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A simple constitutive model for a polymer flow near a polymer-grafted wall

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Synopsis

A simple constitutive model is proposed to describe a polymer flow near a polymer-grafted wall. The model is based on a generalization of the Rolie-Poly equation [A. E. Likhtman and R. S. Graham, *J. Non-Newton. Fluid Mech.* **114**, 1–12 (2003)] to a “bulk+wall” system combined with a microscopic picture of the relaxation of the tethered chains. Different grafting regimes are considered, varying from nonoverlapping to strongly interacting tethered chains. Despite its simplicity, the model allows one to reproduce all the generic features of the flow. Different scaling regimes are predicted, in accord with earlier studies, and the transition between them is quantified. Special attention is paid to a careful comparison to available experimental data: a reasonable agreement is demonstrated and possible shortcomings of the model are discussed. © 2005 *The Society of Rheology*. [DOI: 10.1122/1.2000968]

I. INTRODUCTION

Recently, there has been much attention paid to the role surface anchored polymer chains play in the friction between a flowing polymer melt and a solid interface [see

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Léger *et al.* (1999), and references therein]. The roots of such an interest lie mainly in the practical importance of the issue: an opportunity to manipulate the flow behavior via surface modification could be of great industrial importance, e.g., in extrusion. Moreover, it is believed that the interaction between the adsorbed polymer layer and the bulk material should be held responsible for various flow instabilities in constant speed extrusion [for an excellent review see Denn (2001)]. Though the origin of some instabilities still remains quite poorly understood, it is generally admitted that the so-called “stick-slip” plays a prominent role in the understanding of the phenomena. In this respect, a deeper insight into the processes that take place in a near-wall polymer flow is essential. Even apart from the extrusion instabilities, surface grafting strongly influences the polymer-wall friction and, therewith, introduces a variety of new regimes and possibilities not present in the realm of simple fluids.

The problem itself is quite old, and a number of theoretical and experimental studies, performed largely during the last decade or two, allowed a clarification of many principal points concerning slip in polymer flows. The first important class of studies involved indirect slip observations, e.g., during capillary experiments [Wang and Drda (1996b, a)]. They allowed one to identify, among others, the molecular weight, temperature, and material dependence of the stick-slip transition. However, a number of complicating factors is always present. First of all, the slip velocity is never measured directly and the regime before strong slip sets in is insufficiently studied. Next to this, very little is known about the adsorption process taking place in the vicinity of a solid wall. The surface density of the adsorbed chains as well as the distribution of their tails are unknown factors in this kind of experiment. On the other hand, all the essential features of slip are supposed to depend strongly on these parameters. In this respect, the second class of studies, mainly performed in Léger’s group [Léger *et al.* (1999, 1997); Migler *et al.* (1993); Durliat *et al.* (1997)], was very beneficial. In their model experiments the modified surface had a well-defined grafting density of permanently adsorbed or end-grafted chains, and special care was taken to prevent any further uncontrolled adsorption. Moreover, the novel velocimetry technique used allowed a measurement of the slip velocity in the immediate vicinity of the wall. Hence, the method allowed for a direct observation of slip before and after the stick-slip transition, and captured the transition itself as well.

On the theoretical side, quite a lot of work has been done. Though it is beyond the scope of the present paper to review these numerous studies on stick-slip phenomena, we would like to mention the study by Brochard and de Gennes (1992). Based on an idea that the adsorbed (or tethered) chains should undergo a coil-stretch transition in flow, they explain stick-slip as a disentanglement of the chains fixed at one end from the free-bulk chains. Their relatively simple approach and its more recent refinements [Ajdari *et al.* (1995, 1994); Brochard-Wyart *et al.* (1996); Gay (1999)], allowed one to predict the correct scaling behavior and gain some understanding of the process at the *microscopic* level. Later, Joshi and co-workers utilized some of these ideas to develop a constitutive model for a polymer flow near a grafted wall. They first neglected the interaction between the grafted chains [Joshi *et al.* (2001)], restricting themselves to a so-called mushroom regime, and then removed this restriction in a more complete study [Joshi and Lele (2002)]. Despite the sophisticated nature of their approach based on the model developed in Mead *et al.* (1998) (in the case of steady shear it involves a set of nonlinear partial differential equations), the agreement with the experiments cited above was not always satisfactory. Nonetheless, the grafting density dependence of the critical parameters was qualitatively reproduced quite well and an important step towards constitutive modeling, going beyond simple scaling laws and freed of purely empirical assumptions, was taken.

This shortcoming of Joshi’s model, i.e., its complex structure, seriously hinders pos-

sible further applications, e.g., in flow simulation or other numerical work. Comparing the situation with bulk constitutive modeling, we see that, besides the sophisticated microscopic models, also relatively simple “single-mode” equations have gained increasing popularity [Likhtman and Graham (2003); Marrucci and Ianniruberto (2003)]. Obviously, simplicity is one of their main advantages. Nevertheless, being derived from a more complete molecular model, they inherit the microscopic origin and allow for an easier understanding of the underlying physics than their purely phenomenological counterparts [Bird *et al.* (1987)]. Therefore, it seems to be worthwhile to build the analysis upon one of these simple microscopic models, and then incorporate all the ingredients necessary to describe the interaction between the bulk and the wall layer based on a molecular picture. The combination of these two components—a microscopic view of the processes and a simple constitutive model—should result in computationally tractable equations and, at the same time, incorporate all the physics present in a more complex microscopic approach. The development of such a model is the primary goal of this work. We focus on a polymer flow in the vicinity of a grafted wall, and aim at mimicking all the main features present in a real system. The resulting predictions concerning slip parameters are then critically confronted with experimental data.

The paper is organized as follows. In the next section we outline the different grafting regimes and their influence on the interaction between surface chains. Next, quite some attention is paid to an accurate description of the dynamics of the grafted chains in the linear regime. Finally, a single-mode Rolie-Poly constitutive model [Likhtman and Graham (2003)] is generalized to a “bulk+grafted wall” system, and its outcome is analyzed and compared to the available experiments.

II. GRAFTING REGIMES

Let us consider a surface grafted with chains of Z_I entanglement segments each, in contact with a polymer melt consisting of chains having Z_B segments ($Z_I < Z_B$). It is assumed that the bulk chains do not adsorb on the surface, which corresponds to the conditions in the experiments by Léger *et al.* (1999) where the silica surface was treated specially to suppress this adsorption.

The dynamics of such a system is strongly influenced by the interaction between the bulk and the wall layer. Indeed, the stress is transferred from the bulk to the wall mainly via entanglements between the bulk and the tethered chains. Depending on the grafting density Σ , different regimes can be distinguished. For very small Σ tethered chains interact only with bulk ones. On the other hand, at high grafting densities close to a dry brush, mainly graft-graft interactions play a role. In this section we sketch a possible scenario following the classification proposed by Joshi and Lele (2001).

We examine a layer of the height $a\sqrt{Z_B}$ at the wall, where a is the entanglement spacing. Interaction between bulk and tethered chains mainly takes place in this region: it is the first layer of bulk chains near the wall, and almost all entanglements between bulk and grafted polymer involve these chains. Per area of size $1/\Sigma$ at the wall, there are $\mathcal{N}_B$ bulk chains in the layer

$$\mathcal{N}_B = \frac{V\nu - N_e Z_I}{N_e Z_B} = \frac{Z_I}{Z_B} \left[\frac{\Sigma^*}{\Sigma} - 1 \right], \quad (1)$$

where $V = a\sqrt{Z_B}/\Sigma$, N_e is the number of monomers between entanglements, ν is the volume of one monomer, $\Sigma^* = \sigma_0\sqrt{Z_B}/Z_I$, and $\sigma_0 = a/(N_e\nu)$. These bulk chains are responsible for the interaction with the grafted material. For different grafting densities, the following surface coverage regimes can be defined (see also Table I for a brief summary).

TABLE I. Regimes of surface coverage

1. Mushroom	$\Sigma < \Sigma_c$	$\phi = 1; \chi = Z_B/(\Sigma^*/\Sigma - 1)$
2. Cooperative	$\Sigma_c < \Sigma < \Sigma_o$	$\phi = 1; \chi = Z_B/(\Sigma^*/\Sigma - 1)$
3. Overlap	$\Sigma_o < \Sigma < \Sigma_{dry}$	$\phi = (\Sigma^*/\Sigma - 1)Z_I/Z_B; \chi = Z_I$
4. Dry brush	$\Sigma_{dry} < \Sigma$	Dry brush

- (1.) **Mushroom regime.** In the so-called mushroom regime, grafted chains virtually do not feel each other and are entangled with the bulk chains only. It is convenient to introduce a quantity ϕ —the fraction of bulk-graft entanglements per tethered chain: in this regime $\phi = 1$. The number of bulk-graft entanglements per bulk chain χ is small due to excess of bulk chains, $\chi = Z_I/\mathcal{N}_B < 1$. According to Joshi and Lele (2002), the mushroom regime corresponds to $\chi < 1$ and is realized for $\Sigma < \Sigma_c$, where

$$\Sigma_c = \sigma_0 \frac{\sqrt{Z_B}}{Z_I(Z_B + 1)}. \quad (2)$$

- (2.) **Cooperative regime.** Beyond Σ_c , each bulk chain from the near-wall layer starts to make more than one entanglement with tethered chains, $\chi = Z_I/\mathcal{N}_B > 1$. If Σ grows, χ increases as well until it reaches the value $\chi = Z_I$ at $\Sigma = \Sigma_o$

$$\Sigma_o = \sigma_0 \frac{\sqrt{Z_B}}{Z_B + Z_I}. \quad (3)$$

Still, mainly bulk-graft entanglements are important in this regime.

- (3.) **Overlap regime.** At even higher grafting densities the graft-graft entanglements start to play an important role. In this regime there is less than one bulk chain per grafted chain in the near-wall layer, $\mathcal{N}_B < 1$. The number of bulk-graft entanglements per bulk chain in the layer is saturated at $\chi = Z_I$, but the fraction of entanglements with the bulk per grafted chain starts to decrease, $\phi = \chi \mathcal{N}_B / Z_I < 1$

$$\phi = \frac{Z_I}{Z_B} \left[\frac{\Sigma^*}{\Sigma} - 1 \right]. \quad (4)$$

- (4.) **Dry brush regime.** At certain grafting density Σ_{dry} all the bulk chains are expelled from the region of thickness $h = a\sqrt{Z_I}$ near the wall. This happens if $h/\Sigma_{dry} = \nu N_e Z_I$, i.e.,

$$\Sigma_{dry} = \frac{\sigma_0}{\sqrt{Z_I}}, \quad (5)$$

so that for $\Sigma > \Sigma_{dry}$ the dry brush regime is entered. In this region the grafted layer and the bulk are only weakly entangled, and the interaction between them more resembles conventional Rouse friction [Doi and Edwards (1986)] than entanglement dynamics. This regime is outside the scope of the present paper and is, in some respect, similar to the friction between two incompatible polymer layers [Goveas and Fredrickson (1998); Lam *et al.* (2003)].

Finally, the elastic moduli G_B of the bulk and G_I of the near-wall region can be readily estimated from the presented picture. The bulk modulus is known to be given by $G_B \sim k_B T / (\nu N_e)$ [Doi and Edwards (1986)]. Let us estimate the wall modulus G_I first in the assumption that only bulk-graft entanglements are responsible for the transfer of the

stress from the bulk to the wall [Joshi and Lele (2002); Watanabe (1999)]. In the wall layer of the thickness $a\sqrt{Z_I}$ there are ϕZ_I bulk-graft entanglements per area $1/\Sigma$. Hence, $G_I^{(b-g)} \sim \phi \Sigma \sqrt{Z_I} k_B T / a$ and the ratio between the moduli reads $\psi^{(b-g)} = G_I^{(b-g)} / G_B = \phi \Sigma \sqrt{Z_I} / \sigma_0$. However, the above assumption about only bulk-graft entanglements being responsible for the stress transfer apparently breaks down in the limit of $\Sigma \rightarrow 0$. When no or very few chains are attached, there is still some stress transferred to the wall: not via grafted chains but due to friction between the bulk chains and the wall (we assume no adsorption takes place). A theoretical estimation of this effect is quite a difficult task: apparently, its strength depends on the chemistry of the wall and the bulk material. Still, a simple generalization of the ratio ψ can be proposed

$$\psi = \psi_0 + \phi \frac{\Sigma \sqrt{Z_I}}{\sigma_0}, \quad (6)$$

where ψ_0 is some phenomenological constant, which should be determined from experimental data. The only assumption we made about ψ_0 so far is that it is independent of the molecular weight of the bulk polymer—as it should be if mainly monomeric interactions are responsible for the friction in the $\Sigma \rightarrow 0$ regime.

In fact, it is only the ratio ψ between the moduli, and not the moduli themselves, that we will need further on.

III. LINEAR DYNAMICS OF TETHERED CHAINS

Apparently, the relaxation of the grafted chains is quite different from the bulk ones. The most striking difference is that, being attached by one end, the tethered chains cannot reptate and should relax the stress by retractive motion in a constantly changing environment. On the scaling level, the problem was first addressed by Brochard and de Gennes (1992) and then refined in Ajdari *et al.* (1994, 1995); Brochard-Wyart *et al.* (1996). There, a combination of arm retraction and constraint release is argued to drive the attached chains towards equilibrium. A similar approach was employed in more recent works [Joshi *et al.* (2001); Joshi and Lele (2002)], where a constitutive model for wall slip was proposed.

On the other hand, grafted chains are quite similar to arms of a star polymer, a system relatively well studied in the literature [Doi and Kuzuu (1980); Pearson and Helfand (1984); Ball and McLeish (1989); Milner and McLeish (1997)]. The so-called dynamic dilution theory (DDT) [Ball and McLeish (1989); Milner and McLeish (1997); Milner *et al.* (1998)] is believed to describe arm relaxation adequately and allows one to reach much better agreement with experiment than earlier studies of arm retraction. In that respect, it seems to be feasible to generalize the DDT to the present case, where each tethered chain finds itself in an environment of bulk chains and other tethered chains. This route is taken here to calculate the longest relaxation time of an end-grafted polymer.

According to the star-polymer models [Pearson and Helfand (1984); Ball and McLeish (1989); Milner *et al.* (1998)], the arm retraction process has an “activation” character. In other words, the time t needed to retract an arm of K entanglement segments should be determined from a differential equation [for more details see, e.g., Ball and McLeish (1989)] of the type

$$\frac{dt}{dK} = \frac{2\mu K}{Z_l} t \beta, \quad (7)$$

where $\mu=3/2$ [note the difference with $15/8$ in Ball and McLeish (1989) because of a different definition of entanglement spacing; see also Larson *et al.* (2003)]. In the continuous representation, K labels the position along the primitive path and runs from 0 to Z_l . A “dilution factor” $\beta=1$ would correspond to the picture of an arm retracting in a permanent network [Pearson and Helfand (1984)]. The main idea of the DDT is that, due to constraint release, which takes place on a shorter time scale than arm relaxation itself, the arm becomes more mobile as if it were experiencing some “tube widening.” Thus, $\beta=N_e/N'_e(t)$ is the ratio between the undiluted entanglement spacing N_e and the diluted one, $N'_e(t)$. In the case of star-polymer melts the dilution process is due to the surrounding arms. However, in the case of a grafted chain in the mushroom regime the environment mainly consists of bulk (linear) chains, which retract in their tubes and dilute the tube of the grafted chain. In the overlap regime also the neighboring tethered chains participate in the “dynamic dilution” process exactly as in the case of star polymers [Ball and McLeish (1989); Milner and McLeish (1997)].

According to Milner *et al.* (1998), who studied star-linear blends, different regimes are possible depending on the ratio between the molecular weights of the star arms and the linear chains. Here, we focus on the experimentally most relevant case of short grafted chains, the longest relaxation time of which is shorter than the reptation time of the bulk chains. As shown in Milner *et al.* (1998), in this regime the dynamic dilution picture is valid and both the stars and the linear chains can be considered to be undergoing arm retraction (on the time scale shorter than the reptation time) if each linear chain of Z_B segments is substituted by a two-arm star with arm length $Z_B/2$.

Hence, β is related to the fraction φ of the “initial” constraints which survived up to the moment t : $\beta=\varphi^\alpha$, where either $\alpha=1$, based on a naive picture of the binary entanglements, or $\alpha=4/3$, as suggested by Colby and Rubinstein (1990) for Θ solutions. Here, we follow Milner *et al.* (1998) in using $\alpha=1$, which leads to simpler analytical expressions, although it causes some error in the numerical predictions. This error can be compensated if one takes a value for the entanglement molecular weight N_e about 20% larger than the experimental value [Milner *et al.* (1998)]. In view of other approximations we will make afterwards (single-mode constitutive model, etc.), such accuracy is sufficient for our purposes.

Consider a tethered test chain that has a fraction ϕ of its entanglements with bulk chains and $1-\phi$ with neighboring tethered chains. Then, if all grafted chains chain have retracted an arm of K and all bulk ones of K_B segments (from each end) during time t , the fraction of survived entanglements of the test chain is

$$\varphi = \phi \left(1 - \frac{2K_B}{Z_B} \right) + (1 - \phi) \left(1 - \frac{K}{Z_l} \right). \quad (8)$$

In turn, K_B can be related to the time t passed by an equation like (7) with $\beta=(1-2K_B/Z_B)^\alpha$

$$\frac{dt}{dK_B} = \frac{4\mu K_B}{Z_B} t \left(1 - \frac{2K_B}{Z_B} \right)^\alpha. \quad (9)$$

One can invert (9) to find the function $K_B(t)$ and substitute it back in (8) and (7). Then, Eq. (7) should be integrated to determine the function $t(K)$ with an initial condition $t(0)=\tau_0$, where τ_0 is the inverse attempt frequency: here, we adopt the value $\tau_0 \approx \tau_e Z_l^{3/2}$

[Milner and McLeish (1997)], with τ_e being the Rouse time of one entanglement strand.

In general, (7) is numerically integrated to obtain the longest relaxation time of the grafted chains, $\tau^{(l)} \equiv t(Z_l)$. However, in the grafting regimes where $\phi=1$, the set of equations can be solved explicitly and the longest relaxation time of the tethered chain $\tau^{(l)}$ can be determined directly

$$\tau^{(l)} = \tau_e Z_l^{3/2} \exp \left\{ \frac{\mu Z_B}{6} \left[1 - \left(1 - \sqrt{\frac{2Z_l}{Z_B}} \right)^2 \left(1 + 2 \sqrt{\frac{2Z_l}{Z_B}} \right) \right] \right\}. \quad (10)$$

In the other simple limit, $\phi=0$, the original DDT expression for stars [Ball and McLeish (1989)] is recovered from (7) and (8).

IV. CONSTITUTIVE MODEL OF A BULK/WALL SYSTEM

In this section we aim to develop a simple, yet microscopic, constitutive model for a linear, monodisperse polymer melt in contact with a grafted wall. The simplicity demand restricts our choice to the robust single-mode equations of the type proposed in Likhtman and Graham (2003); Marrucci and Ianniruberto (2003). Though more advanced models [Mead *et al.* (1998); Ianniruberto and Marrucci (2002); Graham *et al.* (2003)] allow one to achieve much better agreement with experimental data in the bulk, they become hardly tractable for more complex systems or geometries. Single-mode equations give us an opportunity to account for all relevant microscopic relaxation mechanisms and, at the same time, possess the simplicity traditionally inherent to phenomenological models [Bird *et al.* (1987)].

Hence, to describe the dynamics of a “bulk+grafted wall” system, the Rolie-Poly model is selected. This constitutive equation has been formulated by Likhtman and Graham (2003) for bulk flows in terms of the velocity gradient tensor $\mathbf{K}_B$ and the dimensionless stress tensor $\boldsymbol{\sigma}_B = \mathbf{T}_B / G_B$ (here, $\mathbf{T}$ denotes dimensional stress tensor)

$$\begin{aligned} \frac{d\boldsymbol{\sigma}_B}{dt} = & \mathbf{K}_B \cdot \boldsymbol{\sigma}_B + \boldsymbol{\sigma}_B \cdot \mathbf{K}_B^T - \frac{\boldsymbol{\sigma}_B - \mathbf{I}}{\tau^{(B)}} - \frac{2}{\tau_R^{(B)}} \left(1 - \sqrt{\frac{3}{\text{Tr } \boldsymbol{\sigma}_B}} \right) \boldsymbol{\sigma}_B \\ & - \frac{2\beta}{\tau_R^{(B)}} \left(\frac{\text{Tr } \boldsymbol{\sigma}_B}{3} \right)^\delta \left(1 - \sqrt{\frac{3}{\text{Tr } \boldsymbol{\sigma}_B}} \right) (\boldsymbol{\sigma}_B - \mathbf{I}), \end{aligned} \quad (11)$$

where $\tau^{(B)}$ and $\tau_R^{(B)}$ are the linear relaxation and the Rouse time of the bulk chains, respectively, and $\mathbf{I}$ is the unit tensor. In the original Rolie-Poly model [Likhtman and Graham (2003)] the relaxation time of a bulk chain in the linear regime is taken equal to the reptation time $\tau_d^{(B)}$. This leaves out the contour length fluctuations, which can be quite important for relatively short chains and lead to the well-known 3.4 power law [Ferry (1970); Doi and Edwards (1986); Doi (1983)]. However, it is possible to take the contour length fluctuations approximately into account by modifying the linear relaxation time as

$$\tau^{(B)} \simeq \tau_d^{(B)} [1 - \xi_d(Z_B)]^2, \quad (12)$$

i.e., assuming an “effective tube shortening” due to very fast relaxation of the chain ends [Doi and Edwards (1986)]. Different estimates of the relaxed fraction ξ_d of the chain are available in the literature. The simplest one, $\xi_d \simeq 1.47 / \sqrt{Z_B}$, is calculated in Doi (1983). Alternatively, Milner and McLeish (1998) presented an approach where each linear chain is treated as a two-armed star with arm length $Z_B/2$. During the disentanglement time, it relaxes a fraction ξ_d of its arm due to retractive motion driven by fluctuations. Equating $\tau^{(B)}$ with the time of a shallow, i.e., driven by fluctuations, retraction $\tau_{\text{shallow}} = (9\pi^3/16)\tau_e(Z_B\xi_d/2)^4$ [Milner and McLeish (1997)], one obtains for ξ_d the equation

$$\tau_d^{(B)}[1 - \xi_d]^2 = \tau_{\text{shallow}}(\xi_d), \quad (13)$$

where $\tau_d^{(B)} = 3Z_B^3 \tau_e$ is the disengagement time without contour length fluctuations and τ_e is the Rouse time of one entanglement strand.

In practice, an approximate solution of (13) as a perturbative series

$$\xi_d \approx \frac{4}{(3\pi^3 Z_B)^{1/4}} \left[1 - \frac{2}{(3\pi^3 Z_B)^{1/4}} + \frac{2}{(3\pi^3 Z_B)^{1/2}} + \dots \right], \quad (14)$$

with small parameter $1/Z_B$ is extremely close to the exact numerical solution of (13) even for $Z_B \approx 10$, and is more than enough for our purposes. The estimated relaxation time $\tau^{(B)}$ of the linear chains (12), with ξ_d given by (14), shows the effective exponent of 3.4 over a wide range of molecular weights before crossing over to the asymptotic exponent 3 for large Z_B [Milner and McLeish (1998)].

Evidently, expression (12) is only a rough approximation, used here to mimic the molecular weight dependence of the linear viscosity. Instead, the phenomenological law $\tau^{(B)} \sim Z_B^{3.4}$ can be used or, if a melt of a certain molecular weight should be simulated, the numerical value of $\tau^{(B)}$ can be directly obtained from the experimental data.

Further, the Rouse-type retraction term in (11) is also written in a one-mode approximation coinciding with the one used in the contour-variable model [Mead *et al.* (1998)] and the pom-pom model [McLeish and Larson (1998)]. Finally, the last term in (11) arises from convective constraint release (CCR): some constraints on a test chain are released because the surrounding polymers move along with the flow [Ianniruberto and Marrucci (2002); Graham *et al.* (2002)]. The frequency of such events is proportional to the Rouse retraction rate. Likhtman and Graham (2003) found, from a comparison with a more sophisticated model [Graham *et al.* (2003)], that $\beta=1$ and $\delta=-1/2$ are reliable estimates.

In what follows, the Rolie-Poly (11) is generalized for a flow in the near-wall region (15). Thanks to the microscopic origin of the equation, it is possible to adjust it term by term to the relaxation processes taking place near the wall. First of all, one has to define the velocity gradient tensor $\mathbf{K}_I$ in this region: it can be determined as the space derivative of the average velocity of the unattached polymers (pieces of the bulk chains penetrating into the wall region). Then, the term corresponding to an affine deformation of the polymer chains by the flow has the same functional form as the first two on the right-hand side in (11). Furthermore, one has to realize that the attached chains do not reptate but relax by arm retraction during some characteristic time $\tau^{(I)}$, as described in the previous section. Also, the Rouse retraction term has the same functional form as in the bulk, but the longest relaxation time is 4 times larger than the Rouse time $\tau_R^{(I)}$ of a *free* chain of Z_I segments [see the fourth term on the right-hand side in (15)].

Finally, the CCR process involving tethered chains needs a bit more attention. Each grafted chain forms entanglements with both bulk and other tethered chains. Hence, each tethered chain experiences CCR with two, possibly very different, rates. Strictly speaking, such a problem needs a treatment similar to the one used to describe CR in binary polymer blends [Rubinstein and Colby (1988)]. However, in our case of grafted chains, which are much shorter than the bulk ones, an ansatz is possible in the spirit of the dilution theories similar to the one used in Doi *et al.* (1987). Indeed, CCR rate is inversely proportional to the Rouse time of the retracting chains [Likhtman and Graham (2003)] and, hence, scales as Z^{-2} . This ensures sufficient time separation between the typical lifetimes of graft-graft and graft-bulk entanglements: the first disappear and reappear much faster than the latter. Therefore, in this limit, one can think of the CCR as of relaxation of a “dilated” grafted chain’s tube with $Z'_I = Z_I \phi$ entanglements which makes

FIG. 1. A sketch of the near-wall region: bulk polymer (gray) is entangled with grafted chains (black). Not to scale.

jumps of $a/\sqrt{\phi}$ with the frequency of the bulk CCR rate. Apparently, besides the condition $Z_I < Z_B$, one should assume that ϕ is not too small—the above ansatz certainly breaks down if only (or mainly) graft-graft entanglements are present. In the addressed here limit, the CCR term takes the form of the last term in (15)

$$\begin{aligned} \frac{d\sigma_I}{dt} = & K_I \cdot \sigma_I + \sigma_I \cdot K_I^T - \frac{\sigma_I - I}{\tau^{(I)}} - \frac{8}{\tau_R^{(I)}} \left(1 - \sqrt{\frac{3}{\text{Tr } \sigma_I}} \right) \sigma_I - \frac{2\beta}{\phi \tau_R^{(B)}} \left(\frac{\text{Tr } \sigma_B}{3} \right)^\delta \left(1 - \sqrt{\frac{3}{\text{Tr } \sigma_B}} \right) \\ & \times (\sigma_I - I). \end{aligned} \quad (15)$$

To summarize: (11) describes the flow in the bulk, and (15)—in the near-wall region with its thickness given by the grafted polymer's coil size $h = a\sqrt{Z_I}$; see Fig. 1. Both equations need to be solved simultaneously, complemented by the condition that the forces that bulk and wall region exert on each other at the interface are equal, i.e., $T_{xy}^{(B)} = T_{xy}^{(I)}$ [Landau and Lifshits (1987)] or, in terms of σ , $\sigma_{xy}^{(B)} = \psi \sigma_{xy}^{(I)}$, where ψ is given by (6). Of course, to be complete, the model should also include the appropriate initial and boundary conditions.

A. Steady shear flow

In this section we apply the Rolie-Poly-based model to the relatively simple case of a steady shear flow in a parallel plate geometry. Despite its simplicity, this particular flow is relevant, especially in the light of the experiments by Léger *et al.* (1999). As these experiments show, surface-anchored chains can strongly influence the friction between a polymer melt and a solid interface. Different friction regimes can be identified with a clear transition between them, also known as “stick-slip” transition. Prediction of the critical shear rate, at which this transition occurs, is one of the primary goals of our investigation: in addition, we also study its dependence upon molecular weight of the bulk and the grafted polymer, grafting density, etc.

Experimental data are usually presented in terms of the slip velocity V_s and the slip length b_s . Theoretically [Brochard and de Gennes (1992); Joshi *et al.* (2001)], these quantities are mapped to the velocity at the top of the grafted layer and the extrapolation length of the bulk velocity profile, Fig. 1. Our goal is to describe quantitatively their dependence on the macroscopic shear rate measured in experiments. Depending on the

value of the slip length b_s we will speak of “weak slip”—below the critical shear rate, and “strong slip,” where b_s is increased by more than an order of magnitude [Léger *et al.* (1999)].

To proceed, we let $K_{xy}^{(B)} = \dot{\gamma}_B$, $K_{xy}^{(I)} = \dot{\gamma}_I$, and $K_{ij}^{(B,I)} = 0$ for $(i,j) \neq (x,y)$ in Eqs. (11) and (15). The steady flow conditions $d\sigma_{I,B}/dt = 0$ simplify the model considerably. It turns out to be convenient to introduce dimensionless variables $\lambda_B = \sqrt{\text{Tr } \sigma_B}/3$ and $\lambda_I = \sqrt{\text{Tr } \sigma_I}/3$, which measure chain stretch. Then, the solution for the bulk region can be obtained analytically, and reads

$$\dot{\gamma}_B = \left\{ \frac{3}{2} \frac{(k_1 + k_2 + 1/\tau^{(B)})^2}{k_1 + 1/\tau^{(B)}} [(\lambda_B^2 - 1)(k_1 + 1/\tau^{(B)}) + \lambda_B^2 k_2] \right\}^{1/2}, \quad (16)$$

$$\sigma_{xy}^{(B)} = \left\{ \frac{3}{2} \frac{k_1 + 1/\tau^{(B)}}{(k_1 + k_2 + 1/\tau^{(B)})^2} [(\lambda_B^2 - 1)(k_1 + 1/\tau^{(B)}) + \lambda_B^2 k_2] \right\}^{1/2}, \quad (17)$$

$$\begin{aligned} \sigma_{yy}^{(B)} = \sigma_{zz}^{(B)} &= \frac{k_1 + 1/\tau^{(B)}}{k_1 + k_2 + 1/\tau^{(B)}}, \\ \sigma_{xx}^{(B)} &= 3\lambda_B^2 - \frac{2(k_1 + 1/\tau^{(B)})}{k_1 + k_2 + 1/\tau^{(B)}}, \end{aligned} \quad (18)$$

where

$$k_1 = \frac{2\beta}{\phi\tau_R^{(B)}} \lambda_B^{2\delta} \left(1 - \frac{1}{\lambda_B} \right)$$

and

$$k_2 = \frac{2}{\tau_R^{(B)}} \left(1 - \frac{1}{\lambda_B} \right).$$

Here, Eqs. (16)–(18) give the flow curve in the bulk region in parametric form with a parameter $\lambda_B \geq 1$.

The flow in the near-wall region is connected to the properties of the flow in the bulk via the interfacial condition and the frequency of CCR. Still, an exact solution of the set of three equations (15) can be obtained. First of all, we note that

$$\sigma_{yy}^{(I)} = \sigma_{zz}^{(I)} = \frac{k_1/\phi + 1/\tau^{(I)}}{k_1/\phi + 8(1 - 1/\lambda_I)/\tau_R^{(I)} + 1/\tau^{(I)}}, \quad (19)$$

$$\sigma_{xx}^{(I)} = 3\lambda_I^2 - \frac{2(k_1/\phi + 1/\tau^{(I)})}{k_1/\phi + 8(1 - 1/\lambda_I)/\tau_R^{(I)} + 1/\tau^{(I)}},$$

$$\dot{\gamma}_I = \frac{\sigma_{xy}^{(B)}}{\psi} \frac{[k_1/\phi + 8(1 - 1/\lambda_I)/\tau_R^{(I)} + 1/\tau^{(I)}]^2}{k_1/\phi + 1/\tau^{(I)}}. \quad (20)$$

Then, the equation for λ_I as a function of λ_B is

$$\begin{aligned} & \frac{2}{3} \left(\frac{\sigma_{xy}^{(B)}(\lambda_B)}{\psi} \right)^2 \frac{[k_1(\lambda_B)/\phi + 8(1 - 1/\lambda_I)/\tau_R^{(I)} + 1/\tau^{(I)}]^2}{k_1(\lambda_B)/\phi + 1/\tau^{(I)}} - \left(\frac{k_1(\lambda_B)}{\phi} + \frac{1}{\tau^{(I)}} \right) \\ & \times (\lambda_I^2 - 1) - \frac{8}{\tau_R^{(I)}} \left(1 - \frac{1}{\lambda_I} \right) \lambda_I^2 = 0. \end{aligned} \quad (21)$$

In fact, this is a fourth-order polynomial equation

$$A_4 \lambda_I^4 + A_3 \lambda_I^3 + A_2 \lambda_I^2 + A_1 \lambda_I + A_0 = 0,$$

which is very simple to solve numerically [for the explicit form of the coefficients $A_i(\lambda_B)$ see the Appendix].

Hence, the summary of the calculation scheme is as follows. For a given stress $\sigma_{xy}^{(B)}$ the corresponding values of λ_B and $\dot{\gamma}_B$ can be computed from (17) and (16). Next (21) allows one to calculate the corresponding λ_I . The flow rate in the near-wall region $\dot{\gamma}_I$ is then determined by (20). Finally, the quantities of interest, such as the slip velocity V_s and the slip length b_s , are obtained from $V_s = h \dot{\gamma}_I$ and $b_s = h \dot{\gamma}_I / \dot{\gamma}_B$.

Some additional insights can be obtained from the analysis of the linear regime. A simple expansion gives

$$\dot{\gamma}_I = \frac{\dot{\gamma}_B}{\psi} \frac{\tau^{(B)}}{\tau^{(I)}}. \quad (22)$$

Rewritten in terms of the slip velocity V_s , this reads as

$$V_s = \dot{\gamma}_B \frac{h}{\psi} \frac{\tau^{(B)}}{\tau^{(I)}}. \quad (23)$$

Finally, the slip length can be readily extracted from (23), i.e.,

$$b_s = \frac{h}{\psi} \frac{\tau^{(B)}}{\tau^{(I)}}. \quad (24)$$

Note that this prediction completely agrees with the scaling proposed in Ajdari *et al.* (1994).

B. Onset of slip

In this section we turn to the prediction of the transition from one friction regime to the other: further on it will be referred as stick-slip transition. The expressions (23) and (24) for slip velocity and slip length are valid only in the linear regime far from the rate $\dot{\gamma}^{(cr)}$, where the stick-slip transition occurs. As will be clarified below, the transition itself is purely a “nonlinear” effect.

For low shear rates the flow in the bulk and the wall layer is stable: relaxation mechanisms, such as reptation in the bulk and arm retraction near the wall, are effective enough to avoid the alignment of the chains in the direction of the flow. The situation changes in nonlinear flows, where CCR becomes responsible for the relaxation. For a bulk molecule in a flow with rate $\dot{\gamma}_B$, the relevant relaxation time scale should be about $1/\dot{\gamma}_B$. As far as the CCR frequency is determined by the other bulk chains, it is of the order of $\dot{\gamma}_B$, which is the same at which the bulk chain is deformed by the flow. Thus, CCR is effective in randomizing the chain configuration and, this way, relaxing the stress. On the other hand, the deformation rate for a tethered molecule is of the order of $\dot{\gamma}_I$, whereas the CCR time scale is governed by the bulk chains and is proportional to $1/\dot{\gamma}_B$.

FIG. 2. A sketch of the dependence $\sigma_{xy}^{(B)}$ vs λ_I as given by (21). Only the “physical branch” with $\sigma_{xy}^{(B)} > 0$, $\lambda_I > 1$ is shown.

This leads to the conclusion, that when $\dot{\gamma}_I$ becomes higher than $\dot{\gamma}_B$, the CCR is not so effective in the wall layer as it is in the bulk [in the terminology of Joshi and Lele (2002); Joshi *et al.* (2001), a tethered molecule experiences *restricted* CCR]. This can lead to an orientation of the tethered molecules in the direction of the flow and their effective disentanglement from the bulk chains, following the scenario of the stick-slip transition described at a scaling level in [Brochard and de Gennes (1992); Ajdari *et al.* (1995, 1994); Brochard-Wyart *et al.* (1996)].

The same conclusion can be drawn from the Rolie-Poly-based model. Here, the analysis is performed based on Eq. (21). As far as γ_B and $\sigma_{xy}^{(B)}$ are connected by (17), Eq. (21) can be interpreted as one giving the average grafted chain stretch λ_I as a function of the stress $\sigma_{xy}^{(B)}$. Qualitatively, this dependence is sketched in Fig. 2. For small $\sigma_{xy}^{(B)}$, in the linear regime, it yields only one root, $\lambda_I \simeq 1$, which corresponds to a coil-like conformation. On the other hand, for very high stress, the only existing root is quite large, $\lambda_I \gg 1$: it corresponds to very stretched grafted chains in the strong slip regime. Gradually increasing $\sigma_{xy}^{(B)}$ from 0 to higher values, we see that the transition between the two regimes, from “stick” (coil-like conformation with $\lambda_I \simeq 1$) to “slip” (stretched, $\lambda_I \gg 1$), occurs at the value of $[\sigma_{xy}^{(B)}]^{(cr)}$, where the function $\sigma_{xy}^{(B)}(\lambda_I)$ has a maximum. To find the position of this maximum, one can perform an expansion of (21) up to second order in the parameter $\lambda_I - 1$. The simple quadratic equation obtained reads

$$C_2(\lambda_I - 1)^2 + C_1(\lambda_I - 1) + C_0 = 0, \quad (25)$$

where $C_2 = \sum_{i=0}^4 i(i-1)A_i/2$, $C_1 = \sum_{i=0}^4 iA_i$, and $C_0 = \sum_{i=0}^4 A_i$. Then, the critical stress, indicated in Fig. 2, at which the stick-slip transition occurs, corresponds to the point where the determinant of (25) vanishes, i.e., the solution of the equation $C_1^2 - 4C_2C_0 = 0$. The values of $\sigma_{xy}^{(B)}$ and $\dot{\gamma}_B$ corresponding to this situation are the critical shear stress and rate, respectively.

Note that a simple algebraic equation must be solved to obtain the critical rate $\dot{\gamma}_B^{(cr)}$. Alternatively, one could analyze the “full” equation (21) to compute the critical stress or critical rate. However, as a numerical calculation shows, the critical values obtained by any of the routes virtually coincide. Moreover, both routes are technically much simpler than those previously proposed in the literature [Joshi *et al.* (2001); Joshi and Lele (2002)] and do not demand any heavy computation.

C. Scaling

Based on the above approach, it is possible to analyze the scaling dependence of the critical shear rate $\dot{\gamma}^{(cr)}$ (further on we use the notation $\dot{\gamma}^{(cr)} = \dot{\gamma}_B^{(cr)}$) on the molecular weight of the bulk and grafted polymer without solving the set (11) and (15). For this purpose we note that the critical stress in the near-wall region is of the order of $T_{xy}^{(cr)} \sim G_I$. At the same time, it should be equal to $\eta_B \dot{\gamma}^{(cr)}$, where $\eta_B \sim G_B \tau^{(B)}$ is the viscosity of the bulk. Comparing these two, one obtains, with the help of (6)

$$\dot{\gamma}^{(cr)} \sim \frac{\psi}{\tau^{(B)}}. \quad (26)$$

Let us first address the dependence of the critical shear rate on the molecular weight of the bulk polymer or, equivalently, on Z_B . The linear relaxation time $\tau^{(B)}$ depends on Z_B in the same way as the viscosity does: $\tau^{(B)} \sim Z_B^{3.4}$. According to (6), the prefactor ψ can have a different scaling, depending on Z_B . If one assumes that the grafting density Σ is fixed, then in the mushroom or cooperative regime, $\Sigma < \Sigma_0$ (3), ψ does not depend on Z_B . This corresponds to $Z_B < Z_B^{(0)}$, where

$$Z_B^{(0)} = \left[\frac{\sigma_0}{2\Sigma} \left(1 + \sqrt{1 + \frac{4Z_I \Sigma^2}{\sigma_0^2}} \right) \right]^2 \sim \left(\frac{\sigma_0}{\Sigma} \right)^2. \quad (27)$$

For higher values of Z_B , $\psi \sim 1/\sqrt{Z_B}$, as follows from (6) and (4). Thus, taking into account $\tau^{(B)} \sim Z_B^{3.4}$, we find

$$\dot{\gamma}^{(cr)} \sim \begin{cases} Z_B^{-3.4} & Z_B < Z_B^{(0)}, \\ Z_B^{-3.9} & Z_B > Z_B^{(0)}. \end{cases} \quad (28)$$

Note that the scaling for Z_B below $Z_B^{(0)}$ coincides with the predictions of earlier works [Brochard and de Gennes (1992); Ajdari *et al.* (1995, 1994)]. However, the result for the regime where interaction between grafted chains becomes important was beyond their scope.

The Z_I dependence of the critical shear rate can be analyzed in a similar manner. For low molecular weight of the grafted polymer, $Z_I < Z_I^{(0)}$, where $Z_I^{(0)} = \sigma_0 \sqrt{Z_B} / \Sigma - Z_B$, the critical rate $\dot{\gamma}^{(cr)}$ increases with Z_I as $\sqrt{Z_I}$. For higher values of Z_I , $Z_I > Z_I^{(0)}$, it is a decreasing function of Z_I

$$\dot{\gamma}^{(cr)} \sim \begin{cases} \Sigma \sqrt{Z_I} / \sigma_0 & Z_I < Z_I^{(0)}, \\ (\sigma_0 / (\Sigma \sqrt{Z_B}) - Z_I / Z_B) \sqrt{Z_I} & Z_I > Z_I^{(0)}. \end{cases} \quad (29)$$

Finally, if Z_I reaches $Z_I^{(dry)} = \sigma_0 / \Sigma$, the dry brush regime is entered where the main role is played by a thin interpenetration layer between the bulk and the brush [similar to Goveas and Fredrickson (1998)] and virtually no dependence on Z_I should be observed.

FIG. 3. (a) An example of the flow curves for the bulk and the wall region: dimensionless stress T_{xy}/G_B vs dimensionless rate in the bulk ($\dot{\gamma}_B \tau_d^{(B)}$) and near the wall ($\dot{\gamma}_I \tau_d^{(B)}$) for $Z_B=100$, $Z_I=10$, $\Sigma/\sigma_0=0.1$. Dashed line corresponds to the unstable branch of the wall flow curve. Dotted lines indicate the critical stress and the corresponding rate. (b) Dimensionless slip velocity as a function of shear rate. The inset shows the same curve in terms of the slip length $b_s=V_s/\dot{\gamma}_B$.

D. Numerical results

The set of equations presented above is solved numerically following the scheme outlined in Sec. IV A for the case of a steady shear flow. The bulk flow curve, which is explicitly given by (16) and (17), is shown in Fig. 3(a). The numerical procedure includes only solving (21) to obtain λ_I for a given bulk flow rate. Then, the flow rate in the wall region can be computed using (20) and is also shown in Fig. 3(a). It is also clear from Fig. 3 how the critical shear rate $\dot{\gamma}^{(cr)}$ must be determined: the maximum in the near-wall flow curve corresponds to a stick-slip transition, and the critical bulk flow rate follows from the bulk flow curve. We want to emphasize the simplicity of the numerical calculation when compared to similar bulk-wall constitutive models [Joshi and Lele (2002); Joshi *et al.* (2001)].

Also, note that the constant ψ_0 in (6) has not been determined yet (it will be computed in the next section, where experimental data are analyzed). Therefore, we shall use $\psi_0 = 0$ in the rest of this section, resorting to the assumption that only grafted chains transfer stress from the bulk to the wall.

In Fig. 3(b) the slip velocity V_s and the slip length b_s are shown against shear rate $\dot{\gamma}_B$. Explosive growth of the slip velocity (or slip length) when the shear rate approaches its critical value is typical for a stick-slip transition. As discussed in the next section, generally three regimes can be distinguished. The first one, at small rates, is characterized by a relatively small and smoothly changing slip velocity—this is what one should associate with a stick or a weak slip. In the marginal regime in the vicinity of $\dot{\gamma}^{(cr)}$, even small increase in the rate leads to a dramatic jump in V_s and b_s . Finally, not shown in Fig. 3(b), a strong macroscopic slip sets in and the slip length attains a quite high value. This scenario has been earlier predicted by Brochard and de Gennes (1992) based on scaling arguments.

Let us further focus on the prediction of the critical shear rate dependence on the molecular weight and the grafting density. In Fig. 4(a), the critical shear rate $\dot{\gamma}^{(cr)}$ is shown against the molecular weight of the bulk chains for different grafting regimes. In accord with previous theoretical work [Brochard and de Gennes (1992); Ajdari *et al.* (1995, 1994); Gay (1999); Joshi *et al.* (2001)] and (28), the critical rate scales as $Z_B^{-3.4}$ in the mushroom and cooperative regimes. This fact is also supported by the available experimental data by Durlat *et al.* (1997). An interesting point, not mentioned in earlier works, is the presence of another regime, where a stronger scaling should be seen, $\dot{\gamma}^{(cr)} \sim Z_B^{-3.9}$ [see the inset in Fig. 4(a)]. This regime has also been predicted based on the scaling analysis in Sec. IV C.

The critical shear rate $\dot{\gamma}^{(cr)}$ is also sensitive to the molecular weight of the grafted polymer, Fig. 4(b). Indeed, for relatively short chains $Z_I < Z_I^{(0)}$, it is proportional to $\sqrt{Z_I}$, as also outlined in Sec. IV C. For longer chains, when interactions between tethered molecules become important and the bulk molecules are gradually expelled from the layer, the critical rate decreases, in accord with expression (29). This behavior is intuitively clear: the density of the bulk-graft entanglements decreases if the bulk chains are expelled from the wall layer and, therefore, a lower stress is needed to cause a cohesive failure.

Knowledge of the grafting density dependence of the critical shear rate can be quite useful: as described in Léger *et al.* (1999), it is possible to control the grafting density experimentally in a quite simple way by changing the polymer concentration in the solution from which the adsorption or the tethering is carried out. The theoretically predicted critical shear rate versus grafting density is shown in Fig. 5. It is very remarkable that $\dot{\gamma}^{(cr)}$ is a nonmonotonic function of the grafting density. For small Σ , in the mushroom and cooperative regimes, critical rate increases linearly with the grafting density. This is what one expects from a system of practically noninteracting tethered chains: the rate is proportional to the stress and, in turn, the total stress, which the wall layer can resist, is simply a sum over all the tethered chains. Completely different behavior is observed in the overlap regime where the interaction between grafted molecules becomes significant. The density of bulk-graft entanglements decreases with increasing Σ and, thus, slip is facilitated. Figure 5 also gives us a hint about the most effective way to postpone slip. For fixed molecular weights of the bulk and the wall polymer, the maximum critical rate $\dot{\gamma}^{(cr)}$ is observed at $\Sigma = \Sigma_o$, where Σ_o is given by (3). The value of $\dot{\gamma}^{(cr)}$ at this maximum, estimated from (26), reads

FIG. 4. (a) Critical shear rate as a function of the bulk polymer molecular weight for $Z_I=10$. For the grafting density $\Sigma/\sigma_0=0.1$ the transition from one scaling law to the other at $Z_B^{(0)}$ is shown [see also the inset and Eq. (28); note $\tau_d^{(B)} \sim Z_B^3$]. (b) Critical shear rate vs Z_I for $Z_B=100$. For $\Sigma/\sigma_0=0.1$: both regimes predicted by (29) are clearly seen.

$$\dot{\gamma}_{\max}^{(cr)} \sim \frac{\sqrt{Z_B Z_I}}{Z_B + Z_I} Z_B^{-3.4}, \quad (30)$$

and increases if the molecular weight of the bulk polymer is decreased. Thus, adding shorter chains into the bulk and choosing the appropriate grafting density allows one to shift the onset of slip to higher values of the shear rate.

Finally, we would like to discuss briefly a possible temperature dependence of the critical shear rate $\dot{\gamma}^{(cr)}$. In Fig. 5 above, the temperature dependence for fixed Z_I , Z_B , and Σ enters only via the reptation time of the bulk chains $\tau_d^{(B)} \sim 1/T$ [Doi and Edwards (1986)]. Hence, the critical shear rate is expected to scale linearly with temperature.

V. COMPARISON WITH EXPERIMENTAL DATA

An ultimate test of the proposed theory is a comparison to the experiments performed within the group of Léger [Léger *et al.* (1999); Durliat *et al.* (1997); Léger *et al.*

FIG. 5. Critical shear as a function of the dimensionless grafting density Σ/σ_0 .

(1997)]—virtually the only available experimental data set in the literature concerning microscopic aspects of the stick-slip transition in the case of a polymer end-grafted wall. The experiments were done in a parallel plate geometry to ensure a well-defined flow profile. The slip velocity was directly measured in the 70 nm layer next to a grafted flat silica plate. Also, special care had been taken to prevent any additional adsorption of the bulk PDMS chains on the surface, so the grafting density is a well-defined and measured quantity [for an excellent review of the results and the techniques employed see Léger *et al.* (1999)]. The main output of the experiments is the measured dependence of the slip velocity V_s on the shear rate in the bulk $\dot{\gamma}$.

Let us start with an estimation of the numerical values of the model parameters. First, we address the available data on the slip velocity versus shear rate for a fixed grafting density $\Sigma=0.0055/(0.5 \text{ nm}^2)=0.022 \text{ nm}^{-2}$ [note that Léger *et al.* (1999) use “a monomer size” equal to 0.5 nm to nondimensionalize the grafting density]. To compute the segmental length of the bulk Z_B and the grafted Z_I chains, a molecular weight between entanglements of $M_e=13\,522 \text{ g/mole}$ and a tube diameter of $a=7.86 \text{ nm}$ are used [Fetters *et al.* (1994)]. Then, the molecular weights $M_B=970 \text{ kg/mole}$ and $M_I=96 \text{ kg/mole}$ yield $Z_B=72$ and $Z_I=7.1$. Making use of the fact that the experimental molecular weight of a monomer is $m=74 \text{ g/mole}$ [Léger *et al.* (1999)] and the mass density of PDMS about $\rho=0.895 \text{ g/cm}^3$ [Fetters *et al.* (1994)], one can compute $\sigma_0=0.313 \text{ nm}^{-2}$.

From the microscopic model described in Sec. III, the relaxation time of a tethered molecule (for the molecular weight and the grafting density given above) is $\tau^{(I)} \simeq 9.1 \times 10^4 \tau_e$. Next, the relaxation time of the bulk chains is computed from (12): $\tau^{(B)}=4.7 \times 10^5 \tau_e$. Note that the ratio $\tau^{(I)}/\tau^{(B)} \simeq 0.19$ is small and, therefore, the approach taken in Sec. III is justified (we recall that an assumption was made that $\tau^{(I)}$ is smaller than the disengagement time of the bulk chains). Finally, the phenomenological constant ψ_0 from (6) is estimated from the data on b_s for low grafting densities: as follows from Durliat *et al.* (1997), $b_s \simeq 1.8 \mu\text{m}$ in this regime, which, together with (24), furnishes $\psi_0 \simeq 0.12$.

Hence, there is the only unknown parameter left—the Rouse time of an entanglement segment τ_e . In practice, it can be calculated via the reptation time of the bulk polymer $\tau_d^{(B)}$, which, in turn, can be expressed via the steady-state viscosity and the elastic modulus measured in experiments. Unfortunately, $\tau_d^{(B)}$ is not directly available in the literature for the PDMS melts at the temperature used in the experiment. However, it can be

FIG. 6. Comparison of the experimental data (points) from 19(c) and (b) in Léger *et al.* (1999) with the model prediction (solid and broken line): (a) slip length vs shear rate; (b) slip length vs slip velocity.

extracted from the data on self-diffusion measurements presented in Léger *et al.* (1996). By fitting the diffusion coefficient D_G as a function of the polymerization index, and using the identity $D_G = Za^2 / (3\pi^2 \tau_d^{(B)})$ [Doi and Edwards (1986)], one can estimate that for the molecular weight $M_B = 970$ kg/mole the reptation time $\tau_d^{(B)}$ is in the range 0.3–0.5 s. In what follows, we shall use $\tau_d^{(B)}$ (or, equivalently, τ_e) as an adjustable parameter to fit the experiment for *one* value of the grafting density, $\Sigma = 0.022 \text{ nm}^{-2}$. Further on, this fitted value of $\tau_d^{(B)}$ will be used to produce a *parameter-free* comparison to the data for the other grafting densities and molecular weights, and will be compared to the above experimental estimate.

The slip velocity and the slip length predicted by the model are compared to the experiment for $\Sigma = 0.022 \text{ nm}^{-2}$ in Fig. 6. The fitted relaxation time has the value $\tau_d^{(B)} \approx 0.15$ s. The quantitative agreement with experiment is satisfactory taking into account the simplicity of the model. The main disagreement present is in the value of $\tau_d^{(B)}$, which is 2–3 times lower than the expected one. This problem may possibly have several origins. The most probable one is the oversimplified view of the physics in the near-wall region. As also mentioned by Joshi and Lele (2002), a simple analysis on the level of Sec.

It probably underpredicts the wall elastic modulus quite substantially. Another bit more subtle reason, lies in the difference in the definition of the slip velocity used in the theoretical works (including this one) and the experiments performed in Léger's group. Indeed, the average velocity measured by the near-field laser velocimetry technique in a layer of 75 nm thick corresponds only approximately to the velocity V_s on top of a 21 nm thick grafted layer, which is used as a theoretical definition of the slip velocity. This also brings some uncertainty into the correspondence between the apparent bulk shear rate $\dot{\gamma}_{\text{app}} = (V_t - V_s)/H$, where V_t is the top plate velocity, H is the distance between the plates [Léger *et al.* (1997)] and the bulk shear rate $\dot{\gamma}_B$ used here.

Apart from the underestimation of $\tau_d^{(B)}$, all the essential features are reproduced quite well. For “slow flows” the slip length remains nearly constant (solid line): it corresponds to a “fully entangled” regime, where a grafted chain has a coil-like conformation. However, in the vicinity of the critical shear rate, around 5 s^{-1} , b_s starts to grow. The following regime, shown as a broken line in Fig. 6, is known as a marginal state [Brochard and de Gennes (1992); Ajdari *et al.* (1995, 1994); Gay (1999)], where the stress is locked at a certain value and only a part of a tethered chain relaxes. Conformationally it corresponds to a “ball-on-stick” or “trumpet” shapes predicted by Ajdari *et al.* (1994). Finally, when the whole chain gets squeezed against the wall, the experimental b_s seems to saturate. This regime, disentangled friction, is beyond the reach of the present model. Indeed, the Rolie-Poly describes entanglement dynamics, whereas the friction after the critical shear rate has mainly a monomeric Rouse-type origin.

As explained before, the bulk relaxation time value obtained can be used to perform a *parameter-free* comparison to the rest of the experimental data. For example, the surface density dependence of the critical shear rate, Fig. 7(a), is quite informative. A reasonable agreement is achieved through a wide range of grafting densities, which have been varied over more than an order of magnitude. As seen from Fig. 7(a), the agreement becomes poorer for higher grafting densities. This is not surprising—as explained in Sec. IV, the CCR term in (15) is written in a “dilution” approximation, which holds only while the grafting density is far enough from the dry brush regime. Some attention also should be paid to the extremely low grafting densities (the very left experimental point). The friction with a bare wall has been left out of the model. This approximation is justified if the friction is totally governed by entanglements between grafted and bulk chains. It implies that the model is valid only until a certain small value of Σ when both effects become equally important.

Finally, the molecular weight dependence of the critical rate is tested against the experiment. Unfortunately, too little data are available in the literature to perform a thorough comparison. Here, we use the data provided in Durliat *et al.* (1997) for two values of the grafting density and four different molecular weights, Fig. 7(b). The linear relaxation time of the bulk molecules of different molecular weights is calculated based on the phenomenological rule $\tau^{(B)} \sim M^{3.4}$ [Ferry (1970); Doi and Edwards (1986)] from the fitted value above. The lack of data makes it hard to judge the quality of the agreement; however, for the low grafting density data, it is within the error margin of the experiment. For the higher grafting density (which is ten times larger than the first one) the agreement is much less favorable but still acceptable taking into account that no adjustable parameter has been used.

VI. CONCLUDING REMARKS

We have presented a simple model describing a polymer melt flow near a polymer-grafted wall. The model is based on the Rolie-Poly description [Likhtman and Graham

FIG. 7. (a) Grafting density dependence of the critical shear rate. Solid line is the prediction of the model; points correspond to the experiment [Léger *et al.* (1999)] for $M_B=970$ kg/mol and $M_I=96$ kg/mol. Dimensionless grafting density, used in Léger *et al.* (1999), is $\sigma=\Sigma \times (0.5 \text{ nm}^2)$. (b) Molecular weight dependence of the critical shear rate for two different grafting densities. Experimental data from Durliat *et al.* (1997) for $M_I=96$ kg/mol.

(2003)] and provides a constitutive equation capable of mimicking the flow up to a stick-slip transition and to predict the critical shear rate at the transition. In combination with a microscopic relaxation model presented in Sec. III, the approach allows one to fit quite accurately (see Fig. 6) the available data for PDMS at a fixed grafting density [Léger *et al.* (1999)], although the fitted value of the reptation time is lower than expected. The relaxation time, obtained from the fitting, has been used to perform a parameter-free comparison with the grafting density and molecular weight dependencies of the critical shear rate, Fig. 7. The outcome for a very wide range of parameter values is in a reasonable agreement with the experimental data.

One of the main advantages of the model is its simplicity, especially in comparison with the earlier proposed approaches [Joshi *et al.* (2001); Joshi and Lele (2002)]: it does not require any extensive numerical calculations and, therefore, potentially can be used in numerical codes for flow simulations in the vicinity of a grafted wall. Despite its simplicity, the model is able to mimic all the generic features of the stick-slip experiments of

Léger. It predicts different flow regimes with some slip always present—there is a weak, or even moderate, slip even for small shear rates, Fig. 6. The value of the slip length in the weak slip regime is reproduced quite well. Also, the scaling obtained from the model is in agreement with the experiments [Durliat *et al.* (1997); Léger *et al.* (1997)] and the earlier theoretical predictions [Brochard and de Gennes (1992); Ajdari *et al.* (1995, 1994); Brochard-Wyart *et al.* (1996); Gay (1999)].

Apart from the agreement with the experiments of Léger *et al.* (1999), there are also areas beyond the reach of the present model in its current form. The Rolie-Poly-based approach describes only the “entangled” regime when the main origin of the friction between the bulk and the wall layer is due to entanglements that the bulk chains form with the grafted ones. However, these entanglements virtually disappear after the onset of strong slip (for shear rates higher than the critical value) and mainly monomeric friction becomes responsible for the physics of the phenomenon. A simple phenomenological approach [see, e.g., Dubbeldam and Molenaar (2003)] and references therein) can be used to include this effect approximately. However, much deeper insight still is needed to achieve a full understanding of the process on a microscopic level.

To summarize, the model presented provides a good basis for quantitative modeling of a polymer flow in the vicinity of a polymer-modified solid wall. A combination of a dynamic dilution-based microscopic model and a simple constitutive equation allows one to reproduce the experimental data quite well for a wide range of grafting densities and molecular weights. Still, a deeper understanding of certain aspects of the slick-slip phenomenon, especially in the strong slip regime, remains a challenge.

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APPENDIX: EXPLICIT FORM OF THE COEFFICIENTS A_i

$$\begin{aligned}
 A_4 &= -B \left(B + \frac{8}{\tau_R^{(I)}} \right), \\
 A_3 &= \frac{8B}{\tau_R^{(I)}}, \\
 A_2 &= B^2 + C \left(B + \frac{8}{\tau_R^{(I)}} \right)^2, \\
 A_1 &= -\frac{16C}{\tau_R^{(I)}} \left(B + \frac{8}{\tau_R^{(I)}} \right), \\
 A_0 &= \frac{64C}{(\tau_R^{(I)})^2}, \tag{A1}
 \end{aligned}$$

where $B = k_1 / \phi + 1 + 1 / \tau^{(I)}$ and $C = (2/3)(\sigma_{xy}^{(B)} / \psi)^2$. Note that k_1 and $\sigma_{xy}^{(B)}$ present in (A1), are functions of λ_B . Thus, (21) allows one to calculate λ_I as a function of λ_B .

References

- Ajdari, A., F. Brochard-Wyart, C. Gay, P. G. de Gennes, and J. L. Viovy, "Drag on a tethered chain moving in a polymer melt," *J. Phys. II* **5**, 491–495 (1995).
- Ajdari, A., F. Brochard-Wyart, P. G. de Gennes, L. Leibler, J. L. Viovy, and M. Rubinstein, "Slippage of an entangled polymer melt on a grafted surface," *Physica A* **204**, 17–39 (1994).
- Ball, R. C., and T. C. B. McLeish, "Dynamic dilution and the viscosity of star-polymer melts," *Macromolecules* **22**, 1911–1913 (1989).
- Bird, R. B., R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids* (Wiley, New York, 1987), Vol. 1.
- Brochard, F., and P. G. de Gennes, "Shear-dependent slippage at a polymer/solid interface," *Langmuir* **8**, 3033–3037 (1992).
- Brochard-Wyart, F., C. Gay, and P. G. de Gennes, "Slippage of polymer melts on grafted surfaces," *Macromolecules* **29**, 377–382 (1996).
- Colby, R. H., and M. Rubinstein, "Two-parameter scaling for polymers in Θ solvents," *Macromolecules* **23**, 2753–2757 (1990).
- Denn, M. M., "Extrusion instabilities and wall slip," *Annu. Rev. Fluid Mech.* **33**, 265–287 (2001).
- Doi, M., "Explanation for the 3.4-power law for viscosity of polymeric liquids on the basis of the tube model," *J. Polym. Sci., Polym. Phys. Ed.* **21**, 667–684 (1983).
- Doi, M., and S. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).
- Doi, M., and N. Y. Kuzuu, "Rheology of star polymers in concentrated solutions and melts," *J. Polym. Sci., Polym. Lett. Ed.* **18**, 775–780 (1980).
- Doi, M., W. W. Graessley, E. Helfand, and D. S. Pearson, "Dynamics of polymers in polydisperse melts," *Macromolecules* **20**, 1900–1906 (1987).
- Dubbeldam, J. L. A., and J. Molenaar, "Dynamics of the spurt instability in polymer extrusion," *J. Non-Newtonian Fluid Mech.* **112**, 217–235 (2003).
- Durliat, E., H. Hervet, and L. Léger, "Influence of grafting density on wall slip of a polymer melt on a polymer brush," *Europhys. Lett.* **38**, 383–388 (1997).
- Ferry, J. D., *Viscoelastic Properties of Polymers* (Wiley, New York, 1970).
- Fetters, L. J., D. J. Lohse, D. Richter, T. A. Witten, and A. Zirkel, "Connection between polymer molecular weight, density, chain dimensions, and melt viscoelastic properties," *Macromolecules* **27**, 4639–4647 (1994).
- Gay, C., "New concepts for the slippage of an entangled polymer melt at a grafted solid interface," *Eur. Phys. J. B* **7**, 251–262 (1999).
- Goveas, J., and G. Fredrickson, "Apparent slip at a polymer-polymer interface," *Eur. Phys. J. B* **2**, 79–92 (1998).
- Graham, R. S., A. E. Likhtman, T. C. B. McLeish, and S. T. Milner, "Microscopic theory of linear, entangled polymer chains under rapid deformation including chain stretch and convective constraint release," *J. Rheol.* **47**, 1171–1200 (2003).
- Ianniruberto, G., and G. Marrucci, "A multi-mode CCR model for entangled polymers with chain stretch," *J. Non-Newtonian Fluid Mech.* **102**, 383–395 (2002).
- Joshi, Y. M., and A. K. Lele, "Dynamics of end-tethered chains at high surface coverage," *J. Rheol.* **46**, 427–453 (2002).
- Joshi, Y. M., A. K. Lele, and R. A. Mashelkar, "Molecular model for wall slip: Role of convective constraint release," *Macromolecules* **34**, 3412–3420 (2001).
- Lam, Y. C., L. Jiang, C. Y. Yue, K. C. Tam, L. Li, and X. Hu, "Interfacial slip between polymer melts studied by confocal microscopy and rheological measurements," *J. Rheol.* **47**, 795–807 (2003).
- Landau, L. D., and E. M. Lifshits, *Fluid Mechanics* (Pergamon, Oxford, 1987).
- Larson, R. G., T. Sridhar, L. G. Leal, G. H. McKinley, A. E. Likhtman, and T. C. B. McLeish, "Definitions of entanglement spacing and time constants in the tube model," *J. Rheol.* **47**, 809–818 (2003).
- Léger, L., E. Raphaël, and H. Hervet, "Surface-anchored polymer chains: Their role in adhesion and friction," *Adv. Polym. Sci.* **138**, 185–225 (1999).

- Léger, L., H. Hervet, G. Massey, and E. Durliat, "Wall slip in polymer melts," *J. Phys.: Condens. Matter* **9**, 7719–7740 (1997).
- Léger, L., H. Hervet, P. Auroy, E. Boucher, and G. Massey, "The reptation model: Tests through diffusion measurements in linear polymer melts," in *Rheology for Polymer Melt Processing*, Rheology series 5, edited by M. Piau and J.-F. Agassant (Elsevier, Amsterdam, 1996), pp. 1–16.
- Likhtman, A. E., and R. S. Graham, "Simple constitutive equation for linear polymer melts derived from molecular theory: Rolie-Poly equation," *J. Non-Newtonian Fluid Mech.* **114**, 1–12 (2003).
- Marrucci, G., and G. Ianniruberto, "Flow-induced orientation and stretching of entangled polymers," *Philos. Trans. R. Soc. London, Ser. A* **361**, 677–687 (2003).
- McLeish, T. C. B., and R. G. Larson, "Molecular constitutive equations for a class of branched polymers: The pom-pom polymer," *J. Rheol.* **42**, 81–110 (1998).
- Mead, D. W., R. G. Larson, and M. Doi, "A molecular theory for fast flows of entangled polymers," *Macromolecules* **31**, 7895–7914 (1998).
- Migler, K. B., H. Hervet, and L. Léger, "Slip transition of a polymer melt under shear stress," *Phys. Rev. Lett.* **70**, 287–290 (1993).
- Milner, S. T., and T. C. B. McLeish, "Parameter-free theory for stress relaxation in star polymer melts," *Macromolecules* **30**, 2159–2166 (1997).
- Milner, S. T., and T. C. B. McLeish, "Reptation and contour-length fluctuations in melts of linear polymers," *Phys. Rev. Lett.* **81**, 725–728 (1998).
- Milner, S. T., T. C. B. McLeish, R. N. Young, A. Hakiki, and J. M. Johnson, "Dynamic dilution, constraint-release, and star-linear blends," *Macromolecules* **31**, 9345–9353 (1998).
- Pearson, D. S., and E. Helfand, "Viscoelastic properties of star-shaped polymers," *Macromolecules* **17**, 888–895 (1984).
- Rubinstein, M., and R. H. Colby, "Self-consistent theory of polydisperse entangled polymers: Linear viscoelasticity of binary blends," *J. Chem. Phys.* **89**, 5291–5306 (1988).
- Wang, S.-Q., and P. A. Drda, "Stick-slip transition in capillary flow of polyethylene. 2. Molecular weight dependence and low-temperature anomaly," *Macromolecules* **29**, 4115–4119 (1996a).
- Wang, S.-Q., and P. A. Drda, "Superfluid-like stick-slip transition in capillary flow of linear polyethylene melts. 1. General features," *Macromolecules* **29**, 2627–2632 (1996b).
- Watanabe, H., "Viscoelasticity and dynamics of entangled polymers," *Prog. Polym. Sci.* **24**, 1253–1403 (1999).