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# Communications to the Editor

## Slip, Concentration Fluctuations, and Flow Instability in Sheared Polymer Solutions

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The local composition of polymer solutions and blends can be significantly affected by flow. For example, shear-enhanced concentration fluctuations in semidilute polystyrene (PS) solutions have been observed via light-scattering and microscopy by a number of groups.[1−8] A purely hydrodynamic mechanism for this phenomenon, in an unbounded flow domain, was proposed initially by Helfand and Fredrickson (HF)[9] and later extended by several authors.[10−14] This mechanism is based on the idea that variations in polymer stress can drive a flux of polymer molecules—indeed, several authors[12,13,15−17] have developed two-fluid models which demonstrate that the polymer flux $\boldsymbol{j}$ in a solution has the form $\boldsymbol{j} = -D\nabla n + (D/k_BT)\nabla\cdot\boldsymbol{\tau}$, where $n$ is the polymer number density, $\boldsymbol{\tau}$ is the polymer extra stress tensor, $D$ is the polymer gradient (collective) diffusivity, $k_B$ is the Boltzmann constant, and $T$ is the temperature. A scattering peak is predicted and observed to arise when the diffusion and relaxation times are equal, which occurs at a wavelength of roughly $\sqrt{D\lambda}$, where $\lambda$ is the longest relaxation time for the solution. For a semidilute PS solution, we note that this scale can be several micrometers, much larger than the equilibrium molecular size.[18]

A recent experimental study by Mhetar and Archer[19] has demonstrated several novel features of shear-enhanced concentration fluctuations in entangled polymer solutions. They studied semidilute solutions of PS in diethylphthalate (DEP), to which tracer particles were added to measure the velocity profile, using a planar Couette cell with (high energy) silica walls. In this situation, wall-slip occurs primarily due to the disentanglement of bulk chains from those adsorbed to the walls, rather than to the formation of a depletion layer, as arises in dilute solutions.[20,21] Three features of the flow of these solutions stand out. First, no turbidity was observed at low shear rates ($\bar{\dot{\gamma}}$) where slip was weak; enhanced concentration fluctuations were observed, however, at large shear rates (Weissenberg number $We = \lambda\bar{\dot{\gamma}} \gg 1$), where slip was significant. The length scale for the fluctuations was observed to be $O(10\ \mu\text{m})$, as was the extrapolation, or slip, length $b$ measured for these solutions. Second, the concentration fluctuation enhancement began near the boundaries, and third, modification of the surface to suppress adsorption, thereby changing the mechanism of slip from disentanglement to “bare” friction between polymer and substrate, delayed the onset on fluctuations to much larger shear stresses. These observations strongly suggest that slip plays a role in the formation and development of these fluctuations. Our goal here is to analyze the coupling between concentration, stress, and slip in bounded shear flow, to elucidate the effects of boundaries on the dynamics and to attempt to capture in a simple model the essential phenomena observed by Mhetar and Archer.

We consider plane shear flow, as shown in Figure 1. To describe the behavior of the solution, we use the two-fluid model derived by Mavrantzas and Beris,[16] simplified to a solution of Hookean dumbbells,[26] and written in terms of the conformation (second moment) tensor, $\boldsymbol{\alpha}$. Nondimensionalizing stresses with $n_0k_BT$, where $n_0$ is the average concentration of the solution, lengths with the characteristic length $\sqrt{D\lambda}$, velocities with $\bar{\dot{\gamma}}\sqrt{D\lambda}$, time with $\lambda$, and concentration with $n_0$ gives, to leading

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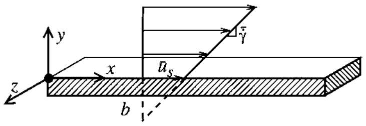

**Figure 1.** Plane Couette geometry showing slip between the solution and solid surface. The flow is in the $x$ direction, $y$ is the gradient direction, and $z$ is the vorticity or neutral direction. The steady state slip velocity is $\bar{u}_s$, $\bar{\dot{\gamma}} = \partial \bar{v}_x/\partial y$ is the steady state shear rate, and $b \equiv \bar{u}_s/\bar{\dot{\gamma}}$ is the extrapolation length.

order when polymer volume fraction $\phi \ll 1$, the following model equations

$$\frac{\partial \boldsymbol{\alpha}}{\partial t} + We\,(\mathbf{v}\cdot\nabla\boldsymbol{\alpha} - \boldsymbol{\alpha}\cdot\nabla\mathbf{v}_p - (\nabla\mathbf{v}_p)^T\cdot\boldsymbol{\alpha}) + \boldsymbol{\alpha} - n\boldsymbol{\delta} = \nabla^2\boldsymbol{\alpha} \tag{1}$$

$$\frac{\partial n}{\partial t} + We\,\mathbf{v}\cdot\nabla n = -\nabla\cdot(-\nabla n + \nabla\cdot\boldsymbol{\tau}) \tag{2}$$

$$-\nabla p + \nabla\cdot\boldsymbol{\tau} + S\,We\nabla^2\mathbf{v} = 0 \tag{3}$$

$$\nabla\cdot\mathbf{v} = 0 \tag{4}$$

where $\mathbf{v}$ is the mass-average velocity, $\mathbf{v}_p = \mathbf{v} + (-\nabla n + \nabla\cdot\boldsymbol{\tau})$ is the polymer velocity (polymer flux/polymer concentration), $S$ is the ratio of the solvent to polymer viscosities, $n$ is the number density of dumbbells, $\boldsymbol{\tau} = \boldsymbol{\alpha} - n\boldsymbol{\delta}$ is the polymer extra stress and $p$ is the pressure. (Here and hereafter, all references to variables refer to their nondimensional form). Equation 1 describes the evolution of polymer conformation. Equation 2 is the polymer species conservation equation. If diffusion of the polymer is neglected, the right-hand sides of eqs 1 and 2 vanish, yielding the Oldroyd-B model. Equations 3 and 4 describe conservation of momentum and mass in the low Reynolds number limit. In presenting the model, we have suppressed any dependencies of properties on concentration—in the analysis below we only consider small perturbations from spatially uniform stress and concentration fields, in which case the terms that reflect these dependencies do not appear. Other phenomenologically motivated models for such systems are virtually identical to this one.[9,10,12−14] Previously, however, only Sun et al.[14] have included the diffusive term in eq 1 in a treatment of scattering.

In Mhetar and Archer's experiments, either high energy (strongly adsorbing silica) or very low-energy (nonadsorbing octadecyltrichlorosilane-coated silica) surfaces were used. In either case, a reasonable first approximation is that in the course of an experiment, adsorbed chains do not desorb to a significant degree in flow, and that no additional bulk chains adsorb. Therefore, we apply no-flux boundary conditions for the polymer and the solvent: $\mathbf{n}\cdot\mathbf{v}_p = \mathbf{n}\cdot\mathbf{v} = 0$, where $\mathbf{n}$ is the unit normal on the boundary. For the same reason, we assume that there are no sources or sinks for polymer conformation at the walls, giving a no-flux boundary condition for the conformation: $\partial\boldsymbol{\alpha}/\partial y = 0$.

The model is completed by specifying the slip boundary condition. We use two simple models here. The first, more suited to the high energy surface, is a simple Navier slip boundary condition $u_s = b\tau_{yx}/We$, with the extrapolation length $b$ taken to be a constant. This model crudely captures the fact that slip is related to polymer stress for the high energy surface (i.e., interaction between adsorbed and bulk chains). The other is a quasisteady relation $u_s = b\dot{\gamma}$, again with $b$ constant. This is the "Newtonian" limit of the Navier model and is appropriate if the slip is due to monomer friction, which will have an extremely short relaxation time, yielding an instantaneous coupling between slip and shear rate.

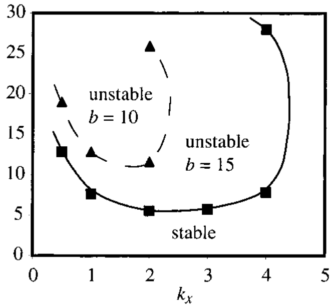

**Figure 2.** Neutral curves for $k_z = 0$, $S = 0.01$, with the stress-dependent slip model and various values of the extrapolation length. Key: (▲) $b = 10$; (■) $b = 15$. The curves are to guide the eye.

We have studied the dynamics of this model by linear stability analysis of the plane shear base state, given (for either slip model) $\boldsymbol{a} = (\bar{v}_x, \bar{v}_y, \bar{v}_z, \bar{\tau}_{xx}, \bar{\tau}_{yx}, \bar{\tau}_{zx}, \bar{\tau}_{yy}, \bar{\tau}_{zy}, \bar{\tau}_{zz}, \bar{n}, \bar{p}) = (y + b, 0, 0, 2We^2, We, 0, 0, 0, 0, 1, 1)$. Infinitesimal normal mode perturbations are added to this base solution: i.e., $\boldsymbol{a} = \boldsymbol{a}(y) + \boldsymbol{a}(y)e^{i\boldsymbol{k}\cdot\boldsymbol{x}}e^{\sigma t}$ + c.c., where $\boldsymbol{k} = (k_x, 0, k_z)$, yielding a generalized eigenvalue problem with eigenvalues $\sigma$. If any $\mathrm{Re}(\sigma) > 0$ then infinitesimal disturbances grow and the flow is unstable. We solve this problem on a semi-infinite domain, mapping $y \in [0,\infty)$ onto the computational domain $\xi \in [-1,1]$, using the mapping $y = 0.1\,(1 + \xi)/(1 - \xi)$, and then performing Chebyshev collocation on the mapped system,[27] using $N + 1$ collocation points. The eigenvalue problem is solved using a public domain routine.[28] Converged results were obtained with $N = 96$.

If the possibility of concentration fluctuations is suppressed in the model (by setting $D$ to zero, thus eliminating the rhs of eqs 1 and 2), plane shear flow with no-slip[22] or either of the above forms of Navier slip[24,25,29] is stable for all Weissenberg numbers. In addition, if concentration variations are permitted but slip is not ($b = 0$), the flow is also stable. In contrast, we find that if Navier slip and concentration variations are allowed, the flow can become unstable when $We$ exceeds a critical value $We_c$, as observed in the experiments of Mhetar and Archer.[19] Two-dimensional disturbances ($k_z = 0$) are the most unstable, in agreement with experiment; Figure 2 shows a neutral curve plotted as $We_c$ vs $k_x$ for $k_z = 0$, with $b = 10$ and $b = 15$—these values of $b$ are consistent with the slip lengths reported by Mhetar and Archer, assuming that $\sqrt{D\lambda}$ is several micrometers.[1−8] For a particular wavenumber $k_x$, if $We$ is in the "unstable" region on the plot for a given $b$, then infinitesimal perturbations of that wavenumber grow. From these results, the critical length scale for the instability is predicted to be $O(\sqrt{D\lambda})$, and it arises when the slip length $b > \sqrt{D\lambda}$. In particular, we find that the dimensionless group $bk_x \approx 20-30$ at criticality. Experimentally, approximating $k_x$ as $2\pi/(10\ \mu\mathrm{m})$ and $b$ as 40 $\mu$m yields $bk_x \approx 25$. The neutral curves turn back on themselves as $k_x$ increases, so sufficiently short wavelength disturbances always decay. Figure 3 shows a gray scale plot of a typical destabilizing concentration perturbation, which is clearly localized near the solid surface, as also seen in the experiments. Finally, if we

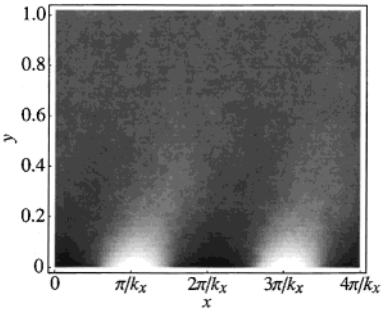

**Figure 3.** Concentration field of the destabilizing disturbance. $k_x = 2.0$, $b = 15$, $We = 6$, and $S = 0.01$. The pattern travels to the right with speed $c \approx \bar{u}_s$. Black indicates a lower concentration than the average, and white, higher.

replace the Navier boundary condition with its instantaneous version corresponding to monomer friction, we observe no instability, again consistent with the experimental observations.

To summarize, these theoretical results corroborate the experimental evidence presented by Mhetar and Archer[19] that the nature of the bounding surfaces plays an important role in the formation of enhanced concentration fluctuations in sheared polymer solutions.

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