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Drag on a Tethered Chain Moving in a Polymer Melt

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Abstract. — A chain of N monomers is attached to a small colloidal particle, and is pulled (at a velocity V) inside a polymer melt (chemically identical, with P monomers per chain). The main parameter for this problem is the number $X(V)$ of P chains entangled with the (N) chain. Earlier estimates of X are criticized, and a new form is proposed: at large N ($N > N_e^2$), we are led to a “Stokes” regime, $X = N^{1/2}$, while at smaller N ($N < N_e^2$), we find a “Rouse” regime, $X = N/N_e$ (where N_e is the number of monomers per entanglement).

1. Introduction

The motion of a long, tethered chain (N monomers) inside a polymer melt (P) is special: the N chain cannot reptate inside the (P) matrix [1]. This occurs in star polymers, and also in two recent experimental situations (Fig. 1):

- a) The N chain is grafted to a colloidal particle (of size smaller than the coil radius R_N of the N chain). The particle can be driven by sedimentation or by optical tweezers (Fig. 1a).
- b) The N chain is grafted on a flat wall, and the (P) melt flows tangentially to the wall (Fig. 1b). (In the following, we assume that the grafting density is very small: no coupling between different N chains).

Problem b) was first considered theoretically (for the low V limit) in reference [2]. The starting point is that a certain number $X(V)$ of P chains are entangled with the N chain. The resulting friction is estimated as follows [3]:

Assume that the N chain has moved by a distance D^* equal to the diameter of an Edwards tube [4] $D^* = N_e^{1/2}a$, where N_e is the number of monomers per entanglement, and a the monomer size. (We take $N_e < N \leq P$). To allow for this motion of the N chain, each (P) chain entangled with (N) must move, along its own tube (of length L_t) by something like L_t .

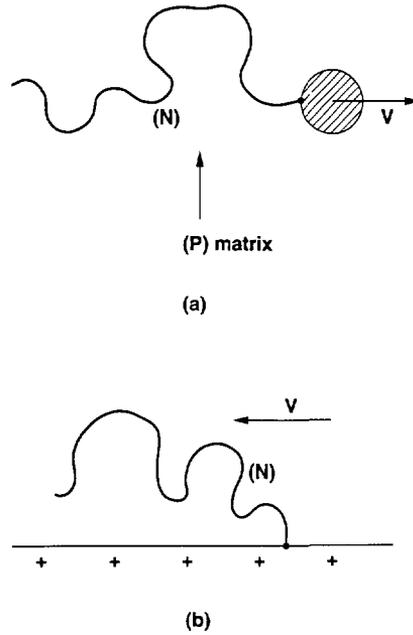


Fig. 1. — Two examples of a tethered chain (N) pulled inside a polymer melt (P). a) Sedimentation (at optical tweezer action) on a colloid grain. b) Shear flow near a weakly grafted surface.

Thus the sliding velocity V_s of this P chain is not the translational velocity V , but is much larger:

$$V_s \cong V \frac{L_t}{D^*} = V \frac{P}{N_e} \quad (1)$$

The dissipation $T\dot{S}$ due to the motion of the tethered chain corresponds to $X(P)$ chains moving at velocity V_s in the ambient melt.

$$T\dot{S} = X\zeta_1 P V_s^2 = f V \quad (2)$$

where $\zeta_1 P$ is the tube friction coefficient of one (P) chain, and f the drag force. Comparing the two expressions of $T\dot{S}$ we get:

$$f = V X(V) a \eta_p \quad (3)$$

where $\eta_p = \zeta_1 a^{-1} P^3 N_e^{-2}$ is the reptation viscosity of the (P) melt.

The crucial question is thus to find $X(V)$. Even in the simplest ($V \rightarrow 0$) limit, where the (N) chain is an unperturbed coil, this problem is difficult, and different answers have been proposed at different times [2, 3]. In Section 2, we reanalyse the problem, using what we call the binary entanglement model. In Section 3, we compare this with a “collective” entanglement model. Section 4 extends our ideas to higher velocities

2. Binary Entanglements

At low velocities, the N chain is an unperturbed coil, of size $R_N \cong N^{1/2} a$ and volume R_N^3 . It experiences in average an entanglement every N_e monomers. Each (P) chain intersecting this

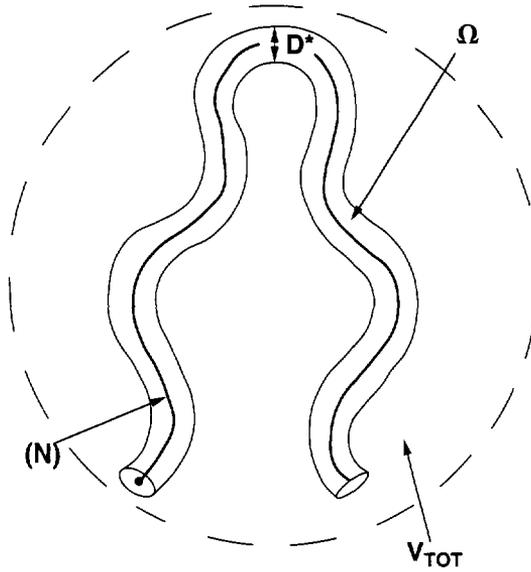


Fig. 2 — The tethered chain at low velocities. coil volume V_{tot} and Edwards tube of volume Ω .

volume uses $\sim N$ monomers in this region. Thus the number of (P) chains which overlap with the (N) coil is $R_N^3/Na^3 = N^{1/2}$.

In reference [2] we simply assumed that all the P chains are entangled with the (N) chain, i.e. $X(V \rightarrow 0) = N^{1/2}$.

The Edwards tube surrounding the N chain (Fig. 2) is a sequence of N/N_e blobs with diameter D^* and total volume:

$$\Omega = N/N_e(D^*)^3 \tag{4}$$

One of the P chains intersecting the volume R_N^3 has $N\Omega/R_N^3$ monomers inside the tube. The number of blobs visited by the P chain is thus:

$$b = (N/N_e)(\Omega/R_N^3) = (N/N_e)^{1/2} \tag{5}$$

Inside one blob, $N_e^{1/2}$ chains coexist (including the N chain). In our binary entanglement model, we assume that a constraint is associated with a *pair* of chains inside the blob. The total number of pairs is $1/2 (N_e^{1/2})^2 \sim N_e$. Thus, the probability that any given pair of chains inside the volume do entangle, is only $N_e^{-1/2}$. The number c of constraints between one (P) chain and the (N) chain is then:

$$c = bN_e^{-1/2} = N^{1/2}/N_e \tag{6}$$

We are thus led to distinguish two very different regimes:

- 1) $N > N_e^2$. In this case c is larger than unity: all the $N^{1/2}$ (P) chains which intersect the coil do entangle with (N). Thus the simple guess of reference [2] is confirmed:

$$X = N^{1/2} \tag{7}$$

We call this the Stokes regime, because the friction force (Eq. (3)) has the scaling form corresponding to a Stokes sphere (radius $N^{1/2}a$) inside a liquid of viscosity η_p .

- 2) $N < N_e^2$. In this case c is smaller than unity, and we cannot use equation (5). When $c \ll 1$, we may say that the probability of entanglement between one (P) chain (intersecting the coil) and the (N) chain is c . Thus:

$$X = N^{1/2}c = N/N_e \quad (8)$$

The friction experienced by the tethered chain is then *linear in* N . Although we deal with an entangled system, the (N) chain is thus described by a Rouse model [6], but the Rouse friction coefficient is proportional to the melt viscosity (as can be seen from Eqs. (3)–(8)).

3. The Collective Entanglement Model

We now wish to describe an opposite limit, where one entanglement site (a blob of diameter D^*) is pictured as a very complex knot, involving $N_e^{1/2}$ chains; the knot is such that eliminating one chain from it removes the constraint. Then the number of constraints released if one P chain moves out of the volume R_N^3 is b , and is larger than unity. All the $N^{1/2}$ “ P -chains” are thus coupled to the N chain.

In this model, it would be enough to select a subset of $(N/N_e)^{1/2}$ “ P -chains” and move them out, to relax the N chain: since $(N/N_e)^{1/2}b = N/N_e$ is the total number of constraints to be removed. This remark leads to the prediction of reference [5]. However, we do not think that this approach is realistic. The N chain, when it moves, has no way of selecting a subset of releasing chains: it drags all of them.

Thus we are led to say that in the collective entanglement model, $X = N^{1/2}$, and the Stokes model holds for all values of N .

4. High Velocities in the Binary Entanglement Model

Under strong flows, and in the simplest picture [7], the N chains become elongated into a cigar shape, with diameter D and length $L = R_N^2/D$. A more sophisticated description has been constructed [5] but is essentially equivalent in practice. We have to distinguish two regimes:

4.1. PARTIAL STRICTION. — $R_N > D > D^*$. Here, a simple repetition of our discussion in Section 2 gives:

$$c = D/(aN_e) \quad (9)$$

If $N < N_e^2$, we always stay in the Rouse regime ($X = N/N_e$).

If $N > N_e^2$, we find a crossover from strong coupling to Rouse upon increasing the velocity (decreasing D).

4.2. MARGINAL REGIME. — Here the cigar diameter D becomes comparable to D^* , and the number of entanglements realised by the N chain can become smaller than N/N_e . The marginal value of X ($X = X^*$) is in fact fixed by the force balance: the stretching force required to reach D^* is [8]:

$$\frac{kT}{D^*} = X^*(V)a\eta_p V \quad (10)$$

and thus X^* is inversely proportional to the velocity. It may be checked that for $V = V^*$ (the onset velocity for the marginal regime) $X^* = N/N_e$ as expected in the Rouse regime and:

$$V^* = kTN_e^{1/2}/(N\eta_p a^2) \quad (11)$$

5. Concluding Remarks

1) The results of the binary entanglement model can be summarized as follows (for the low velocity limit): the number of entangled chains is either $N^{1/2}$ (the number of ambient chains intersecting the mushroom) or N/N_e (the number of constraints acting on the N chain). Each of them is an upper bound for X , and thus X is the smaller of the two.

2) In the collective entanglement model, we are led to $X = N^{1/2}$. (See also [9]). But we do not think that the collective model is fully realistic: complex knots may play a role, but may not dominate the behaviour.

The real situation is probably intermediate between the binary and the collective model, as suggested by the concentration dependence of the modulus of a melt plastified with moderate amount of solvent. The binary model predicts $G_0 \sim c^2$; the collective entanglement approach predicts $G_0 \sim c^3$; and the typical experimental exponent is $G_0 \sim c^{2.2 \sim 2.4}$ (see, e.g., Ref. [10] and Refs. therein). Thus, for many applications, one can stick to the binary model, which is conceptually simpler.

3) It is instructive to discuss the whole distribution function $p(n)$ for the number of entanglements between one given P chain (intersecting the mushroom) and the N chain. Using mean-field arguments, one obtains a Poisson distribution:

$$p(n) = \exp\left(-N^{1/2}/N_e\right) \left(\frac{N^{1/2}}{N_e}\right)^n \frac{1}{n!} \quad (12)$$

This gives:

$$\begin{aligned} X &= N^{1/2}[1 - p(0)] \\ &= N^{1/2}[1 - \exp(-N^{1/2}/N_e)] \end{aligned} \quad (13)$$

Equation (12) is a useful interpolation between equations (7) and (8).

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