Slippage of linear flows of entangled polymers on surfaces

W. Sung
Department of Physics, Pohang University of Science and Technology, Pohang, 790-784, Korea
(Received 29 June 1994)

Using the microscopic boundary layer model [W. Sung, in *Slow Dynamics in Condensed Matter,* edited by K. Kawasaki, M. Tokuyama, and T. Kawakatsu, AIP Conf. Proc. No. 256 (AIP, New York, 1992) and W. Sung and Min Gyu Lee, Phys. Rev. E **51**, 5855 (1995)], I show that there exists an appreciable slippage of entangled polymers on a surface, under linear flow, even with a sizable amount of chains anchored on it. I find the critical anchorage above which the slip to no-slip transition occurs. I discuss the similarities and differences between my results and those of de Gennes and co-workers [C.R. Acad. Sci. (Paris) B **288**, 219 (1979); **314**, 873 (1992); Langmuir **8**, 3033 (1992)].

PACS number(s): 61.41.+e, 83.20.Lr, 83.10.Nn

Due to their long chain structure and the topological constraints, entangled linear polymers either in solution or in melt manifest a fascinating interplay of elasticity and viscosity, namely, viscoelasticity. The molecular description for the flow behaviors of entangled polymers was given by the pioneering works of de Gennes [1] and Doi and Edwards [2]. They envisioned the dynamics of the chain entangled with the background as the reptation in a cage modeled as a tube which undergoes constant relaxation. The relaxation time goes as $N^{\phi}(\phi=3$ in their theories and $\phi=3.4$ in experiments), which means for a large number N of Kuhn segments, the polymers show very slow dynamics, giving rise to very high viscosity.

Compared with the remarkable advances made in understanding the bulk flow properties, little theoretical work on the boundary effects of flow caused by the entanglement has been done, despite it numerous industrial applications. Unlike the fluids of small molecules, the liquids of entangled polymers suffer appreciable slippage on the surface even if the flow is linear, i.e., in the relation between stress and shear rate. The slippage is characterized by the extrapolation (or the slip) length l_s, i.e., the distance from the surface at which the velocity profile extrapolates to zero (Fig. 1). Considering ideal solid surfaces without chain anchorage, de Gennes first showed the slip length [3] is given by

$$l_s \simeq \frac{\eta}{k} \simeq \frac{\eta}{\eta_0} l_0 \ , \tag{1}$$

where k is the frictional force per unit area, and η_0 and l_0 are the microscopic shear viscosity and length characteristic of the monomers. Depending upon η, the viscosity of the polymer which, according to the theory [1,2], scales as $\eta \sim N^3/N_e^2$ (N_e is the segmental number between entanglements), l_s, can be macroscopically large. The suppression of slippage due to the chains grafted onto the surface was also investigated theoretically [4–6]; if the number of grafted chains per unit area is ν, the slip length is reduced to

$$l_s \simeq (\nu R_s)^{-1} \ , \tag{2}$$

where R_s is the average length of a grafted chain. The large slip length and its reduction due to grafted chains is qualitatively in accord with experiments [7–9].

In this paper, a focus is put on the slippage problem in linear and steady-state Couette flow. On a theoretical basis somewhat different from that of de Gennes and his collaborators, I derive the slip length, Eq. (14), which carries finer details on the anchored chains as I discuss below. I find there exists a critical anchorage given by Eq. (19), above which the transition to no slip does occur.

I apply the microscopic boundary layer model developed recently by Sung and Lee for dynamics of a spherical particle of radius R in entangled polymers [10,11]. The $R \to \infty$ limit corresponds precisely to the stationary planar surface on which the polymers flow.

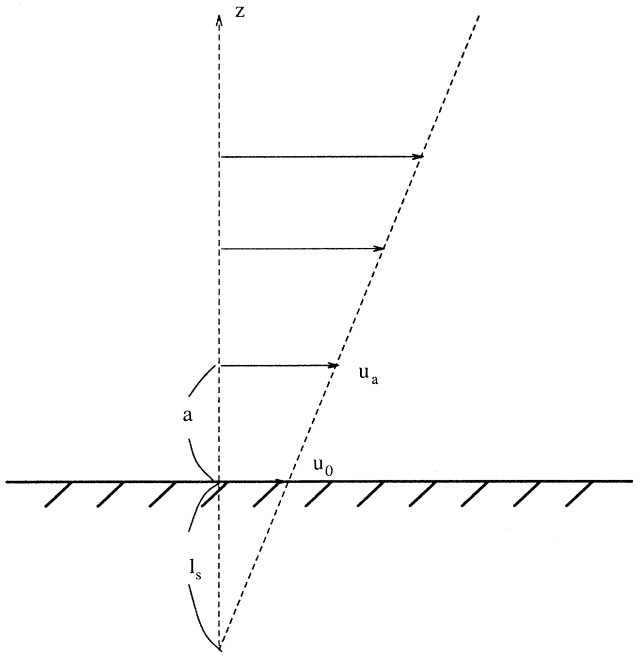

FIG. 1. The extrapolation (slip) length l_s characterizes the slippage.

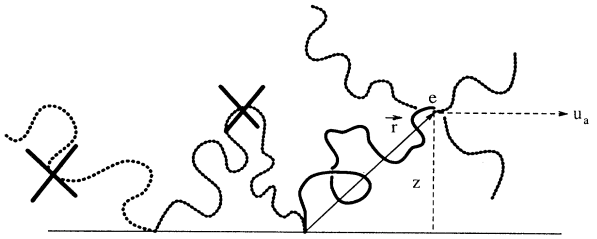

FIG. 2. An elastically effective surface chain (ESC) on surface [the chain from g (grafted) to e (entangled)]. The crossed out dangling chains and loops are not counted as such.

According to the model, the frictional force on the surface is dominated by *the elastically effective surface chains* (ESC's), which, by definition, remain anchored on the surface and entangled with neighboring chains at both ends, respectively, under the linear flow. Because the dangling chains and the loops not engaged with entanglements are not counted as such, the ESC is modeled as a random walk which avoids crossing the surface on the way (Fig. 2). The probability density of the end-to-end distance $\vec{r}$ of an ESC with N_s segments is given by

$$P_{N_s}(\vec{r}) \sim z \exp\left[-\frac{3r^2}{2N_s b^2}\right] , \tag{3}$$

as can be obtained by the image method [11,12]. Here z is the component of $\vec{r}$ normal to the surface and b is the Kuhn segmental length.

The most probable value for z is obtained from Eq. (3) as

$$a = (\tfrac{1}{3} N_s b^2)^{1/2} , \tag{4}$$

which I call the boundary layer size [11]. Suppose that the entangled end (the point e in Fig. 2) of an ESC is displaced by small distance δx along the x axis (along the direction of flow) away from its most probable (normal) position $\vec{r}_a = (0,0,a)$. Then the entropic force incurred the ESC with the other end permanently anchored (grafted) is given by

$$F_1 = -K \delta x , \tag{5}$$

where

$$K = -k_B T \left[\frac{\partial^2}{\partial x^2} \ln P_{N_s}(\vec{r})\right]_{\vec{r}=\vec{r}_a} = \frac{k_B T}{a^2} . \tag{6}$$

The entanglement can sustain this force only during the reptation time $\tau \sim N^{\phi}$ of background chains. Therefore for the linear, steady-state flow of entangled polymers directed along the x axis, the average force can be written as

$$F_1 = -K \tau u_a . \tag{7}$$

Here u_a, the average velocity of the entanglement located at $\vec{r}_a$, can be identified with the fluid velocity at that point. If the surface density of these permanently anchored ESC's is denoted as α_1, they give rise to the force per unit area of the x-y plane at $z = a$:

$$\mathcal{F}_1 = \alpha_1 K \tau u_a . \tag{8}$$

It is conceivable that there are also ESC's with the anchored ends which can slide on the surface. The force on the surface due to this type of ESC's distributed with surface density α_2 is given as

$$\mathcal{F}_2 = \alpha_2 K \tau (u_a - v) . \tag{9}$$

The v is the average velocity of the chain slippage. This is proportional to u_a, so Eq. (9) can be replaced by

$$\mathcal{F}_2 = \bar{\alpha}_2 K \tau u_a , \tag{10}$$

with $\bar{\alpha}_2 < \alpha_2$.

In sum, the force per unit area on the surface due to ESC's is

$$\begin{aligned} \mathcal{F} &= (\mathcal{F}_1 + \mathcal{F}_2) \\ &= (\alpha_1 + \bar{\alpha}_2) K \tau u_a \\ &\equiv \alpha K \tau u_a . \end{aligned} \tag{11}$$

The $\alpha \equiv \alpha_1 + \bar{\alpha}_2$, termed hereafter the effective (permanent) anchorage, is regarded as a constant in the steady flow I consider here. In addition to Eq. (11), it is essential for the problem of slippage to consider the microscopic frictional force due to monomeric collision with the surface, $k u_0$, where k is the frictional coefficient per unit area and u_0 is the average velocity on the surface. Incorporating this force per unit area $k u_0 \equiv \xi u_a$, the total force per unit area on the surface at $z = a$ is given by

$$\mathcal{F} = \alpha K \tau u_a + \xi u_a . \tag{12}$$

In the model given in [10,11], the background polymers beyond the boundary layer are treated as a continuum, according to which the force, Eq. (12), can be matched to the hydrodynamics stress extrapolated to the surface $z = a$:

$$\begin{aligned} \mathcal{F} &= -\sigma_{zx} \\ &= \eta \left[\frac{\partial u}{\partial z}\right]_a . \end{aligned} \tag{13}$$

Matching Eq. (12) to (13) yields my main result for the slip length [13],

$$\begin{aligned} l_s &= \frac{u_a}{(du/dz)_a} - a \\ &= \frac{\eta}{\xi + \alpha K \tau} - a . \end{aligned} \tag{14}$$

When $\alpha = 0$, Eq. (14) is reduced to

$$l_s^0 = \frac{\eta}{\xi} - a . \tag{15}$$

The ξ is the coefficient of monomeric friction per unit area in the same order of magnitude as k, and is given as

$\xi \simeq \eta_0/l_0$ where l_0 is the mean free path of the monomers in collision with the surface. Since $\eta/\eta_0 \simeq N^3/N_e^2$, and thus $\eta/\xi >> a$ for a very large N, I find

$$l_s^0 \simeq \frac{\eta}{\xi} , \tag{16}$$

which is essentially the de Gennes result, Eq. (1).

Equation (14) predicts that for the chain anchorage α above the critical value

$$\begin{aligned} \alpha_c &= \frac{\eta}{K\tau a} \\ &= \frac{G}{Ka} \end{aligned} \tag{17}$$

the slippage diminishes, i.e., $l_s = 0$. Here $G = \eta/\tau$ is the plateau modulus given by

$$G = nk_B T , \tag{18}$$

where n is the volume density of the chains between the entanglements in the bulk. Using Eq. (18) as well as Eq. (6), we find

$$\begin{aligned} \alpha_c &= na \\ &= \frac{ca}{N_e} , \end{aligned} \tag{19}$$

where c is the polymer concentration in the bulk.

Figure 3 shows schematically the variation of the slip length l_s as a function of α given by Eq. (14). The slip length can have the same order of magnitude as l_s^0, which can be macroscopically large, provided that α is less than the crossover anchorage defined by

$$\begin{aligned} \alpha_{1/2} &\equiv \frac{\xi}{K\tau} \\ &\simeq \frac{\eta_0}{\eta}\frac{a^2}{l_0} n \\ &\simeq \frac{N_e}{N^3}\frac{ca^2}{l_0} . \end{aligned} \tag{20}$$

From Eqs. (19) and (20), one finds the ratio

$$\frac{\alpha_{1/2}}{\alpha_c} \simeq \frac{\eta_0}{\eta}\frac{a}{l_0} , \tag{21}$$

which is negligibly small for entangled polymers because of the high viscosity η. This means that, for most of the range of the chain anchorage, the slippage is suppressed due to ESC's, leading to

$$\begin{aligned} l_s &\simeq \frac{n}{\alpha K\tau} - a \\ &= \frac{na^2}{\alpha} - a . \end{aligned} \tag{22}$$

With α much smaller than α_c, Eq. (22) is reduced to

$$l_s^a \simeq \frac{na^2}{\alpha} , \tag{23}$$

which, with $N \simeq a^{-3}$, is comparable to but is not necessarily the same as Eq. (2). Note that the α and a defined here in terms of ESC's can differ, respectively, from ν and R_s in Eq. (2), defined in terms of grafted chains [14], and also, Eq. (23) is valid under a restriction mentioned above.

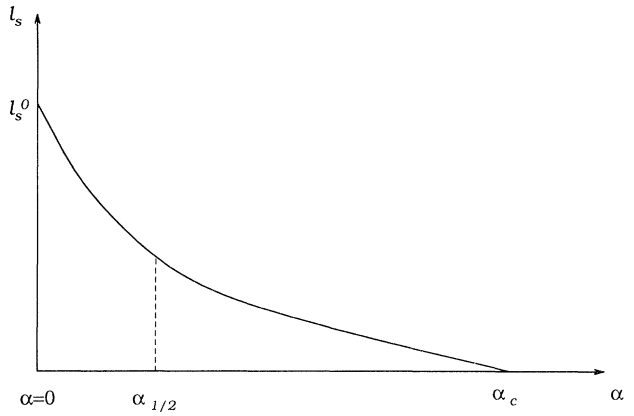

FIG. 3. The slip length l_s vs the effective anchorage α (schematic). The α_c is the critical anchorage [Eq. (19)] below which the transition from no slip to slip occurs. The $\alpha_{1/2}$ [Eq. (20)] is the crossover anchorage, above which slippage is mainly due to ESC's.

For $N = 2000$, $N_e = 200$, $l_0 = 3$ Å corresponding to polystyrene melt ($M \sim 10^5$) [3], and for $a \simeq 100$ Å and $n \simeq a^{-3}$, the following estimations can be made:

$$\alpha_c \simeq a^{-2} = 10^{12}/\text{cm}^2 ,$$

$$\alpha_{1/2} \simeq \frac{N_e^2}{N^3 l_0 a} \simeq 10^8/\text{cm}^2 ,$$

$$l_s^0 = 60\ \mu\text{m} ,$$

$$l_s^a \simeq 1\ \mu\text{m}, \quad \text{with } \alpha = 10^{10}/\text{cm}^2 .$$

Since $\alpha_{1/2}/\alpha_c \ll 1$, the suppression effect of the chain anchorage on slippage is strong (in accord with de Gennes and his collaborators [4,5]), but nevertheless, with appreciable anchorage, the slip length (l_s^a) can remain much larger ($\sim 1\ \mu$m in our numerical estimation) than usually expected (at variance with them [4,5]).

In conclusion, as I demonstrated using the microscopic boundary layer model, a large slippage of an entangled-polymer liquid on a surface can occur due to its *high viscosity*. With the chains anchored on the surface and entangled with the background, the slippage is suppressed, yet operative appreciably due to their *high flexibility*. It is possible to say that the slippage of entangled polymers is another manifestation of their viscoelasticity. The transition to no slip does occur above a critical anchorage given by Eq. (19).

This work was supported in part by RIST, as well as BRSC and CAMP of POSTECH, each funded by Ministry of Education of Korea and KOSEF. Stimulating discussions with P. Pincus are gratefully appreciated.

[1] P. G. de Gennes, J. Chem. Phys. **55**, 572 (1971).
[2] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986).
[3] P. G. de Gennes, C. R. Seances Acad. Sci. Ser. B **288**, 219 (1979).
[4] F. Brochard, P. G. de Gennes, and P. Pincus, C. R. Seances Acad. Sci. **314**, 873 (1992).
[5] F. Brochard and P. G. de Gennes, Langmuir **8**, 3033 (1992).
[6] A. Ajdari, F. Brochard, P. G. de Gennes, L. Leibler, J. Viovy, and M. Rubinstein, Physica A **204**, 17 (1994).
[7] R. Burton, M. Folkes, N. Karm, and A. Keller, J. Mater. Sci. **18**, 315 (1983).
[8] J. Meissner, Annu. Rev. Fluid Mech. **17**, 45 (1985).
[9] K. Migler, H. Hervet, and L. Leger, Phys. Rev. Lett. **77**, 287 (1993).
[10] W. Sung, in *Slow Dynamics in Condensed Matter,* edited by K. Kawasaki, M. Tokuyama, and T. Kawakatsu, AIP Cont. Proc. No. 256 (AIP, New York, 1992).
[11] W. Sung and Min Gyu Lee, Phys. Rev. E **51**, 5855 (1995).
[12] E. A. Di Marzio, J. Chem. Phys. **42**, 2101 (1965).
[13] The definition [Eq. (14)] for l_s is appropriate within our model in that the slope $(du/dz)_a$ is determined by extrapolating the hydrodynamics assumed to be valid for $z > a$.
[14] An ESC as defined here represents only a portion of a grafted chain if the latter is entangled with other chains more than twice.