Shear Thinning Near the Rough Boundary in a Viscoelastic Flow

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Abstract

When polymer melts flow near a corrugated boundary, individual chains go through oscillatory shear due to the perturbed velocity field produced by corrugation. In order to obtain friction constant for this surface, we find total dissipation using the oscillatory strain rate of individual chains. For small slip velocities this friction constant approaches the constant obtained by macroscopic hydrodynamics (P. G. De Gennes, C. R. Acad. Sci. Paris Ser. B, 289:220, 1979). Large slip velocities mean smaller time period of shear oscillation, so less dissipation and we observe shear thinning.

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1 Introduction

Polymer melts behave very differently than ordinary liquids near a boundary. Due to their enormous viscosity, slip velocity at the boundary is observed in many circumstances [1],[2],[3],[4],[5],[6]. This slip is quantitatively described by the slip length which is defined as \( b = \frac{\eta}{f} \), \( \eta \) is the bulk viscosity and \( f \) is the friction constant of the surface. Using macroscopic hydrodynamics, the
friction constant for a corrugated boundary was obtained by P. G. de Gennes [1]. For slip boundary condition, in this hydrodynamic approach, the Navier-Stokes equation is solved where the bulk viscosity term is the steady state shear viscosity. This approach is justified as long as the slip velocity is small. But if the slip velocity is not that small and the time a chain takes to cross a distance $\lambda$ (wavelength of the corrugation) is smaller or comparable to the reptation time $\tau_{\text{rep}}$, traditional hydrodynamic approach will break down. In this situation, in order to find the friction constant, we need to trace the movements of individual chains. For large slip velocities, the individual chains will be under oscillatory shear, not steady state shear. So we need to find dissipation rate considering this oscillation and then from dissipation we will be able to find friction constant. But as the slip velocity decreases, our result should gradually converge to the constant previously obtained by P. G. de Gennes [1].

2 Friction constant for steady state shear

Renewed interest in this viscoelastic flow near the rough boundary originated while studying polymer melt flow in thin capillaries. Polymer melts in thin capillary show several unusual properties [7],[8],[9],[10] and one of the most remarkable is the anomalous molecular mass dependance of flow in capillary rise experiment [11]. In order to explain this molecular-weight dependance, a two velocity model has been proposed [12]. In this paper it is also shown that individual chains will be forced to move along their tube due to the pressure variation near the corrugated surface and this microscopic mechanism of mass transfer will modify the boundary effect. But the consequence of perturbed velocity field on the motion of individual chains is not considered in this article. We will consider the effect of this velocity field. Near the boundary, the individual chains will go through oscillation due to this field. But this is true for all boundaries whether or not the melts are confined. But why then this effect of oscillation did not come to notice before? The reason is the small slip velocity. For very small slip velocities, when a chain moves near the corrugation, it experiences almost a constant strain rate and so the bulk viscosity used by P. G. de Gennes gave the correct result. For large velocities, time period of shear oscillation is small i.e., the elastic property of the chain will play a role to reduce dissipation and hence the friction constant. Below, at first we will recapitulate the hydrodynamic approach.

If a smooth surface is perturbed by $\epsilon g(x)$, the velocity and pressure can be written in perturbation series:

$$V = V'_0 + \epsilon v_1 + \epsilon^2 v_2 + \epsilon^3 v_3 + \ldots$$
$$P = P'_0 + \epsilon p_1 + \epsilon^2 p_2 + \epsilon^3 p_3 + \ldots,$$
where \( V'_0 \) and \( P'_0 \) are velocity and pressure for smooth boundary. Velocity and pressure will satisfy the Navier-Stokes equation \( (\nabla P = \eta \nabla^2 V) \) and incompressibility condition \( (\nabla \cdot V = 0) \). If the slip velocity is \( V_0 \), then the boundary conditions are: \( n \cdot V = 0, \ t \cdot V = V_0 \). For \( g(x) = \cos kx \), the solution of the first order term of velocity is [13]:

\[
\begin{align*}
v_{1x} &= D_y \exp(-ky) \cos kx, \\
v_{1y} &= -(D_y + \frac{D_1}{k}) \exp(-ky) \sin kx, \tag{1}
\end{align*}
\]

where \( D = k^2V_0 \). From pressure and velocity the friction constant within first order perturbation can be obtained which is [13]:

\[
f = \frac{1}{2} \eta \epsilon^2 k^3 \tag{3}
\]

As said in earlier sections, the term \( \eta \) in Navier-Stokes equation is the viscosity for steady state shear. But if we are in the reference frame of a moving chain, we will experience different strain rate as we move. As the melt is viscoelastic, it will retain a fraction of its elastic energy as it passes through a time varying shear. If the total dissipation is calculated using this shear, this will be different from the dissipation obtained by using steady state shear. Below, the total dissipation using an oscillatory shear will be obtained and subsequently related to the friction term.

### 3 Total dissipation for oscillatory shear

From Equations 1 and 2 the velocity field near the boundary is given by [13]

\[
v_1(r) = D_1 y \exp(-ky) \cos kx \hat{x} - \left( D_1 y + \frac{D_1}{k} \right) \exp(-ky) \sin kx \hat{y},
\]

where \( D_1 = \epsilon k^2V_0 \). For a steady flow, within first-order perturbation, if at time \( t = 0 \) the chain experiences the velocity field around point \( x \), then at time \( t \) it will experience the field around point \( x + V_0t \). From the viewpoint of a single chain the velocity field is

\[
v(r, t) = D_1 y \exp(-ky) \cos k(x + V_0t) \hat{x} \\
- \left( D_1 y + \frac{D_1}{k} \right) \exp(-ky) \sin k(x + V_0t) \hat{y} \tag{4}
\]

The constitutive equation is [14]

\[
\sigma_{\alpha\beta}(t) = \int_{-\infty}^{t} dt' G(t - t') \left[ k_{\alpha\beta}(t') + k_{\beta\alpha}(t') \right]
\]
The velocity gradients can be obtained from Equation 4:

\[ k_{xy}(t') = \frac{\partial v_x(t')}{\partial y} = [D_1 - D_1 k y] \exp(-k y) \cos k(x + V_0 t'), \]

\[ k_{yx}(t') = \frac{\partial v_y(t')}{\partial x} = [-D_1 k y - D_1] \exp(-k y) \cos k(x + V_0 t'). \]

Thus,

\[ k_{xy}(t') + k_{yx}(t') = -2D_1 k y \exp(-k y) \cos(kx + V_0 t') \]

This is an oscillatory strain rate which can be written as

\[ \gamma(t) = k_{xy}(t) + k_{yx}(t) = \gamma_0 \cos kx \cos(kV_0 t) - \gamma_0 \sin kx \sin(kV_0 t), \quad (5) \]

where \( \gamma_0 = -2D_1 k y \exp(-k y) \). Letting \( kV_0 = \omega \), \( \gamma_0 \cos kx = \gamma_1 \), and \( \gamma_0 \sin kx = \gamma_2 \), Equation 5 becomes

\[ \gamma(t) = \gamma_1 \cos \omega t - \gamma_2 \sin \omega t, \quad (6) \]

and the constitutive equation becomes

\[ \sigma_{xy}(t) = \int_{-\infty}^{t} dt'G(t-t')\gamma(t') \quad (7) \]

For oscillatory shear the stress can be written in terms of storage and loss modulus [14]. So from Equation 6 and 7, \( \sigma_{xy} \) can be written as

\[ \sigma_{xy} = \left[ \gamma_1 \frac{G'(\omega)}{\omega} \sin \omega t + \gamma_1 \frac{G''(\omega)}{\omega} \cos \omega t \right] \]

\[ - \left[ \gamma_2 \frac{G'(\omega)}{\omega} \cos \omega t + \gamma_2 \frac{G''(\omega)}{\omega} \sin \omega t \right] \]

Because the dissipation corresponds to the product of this stress and the strain rate [15], the dissipation rate \( D'' \) is

\[ D'' = \left[ \left( \gamma_1 \frac{G'(\omega)}{\omega} \sin \omega t + \gamma_1 \frac{G''(\omega)}{\omega} \cos \omega t \right) - \left( \gamma_2 \frac{G'(\omega)}{\omega} \cos \omega t + \gamma_2 \frac{G''(\omega)}{\omega} \sin \omega t \right) \right] \]

\[ \left[ \gamma_1 \cos \omega t - \gamma_2 \sin \omega t \right] \]

Averaging over a time period gives the dissipation rate \( D \) as
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\[
D'' = \frac{\gamma_1}{\omega} G''(\omega) \langle \cos^2 \omega t \rangle - \gamma_1 \gamma_2 \frac{G'(\omega)}{\omega} \langle \cos^2 \omega t \rangle - \gamma_1 \gamma_2 \frac{G'(\omega)}{\omega} \langle \sin^2 \omega t \rangle + \gamma_2^2 \frac{G''(\omega)}{\omega} \langle \sin^2 \omega t \rangle
\]  

(8)

Substituting the values of \(\gamma_1\) and \(\gamma_2\) into Equation 8 and averaging over a wavelength gives

\[
D'' = \frac{\gamma_0^2}{\omega} G''(\omega) \langle \cos^2 k x \rangle \langle \cos^2 \omega t \rangle - \frac{\gamma_0^2}{\omega} G'(\omega) \langle \cos k x \sin k x \rangle \langle \cos^2 \omega t \rangle - \frac{\gamma_0^2}{\omega} G'(\omega) \langle \cos k x \sin k x \rangle \langle \sin^2 \omega t \rangle + \frac{\gamma_0^2}{\omega} G''(\omega) \langle \sin^2 k x \rangle \langle \sin^2 \omega t \rangle
\]

\[
= \frac{1}{2} \gamma_0^2 G''(\omega)
\]

Since \(\gamma_0 = -2D_1 k y \exp(-ky)\),

\[
D''(y) = 2D_1^2 k^2 y^2 \exp(-2ky) \frac{G''(\omega)}{\omega}.
\]

Integration over \(y\) gives the total dissipation rate \(D_t\) as

\[
D_t = \int_0^\infty D''(y) dy
\]

\[
= \frac{1}{2} \frac{D_1^2}{k} G''(\omega)
\]

So

\[
D_t = \frac{1}{2} \epsilon^2 k^3 \frac{G''(\omega)}{\omega} V_0^2.
\]

The dissipation rate can be related to the friction force as \(D_t = FV_0\). Therefore, the friction force is given by

\[
F = \frac{1}{2} \epsilon^2 k^3 \frac{G''(\omega)}{\omega} V_0.
\]

Writing the friction force as \(F = fV_0\), the friction constant \(f\) is

\[
f = \frac{1}{2} \epsilon^2 k^3 \frac{G''(\omega)}{\omega}.
\]

(9)
As the chain moves with velocity $V_0$, the period of the strain rate that it experiences is $T_s = \frac{2\pi}{kV_0}$. So different slip velocities implies different time scale and while using Equation 9, the loss modulus has to be chosen accordingly. The relation between the steady state viscosity and loss modulus is given by the following equation [16]:

$$\eta = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega}.$$ 

Substitution into Equation 9 gives

$$f_{V_0 \to 0} = \frac{1}{2} \epsilon^2 k^3 \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} = \frac{1}{2} \eta \epsilon^2 k^3$$  \hspace{1cm} (10)

Equation 3 and Equation 10 were determined from two different viewpoints. To obtain Equation 3, we use the viewpoint of a laboratory coordinate and see a steady flow with every point in the fluid under constant strain rate. For Equation 10 we use the viewpoint of a single chain. When the chain moves very slowly, the time period of strain rate is so large that we can treat the chain as if it is under constant strain rate. Thus, these two viewpoints will overlap to each other as the velocity becomes smaller, and for $V_0 \to 0$ the friction constants from these two viewpoints exactly match each other.

If $V_0$ is small so that $T_s > \tau_e$, then the reptation model must be used for the value of $G''(\omega)$ [17] and $f$ would be

$$f = \frac{1}{2} \epsilon^2 k^3 \frac{1}{\omega} \frac{ck_BT}{N_e} \sum_{p=1,3,5,...} \frac{8}{\pi^2} \frac{\omega \tau_{rep}}{p^4 + (\omega \tau_{rep})^2}$$

or

$$f = \frac{1}{2} \epsilon^2 k^3 \left[ \frac{ck_BT}{N_e} \right] \tau_{rep} \sum_{p=1,3,5,...} \frac{8}{\pi^2} \frac{1}{p^4 + (\omega \tau_{rep})^2}.$$ 

We know $\left( \frac{\pi^2}{12} \right) \left[ \frac{ck_BT}{N_e} \right] \tau_{rep} = \eta$. So

$$f = \frac{1}{2} \eta \epsilon^2 k^3 \left( \frac{12}{\pi^2} \right) \sum_{p=1,3,5,...} \frac{8}{\pi^2} \frac{1}{p^4 + (\omega \tau_{rep})^2}.$$  \hspace{1cm} (11)

If $\omega \tau_{rep} \ll 1$, i.e., $T_s \gg \tau_{rep}$, then

$$f \propto \eta \epsilon^2 k^3.$$
For \( T_s < \tau_e \), the Rouse model should be used to get the loss modulus [?] and Equation 9 gives

\[
f = \frac{1}{2} \epsilon^2 \kappa^3 \frac{1}{\omega} \left( \frac{c k_B T}{N} \right) \sum_{p=1}^{\infty} \frac{\omega \tau_{pr}}{1 + (\omega \tau_{pr})^2},
\]

where \( \tau_{pr} = \frac{\tau_s}{\tau_e} \). Thus,

\[
f = \frac{1}{2} \epsilon^2 \kappa^3 \left[ \left( \frac{c k_B T}{N} \right) \tau_e \right] \sum_{p=1}^{\infty} \frac{p^2}{p^4 + (\omega \tau_r)^2},
\]

In this case, \( \left( \frac{c k_B T}{N} \tau_e \right) \) is the steady state viscosity for Rouse model, \( \eta_r \). Thus,

\[
f = \frac{1}{2} \eta_r \epsilon^2 \kappa^3 \sum_{p=1}^{\infty} \frac{p^2}{p^4 + (\omega \tau_r)^2},
\]

(12)

Figure 1: Friction constant \( f \) for different slip velocities. Here \( T_s = \frac{2\pi}{k V_0} \), \( \eta \) is the steady state shear viscosity of polymer melt, and \( \eta_r \) is the steady state shear viscosity for the Rouse model. The figure shows how \( f \) depends on \( V_0 \). As the slip velocity is changed, the frequency of the strain rate changes. \( G \) behaves differently for different time scales, resulting in different loss modulus for different slip velocities. Hence the friction constant varies with \( V_0 \).

The relaxation time for entanglement strands is much smaller than the largest Rouse relaxation time. So if \( T_s < \tau_e \) then \( T_s \ll \tau_r \), i.e., \( \omega \tau_r \gg 1 \). In this case we can replace the sum in Equation 12 by integral:

\[
\int_0^{\infty} \frac{p^2}{p^4 + (\omega \tau_r)^2} \, dp
\]

This is a standard integral and its value is \( \frac{\pi}{2\sqrt{2}} \frac{1}{\sqrt{\omega \tau_r}} \). Therefore \( f \) is given by

\[
f = \frac{\pi}{4\sqrt{2}} \frac{\eta_r}{\sqrt{\tau_r}} \epsilon^2 \kappa^3 \frac{1}{\sqrt{k V_0}}.
\]
Figure 1 summarizes the results for different slip velocities. For \( v_0 \to 0 \), friction is independent of velocity. As the velocity increases, friction constant decreases. If \( T_s \) is smaller than \( \tau_{rep} \), then from a rough calculation (see Equation 11) we get \( f \propto \frac{1}{V_0^2} \). If \( T_s < \tau_e \), then \( f \propto \frac{1}{V_0^2} \).

4 Conclusion

Near a corrugated boundary, individual chains go through oscillatory shear. To find the friction constant for this surface, we have calculated the total dissipation rate using the constitutive equation for the polymer melts. Within first order perturbation, the frequency of this oscillation is \( kV_0 \) i.e., the time period is \( T_s = \frac{2\pi}{kV_0} \). So variation of the slip velocity leads to different time scales. As friction constant is \( f = \frac{1}{2} \epsilon k^2 G'(\omega) \), depending on what time scale the period belongs, the loss modulus has to be chosen to find \( f \). Since there is less dissipation for large velocities, the phenomenon of shear thinning of the viscoelastic flow is observed.

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References


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