Unwinding of Globular Polymers under Strong Flows

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ABSTRACT: In poor solvent, a flexible polymer chain (N monomers) collapses into a globule. When stretched at both ends, it switches from a globular to a stretched form by a first-order transition. When the coil is stretched under *a uniform solvent flow* at velocity V, we predict that the transition is second order (continuous). We expect three regimes. (i) $V < V_1$: the globule elongates slightly into an ellipsoid and the resistance is provided by surface tension. (ii) $V_1 < V < V_2$: we have coexistence between a reduced globule and an extended chain. (iii) $V > V_2$: the globule has completely faded out. When stretched under *a shear flow*, we also expect three regimes, but the deformation is now more progressive. In the stem−globule regime, the stem can be either fully elongated or only partially stretched. Finally, we discuss transients, where (i) the chain fully elongated at time $t = 0$ relaxes to the equilibrium collapsed state and (ii) starting from a globule at rest, a uniform flow is suddenly imposed.

I. Introduction

Polymer chains grafted at one end to a flat surface have been intensively studied in the past 10 years in the "brush" regime, where the grafting density σ is high ($\sigma R_0^2 > 1$, where R_0 is the free coil size) and the chains are strongly coupled[1−3] (Figure 1a). The conformation of dense polymer brushes under flow has been studied both theoretically and experimentally. These studies show (i) a swelling of the grafted layer under a shear flow in good solvent,[4] and (ii) a deswelling in a poor solvent.[5] In the present paper, we investigate the effect of uniform and shear flow on a *weakly* grafted layer. By this, we mean the system is in the "mushroom" regime, where different grafted chains do not overlap ($\sigma R_0^2 < 1$) (Figure 1b). Weakly grafted layers are of practical importance as adhesion promoters,[6] in the slippage of polymers,[7] and also in steric stabilization of colloidal particles.

Another experimental situation is the case where one polymer chain is grafted to a colloidal particle, of size smaller than the coil radius R_0. The particle can be driven by optical tweezers[8] or a magnetic gradient for a magnetic particle[9] (Figure 2). Manipulations of single DNA molecules, bound at one end to a colloidal particle, have been performed in the last 4 years. The long DNA molecule can be seen directly under an optical microscope, if suitably decorated by fluorescent dyes. In particular, one series of experiments displayed the conformation of a DNA chain, pulled at one end by a constant force f: (a) *At low f,* the shape is a "trumpet".[10,11] Near the bead all the drag forces add up, giving a relatively large tension; in this region, the trumpet is thin. At the bottom end, the tension is lower and the chain is more contorted. (b) *At large f,* the portion near the bead is under high tension and is completely aligned: we called this the stem.[12] Behind the stem, the rear end is still flexible: we called it the "flower". (c) *At very large f,* the chain becomes fully extended.

Our aim is to extend our previous discussions on the unwinding of one tethered chain under flows[10−12] to the case where the chains are originally compact globules in a poor solvent.

The starting point is a flexible chain of N monomers in poor solvent. At the Θ temperature, the chain is ideal, while at a temperature ΔT below Θ, the chain collapses into a globule if $\Delta T > \Theta/N^{1/2}$. The collapsed chain can be described as a collection of blobs of size ξ containing g monomers per blob. At scales smaller than ξ, the chain is nearly ideal and we have $\xi = (\Theta/\Delta T)a = g^{1/2}a$, where a is the monomer size. Between the blobs, there is an attractive potential of order of $-k\Theta$. Thus, they tend to stick together to build up a globule of radius $r_c = (N/g)^{1/3}\xi$. This globule looks like a liquid droplet with a homogeneous (at scales larger than ξ) monomer concentration $C_b = g/\xi^3$. It is then possible to define a surface tension between the droplet and the solvent $\gamma = kT/\xi^2$.

The process of unwinding collapsed macromolecules may have some importance for the denaturation of proteins under strong shear flows. It may also be important in the formulation of liquid thickener. For example, at ultrahigh shears, the globules will be unwound, leading to a large increase in viscous dissipation; however, for a free chain, one must also include the rotation in shear flows.[13]

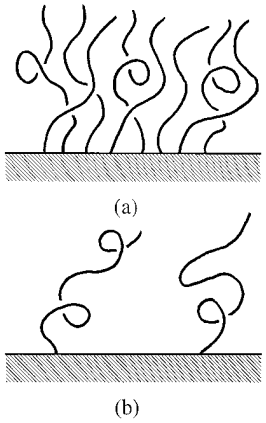

Figure 1. Schematic representation of a polymer brush: (a) high grafting density ($\sigma R_0^2 > 1$); (b) "mushroom" regime ($\sigma R_0^2 < 1$).

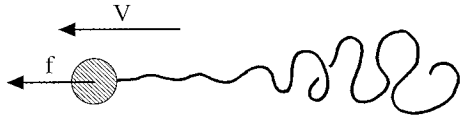

Figure 2. Polymer chain grafted to a colloidal particle under a flow.

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Our motivation is also to investigate the order of the stretching transition by scaling argument. For chains in a good solvent, the deformation in elongational flows, when plotted as a function of shear rate, shows a first-order transition.[14,15] However, no jump is expected for uniform flows and simple shear flows. In a recent paper,[16] Sevick *et al.* discussed coil−stretch transitions for tethered chains in spatially varying flows as a function of the solvent quality, characterized by the Flory exponent ν ($\nu = {}^3/_5$ in good solvent, $\nu = {}^1/_2$ in Θ solvent, and $\nu = {}^1/_3$ in poor solvent). They used a simple model, where the chains are pictured as cylinders. They predicted that the transition will be first order for $\nu \leq {}^1/_2$ under a uniform flow. Under a shear flow, they predicted that the transition should always be second order. Thus for $\nu = {}^1/_3$, we may expect a first-order transition in uniform flow and a continuous transition in shear flow. Moreover, Halperin *et al.*[18] found that under uniform tension, if the chain is stretched at both ends, the transition from the globular form to the stretched form is first order. It is, thus, a challenge to investigate if stretching under flows will be progressive or discontinuous.

In the first section, we start by reviewing the coil−stretch transition of a globular chain under uniform tension; this will be a guide for the more delicate case of tension increasing along the chain. In the second section, we rederive briefly the unwinding of globular chains under uniform flows.[15] In the third section, we focus on strong shear flows, the most important case for practical applications. In the last part of the paper, we consider *transients* where (i) starting from a chain fully elongated, the flow is abruptly supressed, and (ii) starting from a globule, at rest, a flow is suddenly imposed.

II. Free Chain under an External Force

The elongation L of one collapsed chain when an external constraint f is applied has been studied by Halperin and Zhulina.[18]

(1) For small tensions f, the globule, very similar to a liquid droplet, becomes ellipsoidal (Figure 3a), with no change in the internal blob structure. The tension is due to an increase of the surface energy; $F = \gamma \Delta A$, with $\Delta A \approx (L - r_c)^2$, which leads to

$$f = \gamma(L - r_c) \tag{1}$$

(2) For large tensions, the chain can be described as a cylinder of diameter d (Figure 3b), with $\Delta A \approx Ld$. The additional condition of volume conservation $V_c = Ld^2$ gives

$$f = \gamma V_c^{1/2} L^{-1/2} \tag{2}$$

Equation 2 is valid until the chain forms a succession of blobs of size ξ, *i.e.*, $L = (N/g)\xi$ and $f = kT/\xi$.

(3) For very large tensions, the chain elongates as a string of N/g_p blobs of size $\xi_p = kT/f$ (Figure 3c). The deformation is given by Kuhn for ideal chains:

$$L = \frac{R_0^2}{kT} f \tag{3}$$

where $R_0 = N^{1/2}a$.

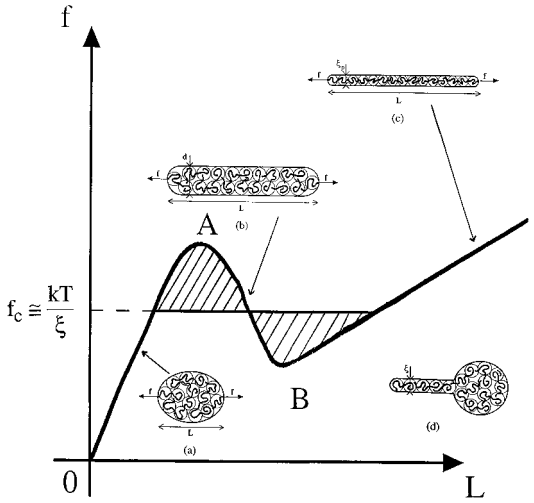

Figure 3. Force f versus deformation L of a globular chain and corresponding conformation: van der Waals loop in the $f(L)$ diagram. (a) Ellipsoidal shape for small tensions; (b) cylindrical shape for large tensions which corresponds to the unstable region A−B of the $f(L)$ curve (Rayleigh instability); (c) string of blobs of size $\xi_p = kT/f$ for very large tensions; (d) in the plateau region $f = f_c$ (given by the Maxwell construction), the conformation of the chain is a globule coexisting with a rod of diameter ξ.

The sequence $f \approx L$, $f \approx L^{-1/2}$, and $f \approx L$ as the deformation increases (Figure 3) describes a van der Waals loop in the $f(L)$ diagram. This is a manifestation of the Rayleigh instability of liquid cylinders. The Maxwell equal-area construction (Figure 3) shows, at $f = f_c = kT/\xi$, a first-order transition from a globular form $L = r_c + \xi$ to a stretched form $L = (N/g)\xi$ (Figure 3d), involving a coexistence of a weakly deformed globule and a stretched string of ξ blobs.

III. Elongation under Strong Uniform Flow

Consider a tethered globular chain subjected to a uniform flow of solvent (viscosity η) at velocity V.[17] This can be achieved easily with one chain attached to a magnetic bead and put into motion by a magnetic gradient.[19]

(1) Small Deformation ($V < V_1$). At low velocity, the chain becomes a slightly elongated ellipsoid, and the balance between the friction force $f_v \cong \eta r_c V$ and the chain tension eq 1 gives

$$\eta r_c V = \gamma(L - r_c) \tag{4}$$

When $f_v = f_c$, the ellipsoid becomes strongly distorted. This defines the threshold velocity:

$$V_1 = \frac{\gamma \xi}{\eta r_c} \tag{5}$$

For $N = 10^4$, $g = 100$, $\eta = 10^{-2}$ SI, and $\gamma = 0.2$ mN·m^{-1}, we find $V_1 \approx$ mm·s^{-1}.

(2) "Stem and Globule" ($V_1 < V < V_2$). For velocities greater than V_1, the chain deformation is nonuniform because the friction force f_v increases from the free end to the fixed extremity. The crucial point is that at the end of the tail there is still a globule of size L_g with a

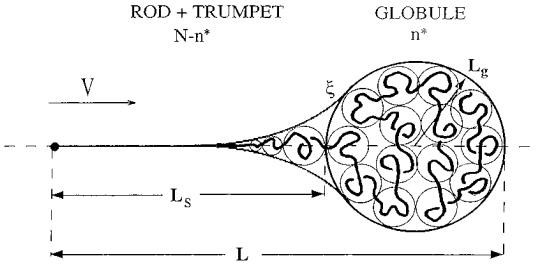

Figure 4. Schematic representation of a collapsed chain deformation in a uniform flow.

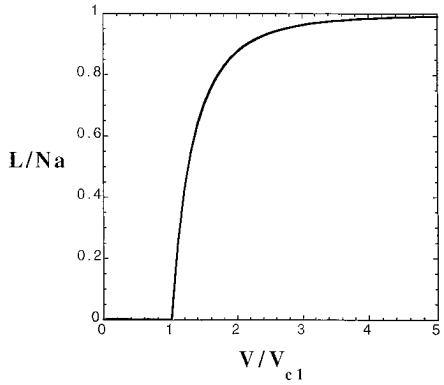

Figure 5. Elongation of the chain in a uniform flow versus solvent velocity in reduced units.

number n^* of monomers (Figure 4). It leads to

$$L_g = (n^*/g)^{1/3}\xi \tag{6}$$

The force on this globule remains equal to the threshold value kT/ξ:

$$\eta L_g V = kT/\xi \tag{7}$$

or

$$L_g/r_c = V_1/V$$

and $n^* = N(V_1/V)^3$. Near the attachment point, we expect a "stem" of $N - n^*$ monomers of length L_s. At scales smaller than ξ, the chain is ideal, and we can use the local equation between force and elongation, assuming an increase of tension[14] from the fixed point to the globule:

$$\frac{kT}{a^2}\frac{\mathrm{d}x}{\mathrm{d}n} = f = \eta x V + \frac{kT}{\xi} \tag{8}$$

where x is the distance from the globule to the monomer. The total extension L is derived by integrating eq 8:

$$L = L_s + L_g = L_g \exp\left[\frac{\eta V a^2}{kT}(N - n^*)\right] \tag{9}$$

where L_g is given by eq 6. The exponential term in eq 9 increases rapidly when V is above V_1 (Figure 5). The length of the stem, which is almost fully elongated, is

$$L_s \cong (N - n^*)a = Na(1 - (V_1/V)^3) \tag{10}$$

There is still a small portion of the chain of length L_f between the globule and the rod where the polymer assumes a horn shape. If n_f is the number of monomers in this horn, eq 8, with $f = kT/a$ leads to $L_f + L_g = L_g \exp[(\eta V a^2/kT)n_f]$, *i.e.*

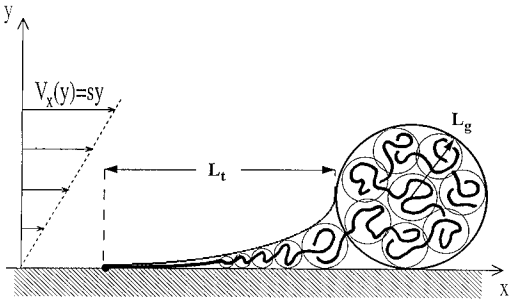

Figure 6. Schematic representation of a sheared collapsed chain.

$$n_f/n^* \cong (g/n^*)^{2/3} \tag{11}$$

For $n^* \gg g$, n_f/n^* is very small and the conformation of the chain is, as assumed by eq 10, a rod terminated by a globule. This regime disappears when the globule size is that of the elementary blob ξ. This corresponds to a solvent velocity V_2 given by eq 7 with $L_g = \xi$:

$$V_2 = \frac{kT}{\eta\xi^2} = \frac{\gamma}{\eta} = \frac{r_c}{\xi}V_1 \tag{12}$$

With the same numerical values, we obtain $V_2/V_1 \approx 5$.

(3) Above V_2. In this regime the globule fades out and the chain is ideal and fully elongated ($L = Na$) because V_2 is much higher than $V_3 = kT/\eta Na^2$, the velocity required to extend completely an ideal chain.

IV. Elongation under Shear Flow

We now consider the case of a solid surface on which a few long flexible chains are grafted, subjected to a shear flow $V_x(y) = sy$ of a poor solvent (Figure 6). To simplify the problem, the chains are assumed to have no interactions (adsorption) with the surface.

Above a threshold shear, the chain will also be in a two-state conformation, where one part of the chain has an ideal behavior (the stem) and the other part has a collapsed chain behavior (the globule). Therefore we review first the unwinding of an ideal chain. This will be useful for the description of the different regimes of a collapsed chain under strong shear flow.

Preamble: Ideal Chain in a Shear Flow. We extend here the discussion of ref 10 performed for chains in a good solvent to ideal coils.

(1) Unperturbed State ($s < s_{c1}$). At low shear rates, the Stokes friction on an ideal chain of radius $R_0 = N^{1/2}a$ is $f_v \cong \eta s R_0^2$, η being the solvent viscosity. When the force f is below kT/R_0, the chain is weakly perturbed. This corresponds to $s < s_{c1}$, where

$$s_{c1} = \frac{kT}{\eta R_0^3} = \frac{1}{\tau_Z} \tag{13}$$

and τ_Z is the characteristic Zimm relaxation time.

(2) "Trumpet" ($s_{c1} < s < s_{c2}$). Above s_{c1}, the chain becomes strongly stretched and can be pictured as a trumpet, *i.e.* a string of blobs of sizes decreasing from the free end (corresponding to the weak friction) to the attached end, where the force is maximum. Consider the nth monomer in the trumpet (counted from the free end) with a distance $x(n)$ to the free end. The friction force on a blob of size y is $\eta s y^2$. The friction force on the chain at a distance x from the free end is $f_v =$

$\int_0^x \eta s y(x)\,\mathrm{d}x$. The size of the blobs $y(x)$ is related to the force by the Pincus rule: $f = kT/y$.

$$\int_0^x \eta s y(x)\,\mathrm{d}x = \frac{kT}{y(x)} \tag{14}$$

Equation 14 leads to $\eta s y(x) = (-kT/y^2(x))(\mathrm{d}y/\mathrm{d}x)$, *i.e.* a trumpet profile:

$$y = \left(\frac{\eta s x}{kT}\right)^{-1/2} \tag{15}$$

With the same approach that led us to eq 8, the elongation can be obtained from the local force balance:

$$\frac{\mathrm{d}x}{\mathrm{d}n} = \frac{a^2}{y} = a^2\left(\frac{\eta s x}{kT}\right)^{1/2} \tag{16}$$

This leads to

$$x(n) = \frac{1}{4} s \tau_Z(n) R_0(n) \tag{17}$$

where $R_0(n) = n^{1/2}a$ and $\tau_Z(n) = \eta R_0^3(n)/kT$ is the Zimm relaxation time of an ideal chain of n monomers. We keep the coefficient in eq 17 only to show that the stretching of the flower is not complete. Thus, the total extension is

$$L = x(N) \cong R_0 s \tau_Z \tag{18}$$

The trumpet regime holds only if the smallest blob (at the tethered end) has a size R_N larger than the monomer size a. This corresponds to $s < s_{c2}$, where

$$s_{c2} = \frac{N^{1/2}}{\tau_Z} = \frac{kT}{\eta N a^3} \tag{19}$$

(3) Stem and Flower ($s_{c2} < s < s_{c3}$). Above s_{c2}, the chain is elongated into a rod of diameter a and is terminated by a flower. The flower size L_f is obtained from eq 15 with $y = a$; at this point, the flower becomes a rod and the number of monomers in this flower is given by eq 17:

$$n^* \cong 2N\frac{s_{c2}}{s}, \qquad L_f \cong (n^*/2)a \tag{20}$$

The length of the rod is $L_r = (N - n^*)a$ and the total length is $L = L_r + L_f$:

$$L \cong Na\left(1 - \frac{s_{c2}}{s}\right) \tag{21}$$

Finally, the chain becomes fully elongated $L = Na$ at $s_{c3} = Ns_{c2}$.

Collapsed Chain in a Shear Flow. *(1) Unperturbed State ($s < s_1$).* We start with a globule of radius $r_c = (N/g)^{1/3}\xi$. At low shear rates, we have a Stokes friction, with a force $f_v \cong \eta s r_c^2$. When the force f is much smaller than kT/ξ, the chain keeps its globular form, and we have a slightly elongated ellipsoid. Things change when we reach the shear rate:

$$s_1 = \frac{kT}{\eta \xi r_c^{\,2}} \tag{22}$$

(2) Two-States Regime ($s_1 < s < s_2$). Above s_1, the chain can be divided into two parts: at the fixed end, we have a *stem* (with an ideal behavior) where monomers are subjected to tensions which are above the plateau in the Maxwell construction (Figure 3); at the free end, we have a *globule* (with a behavior of a collapsed chain) of size L_g.

(A) The Globule. The globule contains n^* monomers. Its length is $L_g = (n^*/g)^{1/3}\xi$. The friction force on the globule ($f_v \cong \eta s L_g^2$) is constant and equal to kT/ξ. This leads to

$$L_g^{\,2} = \frac{kT}{\eta s \xi} \Rightarrow L_g/r_c = (s_1/s_2)^{1/2} \tag{23}$$

and

$$n^* = N(s_1/s)^{3/2} \tag{24}$$

The globule shrinks as s increases, and disappears when $L_g = \xi$; *i.e.*

$$s_2 = \frac{kT}{\eta \xi^3} = (N/g)^{2/3} s_1 = \frac{1}{\tau_\xi} \tag{25}$$

where $\tau_\xi = \eta\xi^3/kT$ is the characteristic Zimm time of the blobs of size ξ.

To conclude, the globule exists only for $s_1 < s < s_2$, and the size of the globule decreases from $L_g = r_c$ at $s = s_1$ to $L_g = \xi$ at $s = s_2$.

(B) The Stem. In the stem, the tension is larger than kT/ξ, the plateau value, and the chain is ideal. In the case of uniform flows, the stem is fully stretched into a rod. In a shear flow, however, the deformation is weaker and more progressive. We shall now see that the stem may only be either partially stretched ("trumpet regime") or fully stretched ("rod regime").

(1) "Trumpet Regime". Consider the nth monomer in the trumpet (counted from the attachment point with the globule) with a distance $x(n)$ to the globule. The friction force on the chain at a distance x from the free end is now $f_v = \int_0^x \eta s y(x)\,\mathrm{d}x + kT/\xi$ (where kT/ξ is exactly the friction force on the globule). Equation 14 becomes

$$\int_0^x \eta s y(x)\,\mathrm{d}x + \frac{kT}{\xi} = \frac{kT}{y(x)} \tag{26}$$

which yields

$$y = \left(\frac{1}{\xi^2} + \frac{\eta s x}{kT}\right)^{-1/2} \tag{27}$$

Equation 16 is replaced by

$$\frac{\mathrm{d}x}{\mathrm{d}n} = \frac{a^2}{y} = a^2\left(\frac{1}{\xi^2} + \frac{\eta s x}{kT}\right)^{1/2} \tag{28}$$

and the solution is

$$x(n) = R_0(n) s \tau_Z(n) + \frac{2R_0^{\,2}(n)}{\xi} \tag{29}$$

The total trumpet length L_t is given by eq 29, with $n = N - n^*$:

$$L_t = R_0(N - n^*) s \tau_Z(N - n^*) + \frac{2R_0^{\,2}(n - n^*)}{\xi} \tag{30}$$

L_t is the sum of two terms: the first term is the

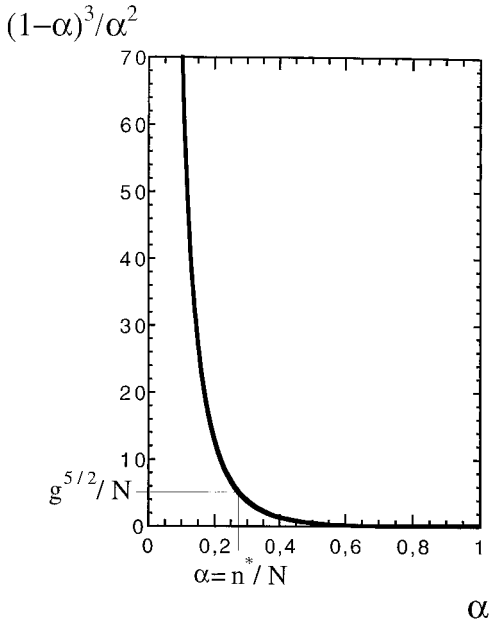

Figure 7. Graphical resolution of eq 31: $(1 - \alpha)^3/\alpha^2 = g^{5/2}/N$.

elongation of a free ideal chain of $N - n^*$ monomers in a shear flow, and the second term is the elongation of the same ideal chain induced by a uniform tension $f = kT/\xi$ ($L = (N - n^*)(fa^2/kT)$).

(2) Rod Regime. The trumpet−globule regime holds only if the smallest blob (at the tethered end) has a size R_N larger than the monomer size a. R_N is given by eq 27: $R_N = (1/\xi^2 - \eta s L_t/kT)^{-1/2}$. Using the value of L_t given by eq 30, we obtain $R_N = ((\eta_s/kT)(N - n^*)a^2 + 1/\xi)^{-1}$. $RN = a$ leads to the threshold shear rate s^* of the rod regime. This equation can be written in terms of $\alpha = n^*/N$ (with eq 24, which becomes $\alpha = (s_1/s)^{3/2}$) as

$$\frac{(1 - \alpha)^3}{\alpha^2} \cong \frac{g^{5/2}}{N} \tag{31}$$

This equation can easily be solved graphically (Figure 7). An analytical solution of n^* can be obtained for the two limiting cases:

$$\frac{g^{5/2}}{N} \ll 1\ ,\ \alpha \approx 1 \quad \text{and} \quad 1 - \frac{n^*}{N} = \frac{g^{5/6}}{N^{1/3}},\ i.e.\ s^* \approx s_1\left(1 + \frac{2}{3}\frac{g^{5/6}}{N^{1/3}}\right)$$

$$\frac{g^{5/2}}{N} \gg 1,\ \alpha \approx 0 \quad \text{and} \quad \frac{n^*}{N} = \frac{N^{1/2}}{g^{5/4}},\ i.e.\ s^* \approx s_{c2} = \frac{kT}{\eta N a^3}$$

Here s^* is the extension of s_{c2}, *i.e.* the shear rate where a rod appears, when there is a globule at the end of the chain.

Two Different Cases May Occur:

(a) $s_{c2} < s_2$ (*i.e.* $g^{3/2} < N$): The conformations of the chain versus increasing shear are pictured in Figure 8a. Below s_1, the globule is only slightly elongated. When the shear rate is above s_1, we enter into the trumpet−globule regime. The length of the stem is given for $s_1 < s < s^*$ by eq 30:

$$L = R_0(N - n^*)s\tau_Z(N - n^*) + \frac{2R_0^2(N - n^*)}{\xi} + \left(\frac{n^*}{g}\right)^{1/3}\xi \tag{32}$$

When we reach the shear rate s^*, a rod appears at the tethered end. This gives a rod−flower−globule regime with a chain length obtained from eq 21:

$$L \cong (N - n^*)a\left(1 - \frac{1}{2}\frac{s_{c2}}{s}\right) + \left(\frac{n^*}{g}\right)^{1/3}\xi \tag{33}$$

It ends at s_2, where the globule fades out ($n^* = 0$). Above s_2, the full chain is ideal and the conformation is a rod terminated by a little trumpet. The length is now given by eq 21. We have plotted in Figure 8b the length $L(s)$ described by eqs 32, 33, and 21.

(b) $s_2 < s_{c2}$ (*i.e.* $N < g^{3/2}$): The trumpet−globule regime is valid in all the range of shear rate $s_1 < s < s_2$ (Figure 9a), and the chain length is given by eq 32. Above $s = s_2$, the chain is ideal, and it leads to

$$L = x(N) \cong R_0 s\tau_Z \quad \text{for } s_2 < s < s_{c2}$$

$$L \cong Na\left(1 - \frac{1}{2}\frac{s_{c2}}{s}\right) \quad \text{for } s_{c2} < s < s_{c3}$$

$$L \cong Na \quad \text{for } s_{c3} < s$$

The curve $L(s)$ for $N < g^{3/2}$ is shown in Figure 9b.

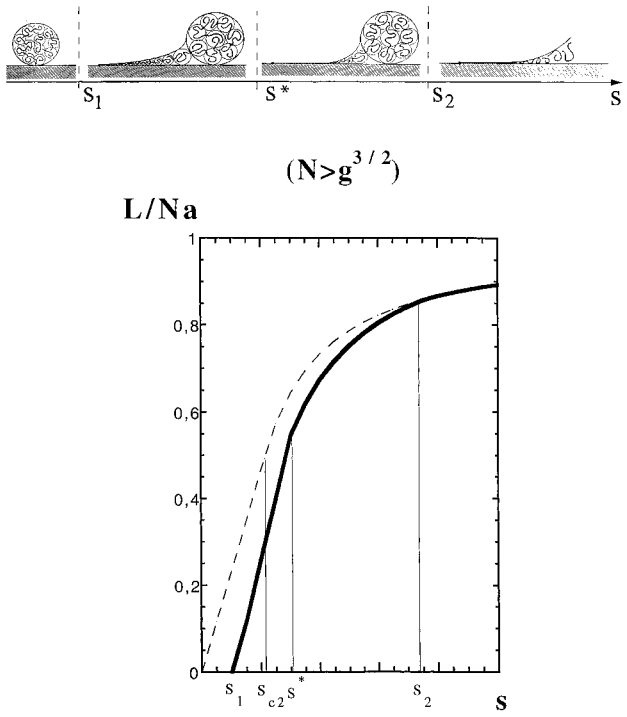

Figure 8. Collapsed chains under shear flow for long chains ($N > g^{3/2}$). (a, Top) Schematic representation of the chain in the four shear rate regimes: (i) ellipsoid; (ii) trumpet/globule; (iii) rod/globule; (iv) rod. (b, Bottom) Elongation of a collapsed chain versus shear rate (the dashed line shows the case of an ideal chain.

V. Relaxation of a Stretched Chain

We consider a chain in a poor solvent which is fully elongated at time $t = 0$. The chain can be tethered or free. As discussed in ref 16, the chain can relax only

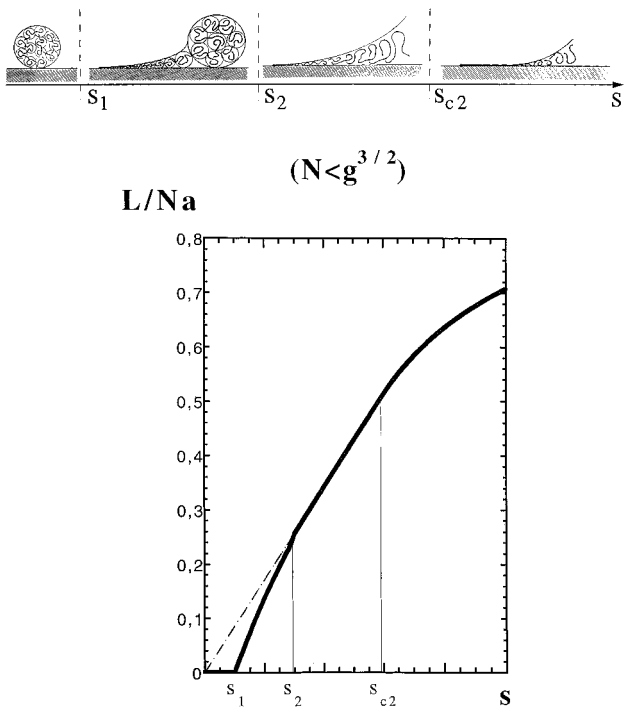

Figure 9. Collapsed chains under shear flow for small chains ($N < g^{3/2}$). (a, Top) Schematic representation of the chain in the four shear rate regimes: (i) ellipsoid; (ii) trumpet/globule; (iii) trumpet; (iv) rod. (b, Bottom) Elongation of a collapsed chain versus shear rate (the dashed line shows the case of an ideal chain).

by its free ends. During the relaxation, the chain is in the two-state model pictured in Figure 4: the globule ($n^*(t)$ monomers, length $L_g(t)$) absorbs the rodlike stem (length $L_s(t) \cong (N - n^*)a$) at velocity $V = -dL_s/dt = a(dn^*/dt)$. The Stokes friction on the globule is given by the plateau value:

$$\eta L_g V = \frac{kT}{\xi} \tag{34}$$

Integrating eq 34 with the boundary condition $L(t=0) = Na$ leads to

$$\eta n^{*4/3} \frac{a\xi}{g^{1/3}} = \frac{kT}{\xi} \tag{35}$$

The terminal time τ_r corresponds to $n^* = N$ in eq 35; *i.e.*

$$\tau_r = \tau_\xi \frac{N^{4/3}}{g^{5/6}} \tag{36}$$

where $\tau_\xi = \eta\xi^3/kT$ is the blob relaxation time. The length $L(t)$ of the chain decreases as

$$L = Na(1 - (t/\tau_r)^{3/4}) \tag{37}$$

We have to plot $L(0) - L(t)$ versus time to fit a scaling law ($t^{3/4}$). This scaling law is very different from the $t^{1/2}$ expected[12] and monitored experimentally[20] for the relaxation of chains either in good ($\nu = {}^3/_5$) or Θ ($\nu = {}^1/_2$) solvent.

Remark: We have assumed a quasi-static equilibrium for the globule. It is correct if the passage time $\tau = L_g/V$ ($=\eta\xi L_g^2/kT$) is equal to or larger than the globule relaxation time τ_g. To estimate τ_g, we consider a small elongation of a globule of size L_g. The relaxation equation is given by eq 4 with $r_c = L_g$:

$$\eta L_g \frac{dL}{dt} = \gamma(L - L_g) \tag{38}$$

The globule relaxes exponentially to equilibrium with a relaxation time

$$\tau_g = \frac{\eta L_g}{\gamma} = \eta \frac{\xi^2}{kT} L_g \tag{39}$$

The passage time $\tau \cong (L_g/\xi)\tau_g$ is always larger than τ_g, and therefore a steady-state approximation for the chain is allowed.

VI. Unwinding by Flow in Poor Solvents

We consider a tethered polymer chain in a poor solvent, in its globular form, subjected at time $t = 0$ to a uniform velocity flow V. During the transient regime, the conformation of the chain is assumed to be a rod terminated by a globule. The friction force on this globule is proportional to the relative globule/solvent velocity $V - \dot{L}$. The globule velocity being equal to the elongation velocity of the stem, we have with eq 10, $\dot{L} = -a(dn^*/dt)$. The balance between the friction force and the restoring force gives

$$\eta L_g(V - \dot{L}) = kT/\xi \tag{40}$$

The expression of L_g in eq 6 leads to

$$(n^*/g)^{1/3}\left(V + a\frac{dn^*}{dt}\right) = \frac{kT}{\eta\xi^2} \tag{41}$$

i.e.

$$a\frac{dn^*}{dt} = \frac{kT}{\eta\xi^2(n^*/g)^{1/3}} - V \tag{42}$$

At small time (as long as $V \gg kT/\eta\xi L_g$), the solution of eq 42 is simply

$$an^* = -Vt + aN \tag{43}$$

This leads to $L(t) \cong (N - n^*)a = Vt$, *i.e.* a simple drift imposed by the external flow.

If $V_1 < V < V_2$, the final state is a stem terminated by a globule, containing $n^*_{eq} = N(V_1/V)^3$ monomers. The drift time to reach this state is from eq 43, $\tau_{drift} = (N - n^*_{eq})a/V$.

If $V > V_2$, the final state is a rod with no globule ($n^*_{eq} = 0$). The drift time is then $\tau_{drift} = Na/V$.

At times $t > \tau_{drift}$, the chain relaxes exponentially to its stationary stretched conformation.

VII. Conclusion

(1) Steady State: Above a threshold velocity or a threshold shear rate, the chain enters in a two-state configuration; we expect a "coil−stretch transition" with a stem and a little globule.

(1) In a uniform flow, the coil−stretch transition is predicted to be sharp, but of second order. The "stem" is rod-like.

(2) In a shear flow, the coil−stretch transition is predicted to be more progressive. Two regimes should show up as a function of N (or as a function of temperature). For large N values ($N > g^{3/2}$), the stem is only partially stretched (trumpet-like) and we predict a crossover at $s = s^*$, toward a fully stretched stem. For

small N ($N < g^{3/2}$), the stem should always have some flexibility and an overall shape which is more open at the rear end.

At a second threshold $V > V_2$ or $s > s_2$, the globule disappears and the chain is fully stretched (except for one special case, namely small chains in simple shear).

(2) Transients: Starting from a rod, the chain relaxes toward a collapsed coil. In contrast to the "sausage" model of the dynamics of collapse,[21] we do not expect that the chain forms a cylinder which becomes thicker and shorter in time. In our model, the globules nucleate and grow at both ends of the chain. This behavior has been observed in numerical simulations for the dynamics of collapse,[22] starting from a chain in good solvent conditions. Thus our approach may also be useful to describe the collapse of a chain in poor solvents without any flow.

Experiments are underway to test all these theoretical predictions.

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Glossary

Θ	Flory temperature
kT	thermal energy
ΔT	temperature difference from Θ
$-k\theta$	attractive potential between the blobs
γ	surface tension globule/solvent
d	diameter of the coil
ΔA	variation of area for the globule
F	free energy
η	viscosity of the solvent
σ	grafting density
f	force applied on the chain
f_v	viscous force
f_c	critical force
a	monomer size
N	number of monomers in the chain
R_0	radius of an ideal chain containing N monomers
$R_0(n)$	radius of an ideal chain containing n monomers
R_N	size of the blob at the attachment point
g	number of monomers per blob
ξ	blob size
r_c	radius of a collapsed chain containing N monomers
V_c	volume of the globule
C_b	monomer concentration in the globule
ν	Flory exponent
ξ_p	blob size of a stretched chain
g_p	number of monomers in a stretched blob
n	nth monomer counted from the attachment point with the globule
n^*	number of monomers in the collapsed part of the chain
n_f	number of monomers in the flower
x	distance from the free end
$y(x)$	size of the blob at x
L	typical length of the chain
L_g	radius of a collapsed chain containing n^* monomers
L_s	length of the stem
L_t	length of the trumpet
V	globule/solvent relative velocity for a uniform flow
V_1	threshold velocity globule → stem and globule
V_2	threshold velocity for the disappearance of the globule
V_3	threshold velocity to extend completely an ideal chain
s	shear rate
s_{c1}	threshold shear rate unperturbed state → trumpet for an ideal chain
s_{c2}	threshold shear rate trumpet → stem and flower for an ideal chain
s_{c3}	threshold shear rate stem and flower → fully elongated chain for the ideal case
s_1	threshold shear rate unperturbed state → two-state regime
s_2	threshold shear rate for the disappearance of the globule
s^*	threshold shear rate where a rod appears
α	reduced number of monomers in the globule
τ_Z	characteristic Zimm relaxation time for the chain containing N monomers
$\tau_Z(n)$	characteristic Zimm relaxation time for the chain containing n monomers
τ_ξ	blob relaxation time
τ_r	terminal time required to achieve relaxation
τ_g	globule relaxation time
τ	passage time
τ_{drift}	drift time

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