A dynamic slip velocity model for molten polymers based on a network kinetic theory

S.G. Hatzikiriakos and N. Kalogerakis

1 Department of Chemical Engineering, The University of British Columbia, Vancouver, BC, Canada
2 Department of Chemical and Petroleum Engineering, The University of Calgary, Calgary, AB, Canada

Abstract: In this paper the slip phenomenon is considered as a stochastic process where the polymer segments (taken as Hookean springs) break off the wall due to the excessive tension imposed by the bulk fluid motion. The convection equation arising in network theories is solved for the special case of a polymer/wall interface to determine the time evolution of the configuration distribution function \( \psi(Q, t) \). The stress tensor and the slip velocity are calculated by averaging the proper relations over a large number of polymer segments. Due to the fact that the model is probabilistic and time dependent, dynamic slip velocity calculations become possible for the first time and therefore some new insight is gained on the slip phenomenon. Finally, the model predictions are found to match macroscopic experimental data satisfactorily.

Key words: Wall slip – dynamic slip – interface – network kinetic theory – polymer melts

Nomenclature

- \( g \): rate of creation of polymer segments
- \( g(Q) \): constant of rate of creation of polymer segments
- \( h \): rate of loss of polymer segments
- \( h(Q) \): constant of rate of loss of polymer segments
- \( h'(Q) \): constant of rate of loss of polymer segments due to destruction of its B-link
- \( H \): Hookean spring constant
- \( k \): Boltzmann's constant
- \( n \): unit vector normal to the polymer/wall interface
- \( n_0 \): number density of polymer segments
- \( n_0' \): surface number density of polymer segments
- \( Q \): vector defining the size and orientation of a polymer segment
- \( Q^* \): critical length of a segment beyond which the tension may overcome the \( W_{adh} \)
- \( t \): time
- \( t_h \): howering time of broken polymer segments
- \( T \): absolute temperature
- \( W_{adh} \): work of adhesion

Greek Letters

- \( \gamma_n \): nominal strain
- \( \gamma \): strain
- \( \gamma_s \): nominal shear rate
- \( \dot{\gamma} \): shear rate
- \( \varepsilon \): dimensionless constant in the expressions of \( h(Q), g(Q) \)
- \( \eta \): viscosity
- \( \kappa \): velocity gradient tensor
- \( \lambda_0 \): time constant
- \( \sigma \): standard deviation of vectors \( Q \) at equilibrium
- \( \sigma_w \): wall shear stress
- \( \tau \): stress tensor
- \( \psi_0 \): equilibrium configuration distribution function of \( Q \)
- \( \psi \): configuration distribution function of \( Q \)

1. Introduction

It is known that molten polymers slip over metal surfaces when the wall shear stress exceeds a critical value (Ramamurthy, 1986; Kalika and Denn, 1987; Hatzikiriakos and Dealy, 1991). In the processing of polymer plastics, the polymer melts are subject to such large and rapid deformations that the shear stress at a solid wall can reach a sufficiently high level and, as a result, the no-slip boundary condition ceases to be valid. To simulate such processes realistically, it is necessary to have available slip velocity models, which can adequately describe both the dynamic and steady-state behaviour of the slip phenomenon.

Experiments have shown that the slip velocity depends on a number of different parameters such as
the wall shear stress, wall normal stress, temperature, molecular weight and its distribution and interface conditions, i.e. material of construction of surface, presence of thin films (Ramamurthy, 1986; Kalika and Denn, 1987; Hatzikiriakos and Dealy, 1991). It is also believed that the slip velocity is associated with poor product appearance in many polymer processing operations, i.e. loss of gloss or in its more severe form appearance of small amplitude periodic distortions (Ramamurthy, 1986; Kalika and Denn, 1987). Thus, the importance of studying the slip velocity is two-fold. Firstly, it is necessary to have a slip velocity expression to use in the simulation of polymer processes and secondly, from a fundamental point of view to understand and explain many of the flow instabilities observed during polymer processing (sharkskin melt fracture, cyclic melt fracture, and gross melt fracture).

Several attempts have been made to model the slip velocity as a function of the above listed parameters (Lau and Schowalter, 1986; Hill et al., 1990; Hatzikiriakos and Dealy, 1992; Stewart, 1993; Hatzikiriakos, 1993). However, these models are capable of describing only the steady-state behaviour of the slip process and thus their use in the numerical simulation of polymer processes is limited. It is clear that a dynamic slip velocity model is needed.

Hatzikiriakos and Dealy (1991) carried out steady and dynamic shear experiments (exponential and large amplitude oscillatory shear) in a sliding plate rheometer to study the slip behaviour of a high density polyethylene (Sclair 56B). They found that the steady-state slip velocity data determined from steady shear experiments could not explain the shear stress response obtained from dynamic experiments. A finite time (slip relaxation time) is required for slip to attain its steady-state value. As they have pointed out, melt slip is a physicochemical process in which the polymer/wall interface may undergo continuous change with time before it takes its steady-state value. In addition, in very rapid deformations slip may not occur even if the shear stress exceeds the critical value provided that the strain is relatively small (Laun, 1983). Thus, the transition from a no-slip to a slip state exhibits characteristics of a relaxation process (Lim and Schowalter, 1989).

Chernyak and Leonov (1986) studied the process of adhesive friction of an elastomer body sliding over smooth rigid surfaces. They considered the slip phenomenon as a stationary stochastic process that consists of the formation and breakage of adhesive linking chains which bind the elastomer body to the surface. The breaking off was believed to be due to either thermal excitations or stress in the link arising from its elongation because of the external force applied to the body. To develop an explicit expression for the friction force, they made use of a linear strain-stress relationship. The developed model is probabilistic and time-dependent but only for the shear stress, while the slip velocity as an input parameter is constant. Therefore, this dynamic model is not suitable to be used for molten polymers where the slip velocity is not an a priori known quantity as in the case of elastomers.

In the present work a dynamic slip velocity model is developed for molten polymers and the results are compared with experimental data to validate its usefulness. The behaviour of a polymer/metal interface is simulated by using a network kinetic theory. Such theories are known to be capable of modelling polymer melts (Bird et al., 1987). The convection equation is solved numerically for the special case of a polymer/wall interface by using a method developed by Petruccione and Biller (1988a,b). This method is based on a direct stochastic interpretation of the convection equation. While the convection equation is solvable analytically for only special cases, using this stochastic interpretation more complex network kinetic theories can be studied efficiently.

2. Polymer network models

Prior to introducing the necessary modifications applied to a polymer-wall interface several relevant concepts from the network kinetic theory are briefly discussed and the basic governing equations are given.

The rheological behaviour of concentrated polymer solutions and melts can be described by an approach which originates from the theory of rubber elasticity (Bird et al., 1987). A rubber is considered to be comprised of strands which are permanently crosslinked at junctions. To allow for a liquid-like behavior these permanent entanglements are considered to be only temporary in the case of polymer melts. Thus, in transient network theories junctions break up and reform continuously. Figure 1a illustrates an idealized network model consisted of polymer segments temporarily crosslinked at junctions. The vectors, \( \mathbf{Q} \), define the size and orientation of the individual segments of the network.

These vectors, \( \mathbf{Q} \), follow the configuration distribution function \( \psi \) whose time evolution is governed by the following PDE which is known as the convection equation in kinetic theory for polymer solutions and melts (Bird et al., 1987).