

Flow-induced migration of polymers in dilute solution

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We investigate the lateral migration of a confined polymer under pressure driven and uniform shear flows. We employ a hybrid algorithm which couples point particles to a fluctuating lattice-Boltzmann fluid. We observe migration in both uniform shear and pressure driven flows, supporting the idea that migration is driven by a combination of shear and hydrodynamic interactions with the wall, rather than by the shear gradient. Recent numerical and theoretical investigations have suggested that polymers migrate toward the centerline when hydrodynamic interactions are included, but our simulations show that in sufficiently narrow channels there is a reversal of direction and the polymers move toward the wall. © 2006 American Institute of Physics. [DOI: 10.1063/1.2186591]

The transport of polymer solutions through microfluidic devices depends on polymer conformation and the center-of-mass distribution across the channel. In the absence of flow, steric repulsion between a globular polymer and the confining walls creates depletion layers on the order of the radius of gyration in free solution, R_g .¹⁻³ In a pressure-driven flow, the shear rate stretches and aligns the polymer along the flow direction, reducing its configurational entropy. Thermodynamic arguments therefore predict that the polymer will migrate to the centerline where the local shear rate is minimized,^{4,5} creating an apparent slip at the boundaries.⁶ The thickness of the depletion layer is observed to increase in a pressure-driven flow,^{7,8} which also implies a net migration of the polymer toward the channel center. By contrast, it has usually been assumed that the depletion layer thins in a uniform shear flow due to reduced steric hindrance between a stretched polymer and the boundary.⁶

Recent theory and simulations have underlined the importance of hydrodynamic interactions in describing polymer migration. Kinetic theories^{9,10} attribute lateral migration to the asymmetry of the hydrodynamic interactions between a stretched polymer and a planar no-slip boundary, which produces a net drift away from the wall. Computer simulations,^{11,12} including full hydrodynamic interactions, showed that the polymer migrates toward the channel centerline in pressure driven flows. On the other hand, simulations neglecting hydrodynamic interactions between polymer segments^{13,14} find migration toward the walls.

There are qualitative differences between the predictions of kinetic and thermodynamic theories of migration. In particular, in a uniform shear flow, no migration is expected on thermodynamic grounds since the polymer extension is independent of position. However, the kinetic theories predict migration toward the channel center in a uniform shear flow as well as in Poiseuille flow. To distinguish between these theories, we have used numerical simulations, with hydrodynamic interactions, to calculate the direction and extent of the lateral migration in pressure-driven and uniform shear

flows. We discovered that migration can occur in both directions, depending upon the degree of confinement; in wide channels the polymers move toward the center, whereas in narrow channels they move toward the walls. The polymer distribution is quantitatively different in shear and Poiseuille flows, but the direction of migration is the same in both cases for the same degree of confinement. This suggests that the primary driving force for migration is hydrodynamic drift from the confining walls, driven by the shear rate rather than its gradient.^{9,10}

The polymer is modeled by beads connected by stiff linear (Fraenkel) springs of finite rest length, each spring representing a Kuhn length. The dynamics of the fluid phase is obtained from a fluctuating lattice-Boltzmann model,^{15,16} which leads to Navier-Stokes equations with local fluctuations in stress.¹⁷ The polymer motion is coupled to the surrounding fluid using a frictional force, based on the difference between the bead velocity and the local fluid velocity.^{18,19} The force exerted by the beads is redistributed to the surrounding fluid nodes so that the total momentum of the coupled particle-fluid system is conserved. Extensive numerical tests have shown that we obtain Oseen level hydrodynamic interactions between beads and between beads and the solid boundaries.¹² In addition, there is a DLVO-like (Derjaguin-Landau-Verwey-Overbeek) repulsion between pairs of beads and between beads and confining walls. The excluded volume sphere has a radius of approximately $b/2$, where b is the distance between beads. The fluctuating lattice-Boltzmann approach has computational advantages over Brownian dynamics,²⁰ which has been the primary numerical method for simulating polymer solutions. First, the computational cost scales linearly with the number of beads, allowing for simulations of chains in excess of a thousand beads.¹² Second, complex geometries, such as porous media or micro devices, can be introduced by mapping the solid surfaces onto the lattice, without having to introduce a new Green's function for each specific geometry.

We study a single polymer chain, confined between two flat plates separated by a gap H . Periodic boundaries are used in the other two directions and the periodic length in these

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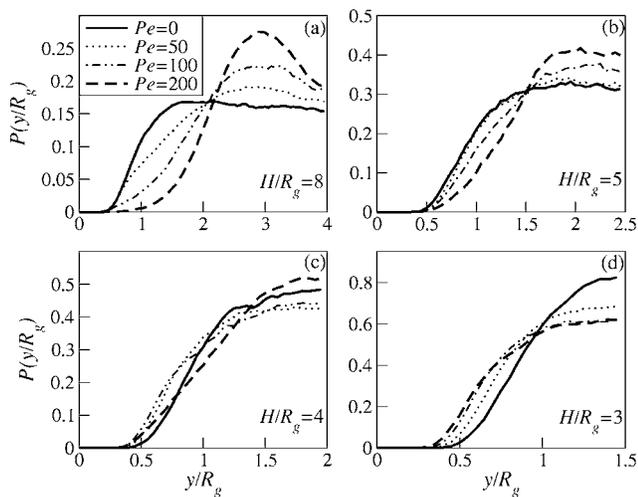


FIG. 1. Center-of-mass distribution for pressure driven flow as a function of Peclet number and channel width. Results are for $N=16$. The distributions are normalized such that $\int_0^{0.5H} P(y/R_g) dy/R_g = 1$. Due to the symmetry of the system, the distribution is plotted up to $0.5H$. The bounding wall is at the origin.

directions is sufficiently large ($L=2H$) that the hydrodynamic interaction between distant images is negligible.¹² The polymer chains are discretized into N beads with most simulations reported in this Letter using $N=16$. Longer chains ($N=32-64$) are used to verify that the equilibrium radius of gyration (R_g) and the free solution center-of-mass diffusion coefficient (D) are the only important parameters, and that the level of discretization of the chain is sufficient. A pressure driven flow was created by applying a uniform force to the fluid, whereas a uniform shear flow was generated by relative motion of the bounding walls. The Peclet number is based on the shear rate and the equilibrium radius of gyration, $Pe = \dot{\gamma} R_g^2 / D$, in both cases. In a uniform shear flow, the shear rate is constant across the channel and given by $\dot{\gamma} = \Delta V / H$, where ΔV is the velocity difference between the walls. In Poiseuille flow, the mean shear rate, $\dot{\gamma} = 2V_{\max} / H$, is used, where V_{\max} is the centerline velocity. The degree of confinement is characterized by the ratio of the gap width to the equilibrium radius of gyration of the polymer chain, H/R_g . For the smallest confinement ratio used in this work, $H/R_g=3$, the polymer coil remains free to rotate in the channel. The simulations are run for a sufficiently long time that a polymer, under equilibrium conditions, would diffuse a distance of at least $50H$. The statistical errors in the figures are less than 5% in the bulk region.

Simulation data for wide channels ($H/R_g > 5$), shown in Fig. 1(a), confirm that polymer chains migrate toward the channel centerline in a pressure driven flow. The mechanism for this migration is not entirely agreed upon. The thermodynamic theory argues that the shear gradient drives the polymer toward low shear regions to attain maximum possible configurational entropy.^{4,5} We have tested this assumption by repeating the simulations in a uniform shear flow. The simulations show that the polymers still migrate toward the centerline [Fig. 2(a)], indicating that a shear gradient is not required for migration. However, due to symmetry, no migration would occur in an unbounded shear flow; therefore

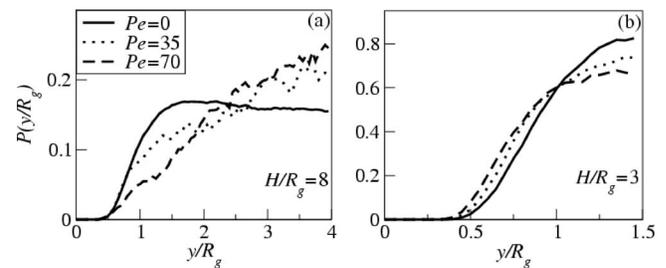


FIG. 2. Center-of-mass distribution for uniform shear flow as a function of Peclet number and channel width. Results are shown for $N=16$. The distributions are normalized such that $\int_0^H P(y/R_g) dy/R_g = 1$.

shear cannot by itself explain the migration either. Hydrodynamic arguments suggest that the tension in the sheared polymer generates a flow away from the wall, due to the asymmetry of the hydrodynamic interactions between a pair of beads and a planar boundary.^{8,10} A kinetic theory¹⁰ of a dumbbell near a planar wall predicts migration toward the channel center in both uniform shear and Poiseuille flows when hydrodynamic interactions are included, in agreement with simulations. A dumbbell is much less flexible than the multibead chains used in our simulations. Moreover, the hydrodynamic center of a dumbbell is also its center of mass, so an external torque leads to a pure rotation rather than tumbling. Despite these limitations, the kinetic theory qualitatively explains the key features observed in simulations of flow in wide channels.

A feature of the polymer distribution in wide channels is a symmetric double peak [Fig. 1(a)] observed at high Peclet numbers.^{11,12} This is a consequence of the interplay of hydrodynamic forces with a spatially varying diffusivity.¹⁰ A sheared polymer undergoes significant extension and alignment along the flow axis [Fig. 3(a)], hence the diffusivity along the confinement direction is reduced with increasing shear rate. The competition between the spatially varying diffusivity and the hydrodynamically induced migration leads to the double peak in the polymer distribution function $P(y/R_g)$ at high Peclet numbers. Kinetic theory¹⁰ would also

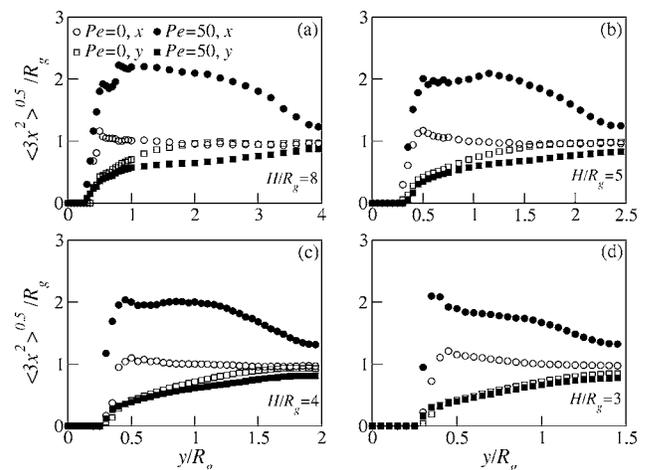


FIG. 3. Components of the radius of gyration along the flow, $\langle x^2 \rangle$, and confinement, $\langle y^2 \rangle$, axes. Results for chains of length $N=16$ are shown at two different Peclet numbers, normalized by $R_g = (\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle)^{0.5}$.

predict a double peak in the distribution function at high Peclet numbers if a spatially varying diffusivity was used in the model.

Figure 1(a) shows that the peak position in the channel is independent of Peclet number. Empirically, we observe that the position coincides with the polymer reaching about 90% of its maximum extension in the flow, as seen by comparing Figs. 1(a) and 3(a). The mobility along the confinement direction, which is a logarithmic function of the aspect ratio, changes little with the marginal additional extension that occurs in the vicinity of the walls. Consequently, the driving force away from the centerline, which is proportional to the gradient of the diffusivity,¹⁰ diminishes very quickly beyond this point. In a uniform shear the distribution has at most a single maximum, since the diffusivity is essentially constant.

As the channel width is reduced with respect to the size of the polymer ($H/R_g=5$), the migration toward the center decreases [Fig. 1(b)]. The extension data [Fig. 3(b)] shows that the polymer shape is similar to that in the wider channels, indicating that the reduced migration is a result of the smaller hydrodynamic force. At a channel width of $H/R_g=4$, migration toward the center is only observed for the highest Peclet number. At lower Peclet numbers the migration is toward the walls [Fig. 1(c)]. In still tighter confinement ($H/R_g=3$), migration is toward the walls at all Peclet numbers. We observe a similar outward migration in uniform shear flow [Fig. 2(b)], although the extent of the migration is lower than in Poiseuille flow. Migration toward the channel walls is further supported by results for the second moment of the center-of-mass distribution (see Ref. 11, Fig. 6). Nevertheless, the evidence for outward migration in that work is by no means unequivocal; indeed the authors conclude that the polymer always migrates toward to the center if hydrodynamic interactions are included.

Polymer kinetic theory¹⁰ accounts semiquantitatively for migration in wide channels, correcting earlier work⁹ based on similar ideas. The key migration mechanism, namely the drift from the wall induced by a sheared polymer, has been validated in previous work,^{11,12} and confirmed in the present study. However, the hydrodynamic interactions in the channel were approximated by superposing the flow fields generated by each wall. This is valid when the polymer is much closer to one wall than the other,^{21,22} but in a narrow channel the Green's function for a slit must be used. In narrow channels, superposition overpredicts the extent of the hydrodynamic interactions, and therefore the degree of migration toward the center. In reality, the hydrodynamic forces that cause migration toward the center are screened by the closely spaced boundaries. We have found that the polymer diffusion coefficient along the confinement axis shows a crossover to Rouse-like scaling in the range $8 > H/R_g > 4$, which supports the screening hypothesis. Previous work^{12,23} demonstrates the effect of confinement on the diffusion of polymer chains which closely follows the theoretical scaling.²⁴ Moreover, computer simulations^{13,14} which neglect intrabead hydrodynamic interactions also show migration toward the walls, independent of the channel size.

The shape of the polymer may also play an important role in the reversal of the direction of migration. The exten-

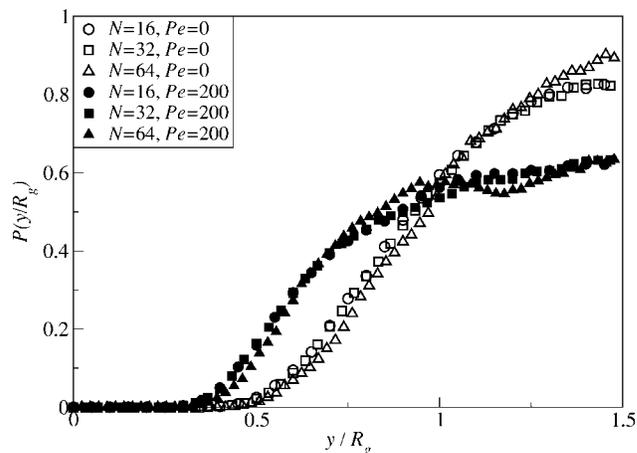


FIG. 4. Center-of-mass distribution for different levels of discretization of the polymer in a tightly confined channel, $H/R_g=3$. The distributions are normalized such that $\int_0^1 P(y/R_g) dy/R_g = 1$.

sion curves [Figs. 3(c) and 3(d)] suggest that equilibrium conformations become distorted within $1.5R_g$ of the walls. Therefore highly confined polymers are anisotropic even at equilibrium and there is no bulk region where the polymer assumes its unconfined globular form. This indicates an analogy with anisotropic rigid particles which also migrate toward the boundaries under flow. This migration is due to the particle aligning in the direction of flow, thereby reducing the diffusivity in the confinement direction.^{25,26} Alignment also reduces the thickness of the depletion layer as a result of a reduced steric force.

The extension of the polymer and the distribution of polymer conformations depends on chain length, especially at high Peclet numbers.²⁷ Resolution of such conformational changes may require a finer discretization of the polymer chain. To assess the accuracy of the results presented, we have repeated some of the calculations using chains of 32 and 64 beads. A finer discretization allows for more conformational flexibility and at the same time improves the accuracy of hydrodynamic interactions.¹² We scale the system volume and pressure gradient to maintain constant confinement ratio and Peclet number, which results in a finer discretization of the fluid grid in comparison to the radius of gyration of the polymer. Longer chains at constant Peclet number also result in lower Reynolds numbers, inversely proportional to their equilibrium radius of gyration. The Reynolds numbers used in this Letter range from 0.6 to 2.3 for the shortest chains in the largest channels and 0.15 to 0.5 for the longest chains. The results shown in Fig. 4 indicate that the level of discretization with $N=16$ is sufficient for this problem. Longer chains show identical distributions within the statistical errors.

In this Letter we have shown that the extent and direction of the migration, in both uniform shear and Poiseuille flow, depends on the degree of confinement as well as the Peclet number. The dynamics in the highly confined channels differ significantly from that in wider channels, where hydrodynamic interactions are stronger. The hydrodynamic screening from the walls reduces the migration toward the centerline at high confinements, and alignment in the flow can then

produce migration toward the walls, similar to what is observed in simulations without intrabead hydrodynamic interactions.¹⁴ We have confirmed that the primary mechanism for migration toward the centerline is a combination of shear and hydrodynamic interactions between the walls and the beads.^{8–10} We also found that the spatially varying diffusivity produces a double maximum in Poiseuille flow,^{11,12} but not in a uniform shear flow. Systematic experiments in comparable parameter regimes would be an interesting confirmation of the results of this study and other recent simulations.^{11,12}

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