LETTER TO THE EDITOR

Polymer depletion-induced slip near an interface

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Abstract
A quantitative description is proposed for the depletion-induced slip thickness
and velocity profile of a polymer solution near the wall–fluid interface in simple
shear flow. The inhomogeneous polymer density profile at a flat wall is inserted
into the equations of motion for the flow of a polymer solution near the flat wall.
The theory is in quantitative agreement with simulation results.

The flow of a dilute polymer solution near an interface, where slippage is thought to be relevant, is an important practical phenomenon [1, 2]. In oil recovery, aqueous polymer solutions are used to sweep oil out of natural porous media in the Earth's subsurface [3]. In that situation the polymer solution flows through narrow pores where a large effective viscosity, as enhanced by the presence of the polymers, is required to flush out the oil. Capillary rheometry is a technique that is often used to measure the viscosity of fluids [4]. It uses the fact that the flow time is inversely proportional to the liquid viscosity. However, for polymer solutions the relative viscosity from capillary rheometry may differ from its value obtained with other rheological methods [4–6]. The self-diffusion of colloidal spheres through a polymer solution cannot be unambiguously described using the Stokes–Einstein equation unless one adjusts the effective viscosity that the colloidal particle experiences [7]. These examples demonstrate the relevance of understanding the depletion-induced flow of an inhomogeneous polymer solution near an interface in order to quantify slip effects. Here we will discuss polymer solutions; for the flow of a polymer melt near a surface we refer to recent reviews [8].

For simple liquids the stick boundary condition has been generally accepted [9], although its correctness has been disputed on the solvent molecular length scale [10, 11]. The stick (or no slip) boundary condition says that the liquid velocity at the solid–liquid interface is zero. In the case of simple shear flow near an interface, the flow field in a solution containing (a) solvent, (b) a polymer solution with adsorbing polymer chains, or (c) a solution with non-adsorbing polymer chains, may be qualitatively described schematically as in figure 1. Since we focus on length scales of the order of and above the typical polymer length scales in solution, we assume that the stick boundary condition is valid for the low molecular solvent molecules, leading to the linear profile in figure 1(a).
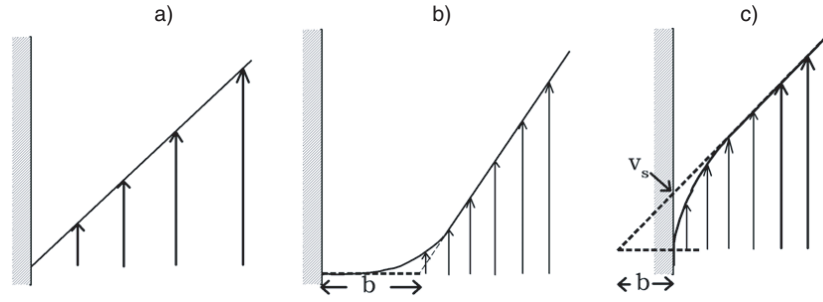
Figure 1. Schematic picture of the simple shear flow profiles of (a) a solvent, (b) a dilute polymer solution with adsorbing polymers, and (c) a dilute polymer solution containing non-adsorbing polymers near a flat wall. The magnitude of the Navier length b is indicated as well as the slip velocity.

In situation (b) where polymers are adsorbed at the surface (or brushes are anchored) the polymer segment concentration and hence the local viscosity increases near the surface, resulting in a decrease of the local shear rate $\dot{\gamma}(x) = \mathrm{d}v(x)/\mathrm{d}x$, where x is the distance from the flat surface, as compared to the bulk value. An effective hydrodynamic layer thickness or Navier length b can be defined, at which the apparent fluid velocity vanishes. The stick boundary condition has shifted from the surface into the fluid [12]. When polymers do not adsorb onto colloidal particles, a depletion layer exists near colloidal particles where the polymer chains are effectively absent (see for example the recent reviews [13]). Therefore the local shear rate increases near the wall as compared to the bulk shear rate for situation (c), leading to a hydrodynamic slip thickness with a finite Navier length b [14], having a negative value. These slip effects can be measured, for instance, by thin film drainage experiments [15]. This slip phenomenon causes problems in the interpretation of rheological data [2], and a quantification of its effects would be helpful for polymer rheologists. As indicated in figure 1(c), there is an apparent slip velocity v_s at the surface. So, when polymer solutions are in contact with a surface, for example a hard wall or a hard sphere, the fluid velocity profile becomes non-linear due to either adsorbed or depleted polymer chains, and the stick boundary condition does not hold for the polymer solution. In this communication the focus is on polymer depletion, and we present an approach that allows, as far as we know, a first analytical quantification of the slip thickness and apparent slip velocity of a dilute polymer solution near a polymer-repelling interface in simple shear flow.

The fluid velocity profile is analysed by starting from the Stokes equation without inertia: $\nabla \cdot \boldsymbol{\sigma} - \nabla \cdot \mathbf{P} = 0$ [16]. In simple shear flow, the pressure $\mathbf{P}$ is isotropic and constant, i.e. $\nabla \cdot \mathbf{P} = 0$, and it follows for the stress tensor $\boldsymbol{\sigma}$ that $\nabla \cdot \boldsymbol{\sigma} = 0$. Near a planar wall this condition suggests [17]

$$\eta(x)\frac{\mathrm{d}v(x)}{\mathrm{d}x} = \sigma, \tag{1}$$

where σ is the (constant) shear stress (component σ_{12} of the stress tensor $\boldsymbol{\sigma}$), $\eta(x)$ is the local viscosity, and $\mathrm{d}v(x)/\mathrm{d}x$ is the local shear rate. Using the stick boundary condition $v(0) = 0$, equation (1) provides an expression for the velocity profile:

$$\frac{v(x)}{\sigma} = \int_0^x \mathrm{d}x' \frac{1}{\eta(x')}. \tag{2}$$

In the case of slip, interesting quantities are the slip thickness or Navier length b and the apparent fluid velocity at the surface v_s. The slip thickness follows as $b = L - \eta_\mathrm{p}v(L)/\sigma =$

$L - \eta_p \int_0^L dx' \, \eta(x')^{-1}$, where L is a distance very far from the wall where $\eta(L) = \eta_p$, the viscosity of the polymer solution in the bulk. The apparent velocity can be defined as the bulk extrapolated velocity at the surface: $v_s = v(L = 0)$, so $v_s = -b\sigma/\eta_p$ [14, 18, 19]. Thus an expression for the local viscosity in the polymer solution near the wall provides the flow velocity near the wall, which subsequently yields the slip thickness and the apparent slip velocity.

The viscosity of a polymer solution η_p (a solvent with neutral Gaussian polymer chains) is generally given by the Huggins equation [20] (see also [4, chapter 11]): $\eta_p/\eta_s = 1 + [\eta]c + k_H([\eta]c)^2 + \cdots$, where η_s is the solvent viscosity, $[\eta]$ is the intrinsic viscosity (a hydrodynamic volume per unit mass), c the polymer concentration, and k_H the Huggins coefficient, which is approximately 0.4. Under conditions where quadratic and higher order concentration terms (caused by hydrodynamic interactions between the chains and due to entanglements) can be neglected, $\eta_p = \eta_s(1 + [\eta]c)$, and we approximate the local viscosity of the solution as

$$\eta(x) = \eta_s(1 + [\eta]c_b\rho(x)), \tag{3}$$

where $\rho(x) = c(x)/c_b$, with $c(x)$ the local segment density concentration, and c_b is the bulk concentration of polymer segments. The local viscosity has the limits $\eta(0) = \eta_s$ at the wall, where $\rho(x = 0) = 0$, and $\eta(\infty) = \eta_p = (1 + [\eta]c_b)\eta_s$ ($\rho(\infty) = 1$) in the bulk.

The concept of local viscosity can be applied to a small region where the local equilibrium holds. In such a small region, the following Green–Kubo formula $\eta = (V/kT) \int_0^\infty dt \langle \sigma_{xy}(t) \, \sigma_{xy}(0) \rangle$ can be used. Here σ_{xy} is the microscopically expressed off-diagonal element of the stress, and V is the volume of the small region. The symbol $\langle \cdots \rangle$ denotes ensemble-averaging. Hence, in order to define the local viscosity depending on the local concentration, the following two conditions should be satisfied in a small region. The first condition is that the longest characteristic relaxation time of the polymer chains τ should be smaller than the reciprocal of shear rate, i.e., $\tau < \dot{\gamma}^{-1}$ in order to satisfy the local equilibrium in a small region. Secondly, the characteristic length scale of the normalized concentration gradient $|(d\rho/dx)/\rho|^{-1}$ should be significantly longer than the size of an effective statistical chain element ℓ in order to have a sufficiently large number of statistical chain elements defining the local concentration inside the volume V, i.e., $\ell \ll |(d\rho/dx)/\rho|^{-1}$.

In the case of the depletion of polymer chains in solution, the following general profile gives a good description of the polymer segment density for ideal [21], mean-field [22, 23], and excluded volume polymer chains [24]:

$$\rho(x) = \tanh^2\left(\frac{x}{\delta}\right). \tag{4}$$

The quantity δ is the depletion layer thickness, which is close to the polymer's radius of gyration R_g in dilute polymer solution. In figure 2 we plot the density profile that follows from equation (4) and compare it to theoretical or simulation results for three types of polymers in solution. The dashed curve is the ideal chain result [25], for which $\delta = 2R_g/\sqrt{\pi}$ [21]. The filled symbols are numerical lattice calculations with mean-field chains (in this example for a segment volume fraction of 0.001, $\chi = 0$, $N = 1000$ but it holds generally) with a depletion thickness given by $\delta^{-2} = \pi R_g^{-2}/4 + \xi^{-2}$, where ξ is the concentration and solvency dependent mean-field correlation length [23]. For chains in the excluded volume limit [24] the filled data points represent the simulation results. Here $\delta = 0.9R_g$, describing the data at $c_b = 0.3$ times the overlap concentration (data courtesy of E J Meijer). The agreement with equation (4) is excellent for the three polymer descriptions. Hence we use equation (4) with a depletion thickness δ that can be specified depending on the conditions of interest. Equation (4) gives $|(d\rho/dx)/\rho|^{-1} = \delta \cosh(x/\delta) \sinh(x/\delta)/2$, so for example at $x = \delta$ (where $\rho \approx 0.58$),
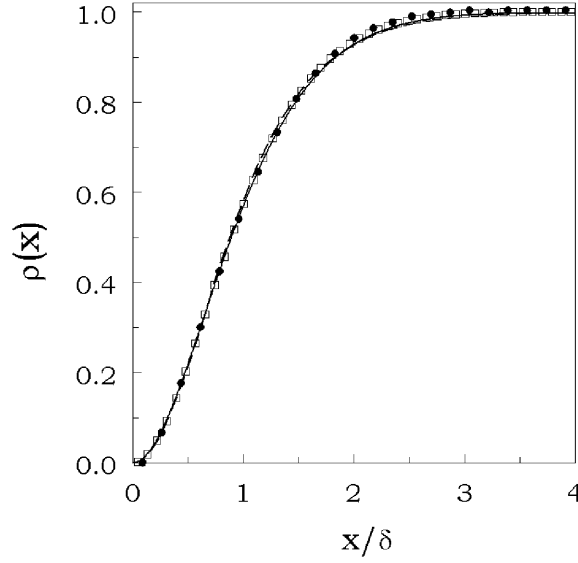
Figure 2. Segment density profile of non-adsorbing polymer at a flat wall. Full curve: equation (4); dashed curve: ideal chain result; open squares: numerical mean-field lattice calculations; and closed circles: simulation results for excluded volume chains.

$|(\mathrm{d}\rho/\mathrm{d}x)/\rho|^{-1} = \delta[\mathrm{e}^2 - \mathrm{e}^{-2}]/8 \approx 0.907\,\delta$. Hence the condition $\ell \ll |(\mathrm{d}\rho/\mathrm{d}x)/\rho|^{-1}$ for this case means $\ell \ll \delta$. The effective size of the segments should thus be much smaller than the depletion thickness.

Using equation (4) for the flow of a polymer solution near a wall, it is implicitly assumed that the equilibrium depletion segment density profile is undistorted due to the flow field. A polymer chain is a strongly fluctuating object that adopts its ensemble-averaged equilibrium configuration when the deformation timescale τ_{def}, set by the inverse shear rate, is sufficiently large. When the longest relaxation timescale in the polymer solution τ is much shorter than τ_{def}, i.e. $\tau \ll \tau_{\mathrm{def}}$, the use of equation (4) is valid. Actually, it is unclear, as yet, what happens in the case $\tau \geqslant \tau_{\mathrm{def}}$. With increasing shear rate, Omari *et al* [26] (indirect experiments) and Duering and Rabin [27] (simulation results) found a weak decrease of the depletion layer thickness, whereas Ausserré *et al* [28] measured an increase of the depletion layer at a wall at large ($>10^2\ \mathrm{s}^{-1}$) shear rates. Numerical calculations of Mavrantzas and Beris [29] suggest there is no significant effect of shear rate on the depletion thickness. Possibly, using equation (4) is not a poor approximation even for $\tau \geqslant \tau_{\mathrm{def}}$.

Insertion of equation (4) and (3) into equation (2) yields

$$v(x) = \frac{\sigma}{\eta_{\mathrm{p}}} \left(\delta\sqrt{[\eta]c_{\mathrm{b}}}\,\arctan\left(\sqrt{[\eta]c_{\mathrm{b}}}\,\tanh\left(\frac{x}{\delta}\right)\right) + x \right). \tag{5}$$

Here σ/η_{p} is the shear rate in the bulk. Far from the wall it follows that the velocity profile becomes linear with the distance from the wall x. Equation (5) yields for the Navier length:

$$b = -\delta\sqrt{[\eta]c_{\mathrm{b}}}\,\arctan\left(\sqrt{[\eta]c_{\mathrm{b}}}\right). \tag{6}$$

For very small $[\eta]c_{\mathrm{b}}$, equation (6) has the limit $b = -\delta[\eta]c_{\mathrm{b}}$, which is also found when the polymer density profile of equation (4) is replaced with a step-function: $\rho(0 < x < \delta) = 0$ and $\rho(x \geqslant \delta) = 1$. The apparent slip velocity follows from equation (5) as

$$v_{\mathrm{s}} = \delta\sqrt{[\eta]\,c_{\mathrm{b}}}\,\arctan\left(\sqrt{[\eta]c_{\mathrm{b}}}\right)\frac{\sigma}{\eta_{\mathrm{p}}}. \tag{7}$$
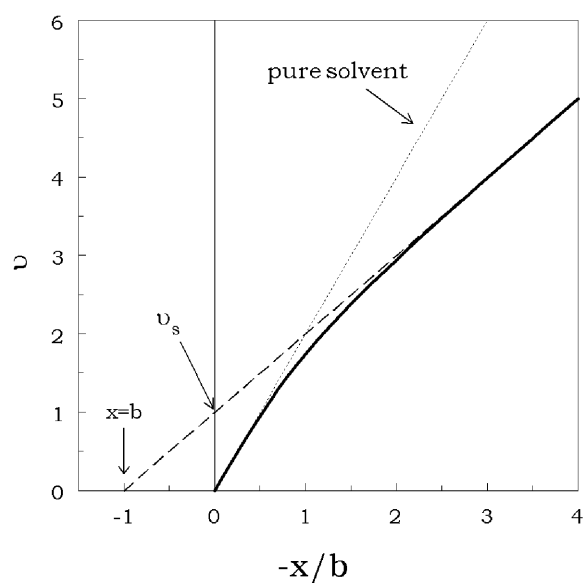
Figure 3. Polymer solution velocity profile near a flat wall. Normalized velocities υ are defined as $\upsilon = -v\eta_\mathrm{p}/\sigma b$. The full curve follows equation (5), and the long-dashed line is the bulk extrapolated velocity from which b can be derived. The short-dashed line is the pure solvent result. The apparent slip velocity υ_s and the Navier length b are indicated as well.
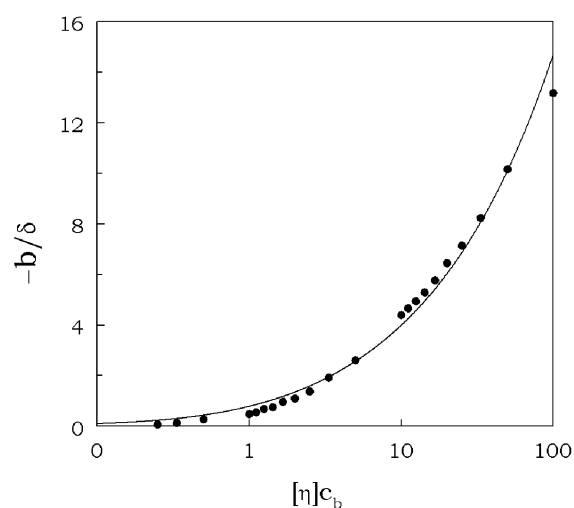

Figure 4. Navier length (normalized with the depletion layer thickness) as a function of the polymer bulk concentration c_b. The full curve follows equation (6), the symbols are redrawn numerical results from [26].

The fluid velocity profile that follows from equation (5) is plotted for $[\eta]c_\mathrm{b} = 1$ in figure 3. This plot demonstrates that the velocity profile is non-linear close to the wall, reflecting the apparent slip due to the presence of non-adsorbing polymer. The pure solvent result, $v_0 = \sigma/\eta_\mathrm{s}$, is plotted as the dotted curve. Extrapolation of the linear bulk profile to the interfacial region gives the finite apparent slip velocity at the surface. Further extrapolation to $\upsilon = 0$ defines the slip length b.

Mavrantzas and Beris [29] numerically studied the simple shear flow of ideal (non-interacting or 'ghost') chains near a wall. They used a non-equilibrium version of the Edwards diffusion equation and inserted that into the equations of motion. The velocity profile near the wall that follows from their simulations matches with the prediction of equation (5): a boundary layer develops at the wall where the fluid velocity increases rapidly. The calculated slip velocity was found to scale linearly with the wall shear stress, which is consistent with a constant depletion layer thickness as a function of shear rate $\dot{\gamma}$. In figure 4 we have redrawn their results (symbols) for the slip thickness as a function of $[\eta]c_b$. The full curve is the prediction of equation (5), which is in quantitative agreement with the numerical results of Mavrantzas and Beris [29]. The theory can be extended straightforwardly to higher polymer concentrations and interacting polymers by taking higher order terms into account in equation (3) and inserting a proper concentration dependence for the depletion layer thickness into equation (4). The slip effects are expected to increase with polymer concentrations beyond the semi-dilute regime. Although the depletion thickness decreases as $\delta \sim c_b^{-3/4}$ [14], the viscosity increase $\eta \sim c_b^{3.4}$ [4] overwhelms it. Extension is also possible in the direction of other geometries (e.g. flow through a capillary).

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