CHAPTER 4

Drift velocity of single ideal polymer chains in microfluidic capillaries†

We use a mesoscopic simulation technique to study the transport of polymers in dilute solution flowing through a cylindrical tube. The simulations use an explicit solvent model to include all the relevant hydrodynamic couplings and a coarse grained ideal chain model for the polymers (appropriate for systems near the theta temperature). For the interactions between the solvent and the tube wall we use a method that ensures continuity of the stress at the interface. We show that the results for the polymer drift velocity are independent of the degree of coarse graining. Further, for the case where the size of the chains is small but not negligible compared to the tube radius, our results are in excellent agreement with experiment. However, they also show that in this regime the “accelerated” drift, relative to the average solvent flow velocity, is described by the steric effect of the tube wall excluding the polymer centre-of-mass from sampling the full cross-section of the tube. Hydrodynamic interactions have little influence in this regime. Consequently, the agreement between experiment and theories that approximate the former but include the latter is fortunate. When the undisturbed polymer radius approaches or exceeds the tube radius, the hydrodynamic interactions do have a significant effect. They reduce the drift velocity, in qualitative agreement with theoretical predictions. The accelerated drift still approaches the maximum value one would expect based on a Poiseuille flow but more slowly than if one neglects hydrodynamics. Based on our results we propose an empirical fit that accurately describes data in the intermediate regime. We conclude the chapter with a short discussion on the nature of ordering of polymer chains at higher flow velocities.

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4.1 INTRODUCTION

With the development of novel fabrication techniques it is now possible to construct microscopic flow devices. Consequently, the behaviour of fluids on this micrometer scale, micro-fluidics, is topical. Computer simulation techniques capable of describing these systems are a useful complement to experiment and theory because of their predictive power and the detailed microscopic information they provide. In this chapter we apply such an approach to perhaps the simplest non-trivial problem. That is, a dilute polymer solution flowing in a tubular capillary.

A separation technique, hydrodynamic chromatography, is based on this system.\(^{104,105}\) Basically, it works as follows. At low Reynolds numbers the flow profile of a pressure-driven flow through a cylindrical tube is parabolic. Solvent molecules located near the centre therefore have a higher velocity, on average, than those close to the wall. At the wall itself the average solvent velocity approaches zero. Due to steric hindrance, the centre-of-mass of larger molecules cannot approach the walls as closely as those of the smaller solvent particles. Because of this “depletion” effect large molecules, polymers for example, spend less time in the low velocity region close to the wall. Their average drift velocity is therefore higher than the average solvent flow velocity. Because the magnitude of this “accelerated” drift velocity depends on the molecular size, solutes of different size elute at different times. This assumes of course that the solute molecular size is not small compared to the capillary radius (otherwise the effect is negligible). Consequently, narrow capillaries are required for efficient separation. For polymeric solutes, proteins for example, this typically means capillaries not larger than a micron.\(^{106,107}\) Larger capillaries are also possible (up to the order of a centimeter).\(^{108}\) However, in that case the capillary must be packed in some way, using small nonporous particles for instance. In Fig. 4.1 we show a schematic representation of hydrodynamic chromatography.

In the micron range, the solvent flow rate is typically limited to the regime where both the Reynolds number for the flow and the Péclet number for the solute is low. The former means that fluid inertia is negligible. The latter implies that, in the case of polymeric solutes, the conformational distribution is not significantly perturbed from equilibrium by the flow. Under these circumstances it makes sense to estimate the solute drift velocity \(V_p\) in the following simple manner. The equation describing the (radially symmetric) velocity of a solvent at low Reynolds number at a distance \(r\) from the centre
of a tube is known:102

\[ V_s(r) = \frac{\tilde{F}R^2}{4\eta} \left[ 1 - \left( \frac{r}{R} \right)^2 \right]. \tag{4.1} \]

Here \( \tilde{F} \) is the force density acting on the fluid, \( R \) is the radius of the capillary and \( \eta \) is the shear viscosity. The solute is now represented only by its centre-of-mass. This is further assumed to drift with the unperturbed solvent flow velocity (Eq. 4.1). This being the case, the drift velocity \( V_p \) is

\[ V_p = \frac{1}{\pi R^2} \int_0^R 2\pi r P(r)V_s(r) dr, \tag{4.2} \]

where \( P(r)dr \) is the probability that the centre of mass is located a distance \( r \) from the centre of the tube. To calculate \( V_p \) we only need to know \( P(r) \). One approximation is to simply say that the polymer cannot approach within a distance \( R_p \) of the wall, but otherwise its distribution is uniform. In this case, Eq. 4.2 yields

\[ \frac{V_p}{V_s} = 1 + 2\left( \frac{R_p}{R} \right) - \left( \frac{R_p}{R} \right)^2, \tag{4.3} \]

where \( V_p/V_s \) is the solute velocity relative to the mean solvent velocity \( V_s \). This approach is “termed” the quadratic model. More complicated models also take into account the fact that if the analytes are rigid they will rotate due to the velocity gradient. In theory, this hydrodynamic effect modifies the drift velocity such that for “refined quadratic” theories

\[ \frac{V_p}{V_s} = 1 + 2\left( \frac{R_p}{R} \right) - C\left( \frac{R_p}{R} \right)^2, \tag{4.4} \]

where \( C \) is a model dependent value that is not unity, as in the quadratic
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In general, treating the solute as a solid rigid sphere results in lower estimates for $C$ (starting at $C = 2.33$) than treating it as a porous rigid sphere (starting at $C = 4.03$). The consensus is thus that hydrodynamic interactions reduce the "accelerated" drift velocity. However, by how much depends on the method used to estimate it.\textsuperscript{104,109–111}

While this simple approach gives a quantitative estimate of the drift velocity, it has some limitations. Firstly, a polymer is flexible so the definition of a particle radius is not specific. The quantity $R_p$ is therefore to some extent an adjustable parameter. Further, if the polymer is large compared to the capillary then it cannot reasonably be regarded as spherical. Nonetheless, in the $R_p/R \ll 1$ regime the refined quadratic model for a solid sphere, treating the sphere radius as the polymer radius of gyration, gives a very good correlation with experimental measurements.\textsuperscript{111} One might expect that a permeable sphere is a better representation of a polymer. Surprisingly, the prediction of the refined quadratic model for a permeable sphere compares less well with experimental results. Because the refined quadratic model still uses an approximate form for the solute probability distribution it is impossible to deduce whether deviations from the model are because it neglects hydrodynamic effects or because it simplifies $P(r)$. One way to resolve this question is to use the correct $P(r)$ for a polymeric solute in Eq. 4.2 and compare with simulations that include the hydrodynamics. This is one of our aims here.

Because polymers are very large molecules their dynamics in solution are slow on a molecular timescale. This makes their influence on the solvent complex. Simulating such a system with thermal fluctuations and all the hydrodynamic couplings is a non-trivial problem. An elegant method for doing so is Brownian dynamics (BD). This method treats the solvent as a continuum and its influence is included implicitly through the configurationally dependent mobility matrix.\textsuperscript{39} Recently it was applied to study the dynamics of single DNA molecules confined in a microfluidic capillary.\textsuperscript{42–44} However, using BD also has some drawbacks. Including a solid/liquid interface within the framework of BD is not straightforward (although Jendrejack et al. show that it is feasible if one uses another method to calculate the contribution of the solid geometry to the mobility\textsuperscript{42}). Moreover, because of the long range nature of the hydrodynamic interactions, the scaling of the computational work required with increasing number of polymers is dramatic without the use of a sophisticated algorithm. This is not relevant for the single polymer system we study here, but we choose a methodology that, in principle, extends straightforwardly to the many polymer case. For these reasons we use an explicit solvent model. That is, the hydrodynamic couplings arise as a result of the motion of solvent particles. There are a number of techniques
for modelling a simplified solvent using particles. One method is to couple model polymers to a discretized solution of the fluctuating Boltzmann equation. Stochastic rotational dynamics has also been used to study polymer dynamics. This method works with particles that move in continuous space and interact by a rule that conserves energy. Consequently, out of equilibrium a thermostat is necessary to suppress heating in the system. Similarly, Dissipative Particle Dynamics (DPD) uses particles moving in continuous space. A “built in” thermostat sets the temperature. This thermostat is Galilean invariant and conserves momentum, so hydrodynamic behaviour is recovered. DPD particles usually interact through a soft repulsive potential. However, if one is just interested in the hydrodynamics, the repulsive potential is an unnecessary complication. If it is omitted, the model solvent is an ideal gas. Nevertheless one can still recover realistic fluid behaviour by requiring that the ratio of the viscosity to the diffusion coefficient (the Schmidt number, $Sc$) significantly exceeds unity. Here we choose to use a thermostat closely related to the DPD thermostat (in that it recovers hydrodynamic behaviour), the Lowe-Andersen (LA) thermostat.

In this chapter we describe how we develop this methodology to study numerically polymer drift in a capillary. The questions we address are firstly, how well can the simulations describe what is observed in experiment? Secondly, to what extent can the simplified theories above adequately describe polymer drift in a capillary when $R_p/R < 1$? Thirdly, what do we expect for the regime $R_p/R > 1$, where quadratic models break down.

### 4.2 METHODOLOGY

One of the questions we will investigate in this chapter is how accurate the quadratic model is if we allow for the non-uniform distribution of the centre-of-mass and the deformation of the polymer chain, when the polymer is not small compared to the width of the capillary. That is, if we use Eq. 4.2 but compute $P(r)$ numerically. The procedure is as follows: configurations of ideal chains were generated and then inserted randomly in the tubular geometry. If the chains overlap the tube wall, the configuration is rejected, otherwise the position of the centre-of-mass is taken into account for the calculation of $P(r)$. Because the acceptance rate drops dramatically when the size of the polymer is very large compared to the size of the tube it is increasingly difficult to obtain accurate results and more advanced techniques are required. However we found this method adequate for our purposes here. It is basically a simple Monte Carlo algorithm, therefore we refer to it as MC.
Computationally, as noted above, the full dynamic simulations are more involved. The approach we use to address the various aspects of the problem are itemized below.

4.2.1 POLYMER MODEL

For the polymer, we take the simplest plausible model: an ideal chain. Adjacent beads are connected via a harmonic potential:

\[ U = k_B T \sum_{i=1}^{N_b-1} \frac{3}{2 b^2} (\vec{r}_i - \vec{r}_{i+1})^2, \]  

with \( U \) being the energy, \( k_B \) is Boltzmann’s constant, \( T \) the temperature, \( N_b \) the number of beads in the polymer, \( b \) the Kuhn length and \( \vec{r}_i \) the position of particle \( i \). Using this form of the potential, the distribution of the end-to-end vector is Gaussian for any number \( N_b \) of beads. The beads do not interact, so this model is only valid for a polymer at or near to the theta temperature. However, in principle, this restriction can be relaxed.\(^4^2\)

Lowe et al. have shown that for a specific choice of the hydrodynamic radius of a polymer bead \((a = k_B T/6\pi\eta D_0, \text{ where } D_0 \text{ is the diffusion coefficient of a single bead})\) over the Kuhn length we can obtain long polymer scaling \((D/D_0 \propto 1/\sqrt{N_b})\), even for a finite number of beads. In this sense the hydrodynamics of the polymer are coarse grained. To achieve this the ratio \(a/b\) should be set such that \( b = 4.04a \). In this case \( a = 0.21r_c \) (with \( r_c \) being the cut-off radius) which defines the Kuhn length \( b = 0.84r_c \).\(^9\)

4.2.2 SOLVENT MODEL

The LA thermostat method works as follows. Each time step \( \delta t \) all pairs of particles within a certain cut-off radius \( r_c \) have a certain probability \( \Gamma \delta t \) of undergoing a “virtual” collision. A virtual collision involves generating a new relative velocity from the Maxwell-Boltzmann distribution along the line of centers. Since the forces act along this vector, angular momentum is conserved. The new absolute velocity is specified such that linear momentum is also conserved. Additionally, because only relative velocities are involved the method is Galilean invariant. Taken together, these properties mean that on long enough time and length scales full non-linearized hydrodynamic behaviour is recovered.\(^7\)
There are two solvent parameters to specify. Firstly, we have to set the cut-off radius $r_c$. It must of course be larger than the interparticle separation or the particles will hardly interact with each other. However, for computational reasons a large value for the cut-off radius is inconvenient. Here we choose that value such that on average each solvent particle interacts with 8 others. Secondly, we have a Knudsen-like parameter, $\Lambda = \sqrt{\frac{k_B T}{(\Gamma^2 r_c^2 m)}}$, that characterizes the ratio of the typical decay time for relative velocities to the time it takes ballistic motion to move a particle a distance $r_c$. Here $m$ is the mass of a solvent particle. Unsurprisingly, to reproduce hydrodynamics on short time and length scales this parameter should be small. Similarly, it must be small to satisfy $Sc \gg 1$. We choose $\Lambda = 0.03$ which sets $Sc \sim 75$. We deliberately do not choose a smaller value for the following reason. An ideal gas solvent is generally more compressible than a real solvent. However, we will restrict ourselves to low velocities well below the speed of sound $C_s$, so the Mach number (the ratio of the average flow velocity and the speed of sound) is much less than unity. This being the case, one expects that the compressibility of the solvent is irrelevant. Lowering $\Lambda$ decreases $C_s$ and consequently restricts the maximum flow velocities. The value we use is a trade-off between the requirement for high Schmidt numbers and relative incompressibility.

There seems to be some confusion as to the regime where this methodology applies. Here we would like to point out that using either the LA method or DPD, $Sc$ can be varied freely. This is not an inherent property of the “Lowe” fluid. It is simply that in this regime the LA method is advantageous because it allows significantly longer time steps than DPD.

### 4.2.3 SOLID GEOMETRY

The final piece in the jigsaw is including the confining solid geometry. Our basic requirements are as follows. Firstly that we recover a stick boundary. That is, the average flow velocity at the boundary should be zero. Secondly, the presence of the interface should not perturb the transport properties of the solvent. The first condition is straightforward to enforce. Using a bounce back rule (that is, the direction of the velocity of particles impinging on the interface is reversed), the only possible steady state velocity at the interface is zero. The second is more problematic. Clearly the interface should not influence the density profile, otherwise it generates a local varying viscosity. Similarly, the number of interactions a particle experiences with its neighbours cannot change, or again an artificial local variation in the viscosity is introduced. This means that at the very least a “dummy” system
is needed up to distances $r_c$ on the other side of the boundary.

In our case, where the solvent is an ideal gas, one method is to fix the velocity distribution for particles in the wall region to the appropriate Maxwellian. While this is probably adequate here, we prefer to use a novel method that goes a step further and requires continuity of the velocity across the interface between the dummy region and the real system. Moreover, it applies for any axially symmetric flows. More formal details are given in chapter 3, here we just outline the physical reasoning.

The dummy region, with a width equal to the cut-off radius, is filled with particles, at a density equal to the system density. Interactions between the system particles and wall particles are evaluated in the normal way: there is no difference between particle types. The system particles and the wall particles are separated by a no-slip boundary. That is, a bounce-back is performed whenever a wall or system particle impinges on the boundary. To complete the system we have a slip boundary, confining the particles within the dummy region. The slip boundary is enforced by reversing just the perpendicular velocity. This operation does not change the momentum along the axis. The flow in the system is driven by applying a uniform force density $\tilde{F}$. For the wall region we also apply a uniform force density. However, this force acts in the opposite direction such that the total force acting on the system is zero. The only force the system can exert is at the interface of the dummy region and the real system. Since the total applied force is zero, in the steady state the force on the inner wall must also be zero. That is, the force exerted by the system on the system side of the interface is equal and opposite to the force exerted by the dummy region on its side. Hydrodynamically, the force the fluid exerts is proportional to the gradient of the velocity field. Thus, we know that the derivative of the velocity field is the same on both sides of the interface. At the interface itself the velocity field is continuous.

4.3 RESULTS

This is meant to be a course grained representation of a well defined (model) polymer system, so it is important to verify that the results are independent of the degree of coarse graining (the number of beads in the model polymer chain). Only if this is true can we establish a link between the simulation results and real systems, where the number of monomers is considerably larger than is practical to use in the simulation. Using similar methodology, Lowe and Dreischor$^9$ verified that this was the case for equilibrium simula-
4.3 Results

Figure 4.2: Influence of the number of beads on the centre-of-mass diffusion of the polymer (○) and on the relative polymer drift velocity (□). In this case $R_g/R = 0.326$.

...tions, as long as $N_b \gtrsim 16$. Does this also hold for the non-equilibrium case we consider here? To answer this question we performed a series of simulations to test our model system. If the model is correct the hydrodynamic behaviour of polymers with the same size relative to the tube diameter should be independent of $N_b$. As a measure of polymer size we take the radius of gyration $R_g$ of the ideal chain:

$$R_g^2 = \frac{(N_b + 1)(N_b - 1)}{6N_b}$$  \hspace{1cm} (4.6)

In Fig. 4.2 we plot the ratio of the polymer drift velocity to the mean solvent velocity for chains of 8 to 64 beads, for the case where $R_g/R = 0.326$. Clearly, the results for the accelerated flow velocities in these dimensionless terms do not significantly depend on the number of beads in the chains. We have verified that this is also the case for the results at all values of $R_g/R$ studied. The simulation results we describe here are therefore independent of $N_b$ as we require. Also plotted are centre of mass diffusion coefficients $D$ calculated for the model polymers in the absence of the tube. They follow long polymer scaling $D \sim D_0/N_b^{1/2}$. This is as expected for this choice of parameters (although for short model polymers it is not generally the case).

To differentiate the effects of hydrodynamic interactions from the depletion effect, we first need to carefully examine what the simplified model predicts when the latter is included correctly. That is, using the exact $P(r)$ in Eq. 4.2. In Fig. 4.3 we show plots of the distribution of the polymer centre of mass as a function of distance from the centre of the tube. As the plot shows, even at relatively small values of $R_g/R \sim 0.15$ the distribution is poorly approximated by the step function simple theories assume.
Figure 4.3: Normalized probability distributions of polymers with values for the radius of gyration over the radius of the tube of $R_g/R = 0.151 (~-~)$, 0.326 (···), 1.00 (~—~) and 1.40 (~·~).

Figure 4.4: Average polymer radius of gyration parallel and perpendicular to the tube axis as a function of $R_g/R$. Results are plotted for LA simulations and MC simulations. For a non-distorted polymer $R_g/R_0 = 1$. 
In Fig. 4.4 we have plotted values of $R_g$ perpendicular and parallel to the tube axis. In the limit $R_g/R \to 0$ these quantities are equal. The polymer can in this sense be considered “spherical”. As the plot shows, this approximation holds up until $R_g/R \sim 0.25$. For higher values the component along the axis follows the usual unconfined polymer scaling ($R_g \sim b N_{p}^{1/2}$), whereas the radial components approach a constant because of the confinement in the radial direction. Combined with the observation above, this means that in the regime $R_g/R < 0.25$ it is reasonable to consider the polymer as a “soft” rather than hard sphere. For values of $R_g/R > 0.25$ the configurations of the polymer are so perturbed by the tube that it hardly makes sense to approximate the polymer as a spherical particle.

To confirm that the results we obtain from the full dynamic calculation are valid in the low Péclet number regime, in Fig. 4.4 we have also plotted values for the radius of gyration parallel and perpendicular to the tube axis calculated from this simulation. As the plot shows, the values are identical to the equilibrium values for all $R_g/R$, confirming that the distribution of polymer configurations in the dynamic simulations is not influenced by the ambient flow.

The results for the accelerated drift velocity from the full hydrodynamic calculation, using the particle model, are plotted in Fig. 4.5. Also shown is the result for the quadratic model treating the polymer hydrodynamically as a hard sphere ($C = 2.33$). We labeled this result “experiment” because it best
described the experimental results obtained by Tijssen. These experimental results were obtained for a solution at the theta temperature, matching the model, but for smaller values of $R_g/R$ than those we have studied ($R_g/R < 0.15$). Clearly the agreement with experiment is very good. However, in the plot we also show the results we obtained for the simple model using the correct centre of mass distribution function for the polymer (see Fig. 4.3). Note that this model does not include hydrodynamic interactions. Nonetheless, it is in agreement with both the full hydrodynamic simulation and experimental results in the regime $R_g/R < 0.25$. Apparently in this regime the hydrodynamic interactions have little effect, even though the theory that best describes the experimental results includes a hydrodynamic effect. For $R_g/R > 0.25$ we see that the hydrodynamic interactions do have an effect. This is clear because the full simulation results predict a systematically lower value for the accelerated drift velocity than the simpler depletion model does. That is, the effect of the hydrodynamic interaction is to decrease the polymer drift velocity, although not very dramatically. In the regime $0.5 < R_g < 1.5$ the typical effect of the hydrodynamic interaction is only to reduce the drift velocity by approximately 15%. However, from the point of view of hydrodynamic chromatography this is not a trivial effect because the difference in elution time for polymers of different sizes is also proportional to the capillary length. So the difference in elution times when one includes hydrodynamic interactions can be arbitrarily large, depending on this length.

We have attempted to fit the values we have calculated for the accelerated drift velocity to a form predicted by the refined quadratic model, including higher order terms. However, such an expansion appears to be unable to describe our data. This suggests that an expansion of this form is either divergent or very slowly convergent. Empirically we found that the function

$$\frac{V_p}{V_s} = 1.74 + 0.28 \ln \left( \frac{R_g}{R} \right)$$

(4.7)

accurately describes our data in the intermediate regime $0.25 < R_g < 2$. We do not believe this function applies for $R_g/R \gg 2$ for the following reason. There is a striking and somewhat unexpected feature of the results we obtain for the accelerated drift velocity of the polymer when we include hydrodynamic interactions. For $R_g/R \gg 1$ it appears that $V_p/V_s \to 2$ (which is inconsistent with Eq. 4.7). That is, even with depletion and hydrodynamic effects included, the prediction of highly simplified models, that in this limit the polymer simply drifts with a velocity equal to the maximum of the ambient Poiseuille velocity profile, remains valid. If all other effects are included it appears that this limit is just approached more slowly with increasing $R_g/R$.

Thus far we only considered the regime where the Reynolds number and
Péclet number are very small. Consequently the distribution of the polymer in the capillary is not perturbed from its equilibrium value. This is appropriate for microscopic capillaries. For larger geometries and/or higher flow rates this is no longer true. What is more, it is well established experimentally that in this regime the distribution is perturbed by the flow.\textsuperscript{118,119} In fact, the polymer has a preferred location at some point between the capillary wall and mid point. The same effect is seen in computer simulations.\textsuperscript{62,120–122} Indeed, we see this effect too if we operate our model in this regime. Because we have not analyzed the effect in sufficient detail these results are not reported here. However, what we do want to address is the mechanism that causes the effect. The importance of polymer hydrodynamic interactions is undisputed. In what way is a matter of debate. Graham et al.\textsuperscript{123} predict polymer migration away from the walls and attributes this effect to wall-polymer hydrodynamic interactions and a gradient in chain mobility. On the other hand, Ladd et al.\textsuperscript{122} propose that polymer migration can proceed both away from and to the wall, and is determined by the balance of several effects: hydrodynamic lift, rotation and drift of the polymer. The latter suggests that a polymer behaves in a similar way to a rigid colloidal sphere. Although this may seem a crude approximation, in Fig. 4.4 we showed that for low degrees of confinement, in the microfluidic regime it is a reasonable approximation. Continuing the analogy, for rigid spheres there is the well known Segre-Silberberg effect: there is a preferred off-centre location for the particle.\textsuperscript{124} The precise location is determined by two competing effects. The first is a hydrodynamic repulsion from the wall due to the particle-wall hydrodynamic interaction. The second is a hydrodynamic attraction toward the point with highest shear. Although this is generally the wall itself, this effect does not require the presence of the wall. Whereas the hydrodynamic force tries to push the particle to this specific location, thermal diffusion always counters this. The degree to which particles are confined to a preferred location is a competition between these two effects. Here we try to see how close the analogy is between the colloidal sphere and a polymer by removing one effect, namely the wall.

Importantly, all the above is an effect of fluid inertia (the non-linear term in the Navier-Stokes equations). Any simulation method that is based on the linearized Navier-Stokes equations, which completely neglects inertia, can never describe this phenomenon. An example would be Brownian Dynamics. However, as we pointed out, our approach is not limited in this way. It correctly includes inertia because it is Galilean invariant. As it also includes the other important effect correctly, namely thermal diffusion, it is an appropriate tool for studying this problem. To do so we have considered a system that has no boundary but does have a non-uniform shear rate. Specifically, we apply an external force such that the flow profile is one wavelength of a sinu-
Figure 4.6: The distribution of polymer chains (bottom figure) in a non-uniform flow (top figure). The flow is generated using the periodic Poiseuille flow method.\textsuperscript{101}

soidal wave (this is then repeated to infinity by the use of periodic boundary conditions).\textsuperscript{101} The solvent is modelled as described above and a single polymer in the system is allowed to diffuse in the resultant flow field. In figure 4.6 (top) we show the flow profile we observe (normalized by the maximum flow velocity). The polymer concentration is negligibly low so we do not expect any significant non-Newtonian behaviour. Indeed we observe a sinusoidal profile, as one would expect for a Newtonian fluid. In the lower part of the figure we have plotted the distribution of the location of the centre of mass of the polymer (averaged over different uniformly distributed starting points and a considerable length of time). The two sets of results correspond to two different magnitudes of the driving force resulting in two different flow velocities. Between the two simulations the ratio of the magnitude of any inertial force (characterized by the Reynolds number) to the diffusive force changes. The magnitude of the latter is characterized by \(1/(\gamma \tau_D)\), where \(\gamma\) is the maximum shear rate, and \(\tau_D\) a characteristic diffusive time \((\tau_D = D/R_0^2)\). As the figure shows, even though we have no walls in the system, we still observe ordering. The polymer is not uniformly distributed. There are two preferred locations (the centre and edge of the simulation box) and these correspond to the positions of maximum shear rate. That is, qualitatively we see exactly the behaviour one would expect for a rigid sphere in this system when inertia is taken into account. Furthermore, as we increase the Reynolds number (so any inertial force is increased while the opposing diffusive force is decreased) the non-uniformity of the distribution takes the same form but increases
in magnitude. Again this is in line with what one would conclude from the analogy with a rigid sphere.

It would be useful at this point to see if the magnitude changes quantitatively in the same way, but unfortunately (and despite quite a lot of computer time) the data is too inaccurate to make a meaningful comparison. What we can conclude is that even in this unbounded system there is a preferred location for the polymer. This is the same preferred location as for a rigid sphere. Both observations support the mechanism proposed by Ladd et al.\textsuperscript{122} to explain the ordering effect observed in capillaries.

\subsection*{4.4 DISCUSSION AND CONCLUSIONS}

We have developed and implemented a scheme for simulating the dynamics of ideal polymers in a solvent flowing through a tube. To do so we used a novel method that accurately describes the behaviour of the fluid at the solid/fluid interface. In dimensionless terms we show that the predictions for the model do not depend on the number of beads in the model polymer chains. This means that we can reasonably extrapolate our results to real systems. Doing so, we find excellent agreement between our simulation results and experiments for the values of $R_g/R$ studied experimentally. We show that in this regime a simplified model that neglects hydrodynamic interactions but includes the depletion effects correctly is accurate. We conclude from this that in this regime the hydrodynamics actually play a very minor role. The agreement between the experimental results and theories that simplify the depletion effect but include hydrodynamic interactions for either a rigid sphere or a porous sphere are therefore fortuitous. As Tijssen et al. commented, it was a surprise that the hard sphere model provided a better description of the results than the more realistic porous model does.\textsuperscript{111} Clearly, the reason is that in this regime a correct description of the depletion effect is far more important than a correct description of the hydrodynamic interactions. The fact that both models make the wrong approximation for the depletion effect means that one cannot conclude that the porous sphere model gives a less realistic description of the hydrodynamics. Hopefully this observation will help guide the development of better theories.

For higher degrees of confinement ($R_g/R > 0.25$) the hydrodynamics do play a role. They reduce the accelerated drift velocity relative to the velocity that one would expect from the simple model. In this respect our results are in qualitative agreement with theory. From an experimental point of view this means it would be advantageous to screen the hydrodynamic interactions if
possible. Based on our simulation results we have given an empirical fit for our predictions that can be tested experimentally when higher values of \( \frac{R_g}{R} \) are studied. Given that the simulation results are independent of the number of beads in the model chain we have good reason to believe that this will be the case. In the limit where the size of the polymer is much greater than the width of the capillary, the simulation shows that the accelerated drift velocity approaches its maximum of twice the average solvent drift velocity. This is exactly the same as the theoretical maximum one would expect from the simple depletion model, even in a regime where one could hardly expect such a simple model to work. Presumably this is because at such high degrees of confinement the effect of the hydrodynamic interactions is to generate a local “plug flow” solvent velocity profile, with a velocity equal to the maximum flow velocity of the ambient Poiseuille flow.

We conclude by noting that the simulations we report here consider a relative special case. That is, a polymer solution at its theta temperature. However, they deal with what is, in computational terms, a complex mesoscopic problem and provide a quantitative prediction for a parameter regime not yet studied experimentally. In this sense we hope that it again shows that mesoscopic simulation techniques have predictive as well as diagnostic potential. Furthermore, we believe it should be possible to extend the simulation methodology to more general cases where the polymer solution is not at the theta temperature and where the geometry is more complex. Notably, one might expect that the effect of being above the theta temperature could be accounted for by simply allowing for the fact that the polymer is relatively expanded in this case. However, the experimental results showed that for this case a different constant in the refined quadratic model described the results. This suggests that in this case hydrodynamic interactions are important even in the regime where for ideal chains they are not.