MACROMOLECULES IN NONHOMOGENEOUS VELOCITY GRADIENT FIELDS:

RHEOLOGICAL AND DIFFUSION PHENOMENA

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INTRODUCTION

Kinematically nonhomogeneous* flows are common in rheological measurement situations and in flows of technological importance for polymers. Rheological anomalies1,2 and migration phenomena3-5 have been observed and/or speculated upon in these flows. Apparent "slip" at liquid-solid interfaces (for example, viscosity decreasing with channel size in small capillaries) has been reported in some such flows of macromolecular liquids. Much discussion has centered on the molecular origins of the observations leading to these reports.6,7 At least three identifiable alternatives are possible. 1. When large molecules are present in the liquid, they sample a larger portion of the flow. Thus, they "detect" in some sense the nonuniform velocity gradient field and this in turn affects the contribution they make to the fluid stress. 2. Macromolecules migrate away from the walls leaving a concentration-depleted layer which produces lower fluid viscosity in those regions and apparent "slip". Restricting our attention to infinitely dilute polymer solutions, where a macromolecule may plausibly, if not very accurately, be represented as a deformable ellipsoid, there are hydrodynamic forces which can cause particles to migrate across streamlines, either in unbounded fluid or in the vicinity of a wall.8,9 The details of the particle motion depend on particle shape and on the undisturbed kinematics of the flow. Speculation has been advanced that, quite apart from the above-mentioned hydrodynamically driven migration, macromolecules may move toward

*Nonhomogeneous in this paper refers to spatial variation of velocity gradients.
minimum velocity gradient regions in order to avoid the stretching and configurational entropy reduction imposed by the high velocity gradient regions, a thermodynamically-driven migration.\(^5,6\) In Poiseuille flow, such a migration, if it occurs, could account for apparent "slip". 3. The presence of the wall could affect the configurational distribution of the macromolecules, preferentially aligning them parallel to the surface of the wall. Brunn\(^10\) has analyzed such a situation and shown how apparent "slip" could arise. We point out that such an analysis depends crucially on the texture of the wall surface. (Brunn assumed that it had none.) If the size scale of any wall roughness elements is of order macromolecular size or larger, the situation and result will be quite different from the smooth wall result.

In this paper we explore the first two alternatives in more detail. Bead-spring model macromolecules with equivalent beads and linear zero-rest-length springs (i.e. Rouse and linear elastic dumbbell) will be the subjects of our analysis and discussion.\(^11\) We will show how the contribution to the viscosity of the Rouse model is different in a nonhomogeneous flow than in a homogeneous flow at the same velocity gradient level. We examine what sort of relative motions of macromolecule and solvent are predicted by introducing nonhomogeneous kinematics into the otherwise standard bead-spring kinetic theory. Nonuniform concentration profiles develop in some, but not all, nonhomogeneous flows. Parallels are pointed out between these results and those for other types of particles. Comparison between analysis and experiment on dilute solutions of macromolecules can be made in a few cases which we illustrate. This type of comparison makes for a novel way of testing molecular rheological models.

RESULTS ON BEAD-SPRING MODELS IN NONHOMOGENEOUS FLOWS

Consider the following expression of fluid velocity \(\mathbf{v}(\mathbf{r})\) at a point \(\mathbf{r}\) in terms of a Taylor series expansion about an origin at \(\mathbf{r} = 0\) [\(\mathbf{v}(0) = \mathbf{v}_0\)]:

\[
\mathbf{v}(\mathbf{r}) = \mathbf{v}_0 + \mathbf{r} \cdot \nabla \mathbf{v}_0 + \frac{1}{2} \mathbf{r} \cdot \nabla \mathbf{v} \mathbf{v}_0 + \ldots
\]

For homogeneous flows the last and all higher order terms are zero. The kinetic theory of bead-spring models in homogeneous flows is extensively developed. The Rouse model and its configurational vectors is illustrated in Figure 1. (The dumbbell is the two bead case so that \(\mathbf{r}_2 - \mathbf{r}_1 = \mathbf{0}\) \(\equiv \mathbb{R}\).) The standard starting point for bead-spring kinetic theory is the force balance about the \(i\)th bead (accelerations assumed negligible):

\[
0 = -\zeta [\dot{x}_i - \mathbf{v}(\mathbf{r}_i)] - kT(\partial / \partial x_i) \mathbf{v} \mathbf{v} + \mathbf{F}_i
\]

\[(2)\]