\eta L^2} \tag{18}$$

For a wave vector q [$q = (p + 1/2)(\pi/L)$, the deformation $U_{\tilde{n}}(t)$ can be written as

$$u_{\tilde{n}=(x/\xi),q} = \alpha_q \sin(qx)e^{-t/\tau_q}$$

$$1/\tau q = (f/\eta)q^2, \quad x = \tilde{n}\xi \tag{19}$$

(B) Nonuniform Stretching (Figure 4). We now study the eigen modes of a chain stretched by an external uniform flow. As shown in Figure 4, the size of the blobs decreases and the Rouse equation is modified. We shall picture the chain as a sequence of $\tilde{N}$ blobs ($\tilde{N} = \int_0^L dx/y = L^2/R_1^2$). The elastic force on the $\tilde{n}$th blob is now

$$f_{el} = \left[\frac{kT}{y_{\tilde{n}+1}^2}(\tilde{u}_{n+1} - \tilde{u}_n) - \frac{kT}{y_{\tilde{n}}^2}(u_{\tilde{n}} - u_{\tilde{n}-1})\right] \tag{20}$$

Table 1. Zero of the J_0 Bessel Function

p	1	2	3	4	5
x_p	2,4	5,6	8,6	11,7	14,9

If we go to the continuum limit, eq 20 leads to

$$f_{el} = \frac{\partial}{\partial\tilde{n}}\left(\frac{kT}{y^2}\frac{\partial u}{\partial\tilde{n}}\right) \tag{21}$$

The Rouse equation $f_{el} = f_v$ becomes

$$\frac{\partial}{\partial\tilde{n}}\frac{kT}{y^2}\frac{\partial u}{\partial\tilde{n}} = \eta y\frac{\partial u}{\partial t} \tag{22}$$

We set $ds = (y^2/R_1^2)d\tilde{n}$, where $R_1^2 = kT/\eta V$ is the size of the largest blob. Equation 22, using eq 8, becomes

$$\frac{\partial^2 u}{\partial s^2} = \frac{x}{V}\frac{\partial u}{\partial t} \tag{23}$$

We must solve eq 23 with the following boundary conditions:

$$u(x = L,t) = 0 \qquad \text{grafted chain end}$$

$$\partial u/\partial s = 0 \qquad \text{free end} \tag{24}$$

We can also write eq 23 as a function of x and t. With $y = -(dx/d\tilde{n})$ and $ds = -(dx/x)$, eq 23 becomes

$$\frac{\partial}{\partial x}x\frac{\partial u(x,t)}{\partial x} = \frac{1}{V}\frac{\partial u(x,t)}{\partial t} \tag{25}$$

We look for a solution $u(x,t) = u(x)\exp-(t/\tau)$. Equation 25 leads to

$$\frac{\partial}{\partial x}x\frac{\partial u(x)}{\partial x} + \frac{1}{V\tau}u(x) = 0 \tag{26}$$

The general solutions of eq 26 are the Bessel function of order zero, which have to satisfy boundary conditions (eq 24). We have then

$$u(x,t) = AJ_0\left(2\sqrt{\frac{x}{V_\tau}}\right)\exp-\frac{t}{\tau} \tag{27}$$

$$\text{where} \quad J_0\left(2\sqrt{\frac{L}{V\tau_p}}\right) = 0 \qquad p = 1, 2, \ldots \tag{28}$$

$dJ_0/dZ = -J_1(Z) \sim Z$ and the free end condition is well satisfied. The dispersion relation is given by the zero of $J_0(Z)$, which are listed in Table 1. The normal modes for $p = 1, 2, 3$ are shown in Figure 5.

We have also solved eq 23 using the WKBJ approximation. Equation 23, with $u = u(s)e^{-t/\tau}$ becomes

$$\partial^2 u/\partial s^2 + K^2 u = 0 \tag{29}$$

where $K^2 = x_1e^{-s}/V\tau = x/V\tau$. The JWKB solution is

$$u = u_0\left(\frac{x}{V\tau}\right)^{-1/4}\exp\pm i\int K\,ds \tag{30}$$

The integral in eq 30 is $\int K\,ds = 2(x_1^{1/2}e^{-s/2}/(V\tau)^{1/2}) = 2(x/V\tau)^{1/2}$, and the solution that satisfies the boundary conditions (eq 24) is

$$u = u_0\left(\frac{x}{V\tau}\right)^{-1/4}\cos 2\sqrt{\frac{x}{V\tau}}$$

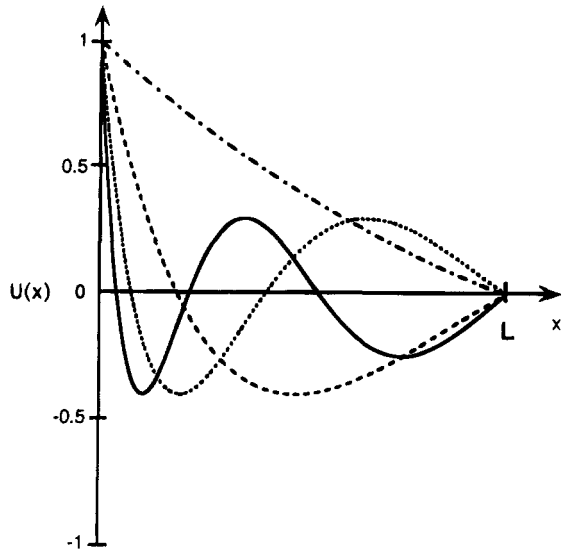

Figure 5. Normal modes of a trumpet for $p = 1, 2, 3, 4$.

$$\cos 2\sqrt{\frac{L}{V\tau}} = 0, \quad 2\sqrt{\frac{L}{V\tau_p}} = (p + {}^1/_2)\pi$$
$$p = 0, 1, 2, \ldots \quad (31)$$

The longest relaxation time $\tau_{p=0}$ is given by $\tau_{p=0} = (L/V)(4/\pi)^2$. If we set $q = (p + {}^1/_2)(\pi/L)$, the mode can be written as

$$u = u_0\left(L\frac{x}{4}q^2\right)^{-1/4}\cos\sqrt{xLq^2}$$

$$1/\tau_q = VLq^2 \quad (32)$$

Notice that eq 32 corresponds to the expansion of the Bessel function $J_0(Z)$ for large arguments.

The same scaling relationship (eq 32) can be obtained in the "monoblock" picture (eqs 17 and 18), with $f = \eta LV$. We expect the same behavior for ideal or swollen chains. The only difference is the $L(V)$ relationship.

In conclusion, we have calculated the scaling relationship of a strongly stretched polymer chain under a force and under a flow. Under a force, we have a Rouse chain with renormalized units (the blobs instead of monomers) and we find the classical modes of Rouse chains. Under a flow, the shape of the chain is a "trumpet", pictured by blobs of decreasing sizes. This description leads to a generalized Rouse equation, with a diffusion coefficient x dependent [$\tau_B = kT/\xi^3 \rightarrow \tau = x/V$]. The solutions $u(x)$ are now Bessel functions instead of sinusoidal functions. For both cases, the mode dispersion relationships are of the Rouse type and can be written as

$$1/\tau_q \cong (f/\eta)q^2 \quad (33)$$

with $q = (p + {}^1/_2)(\pi/L)$ and $f = \eta LV$ for case B.

In the blob picture, i.e., renormalized unit, the swelling properties do not show up and we expect the same laws for an ideal or swollen chain. On the other hand, inside one blob, the chain is ideal or swollen, depending upon the nature of the solvent.

III. Observation of Normal Modes: Response to Small Oscillatory Perturbations

We discuss now how these modes can be seen by monitoring the response of the stretched chain to oscillatory perturbations.

(A) Case 1: External Force. Let us consider the polymer chain stretched by an external force f. This is the case observed in ref 1 with a tethered chain attached by its free end to a magnetic bead of radius b and submitted to a flow at velocity V: the force f is the Stokes force $f = 6\pi\eta bV$. We superimpose now a small oscillatory force $f_{1\omega} = f_1 \cos \omega t$, by using oscillatory magnetic fields. We calculate the response of the chain in the limit $f_1/f = \epsilon \ll 1$. The position of the $\tilde{n}$th blob can be written as

$$x_{\tilde{n}} = \tilde{n}\xi + u_{\tilde{n}}(t) \quad (34)$$

The equation for u_n is the Rouse equation (14') with the boundary conditions

$$u_{\tilde{n}=0}(t) = 0 \qquad \left.\frac{\partial u}{\partial \tilde{n}}\right|_{\tilde{N}} = \epsilon\xi e^{i\omega t} \quad (35)$$

where $\epsilon = ({}^2/_3)(f_1/f)$ for a swollen chain and $\epsilon = f_1/f$ for ideal chains. The solution of eq 14 is

$$u_{\tilde{n}}(t) = \zeta\epsilon e^{i\omega t}\frac{\sin q\tilde{n}}{q\cos q\tilde{N}} \quad (36)$$

with $q^2 = -i\omega\tau_b$, leading to $q = \pm(1 - i)(\omega\tau_b/2)2^{1/2}$. Then

$$u_{\tilde{n}}(t) = \frac{\epsilon\xi}{\sqrt{\omega\tau_b}}e^{i(\omega t+(\pi/4))}\frac{\sin[(1 - i)\sqrt{\omega\tau_b/2}\tilde{n}]}{\cos[(1 - i)\sqrt{\omega\tau_b/2}\tilde{N}]} \quad (37)$$

In the limit $\omega\tau_b\tilde{N}^2 \gg 1$, the response $u_{\tilde{n}}(t)$ becomes

$$u_{\tilde{n}}(t) = \epsilon\xi\frac{e^{-(\tilde{N}-\tilde{n})}\sqrt{\omega\tau_b/2}}{\sqrt{\omega\tau_b}}\cos\left[\omega t - \frac{\pi}{4} + \sqrt{\frac{\omega\tau_b}{2}}(\tilde{N} - \tilde{n})\right] \quad (38)$$

The amplitude of the last monomer response is then

$$u_{\tilde{N}}(t) = \epsilon\bar{x}, \quad \text{with } \bar{x} = \xi/\sqrt{\omega\tau_b}$$

The penetration of the deformation is limited to $\tilde{m}$ blobs, with $\tilde{m} \sim (\omega\tau_b)^{-1/2}$, i.e., to $\bar{m}$ monomers, with $\bar{m} = g\tilde{m}$. If x is the distance from the free end, the distortion of the chain is limited to a distance $\bar{x} = \tilde{m}\zeta$. $\bar{x}$ and ω are related by the dispersion relation

$$\omega \cong f/\eta\bar{x}^2 \quad (39)$$

$$\text{i.e., } \bar{x} = \sqrt{f/\eta\omega}$$

(B) Case 2: Tethered Chain under Flow. We consider now the response of one chain stretched under a uniform flow and submitted to a small oscillating force acting on the free end ($f_\omega = f_1 \cos \omega t$).

We have to solve the generalized Rouse equation (eq 25) with the boundary conditions

$$\begin{cases}\text{attachment point} & u(x=L,t) = 0 \\ \text{free end} & -x\left.\dfrac{\partial u}{\partial x}\right|_{x=0} = \epsilon e^{i\omega t}\end{cases} \quad (40)$$

where $\epsilon = f_1/\eta V$. The solutions are the zero-order Bessel functions:

$$u(x) = Z_0[2\sqrt{-(i\omega x/V)}] \quad (41)$$

The solution that satisfies the boundary conditions is

$$u(x) = -\pi\epsilon N_0(2\sqrt{-(i\omega L/V)})\left[\frac{N_0(2\sqrt{-(i\omega x/V)})}{N_0(2\sqrt{-(i\omega L/V)})} - \frac{J_0(2\sqrt{-(i\omega x/V)})}{J_0(2\sqrt{-(i\omega L/V)})}\right] \quad (42)$$

The distortion induced for the small perturbation penetrates up to a distance $\bar{x}$ from the free end, related to ω by

$$\bar{x} = V/\omega \quad (43)$$

The number of monomers $\bar{m}$ that respond to the force is deduced from eq 10 for a chain in good solvent condition:

$$\bar{m} = \bar{x}^{1/3}(R_1^{4/3}/a^{5/3}) \quad (44)$$

and from eq 11 for a chain in a θ solvent

$$\bar{m} = (R_1^2/a^2)\log(\bar{x}/R_1) \quad (45)$$

Concluding Remarks

A tethered chain deformed by a flow has a complex configuration. We can imagine several experiments to investigate this conformation: (i) measurements of the steady state regime, by monitoring the extension versus the amplitude of the flow; (ii) nonlinear dynamic measurements monitoring the relaxation of the chain if at time $t = 0$ the flow is suppressed; (iii) studies on the response of the stretched chain to a small oscillating force; this may provide a precise probe of the deformed state. We have set up a theoretical frame for the type iii experiments, discussing both uniformly (case 1) and nonuniformly (case 2) stretched chains.

For case 1, we expect a simple Rouse behavior even when we are in good solvent conditions, provided that we discuss chain of "blobs". The deformation $u_p(x)$ in the p'th mode is sinusoidal [$u = u_0 \sin((p + 1/2)(\pi/L)x)$-$e^{-t/\tau_p}$], and the relaxation of p'th mode is $1/\tau_p = (f/\eta)(p + 1/2)^2(\pi^2/L^2)$.

For case 2, the situation is more complex because the blob size decreases when we go from the free end to the tethered end of the chain. The structure of the modes is different, $u = u_0 J_0(2(x/v\tau_p)^{1/2})e^{-t/\tau_p}$, but the dispersion relations $1/\tau(p)$ (eqs 28 and 31) are very similar for large p. When a small oscillatory force is applied at the free end, we find that the chains are distorted on a typical distance $\bar{x}(\omega)$ given by $\bar{x} = (f/\eta\omega)^{1/2}$ for case 1 and $\bar{x} = V/\omega$ for case 2 (for both good or θ solvents!). Here case 1 and case 2 are quite different. The trumpet region is limited: at higher velocities, experiments[12] and theory[13] are in favor of a "stem and flower" conformation with a completely stretched portion (the stem) terminated by a trumpet (the flower). Our discussion remains valid for the trumpet part of the deformed chain.

On the whole, our description based on a renormalized Rouse chain has allowed us to analyze relatively simply the complex behavior of a stretched chain, from both ideal and swollen flexible polymers. Experiments to apply an oscillating magnetic field to the anchored DNA with a magnetic particule at its end and stretched in strong flows are underway.[10] Our results can also be extended to the deformations of polymer brushes in the mushroom regime, where the grafted chains are well separated. It does not apply to the dense regime studied by Johner and Joanny[11] because the flows are screened and the friction acts only on the tails of the grafted chains.

Acknowledgment

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Appendix

Discrete Description of Stretched Chains under Flows. In this approach,[6] the chain is pictured as a serie of blobs (Figure 2) of decreasing radii $R_{\tilde{n}}$ (because the tension increases from the tail to the head). In steady state, mechanical equilibrium relates the tension $f_{\tilde{n}}$ on blob $\tilde{n}$ ($\tilde{n}$ numbered now from the tail) to its friction coefficient:

$$f_{\tilde{n}+1} - f_{\tilde{n}} = \zeta_{\tilde{n}}V \quad (A.1)$$

The friction coefficient $\zeta_{\tilde{n}}$ is related to the blob size $R_{\tilde{n}}$ by a Stokes equation:

$$\zeta_{\tilde{n}} = \eta R_{\tilde{n}} \quad (A.2)$$

where η is the solvent viscosity.

From eqs A.1 and A.2, one can relate the tension $F_{\tilde{n}}$ to the abscissa x:

$$f_{\tilde{n}} = \eta V\sum_{\tilde{i}} R_{\tilde{i}} = \eta V x \quad (A.3)$$

The size of the blobs $R_{\tilde{n}}$ shrinks from tail to head, as $R_{\tilde{n}} = kT/f_{\tilde{n}}$. The size of the largest blob is in perfect agreement with eq 6. R_1 is then given by

$$R_1 = kT/\eta V R_1 \quad (A.4)$$

From eq A.3, we can derive the profile of the trumpet y as a function of abscissa x:

$$y = (a^2/x)(V_0/V) \quad (A.5)$$

where $V_0 = kT/\eta a^2$. Each blob $\tilde{n}$ contains $g_{\tilde{n}} = (R_{\tilde{n}}/a)^{1/\nu}$ monomers. The number n of monomers from the free end at abscissa x is

$$n(x) = \sum_{\tilde{n}} g_{\tilde{n}} \quad (A.6)$$

Using the relation $dx = R_{\tilde{n}}\, d\tilde{n}$, the continuous limit of eq A.6 leads to

$$n(x) = \int\left(\frac{V_0}{V}\right)(1/\nu)^{-1}\left(\frac{x}{a}\right)^{1-(1/\nu)}\frac{dx}{a} \quad (A.7)$$

(i) In good solvent, $\nu = 3/5$, the solution reads

$$n(x) = (V_0/V)^{2/3}(x/a)^{1/3} \quad (A.8)$$

The full extension $x = L$ corresponds to $n = N$ in eq A.8 in

$$L = a\,(V/V_0)^2N^3 = N^3(a^5/R_1^4) \quad (A.9)$$

(ii) In θ solvent, $\nu = 1/2$, we find

$$n(x) = (V_0/V)\log(x/R_1) \quad (A.10)$$

This leads to an exponential law for $L(N)$

$$L = R_1 \exp N(V/V_0) = R_1 \exp(Na^2/R_1^2) \quad \text{(A.11)}$$

in agreement with eq 11.

The discrete description[6] is identical to the local force/deformation approach[5] in the model of discrete blobs $\tilde{n}$, located at abscissa $x_{\tilde{n}}$:

$$dx/d\tilde{n} = R_{\tilde{n}} \quad \text{(A.12)}$$

$\tilde{n}$, the number of blobs, is related to n, the number of monomers, by $dn = g_{\tilde{n}}\, d\tilde{n}$, with $g_{\tilde{n}} = (R_{\tilde{n}}/a)^{1/\nu}$. $R_{\tilde{n}}$ is related to the local tension by the Pincus relationship ($fR_{\tilde{n}} = kT$). Then

$$\frac{dx}{dn} = \frac{dx}{d\tilde{n}}\frac{d\tilde{n}}{dn} = \frac{R_{\tilde{n}}}{g_{\tilde{n}}} = a\left(\frac{fa}{kT}\right)^{(1-\nu)/\nu} \quad \text{(A.13)}$$

which is exactly the relation between local deformation and force.

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