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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  $L_t$ .

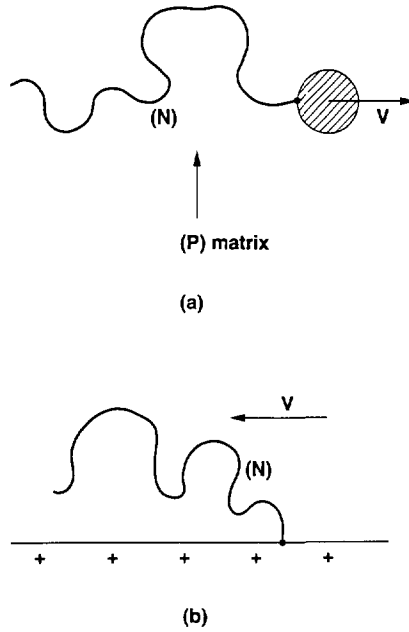


Fig. 1. — Two examples of a tethered chain ( $N$ ) pulled inside a polymer melt ( $P$ ). a) Sedimentation (at optical tweezer action) on a colloid grain. b) Shear flow near a weakly grafted surface.

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

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

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.

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

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:

$$f = V X(V) a \eta_p \tag{3}$$

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

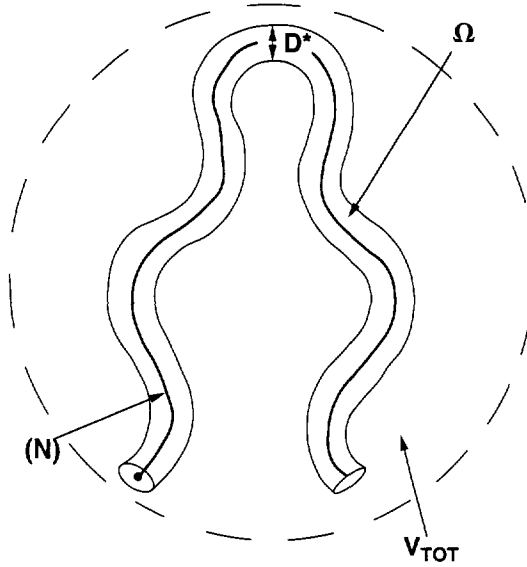


Fig. 2 — The tethered chain at low velocities. coil volume  $V_{tot}$  and Edwards tube of volume  $\Omega$ .

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  $\eta_p$ .

- 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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