Wall-Slip and Polymer-Melt Flow Instability

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(Received 12 March 1996; revised manuscript received 13 May 1996)

Instabilities and complex time dependence are often associated with wall slip in polymer-melt flows. We present here a phenomenological slip model that takes into account the unsteady-state kinetics of the wall-polymer interactions. In this model, both the shear and normal stresses arise, in contrast to other models used in stability analyses of shear flow, which incorporate only shear stresses and yield only stable flow. Asymptotic analysis of viscoelastic shear flow with this slip model predicts instability with respect to short wavelength fluctuations at sufficiently high shear rates, showing that slip can lead to instability in viscoelastic shear flow. [S0031-9007(96)00776-4]

PACS numbers: 83.50.Lh, 47.20.–k, 47.50.+d, 68.45.Kg

The behavior of polymers near interfaces is interesting and important from several points of view. At the most fundamental level, the kinetics of adsorption and diffusion of polymers near interfaces are fundamentally different than for small molecules, and are topics of active research (see, e.g., [1–3]). We present here theoretical evidence that this fact has important implications at the macroscopic level, for the fluid dynamics of polymer melts. At very high shear stresses, polymer-melt flows violate the classical no-slip hydrodynamic boundary condition at solid surfaces, and exhibit flow instabilities and complex nonlinear dynamics whose mechanisms are as yet poorly understood. In this Letter, we develop a simple phenomenological model for the slip process and show for the first time that a well-posed, single valued slip model, in conjunction with viscoelasticity, can exhibit shear flow instabilities consistent with those observed experimentally.

Wall slip has been reported in polymer-melt flows since the work of Mooney in 1931 [4] and has long been suspected to contribute to the melt fracture instabilities observed in polymer-melt extrusion processes [5]. Melt fracture is a macroscopic change in the surface morphology that varies from small scale (100 μm) roughness ("sharkskin") to large scale distortion of the entire extrudate. The site of initiation of these instabilities remains controversial, but a number of experimental studies demonstrate that at least in some cases, instability is not due to processes at the die entry or exit, but is coincident with the onset of slip in the die land (flow channel) [6–8]. Very large degrees of slip, however, may lead to stable flow because slip reduces the stress in the fluid. Most often, the evidence of slip is indirect. For example, slip may be inferred from the observation of an anomalously high flow rate for a given pressure drop. In many experiments, the onset of slip depends on the material of construction of the boundary, strongly suggesting that the wall-polymer interaction is important [2,7,9]. These experiments and others indicate that the no-slip condition seems to be valid until the shear stress reaches a critical value, above which the steady-state slip velocity u_s roughly follows a power law in the wall shear stress τ_w [2,6,10]. Data and analyses suggest that slip velocity also depends on pressure, decreasing as pressure increases [10,11]. Recently, direct optical observations of slip have been made. Archer, Larson, and Chen [12] observed the motion of microscopic beads within a few μm of a solid surface during simple shear flow of polystyrene solutions. Migler, Hervet, and Leger [13] used evanescent-wave-induced fluorescence in combination with fringe pattern fluorescence recovery after photobleaching to observe slip in a region less than 70 nm from the wall during shear flow of polydimethylsiloxane on silica.

Several theoretical approaches have been developed to understand slip in polymer melts. de Gennes and coworkers [14] and Sung [15] have modeled slip during steady shear flow of polymer melts at surfaces containing grafted chains. This model is based on the disentanglement of the bulk chains from the grafted chains, and predicts that the slip velocity jumps sharply at a critical value of the shear stress, as is observed in experiments [16]. Chemical interactions between melt and surface are only considered as a mechanism for providing grafted chains. In contrast, Lau and Schowalter [17] take chemical interactions to be dominant. They postulate that the shear stress alters the activation energies for the formation and destruction of bonds between melt and surface. Hill, Hasegawa, and Denn [10] argue that the work of adhesion must be included in a slip theory and that normal stresses rather than shear stress control the onset of slip. Stewart [18] and Hatzikiriakos [19] modify Eyring's theory for the viscosity of a liquid (cf. [20]) to describe slip. As in Lau and Schowalter's theory, but unlike that of Hill *et al.*, their expressions for slip velocity depend on shear stress, but not normal stress. In the model we present below, both the shear and normal stresses arise, and the normal stress dependence is necessary for instability.

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In capillary flow, the shear rate is nonuniform and cohesive failure ("constitutive instability") within the material has been proposed as an alternate mechanism for the onset of slip. This view reflects the fact that some constitutive models of polymer-melt flows can exhibit multiple shear rates for the same shear stress, at sufficiently high shear stresses [21]. If a high shear rate region is localized at the boundary, as would be the case in capillary flow, apparent slip will occur. In this view, however, slip is only affected by the bulk polymer properties, rather than the interfacial properties, a prediction that is not consistent with observations.

The experimental observations of melt flow instabilities and their association with slip have motivated a number of stability analyses attempting to understand their origin, with notably little success. The important dimensionless parameter in these flows is the Deborah number, $\mathrm{De} = \lambda\dot{\gamma}$, where λ and $\dot{\gamma}$ are the fluid relaxation time and shear rate, respectively. With no-slip boundary conditions, steady inertialess plane Poiseuille and Couette flows of Oldroyd-B fluids are linearly stable at all Deborah numbers [22,23]. Steady state or static slip models [i.e., algebraic models of the form $g(u_s, \tau_w) = 0$] have been applied to shear flows, but only predict instability when $du_s/d\tau_w < 0$ for a range of τ_w [24,25], a condition which has neither been observed nor theoretically predicted for polymer melts.

Use of an algebraic model for slip in a dynamical analysis is tantamount to assuming that the slip velocity responds instantaneously to changes in stress at the wall. However, measurements reveal surprisingly slow surface processes at polymer-solid interfaces [1–3], suggesting that stability analyses should incorporate the possible dependence of slip on the stress history at the boundary. Prior to the work presented here, the only such model that had been studied in the context of polymer-melt instabilities [26,27] was an *ad hoc* evolution equation introduced by Pearson and Petrie [24]:

$$u_s + \mathrm{De}_s \frac{Du_s}{Dt} = f(\tau_w), \tag{1}$$

where $\mathrm{De}_s = \lambda_s\dot{\gamma}$ is the "slip Deborah number"; λ_s is the characteristic time for the slip process. Here D/Dt is the usual substantial derivative, evaluated at the boundary under the assumption that the fluid velocity at the boundary is always tangent to the boundary. Renardy [26] showed that this boundary condition applied to inertialess shear flow of an upper convected Maxwell fluid leads to an ill-posed problem: the growth rate of fluctuations increases without bound as wavelength decreases. This pathology may stem from the unphysical property that even if the shear stress vanishes, the model allows a finite slip velocity to persist.

Our goal here is to introduce a well-posed phenomenological continuum model of slip that encompasses the ideas of the microscopic theories, but allows us to perform analysis and make predictions at the macroscopic, fluid dynamical level. The model is based on the ideas that the material structure very near a solid boundary is different from that in the bulk, and that this structure affects the slip behavior. We denote the structure with a dimensionless scalar X, the fraction of available polymer segments that are strongly interacting with the solid surface. Generically, X is analogous to the network junction density in transient network theories for bulk melt behavior [28]. In the disentanglement picture of slip, X roughly corresponds to the density of entanglements between bulk chains and chains attached to the surface. We take the structure creation (attachment) rate to be proportional to the number of free segments and the destruction (detachment) rate to be proportional to the number of bound segments and the elastic stress in the segments, measured by $\mathrm{tr}\boldsymbol{\tau}_w$, the trace of the polymer stress tensor evaluated at the wall (cf. [28,29]). The resulting evolution equation for X is

$$\frac{DX}{Dt} = \frac{1}{\mathrm{De}_s}[(1 - X) - sX\mathrm{tr}\boldsymbol{\tau}_w]. \tag{2}$$

Here De_s and s are positive constants; s is the ratio between the dimensionless detachment and attachment rate constants and De_s is the dimensionless attachment time constant (slip Deborah number). Time has been scaled with the inverse nominal shear rate and stress with the shear modulus. This equation is to be evaluated at all points on the polymer-solid boundaries of the domain; an appropriate initial condition is the equilibrium solution $X = 1$. Given this evolution equation, we now relate the structure at the wall to the velocity there. If the drag on a free segment is given by Stokes' law with a drag coefficient proportional to the number of bound segments, a reasonable form for its velocity is $u_f = \epsilon\tau_w/X$, where ϵ is a constant. If the overall slip velocity u_s is the average velocity of the free and bound (stationary) segments [17], then

$$u_s = (1 - X)u_f = \epsilon\frac{1 - X}{X}\tau_w. \tag{3}$$

In steady shear flow, or in the limit as $\mathrm{De}_s \to 0$ (fast interfacial kinetics), $u_s = \epsilon s(\mathrm{tr}\boldsymbol{\tau}_w)\tau_w$.

To examine the effect of this model on polymer-melt flow, we consider the stability of inertialess plane Couette flow of viscoelastic liquid, replacing the usual no-slip boundary condition with Eqs. (2) and (3). To facilitate a closed form solution, we consider the upper convected Maxwell (UCM) model for viscoelasticity and perform an asymptotic analysis, using ϵ from Eq. (3) as the small parameter and considering short [$O(\epsilon)$] wavelength fluctuations localized near the solid surface $y = 0$. In this limit, the analysis and results presented here also apply to Poiseuille flow.

The governing equations are the UCM constitutive equation and the equations of motion and continuity [30]:

$$\frac{\partial\boldsymbol{\tau}}{\partial t} + \boldsymbol{v}\cdot\nabla\boldsymbol{\tau} - \{(\nabla\boldsymbol{v})^T\cdot\boldsymbol{\tau} + \boldsymbol{\tau}\cdot\nabla\boldsymbol{v}\} + \frac{1}{\mathrm{De}_n}\boldsymbol{\tau} = \{\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^T\}, \tag{4a}$$

$$\nabla \cdot \boldsymbol{\tau} - \nabla p = 0, \tag{4b}$$

$$\nabla \cdot \boldsymbol{v} = 0. \tag{4c}$$

The polymer stress tensor $\boldsymbol{\tau}$ and pressure p are scaled with G, the shear modulus, velocity $\boldsymbol{v}$ with V, the velocity of the upper surface, lengths with l, the gap width, and time with the inverse nominal shear rate l/V. The nominal Deborah number De_n is $\lambda V/l$, where λ is the polymer relaxation time. Because of slip, the true Deborah number De_t is smaller than the nominal one, but this difference is negligible to leading order in ϵ. The physical setup of the problem is shown in Fig. 1; to leading order the steady state solution (denoted with overlines) is $\bar{\tau}_{xx} = 2\mathrm{De}_n^2, \bar{\tau}_{yx} = \mathrm{De}_n, \bar{\tau}_{yy} = 0, \bar{u} = \bar{u}_s + (1 - 2\bar{u}_s)y, \bar{v} = 0, \bar{X} = \left(1 + 2s\mathrm{De}_n^2\right)^{-1}$, with the steady state slip velocity $\bar{u}_s = 2\mathrm{De}_n^3 s\epsilon$. Only two-dimensional disturbances of the base flow (denoted with circumflexes) will be considered, since Squire's theorem holds for the UCM equation [31]. Linearization of Eqs. (4a)–(4c) around the steady state values results in a system of six coupled partial differential equations for the disturbances. A solution of the form $\hat{a}(\tilde{y})e^{i\alpha(x-\epsilon ct)}$ is proposed for each of the disturbance variables, where the wave number α is large ($\alpha = \epsilon^{-1}$) and $\tilde{y} = y\epsilon^{-1}$ is the stretched vertical coordinate. The wave speed (ϵc) is explicitly made $O(\epsilon)$, as we expect it to scale with the fluid velocity near the wall. Instability occurs when the imaginary part of c becomes positive. The amplitudes, $\hat{a}(\tilde{y})$, and the eigenvalue, c, are written as asymptotic expansions in ϵ and we consider here only the leading order behavior.

After incorporating the scalings, the stability problem can be reduced to a single equation for the $\tilde{y}$ velocity $\hat{v}$ (cf. [23]):

$$\left(Q^2\frac{d^2}{d\tilde{y}^2} - 2Q\frac{d}{d\tilde{y}} + 2 - Q^2\right) \times \left(\frac{d^2}{d\tilde{y}^2} + 2iDe_n\frac{d}{d\tilde{y}} - 1 - 2De_n^2\right)\hat{v} = 0, \tag{5}$$

with boundary conditions at $\tilde{y} = 0$:

$$\hat{u} = i\hat{v}' = B\hat{\tau}_{yx} + G\hat{X}, \tag{6a}$$

$$[(i\bar{u}_w - ic)\mathrm{De}_s + A]\hat{X} = -D(\hat{\tau}_{xx} + \hat{\tau}_{yy}), \tag{6b}$$

where $Q(\tilde{y}) = \tilde{y} + \bar{u}_w - c - i/\mathrm{De}_n$ and $\bar{u}_w = \bar{u}_s\epsilon^{-1} = 2\mathrm{De}_n^3 s$. The values of c where $Q = 0$ define a stable continuous component of the eigenvalue spectrum. The constants A, B, D, and G arise from the linearization of Eqs. (2) and (3): $A = 1 + s\bar{\tau}_{xx}$, $D = s\bar{X}, B = \frac{1-\bar{X}}{\bar{X}}, G = -\frac{\bar{\tau}_{yx}}{\bar{X}^2}$. Considering only solutions that decay as $\tilde{y} \to \infty$, we find

$$\hat{v}(\tilde{y}) = K_1 e^{(-i\mathrm{De}_n - \sqrt{1+\mathrm{De}_n^2})\tilde{y}} + K_2(\tilde{y} + \bar{u}_w - c)e^{-\tilde{y}}. \tag{7}$$

Application of the boundary conditions at $\tilde{y} = 0$, Eqs. (6), leads to a fifth order polynomial for the eigenvalue c. At low De_n, the imaginary parts of all five roots are negative. At higher De_n, one of the roots becomes positive, indicating flow instability. The critical Deborah number for instability, De_c, is shown graphically in Fig. 2. Instability occurs at all values of De_s if De_n is sufficiently large. Figure 3 shows a snapshot of the $\hat{\tau}_{xx}$ component of the structure of the destabilizing disturbance when $s = 0.01, \mathrm{De}_s = 0, \mathrm{De}_n = \mathrm{De}_c = 10.7256$. The destabilizing fluctuations are localized very near the wall and the elastic stress $\hat{\tau}_{xx}$ dominates the stress fluctuation. The wave speed $\mathrm{Re}(c)$ is essentially identical to the slip velocity so the fluctuation travels downstream with the steady base flow. As material that has undergone this instability is extruded from a channel, the normal stress perturbations will lead to small scale corrugation of the polymer surface, as occurs in mild melt fracture.

Figure 2 shows that instability occurs only when De (i.e., the effect of elasticity) is sufficiently large. As $s \to 0$, $\mathrm{De}_c \sim s^{-1/4}$, consistent with the classical result of Gorodtsov and Leonov [23] that Couette flow in the absence of slip ($s = 0$) is stable at all De. Furthermore, we have found that if the detachment kinetics in Eq. (2) are modified to depend on $2\tau_w^2$, the steady state value of $\mathrm{tr}\boldsymbol{\tau}_w$, rather than $\mathrm{tr}\boldsymbol{\tau}_w$ itself, the flow is again always stable. Thus both slip and elasticity are necessary for instability and the normal stress dependence of the interfacial interactions is an essential element of the instability mechanism.

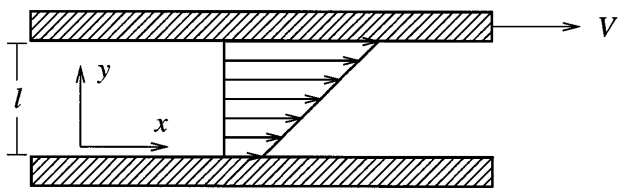

FIG. 1. Simple shear (Couette) flow geometry, showing the steady state velocity profile with slip.

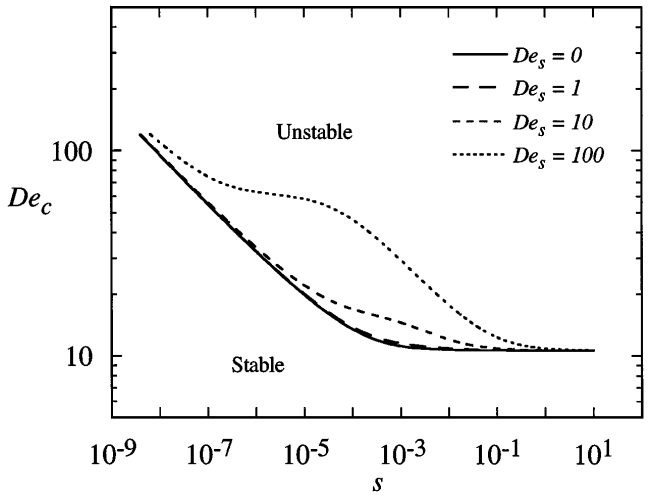

FIG. 2. Critical Deborah number De_c for instability as a function of De_s and s.

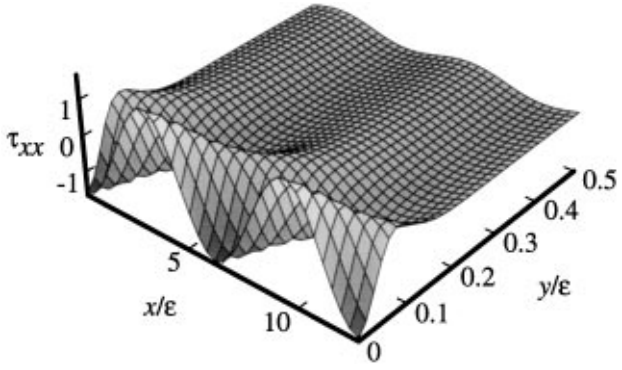

FIG. 3. Structure of the first normal stress perturbation $\hat{\tau}_{xx}$ at the onset of instability.

As s increases, De_c approaches a constant value of about 10.67, suggesting the existence of a lower bound on the stress required for instability. The analysis presented here is only valid for $\epsilon s \ll 1$; when s is large, slip significantly reduces De_t (the actual shear stress) relative to De_n. In fact, when $\epsilon s > 2.05 \times 10^{-4}$, De_t never exceeds 10.67, suggesting that the flow will be stable at all De. A more detailed analysis [32] confirms this prediction: $\mathrm{De}_c \to \infty$ as $\epsilon s \nearrow 2.05 \times 10^{-4}$. Therefore the model predicts the existence of a window in ϵs where instability occurs at a given De. Since s is a measure of the tendency of a polymer to detach from a particular surface, this prediction may unify disparate experimental results showing that instability may be avoided both by surface modifications that enhance slip and ones that minimize it.

Clearly, more work is necessary to solidify the relationship between our phenomenological evolution equation for X and the actual physics near the wall (e.g., the dependence of slip on pressure), as well as to study more realistic constitutive equations and flow geometries. Nevertheless, the present results do predict instabilities at short wavelengths, localized near the polymer-solid interface, which are intimately related to both the slip (interfacial) and bulk (elastic) properties of the polymer. These predictions accord with experimental observations and clarify the role of the polymer-solid interface in extrusion and other polymer-melt flow instabilities.

The authors gratefully acknowledge the support of this work through a Shell Faculty Fellowship, an NSF CAREER award, an ACS/PRF starter grant, and the Industrial and Economic Development Research Program of the State of Wisconsin.

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