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Multiscale modeling of polymer flow-induced migration and size separation in a microfluidic contraction flow

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ABSTRACT

We study polymer migration in a periodic pressure-driven sudden contraction-expansion flow with contraction dimension comparable to the polymer radius of gyration, for which several polymer migration mechanisms can be important: (1) sieving by the thin channel of polymers too large to easily enter them; (2) deformation-hydrodynamic coupling, including wall-hydrodynamic interaction, which causes polymers to drift away from the walls towards the center of the channel; (3) streamline-curvature-induced migration, in which polymers traveling along curved streamlines migrate towards the center of curvature; and (4) depletion-convection coupling, in which depletion layers in thin channels are convected across wide side chambers, creating a one-sided diffusion barrier that leads to depletion from the side chamber. We use both Stochastic Rotation Dynamics (SRD), which includes hydrodynamic interaction (HI), and simple Brownian dynamics (BD), with HI omitted and flow field given by finite element analysis. The similarity in results from SRD and BD at Weissenberg number Wi less than 10 (where Wi is based on the shear rate in the narrow region of the contraction channel) shows that HI (Mechanism 2) has only a weak effect on polymer migration in our tight geometry. At Wi > 1, the polymer migrates towards the centerline in the wide region, due mainly to streamline-curvature-induced (SCI) migration (Mechanism 3), but also to depletion-convection-induced migration (Mechanism 4). And we demonstrate these two mechanisms more explicitly in a pressure-driven flow in a grooved channel that is significantly wider than the polymer. SCI migration dominates in the contraction geometry, and produces a migration velocity proportional to Wi^2. Using the central limit theorem, we accurately predict the position and width of a band of polymer passing through N periodic contractions, thereby demonstrating the potential for SCI migration as a mechanism of size separation in a multi-step planar contraction channel. We find that the best separation is achieved at Wi around 2, where SCI migration has the greatest resolving power between polymers of different size. We also find that sieving (Mechanism 1) is dominant at low Wi less than unity, where the chains with large radius of gyration are delayed in their entry to the thin channel, relative to shorter polymers. This sieving separation mechanism differs from that of size-exclusion chromatography which yields faster migration by the shorter chains. Our strategy of combining simulation methods with the central limit theorem could also be used to predict separation efficiencies of a wide variety of polymers and colloids in microfluidic geometries.

1. Introduction

Owing to recent advances in micro-fabrication technology, microfluidic devices can be fabricated inexpensively and reliably with tailored complex geometries. These devices commonly rely on pressure-driven or electrokinetically-driven flows to stretch polymer chains far from equilibrium. Such geometries provide a powerful platform to study non-equilibrium polymer dynamics, polymer-solvent interactions, and macromolecular transport phenomena. A comprehensive understanding of polymer dynamics in micro-fluidic devices is important for many potential applications, including polymer separation.

The most conventional and widely used polymer separation technique is size-exclusion chromatography (SEC), which was first developed in 1955 by Lathe and Ruthven [1]. A typical SEC method is gel permeation chromatography (GPC), which can be traced back to Moore [2]. GPC techniques separate based on polymer size or radius of gyration. The flow rates in GPC columns are typically too small to deform the polymer molecules; that is the

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Weissenberg number Wi, which is the characteristic shear rate multiplied by the polymer relaxation time, is usually very small, much less than unity ($<10^{-2}$) [2].

Meanwhile, techniques for separating biological molecules of different sizes have been developed in parallel with the evolution of molecular biology. Decades ago, Dill and Zimm [3,4] proposed a rheological separation method for DNA molecules based on the radial migration of the DNA that occurs when DNA solutions are subjected to flow between rotating concentric cylinders or cones. This radial migration results from a coupling between the polymer deformation and the streamline-curvature of the flow field.

Very recently, Faivre et al. [5] reported that size exclusion of cells from the wall can be enhanced in a contraction/expansion geometry, and proposed an application of this for separation of red blood cells from the suspending plasma. This effect actually results from the convection of a wall depletion zone across the wide channel of the contraction geometry, as discussed in more detail later.

In this paper, we study polymer migration and separation in a periodic planar contraction channel, using two mesoscopic simulation methods. The first method is Stochastic Rotation Dynamics (SRD), which is a particle-based method of solving for polymer and fluid dynamics simultaneously, including the effects of hydrodynamic interaction (HI) within individual chains, between different chains, and between chains and the walls of the geometry. The SRD method is briefly described below in Section 2. The second method is Brownian dynamics (BD), in which we use the flow field in the absence of polymer, drawn either from a finite element solution or from SRD simulations, as the convection term in a Langevin differential equation that, as used here, neglects all hydrodynamic interactions and also neglects the modification in the flow field produced indirectly by the polymer molecules through the momentum balance equation. In Section 3, by comparing results from SRD with those from Brownian dynamics (BD) for a single polymer chain without HI, we show that HI has only a weak effect on the polymer dynamics in our geometry for the flow rates considered, and that BD simulations without HI predict the polymer migration accurately. We investigate in Section 4 the migration mechanisms, which determine the spatial distribution and residence time distribution of the polymer, and show that the polymer migration toward the center of the channel observed in both SRD and BD simulations is due to the large curvature of the contraction flow streamlines on the scale of the polymer size, and to a lesser extent by the convection of a wall depletion zone, as alluded to above. To demonstrate these phenomena more clearly, we examine polymer migration in a second flow, that of a pressure-driven flow in a grooved channel that is significantly wider than the polymer. Finally, in Section 5, we first show that the standard deviation of the residence time distribution in the contraction geometry can be used to determine the polymer dispersivity using the theory of Taylor, and, by using the central limit theorem, we compute the accumulated polymer separation that can be achieved in a periodic contraction geometry. We summarize our results in Section 6.

2. Migration of a single polymer chain with HI, simulated using SRD

In this section, we investigate migration of single polymer chains with HI using Stochastic Rotation Dynamics (SRD). SRD is an especially promising method for situations in which fluctuating or time-dependent HI is potentially important, but the geometry is so complex that Brownian dynamics with full HI is difficult to implement. Earlier studies [6,7] have shown that SRD can accurately capture HI in the relaxation dynamics of an isolated chain in the absence of flow. Studies [8,9] have also shown that SRD captures the HI between the solid boundaries and the polymer in shearing flows. In principle it should also capture the influence of polymeric stresses on the flow field.

2.1. Algorithm

In SRD simulations, the fluid is modeled by N solvent beads. The polymer is, as usual, modeled as a chain of N_b polymer beads connected by $N_s = N_b - 1$ springs. The algorithm consists of two steps: a *streaming* step followed by a *collision* step after a discrete time step Δt, which is referred as the collision time. In the *streaming* step, the solvent/polymer beads simply follow Newton's law, with the positions $\mathbf{r}_i$ and velocities $\mathbf{v}_i$ determined by integration using the velocity Verlet algorithm:

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t)\Delta t + \frac{1}{2}\frac{\mathbf{f}_i(t)}{m}\Delta t^2 \tag{2.1}$$

$$\mathbf{v}_i(t+\Delta t) = \mathbf{v}_i(t) + \frac{1}{2}\frac{\mathbf{f}_i(t)+\mathbf{f}_i(t+\Delta t)}{m}\Delta t \tag{2.2}$$

where $\mathbf{f}_i$ is the force exerted on the i-th bead and m is the bead mass. The masses of the solvent and polymer beads are not the same, and the mass ratio is chosen to optimize transport of momentum from the polymer to the solvent so that hydrodynamic interactions are most accurately captured [7]. Usually the polymer beads are more massive than the solvent beads, so that the integration time step for the polymer beads can be the same as Δt without losing accuracy at the relatively low shear rate applied in SRD simulations in this paper. In the *collision* step, the solvent/polymer beads are sorted into the cells of a d-dimensional cubic lattice (where typically $d = 3$) with lattice spacing a. The beads exchange momentum following a "collision" rule in which their velocities are updated after the collision as follows:

$$\mathbf{v}_i(t^+) = \mathbf{v}_{\mathrm{CoM},i}(t^-) + \mathcal{R}(\alpha)\cdot\left[\mathbf{v}_i(t^-) - \mathbf{v}_{\mathrm{CoM},i}(t^-)\right] \tag{2.3}$$

where $\mathcal{R}(\alpha)$ is a stochastic rotation matrix which rotates the velocity vector in a random direction through an angle α, $t^{+/-}$ refers to the time after/before the collision and $\mathbf{v}_{\mathrm{CoM},\,i}$ is the center of mass velocity of all beads in the collision cell where the i-th bead is located. This collision rule ensures that the kinetic energy and linear momentum in the cell are conserved during the collision. Therefore in SRD, the flow field is discretized with a resolution determined by the cell size a. After each *collision* step, a thermostat is applied to adjust the local temperature of each collision cell to the imposed temperature [8,10]. To guarantee Galilean invariance over long runs, a random shift of particles before executing the *collision* step has to be performed, and after the *collision* step, the particles are shifted back to their original positions [11].

2.2. Geometry and boundary condition

The geometry of a planar contraction channel in our simulation is shown in Fig. 1. The simulation box has dimensions $L_1 \times L_2 \times L_3$ where L_3 is the out-of-plane dimension, not shown in Fig. 1. The lower and upper wide chambers are connected by a narrow channel with width w and length h. A constant acceleration $\mathbf{g}$ is applied along the y direction on each solvent bead to drive the flow.

Along the y and z directions, we apply periodic boundary conditions; thus the geometry between the dashed lines shown in Fig. 1 is extended infinitely along those directions. Therefore we are actually simulating a periodic contraction channel. The flow field is invariant along the z-direction and thus two-dimensional, although in SRD we solve the problem in three dimensions to allow isotropic random velocity fluctuations from Brownian motion. Along the walls, we apply a no-slip boundary condition. To realize the no-slip boundary condition, in the *streaming* step the bounce-