Viscous finger narrowing at the coil-stretch transition in a dilute polymer solution

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We present results of an experimental study of Saffman-Taylor fingers in dilute solutions of polystyrene in dioctyl phthalate (DOP). While fingers in pure DOP obey classical scaling laws, we observe transitions to narrow fingers in polystyrene solutions of concentrations as low as 1 part per million. The onset of narrowing occurs at a shear rate which roughly equals the inverse of the polymer Zimm relaxation time and depends only weakly on concentration. The onset of instability occurs earlier than in Newtonian fluids and is often initiated by small-amplitude oscillations.

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Dilute polymer solutions display interesting flow phenomena, such as turbulent drag reduction. Despite recent progress in experiments [1] and theory [2], these effects are not completely understood. The difficulty is that polymeric effects only seem to appear after the transition to turbulence, making them hard to study. Therefore, it seems useful to try to look for effects in simpler flows. Theories predict that a polymer coil will begin to unravel if subjected to sufficiently rapid elongational flow, and that the transition from a coiled to a stretching state is abrupt. The problem is to understand the back effect of stretching polymers on the flow. Typically, rheological measurements have only revealed polymer effects at concentrations near or above static chain overlap, and have not provided evidence for the sharp coil-stretch transition expected in very dilute solutions. Birefringence measurements have revealed polymer transitions in dilute solutions [3], but are not very useful for studying the flow. Recently, light scattering was used to study velocity gradients in a controlled extensional flow [4]. In that experiment, concentration-dependent flow effects were observed at shear rates distinctly higher than the shear rate at the coil-stretch transition.

In this paper we present an alternative way to study the effects of small concentrations of polymers on hydrodynamics. The dynamics of viscous fingers in Newtonian fluids [5] has been studied in detail experimentally [6] and theoretically [7], and is now well understood. Here we report results of a study of viscous fingers in dilute polymer solutions. We begin by reviewing relevant aspects of the problem and by applying the Zimm model for polymer deformation.

In the experiment, a finger of air penetrates into a cell containing a viscous fluid between two narrowly separated parallel plates. The cell is characterized by its width \( W \) and thickness \( b \), and the finger by the ratio \( \lambda \) of its width to that of the cell. In order to describe the behavior of the system, theory [7] and experiments [6] have shown it is useful to consider the dimensionless parameter

\[
\frac{1}{B} = 12 \frac{\eta V}{\sigma} \left( \frac{W}{b} \right)^2,
\]

where \( \eta \) is the viscosity, \( \sigma \) is the surface tension, and \( V \) is the finger velocity. One finds essentially universal scaling of \( \lambda \) vs \( 1/B \) for Newtonian fluids. The finger becomes unstable at \( 1/B \approx 7000 \) (experimentally), but the exact value depends on perturbations caused by imperfections in the cell and fluid. Neglecting surface tension, Saffman and Taylor [5] found the following family of solutions for the finger shape:

\[
x = \frac{1 - \lambda^2}{\pi} \ln \left[ \frac{1}{2} \left( 1 + \cos \frac{\pi x}{\lambda} \right) \right].
\]

For nonzero surface tension, these solutions accurately describe fingers with \( \lambda \) near \( \frac{1}{2} \), but fail for wider fingers in which surface tension plays a larger role. Recent experiments and simulations have shown that local perturbations in the form of threads [8], grooves [9], or bubbles [10], when located near the finger tip, increase the stability of the finger and lead to narrowing of the width of fingers over the entire range of \( 1/B \).

We now consider the effect of the polymers on the flow. In a sufficiently dilute solution we expect an abrupt coil-stretch transition, so it may be reasonable to look for flow modification at the transition point. Experiments [6] and calculations [11] show that the flow partly converges toward the interface, leading to a rolling motion in three dimensions in a narrow region just in front of the finger tip. The qualitative behavior of the flow is shown schematically in the inset of Fig. 1. There is a point of near stagnation just in front of the finger tip and the fluid elongates in the forward direction ahead of this point. By considering the smallest length scale which constrains the flow, which is the cell thickness \( b \), we estimate the maximum shear to be of order \( V/b \) near the finger tip. The theory for dilute polymer deformation proposed by Zimm [12] predicts a characteristic relaxation time for a polymer chain given by

\[
\tau_{\text{Zimm}} = 2.93 R^3 \eta/kT,
\]

where \( R \) is the polymer radius of gyration, \( \eta \) is the solvent viscosity, \( k \) is Boltzmann’s constant, and \( T \) is the temperature. Experimental studies using birefringence [3,13] confirm this theory, as do molecular-dynamics simulations [14]. To estimate the value \((1/B)^t\) at which we expect the coil-stretch transition to occur, we compare the shear rate
FIG. 1. $\lambda$ vs $1/B$ for pure DOP (●), and for stable (○) and oscillating (○) fingers in the 80-ppm solution of $2\times10^{10}$ g/mol polystyrene. Inset: Schematic picture of the flow near the finger tip.

$V/b$ to the inverse of the polymer relaxation time using (1) and (3) to obtain

$$(1/B)^2 = 4.09W^2 kT/R^3 \rho b.$$  \hspace{1cm} (4)

Note that the result does not depend on the viscosity. The aim, then, is to sweep through a parameter range containing $(1/B)^2$ and to study the flow.

We now present experimental results. Most of the measurements were made in a cell of width $W = 4.13$ cm and thickness $b = 0.0457$ cm (aspect ratio $\Gamma = W/b = 90.4$). Additional measurements were performed in a cell with $W = 4.52$ cm and $b = 0.0254$ cm ($\Gamma = 178$). The plates were made of glass (or glass coated with acrylic floor polish [15]), separated by stainless-steel spacers, and assembled under a clean hood. The thickness of the cell was adjusted to be uniform using laser interferometry, giving a uniformity of about 10 μm. Fingers were visualized by diffuse light reflected through the bottom of the cell to a video camera mounted above. The cell was supplied with viscous fluid by a reservoir connected to one end, and open to air or compressed nitrogen at the other end.

Diocetyl phthalate (DOP) (Aldrich Chemical Co.) was used as the solvent and polystyrene as the polymer. DOP has an experimentally desirable viscosity of 63 cP at room temperature. Measurements in a rotational viscometer showed no dependence of the viscosity on shear rate and the slope of the viscosity change with temperature near 22°C was measured to be about 3.7 cP/°C. The surface tension was determined by be 27.2 dyn/cm² at 22.0°C by the Wilhelmy plate method. Monodisperse polystyrene ($M_{w}/M_{n} = 1.3$) (Pressure Chemical Co.) of molecular weights $2\times10^{6}$ and $2\times10^{6}$ g/mol were dissolved by slow rotation in a small jar under a heat lamp, diluted to concentration, and filtered through 11-μm filter paper. Measurements showed that the viscosity and surface tension of the solutions varied slightly from that of DOP, but not appreciably as far as the rheology is concerned. The scattering of a He-Ne laser at 90° by the 80-ppm solution was no more than twice that of the pure solvent and even less for the lower concentrations, indicating that the polymers were well dissolved.

DOP is a Θ solvent at 22.0°C [16], where the long-range attractive van der Waals forces between monomers which cause concentration are just balanced by the polymer-solvent interactions which cause the polymer coil to expand. The result is a random walk of the monomer units, yielding a theoretical estimate [17] of the equilibrium radius of $R = 3.02\times10^{-2} M^{1/2}$ nm, where $M$ is the molecular weight. This gives $R = 135$ nm for $2\times10^{6}$ g/mol and 42.7 nm for $2\times10^{6}$ g/mol. By calculating the static volume of the polymers, one may estimate the critical concentration $c^*$ at which they will overlap. $c^* \approx 3160$ ppm (mass) for $2\times10^{6}$ g/mol and $2\times10^{8}$ g/mol. By keeping our concentrations far below these amounts we expected to avoid entanglement effects at the coil-stretch transition.

First, we verified that Saffman-Taylor fingers in pure DOP obeyed the scaling laws for Newtonian fluids. The finger scaling ($\lambda$ vs $1/B$) agreed with previous measurements in silicon oil [4]. The instability in pure DOP first occurred at $1/B \approx 7000$. We proceeded to study the behavior in solutions of $2\times10^{6}$ and $2\times10^{6}$ g/mol polystyrene at room temperature ($22 \pm 1.0^\circ$C), which is roughly the Θ point. A plot of $\lambda$ vs $1/B$ for fingers in an 80-ppm solution of $2\times10^{6}$ polystyrene in the $\Gamma = 90.4$ cell is shown in Fig. 1. Three striking features are apparent: (i) There is a transition to narrow fingers, (ii) the family of narrow fingers fills a region in the $(1/B, \lambda)$ parameter space, and (iii) the onset of instability occurs at a significantly smaller $1/B$ than for Newtonian fluids.

We observed transitions to narrow fingers in solutions of $2\times10^{6}$ g/mol polystyrene with concentrations ranging from 1 to 500 ppm. The dependence of the onsets of narrowing on concentration in the $\Gamma = 90.4$ cell are shown in Fig. 2. The value of $1/B$ at which we saw finger narrowing in the $2\times10^{6}$ g/mol polystyrene agrees quite well with the theoretical prediction $1/B \approx 932$, given by Eq. (4). As seen in Fig. 2, there is excellent agreement for concentrations ranging from 20 to 500 ppm. However, in the 0.5 and 1 ppm concentrations the onset is roughly a factor of 2 greater than that predicted by Eq. (4).

FIG. 2. The dependence of the onset of narrowing (○) and instability (●) on concentration in the solutions of $2\times10^{6}$ g/mol polystyrene and the onset of instability (●) in the solutions of $2\times10^{6}$ g/mol polystyrene. The dashed line is the theoretical estimate from the Zimm model for solutions of $2\times10^{6}$ g/mol polystyrene.
plitude of narrowing is approximately constant in the solutions \( \geq 5 \text{ ppm} \) \((\Delta A_{\text{max}} \approx 0.05)\), but it is noticeably smaller in the 1-ppm solution \((\Delta A_{\text{max}} \approx 0.025)\). Figure 3 shows the observed shape of a typical narrow finger in a solution of \(2 \times 10^6\) g/mol polystyrene. The finger appears to have a slightly sharper tip than that predicted by the Saffman and Taylor solution (2). By decreasing \(b\), we increased the shear rate and found, in a solution of 80-ppm \(2 \times 10^6\) g/mol polystyrene in the \(i = 178\) cell \((b = 0.0254\) cm), the onset of narrowing occurred at \(1/B = 1900 \pm 250\). The value predicted by Eq. (4) is \((1/B)^\prime = 2001\).

We observed no narrow fingers in the solutions of \(2 \times 10^6\) g/mol polystyrene, up to the point of the onset of dynamical instability. This is understandable because the onset of instability for \(2 \times 10^6\) g/mol polystyrene comes at a \(1/B\) far smaller than the predicted point of \((1/B)^\prime = 29340\) for the coil-stretch transition.

The fact that there is a distribution of possible finger widths for a single \(1/B\) suggests that the polymers act as a variable perturbation which depends on the exact evolution (history) of the interface. A few times we saw a stable finger undergo a spontaneous widening or narrowing, followed by stability. The possibility of dynamical effects due to adsorption of polymers on the interface should be considered, and might explain the variations in onset and deviation at the smallest concentrations.

As seen in Fig. 2, the values of \(1/B\) at which the instabilities in the polymer solutions occur are significantly lower than for Newtonian fluids. The transition from stable to unstable behavior is often initiated by weak transverse oscillations of the finger tip, such as that shown in Fig. 4. The oscillation appears to be only marginally stable, as it quickly decays into side instabilities or tip splitting. The decrease in stability with polymers might be contrasted with the increase in stability of narrow fingers found with local fixed perturbations \([8,10]\), suggesting that polymers increase the noise level of the system. Figure 2 shows that the onset of instability depends on the polymer size and concentration. Fingers in the solutions of \(2 \times 10^6\) g/mol polystyrene are stable up to a \(1/B\) approximately 2 times greater than in the solutions of \(2 \times 10^6\) g/mol polystyrene and the onset of instability appears to be weakly (at most logarithmically) dependent on concentration. Note that before changing polymer concentrations we flushed the cell with nitrogen and DOP, and occasionally repeated the set of measurements with pure DOP.

In summary, we have identified a transition in the flow which occurs at the polymer coil-stretch transition. We suspect that other pattern formations in fluids may also be affected by small concentrations of polymers. In preliminary investigations we found that the dynamics of thermal plumes, believed to be fundamental objects in turbulent convection, may be changed dramatically by a small concentration of polymers \([18]\). The formation of coherent structures, such as vortices, are a basic feature of flow-induced turbulence as well. The modification of such structures by unraveling polymers may be an important aspect of drag reduction. Other fluctuating polyatomic structures, such as surfactant vesicles and membranes may also influence flows in ways analogous to those reported here.

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[15] The fluid must wet the cell in order to obtain proper finger movement. For the $\Gamma = 90.4$ cell, we had success with glass plates washed gently with water and Micro Lab Cleaner. However, after a second washing, the glass could not be wet again even after a rigorous cleaning with nitric acid. This led us to suspect that we had removed some coating from the surface. Wetting was reattained by applying a microlayer of acrylic polish to the surface. The layer did not affect fingers in pure DOP.
[18] For example, we found that a plume created with 20 W power from a localized heat source became unstable (turbulent) in water, but remained stable in a solution of 50-ppm xanthan gum.
FIG. 4. A typical oscillating finger in a solution of 80-ppm 20×10^6 g/mol polystyrene.