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Slippage of Polymer Melts on Grafted Surfaces

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ABSTRACT: We study the slippage of a highly viscous polymer melt (P monomers per chain) on a solid substrate grafted by a few smaller chains in the mushroom regime (N monomers per chain, grafting density ν). The friction is provided by the sliding motion of the P chains of the "skin" (thickness $R_p = P^{1/2}a$) which are entangled with the tethered chains. At low grafting densities, only a fraction of the P chains in the skin are coupled to the N chains, and the friction on the mushrooms is additive. Above a threshold ν_c, all P chains of the skin are trapped, and the low-velocity friction becomes independent of the grafting density. Above a certain threshold slippage velocity $V^*(\nu)$, the N chains are strongly stretched and reach a "marginal state", corresponding to a constant shear stress. We expect that for $\nu > \nu_c$, $V^*(\nu)$ increases linearly. Depending on N, P, ν, and V, we predict a cascade of regimes, where the N chains may be ideal, stretched, or "marginal", while the trapped chains may be ideal or stretched and progressively disentangle from the N chains.

I. Introduction

Entangled polymers do not flow like usual liquids. One of us[1] predicted that polymer melts slip on a "smooth, passive" surface. More generally, the slippage is characterized by the extrapolation length b, defined by the distance to the wall at which the velocity extrapolates to zero. The ratio between the shear stress σ at the S/L interface and the surface velocity V defines a friction coefficient k:

$$\sigma = kV \tag{1}$$

The polymer melt has a huge viscosity η_p. By equating the two forms of the shear stress,

$$\sigma = \eta_p \left.\frac{dv}{dz}\right|_0 = kV \tag{2}$$

one can relate the extrapolation length b to k:

$$b = \eta_p/k \tag{3}$$

For *ideal conditions*, with an ungrafted surface, $k = k_0 = \eta_0/a$, where η_0 is a monomer viscosity and a a molecular size. The viscosity η_p is huge, $\eta_p \cong \eta_0 P^3/N_e^2$, where N_e is the number of monomers per entanglement. Equation 3 leads to

$$b_\infty = a\frac{P^3}{N_e^{\,2}} \tag{4}$$

(typically, $b = 10\ \mu$m for $P \approx 10^3$ and $N_e \approx 10^2$).

Some time ago, we studied *semiideal conditions*, where a few long N molecular chains ($N < P$) have been grafted on the solid surface, in the mushroom regime ($\nu < 1/R_N^2$, where $R_N = N^{1/2}a$ is the coil size of the grafted chains). We found[2] that these few chains lead to a huge friction in the low-velocity regime ($V \to 0$):

$$\sigma = [k_0 + \nu\eta_p R_N]V \tag{5}$$

At most practical values of ν, the second term dominates and b reduces to

$$b_0 \cong (\nu R_N)^{-1} \tag{6}$$

Equation 6 gives b values which are extremely small ($b_0 \sim 100$ Å). Slippage is suppressed at small velocities.

Experiments[3] have shown that slippage is progressively *restored* above a critical velocity V^*. We have interpreted these results[4] by a coil−stretch transition of the N chains, which disentangle from the melt.

In refs 2 and 4, we showed the dissipation is due to the sliding motion of the P chains, which are entangled with one grafted chain. However, above a threshold ν_c, one P chain is entangled with more than one mushroom, and the sliding motion of a melt chain releases many entanglements. Our aim here is to include this cooperative effect, which will decrease the effective dissipation per chain. In section II, we go back to low grafting densities where the effect of the grafted chains is additive. In section III, we look at higher grafting densities, at which the cooperative effect described above plays a role.

The main difficulty, encountered in section II, is related to the number X of mobile chains which are trapped by a single mushroom. It turns out that X depends on a very detailed description of entanglements, as pointed out in ref 5. Opposite limits correspond to (a) binary entanglements (where only *two* chains build up a constraint) and (b) collective entanglements (where a number $\sim N_e^{1/2}$ of chains are required to construct one constraint, following an interesting idea of Kavassalis and Noolandi.[6]

The "binary" assumption is described in detail in ref 7. It is somewhat simpler to explain: for this reason, we use it in our discussion of section II. Fortunately, the distinction between (a) and (b) drops out when we come to the case of interest in this paper, namely, higher grafting densities, ν, where *all* the mobile chains which touch the surface are trapped, independently of a detailed model of entanglements.

We also simplify section II by assuming that the grafted chains are not exceedingly long ($N < N_e^2$). The opposite limit ($N > N_e^2$) is described in Appendix A. Appendix B shows the explicit link with experimental parameters.

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II. One Single Chain and the Low Grafting Density Limit

This case will be important at small grafting densities $\nu < \nu_c$. It can also be observed directly by manipulating one single chain immersed in a melt, using optical tweezers.[8] Let us first return to the calculation of the friction F_v experienced by one single tethered chain in the limit $V \to 0$.[2] When the mobile chains (P) move at velocity V with respect to the N grafted chain, the P chains which are entangled have to slide.[5] To move one entanglement a distance D^*, each P chain must slide over its tube length $L_t = Pa^2/D^*$. The tube velocity of the P chain is then $V_t = (P/N_e)V$. The friction force per sliding chain is

$$f_v = \eta_0 aP\left(\frac{P}{N_e}\right)^2 V = \eta_p aV \tag{7}$$

where η_p is the viscosity of the P melt.

The total friction force acting on the grafted chain is then given by

$$F_v = Xf_v = Xa\eta_p V \tag{8}$$

where X is the number of trapped chains: i.e., P chains entangled with the mushroom.

Different forms have been proposed for X.[2,4,5,7] Here, we shall simply summarize the results of the "binary entanglement model" described in ref 7, assuming $P \geq N$. There are two upper bounds for X:

(a) X cannot be larger than the total number of P chains which intersect the (N) "mushroom": the corresponding volume is $N^{3/2}a^3$ and each intersecting P chains puts $\sim N$ monomers in this region. Thus the total number of P chains concerned is $N^{3/2}/N = N^{1/2}$.

(b) X cannot be larger than the number of constraints experienced by the N chain, namely N/N_e.

Ultimately, for binary entanglements, it turns out that X is the smaller of these two bounds.[7] Thus

$$\left.\begin{aligned} X &= N/N_e \quad (N < N_e^2) && (9a)\\ X &= N^{1/2} \quad (N > N_e^2) && (9b)\end{aligned}\right\}$$

In most practical cases, $N_e \gtrsim 100$ and $N < N_e^2$. Then, the friction force in eq 8 is proportional to N: we call this the *Rouse regime*. There may be some (rare) cases where $N > N_e^2$. Then, the friction force in eq 8 should be proportional to the radius of the mushroom $N^{1/2}a = R_n$ and to the melt viscosity: it is similar (at the level of scaling laws) to the Stokes friction on a hard sphere of radius R_N. We call it the *Stokes regime*.

In what follows, we focus our attention on the Rouse regime. The opposite limit $N > N_e$ is discussed in Appendix A.

The friction form at low velocity is thus, from eqs 5, 8, and 9a,

$$\begin{cases} F_v = \dfrac{N}{N_e} a\eta_p V & (10a)\\[2ex] \sigma = \nu F_v = \nu \dfrac{N}{N_e} a\eta_p V & (10b)\end{cases}$$

This corresponds to a slippage length

$$b = \frac{N_e}{\nu a N} \tag{11}$$

The linear regime described by eq 10 will hold when $F_v < kT/R_N$, or equivalently at velocities $V < V_1$, where

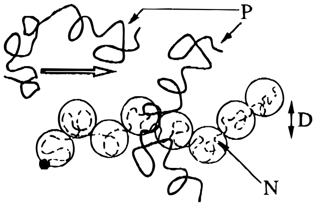

Figure 1. A tethered chain (N monomers) is elongated into a sequence of blobs of size D. Some of the melt chains (moving with velocity V) are entangled with it. In the marginal state ($D = D^* = aN_e^{1/2}$), each blob contains N_e monomers.

$$V_1 = \frac{kTN_e}{a^2\eta_p N^{3/2}} \tag{12}$$

V_1 can be found by two methods: (i) by equating the friction force F_v and the elastic force required to get an elongation $\sim R_N$:

$$\frac{N}{N_e} a\eta_p V_1 \equiv kT\frac{R_N}{Na^2}$$

(ii) by considering the coil relaxation time in the melt flow. If δR is the end-to-end vector of the grafted chain, we can write down the force balance:

$$kT\frac{\delta R}{Na^2} = \frac{N}{N_e} a\eta_p (V - \delta\dot{R})$$

As a matter of fact, if the coil is elongating ($\delta\dot{R} > 0$), monomers experience a flow at a reduced speed. We calculate therefrom a typical relaxation time:

$$\frac{1}{\tau_{\mathrm{rel}}} = \frac{kT}{\eta_p a^3}\frac{N_e}{N^2}$$

The threshold velocity V_1 for large elongations ($\delta R > R_N$) is then given by $V_1 = R_N/\tau_{\mathrm{rel}}$.

At higher velocities, the grafted chains are elongated into a cigar shape (as assumed in ref 4) or more precisely into a trumpet shape (as shown in ref 5), because the cumulative friction on the chain increases from the free end to the attachment point. Both descriptions are essentially equivalent in their final results. Here, for simplicity, we use the simpler picture, where the N chain is deformed into a cigar of diameter D, length $L = Na/D$, under the viscous friction force due to the sliding motion of the P chains entangled with it.

Elongation always favors a Rouse regime. (This is shown in detail for binary entanglements.) Thus, even for $V > V_1$, we keep $X = N/N_e$ for the distorted chain, and eqs 10 and 11 remain valid. The diameter of the cigar is derived from the Pincus law:[9]

$$D = kT/F_v = R_N\frac{V_1}{V} \tag{13}$$

When V increases, D decreases, and ultimately we reach the *marginal regime* where $D = D^* = aN_e^{1/2}$ (the tube diameter) (Figure 1). At this point, the N chain is on the verge of disentangling from the melt. But, if it did so, the drag force would decrease, D would increase, and entanglements would reappear. Thus we stick to $D = D^*$, and the shear stress σ reaches a plateau value:

$$\sigma^* = \nu kT/D^* \tag{14}$$

The corresponding velocity is

$$V_0^* = \frac{kTN_e^{1/2}}{Na^2\eta_p} \tag{15}$$

When $V > V_0^*$, σ sticks to the value σ^*, and the slippage length is linear in V:

$$b = \frac{\eta V}{\sigma^*} \qquad (V > V_0^*) \tag{16}$$

What happens at velocities $V \gg V_0^*$? First, the number of trapped chains $X(V)$ decreases. The friction per chain in the marginal regime is constant and equal to kT/D^*. The friction per sliding chain increases linearly with velocity V. Thus

$$X(V) = X(0)V_0^*/V$$

Ultimately, at a certain (high) velocity V^{**}, the melt chains decouple from the (N) chains. This process may be understood as follows:

The tube velocity of one (P) chain disentangling from the (N) chain is of order

$$V_t = \frac{L_t}{D^*}V \tag{17}$$

where $L_t = PD^*/N_e$ is the tube length. Equation 17 ensures that when the N chain has moved by a distance D^* with respect to the fluid, the P chain has released one constraint (and thus moved by $\sim L_t$ inside its tube). This removal of constraints is balanced by the establishment of new entanglements. The trapped P chains will be deeply perturbed if their relaxation time $T_{rep}(P)$ becomes longer than the tube evacuation time:

$$T_{rep}(P) > L_t/V_t = D^*/V \tag{18}$$

The nature of the perturbed state has recently been discussed by Ajdari for a related problem:[10] it may in fact lead to stick slip instabilities. From the present point of view, we conclude that there is a limiting velocity:

$$V^{**} = D^*/T_{rep} \tag{19}$$

Using standard relations for entangled media, we can write a relation between T_{rep} and the P melt viscosity η_p, namely

$$\eta_p = \frac{kT}{N_e a^3}T_{rep} \tag{20}$$

where $kT/N_e a^3$ is the plateau modulus of the melt. Combining eqs 19 and 20, we arrive at

$$V^{**} = \frac{kT}{D^* a\eta_p} \tag{21}$$

Notice that the pulling force $a\eta_p V^{**}$, acting on a P chain entangled with the N chain, is just equal to the marginal value kT/D^*: the P chains become marginal at $V = V^{**}$. The number of trapped chains per grafted chain also happens to be equal to unity at this stage: $X(V^{**}) = 1$.

III. Higher Grafting Densities

(1) From Separate Mushrooms to Cooperative Behavior. The central question here is to find how many P chains are entangled with the mushrooms: we call them *trapped chains*. Their number (per unit area) is designated by ν_p.

(a) At very low grafting densities ($\nu \to 0$), we must simply add up the contributions of independent mushrooms, and this gives (in the binary entanglement model)

$$\nu_p = X\nu = \frac{N}{N_e}\nu \qquad (N < N_e^2) \tag{22}$$

(b) At some critical value of the grafting density ($\nu = \nu_c$), the number of trapped chains saturates. All the trapped chains are confined in a certain "skin" of thickness $R_p = aP^{1/2}$ near the solid surface. The maximal number of trapped chains is thus

$$\nu_{pm} = \frac{1}{Pa^3}R_p = a^{-2}P^{-1/2} \tag{23}$$

and (by comparison with eq 22) this defines

$$\nu_c = \frac{N_e}{Na^2P^{1/2}} \tag{24}$$

In order to understand how ν_p saturates for $\nu > \nu_c$, it is also instructive to calculate ν_p as the total number of available entanglement points with the grafted chains $\nu N/N_e$, divided by the number of C of constraints that each entangled melt chain makes with grafted chains; C is evaluated by appropriate counting. This viewpoint will be discussed separately. Note that when $P > N_e^2$, the quantity $\nu_c Na^2 = \nu_c R_N^2$ is smaller than unity: the mechanical effects of the grafted chains are not additive, *although the mushrooms do not overlap*!

(c) It is of some interest to compare this discussion with another feature, related to the statistics of the grafted chains: at a certain grafting density ν_b, we cross over from mushrooms to extended chains. In this "brush" regime, the free energy per N chain has the scaling form[11]

$$\frac{F_N}{kT} = \frac{L_b^2}{Na^2} + \frac{N\phi}{P_{eff}} \tag{25}$$

The first term describes the entropic elasticity of deformed chains: L_b is the thickness of the brush. The second term describes repulsive interactions between grafted monomers. The volume fraction inside the brush is

$$\phi = \nu\frac{Na^3}{L_b} \tag{26}$$

The repulsive interactions inside the brush are screened by the P matrix:[11] hence the factor P_{eff} in eq 25. If the P chains were small ($P < N$), we would simply have $P_{eff} = P$. In our case ($P > N$), it is legitimate to take $P_{eff} = N$ (the effective length of the P chain portions which penetrate). To discuss ν_b, we are interested in the onset of the brush regime—i.e., when the second term of eq 25 (estimated via eq 26 with an unperturbed thickness

$L_b \sim N^{1/2}a$) becomes of order unity, extension starts. This leads to

$$a^2\nu_b = N^{-1/2} \tag{27}$$

Comparing ν_b (eq 27) and ν_c (eq 24), we see that

$$\frac{\nu_b}{\nu_c} = \frac{(NP)^{1/2}}{N_e} \tag{28}$$

This ratio is always larger than unity (since $N > N_e$ and $P > N_e$). Thus, upon increasing ν, the dynamical coupling occurs before the onset of a brush.

(2) Dynamical Behavior of the *N* Chains in the Coupled Regime ($\nu > \nu_c$).

(a) Onset of Distortions on the *N* Chains. At low V, each trapped P chain contributes a shear force $\eta_p aV$. The number of trapped chains per unit area is $P^{-1/2}a^{-2}$, and the resulting stress is

$$\sigma = P^{-1/2}a^{-2}\eta_p aV \tag{29}$$

corresponding to a length $b \sim P^{1/2}a$ (the thickness of the trapped layer).

The force F_v on one N chain is such that $\sigma = \nu F_v$. When this force becomes equal to kT/R_N, the N chain begins to distort. Using eq 29, this gives a crossover velocity

$$V_1 = \frac{\nu\, kTP^{1/2}}{\eta_p N^{1/2}} \tag{30}$$

Note that eqs 12 and 30 coincide at the crossover point $\nu = \nu_c$.

(b) Marginal Regime of the *N* Chains. The velocity $V^*(\nu)$ at which the N chains become marginal is derived directly from the force balance, writing the stress in two forms:

$$\sigma = \nu\frac{kT}{D^*} = P^{-1/2}a^{-2}\eta_p aV^* \tag{31}$$

Thus V^* is linear in ν:

$$V^*(\nu) = V_0^*\frac{\nu}{\nu_c} \tag{32}$$

where V_0^* is the value for a single mushroom (eq 15).

(c) Decoupling of the *P* Chains. For $V > V^*$, the number of coupled chains decreases and as explained in section II, the P chains are seriously affected at velocities $V > V^{**}$, where V^{**} is given by eq 21 and is independent of ν. We have no deep knowledge of what happens at $V > V^{**}$, but we suspect that the P chains are torn out from the grafted chains and that a completely novel regime follows: this will require a separate study. The various regimes (a, b, c) are summarized in Figure 2.

It must also be emphasized that, above a certain velocity $V_{1p} = kT/a^2\eta_p P^{1/2}$ (which is reached before V^{**}), the trapped chains are also deformed: their density ν_p has to be counted somewhat differently. However, we find that this does not lead to any deep alteration of the scaling laws. Thus the regimes found above do extend up to V^{**}.

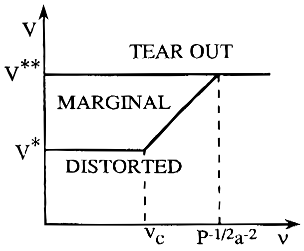

Figure 2. Various regimes for a weakly grafted solid (grafting density ν) under shear flow (slippage velocity V). Here, the surface is grafted with moderately long chains ($N_e < N < N_e^2$).

IV. Concluding Remarks

(1) The main surprise is the correlated behavior between mushrooms which occurs at grafting densities $\nu > \nu_c$. In this regime, (a) all chains of the skin are coupled and (b) the grafted polymer becomes denser and stronger upon increasing ν, while the number of trapped melt chains saturates at $\nu > \nu_c$. Thus the interface chains become less deformed (at fixed V), or equivalently the characteristic velocities V_1 (for deformation) and V^* (for marginal behavior of the grafted chains) increase. Ultimately, we should go back to the case of strong brushes in strong flows. A related problem has been discussed by Alexander and Rabin[12] and by Barrat.[13] However, their analysis applied for a liquid of small molecules ($P = 1$) facing a wet brush while, here, we are talking of a melt ($P > N$) facing a dry brush.

(2) The marginal velocity $V^*(\nu)$ in eq 33 in the cooperative regime is independent of the model chosen for entanglements: “binary” or “collective” (or other).

(3) We assumed long mobile chains ($P > N$). But the problems at small P ($P < N$) are also interesting; they will be discussed separately.

(4) At very high N ($N > N_e^2$), a single mushroom (at low ν) has a Stokes behavior rather than a Rouse behavior, and the diagram of Figure 2 becomes more complex. This is discussed in Appendix A. However, once again, the main formulas—in particular, $V^*(\nu)$ in eq 32—are quite independent of the precise choice of X for a single mushroom.

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Appendix A: Grafted Surface with Ultralong Chains

When $N > N_e^2$, two main differences show up:

(1) Friction on One Single Chain ($\nu \to 0$): Zimm to Rouse Behavior. The number $X(V=0)$ of coupled chains is now $N^{1/2}$. The friction forces the grafted chain as the P melt moves at velocity V ($V \to 0$) is a Stokes friction:

$$F_v = N^{1/2}\eta_p aV = \eta_p R_{0N} V \tag{A1}$$

The chain starts to be deformed at a velocity V_1:

$$\eta_p R_{0N} V_1 = \frac{kT}{R_{0N}}$$

i.e.

$$V_1 = \frac{kT}{a^2\eta_p N} \tag{A2}$$

As in the case of smaller chains, V_1 can be found by considering the relaxation time coming from the equation $kT\delta R/Na^2 = N^{1/2}a\eta_p(V - \widehat{\delta R})$.

For $V > V_1$, the chain undergoes an abrupt coil—stretch transition[5,14] and the deformation L increases exponentially ($L \sim \exp(V/V_1)$). At a velocity V_c close to V_1, the friction becomes of the Rouse type: the chain can be pictured as a string of blobs, size D, containing each $g_D = D^2/a^2$ monomers. If $g_D > N_e^2$, the friction on each blob is a Stokes friction. If $g_D < N_e^2$, the friction becomes a Rouse friction ($X(V > V_c) = N/N_e$), and we go back to the previous discussion: thus the threshold velocity V_0* to enter the marginal regime is still given by eq 15.

(2) "Locking" Transition of the Skin at Increasing Velocity. At zero velocity, the grafted chains are unperturbed and the number of coupled P chain is

$$\nu_p = \nu N^{1/2} \tag{A3}$$

All the skin is coupled when $\nu_p = 1/P^{1/2}a^2$, i.e., when the grafting density reaches

$$\nu a^2 = \nu_{c2}a^2 \equiv \frac{1}{(NP)^{1/2}} \tag{A4}$$

Between V_1 and V_c, each chain is deformed and traps an increasing number of free P chains. Above V_c, X saturates at a constant value N/N_e, and the threshold density to couple to the whole skin is again

$$\nu_c a^2 = \frac{N_e}{NP^{1/2}} \tag{A5}$$

The threshold velocity $\tilde{V}_1$ to deform the chains in the cooperative regime is given by

$$\frac{1}{P^{1/2}a^2}\eta_p a\tilde{V}_1 = \nu\frac{kT}{R_{0N}}$$

i.e.

$$\tilde{V}_1 = V_1\frac{\nu}{\nu_{c2}} \tag{A6}$$

The marginal velocity, for $\nu > \nu_c$, is still given by eq 32. The different regimes are shown in Figure 3.

Appendix B: Experimental Conditions

The situation discussed in the present paper may be tested by various experimental methods. One of them, ref 3, involves a moving plate (at a distance d from the surface of interest). At the moving plate, there is no slippage, and the velocity has an imposed value V_t. The slippage velocity V, shear rate $\dot{\gamma}_p$, and extrapolation length b can be measured by optical means. The shear stress is $\sigma = \eta_p\dot{\gamma}_p$. We have

$$V = V_t\frac{b}{b + d} \tag{B1}$$

and

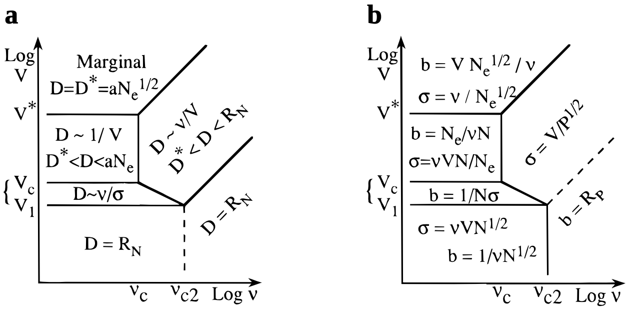

Figure 3. Slippage velocity V versus grafting density ν diagram for a long chain grafted surface ($N > N_e^2$): grafted chain deformation (a) and melt flow parameters (b). The $V_1 < V < V_c$ region describes an abrupt transition in terms of slippage velocity; however, all quantities vary continuously with the shear stress σ. Dimensional factors (a, kT, η_p) have been ignored.

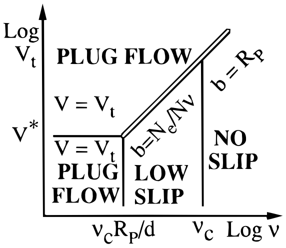

Figure 4. In some experiments, the polymer sample top velocity V_t is monitored. For moderately long grafted chains ($N < N_e^2$), the V_t versus ν diagram is shown. Slippage velocity V and extrapolation length b display strong variations across the double line; on the other hand, the shear stress σ is continuous. Dimensional factors (a, kT, η_p) have been ignored.

$$\dot{\gamma}_p = \frac{V_t - V}{d} = \frac{V_t}{b + d} \tag{B2}$$

We therefore expect regime transitions when b becomes comparable to d:

$$b > d \begin{cases} V = V_t & \text{(B3)} \\ \sigma = \eta_p\dfrac{V_t}{b} & \text{(B4)} \end{cases}$$

$$b < d \begin{cases} V = V_t\dfrac{b}{d} & \text{(B5)} \\ \sigma = \eta_p\dfrac{V_t}{d} & \text{(B6)} \end{cases}$$

We can now predict the different regimes in terms of the top velocity V_t and the grafting density ν. They are presented for short grafted chains ($N < N_e^2$) in Figure 4. We review now the behavior of observable quantities under these circumstances.

A plug flow ($V \simeq V_t$: the whole sample moves at roughly the same speed with respect to the grafted surface) should be observed in two regions: 1. For $V_t < V^*$ and $\nu < \nu_c R_p/d$, the observable parameters vary as follows:

$$\begin{cases} V = V_t \\ b = \dfrac{N_e}{N}\dfrac{1}{\nu a} \\ \sigma = \dfrac{N}{N_e}\nu V_t a\eta_p \end{cases} \tag{B7}$$

2. For $V_t > V^*$ and $V_t > (\nu d/N_e^{1/2})kT/a\eta_p$ (marginal state $D = D^*$), we have

$$\begin{cases} V = V_t \\ b = N_e^{1/2}\dfrac{V_t}{\nu}\dfrac{a\eta_p}{kT} \\ \sigma = \dfrac{\nu}{N_e^{1/2}}\dfrac{kT}{a} \end{cases} \tag{B8}$$

Slippage is lowered in a transition region: 3. For $\nu_c R_p/d < \nu < \nu_c$ and $V_t < (\nu d/N_e^{1/2})kT/a\eta_p$, we have

$$\begin{cases} V = \dfrac{N_e}{N}\dfrac{V_t}{a\nu d} \\ b = \dfrac{N_e}{N}\dfrac{1}{\nu a} \\ \sigma = \dfrac{V_t}{d}\nu_p \end{cases} \tag{B9}$$

Eventually, slippage is visible only at the molecular scale ($b = R_p$); i.e., it is macroscopically suppressed: 4. For $\nu > \nu_c$ and $V < (\nu d/N_e^{1/2})kT/a\eta_p$, we get

$$\begin{cases} V = V_t\dfrac{R_p}{d} \\ b = R_p \\ \sigma = \dfrac{V_t}{d}\eta_p \end{cases} \tag{B10}$$

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