The dynamics of polymers by novel mesoscopic methods
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CHAPTER 5

Flow of concentrated polymer solutions in microfluidic capillaries - simulation and theory

We describe the results of simulations of the flow of concentrated solutions of ideal chains in microfluidic capillaries. With increasing concentration, the mean flow rate of the solution significantly exceeds that of a Newtonian fluid with equivalent viscosity. Further, the results show that with increasing concentration the flow profile becomes increasingly “blunt” compared to the normal parabolic profile characteristic of a simple Newtonian fluid. This is all in agreement with experimental observations. However, the form of the profile we observe cannot be explained by existing theories because the characteristic length that determines the shape of the profile is a function of the volume fraction of the solvated polymers and not of their size. Using this observation we develop a “slight-slip” theory, using the conjecture that the drift of the polymers differs slightly from the ambient local solvent velocity. The slight-slip theory predicts velocity profiles in excellent agreement with the simulations for concentrations ranging from dilute to semi-dilute. It also accurately describes profiles measured experimentally and accurately predicts flow profiles for bi-disperse polymer mixtures. By studying this system we are able to calculate how the efficiency of hydrodynamic chromatography is affected relative to the dilute, mono-disperse, case studied in chapter 4.
5.1 INTRODUCTION

Dissolving polymers in a simple Newtonian solvent can have a remarkably dramatic effect. The slow relaxation processes of the polymer molecules, up to seconds or even minutes, result in an extra non-linear stress term in the Navier-Stokes equations. Examples of phenomena caused by this non-linearity are: elastic turbulence, where flow is chaotic even for small flow velocities; shear thinning, where the viscosity of the polymer solution decreases with increasing shear rate and turbulent drag reduction, where adding a small amount of polymer to a turbulent flow results in a spectacular increase in the flow rate. Despite a large volume of literature on these topics, it is fair to say that generally the underlying mechanisms that drive these effects are not yet fully understood. In this chapter we apply the methodology developed in previous chapters to study numerically the flow of concentrated polymer solutions through cylindrical capillaries. Again we will focus on the micro-fluidic regime. Even though a number of possible mechanisms that generate complexity in the flow of polymer solutions are absent in this regime (for example, a shear rate dependence of the viscosity), the presence of the polymers still has a profound influence on the flow characteristics.

At the most basic level, the presence of solvated polymers has the following effect. The viscosity of the polymer solution is higher than the viscosity of the pure solvent (that is, the solvent in the absence of polymer molecules). The additional contribution to the solvent viscosity $\eta_s$, in the dilute limit, is characterized by the intrinsic viscosity $[\eta]$. For low polymer volume fractions, $\phi \ll 1$, the intrinsic viscosity is defined by:

$$[\eta] = \lim_{\phi \to 0} \frac{\eta - \eta_s}{\eta_s \phi}$$  \hspace{1cm} (5.1)

In this equation we define the polymer volume fraction $\phi$ as the total volume of all polymer chains over the total accessible volume in the system. We define the total polymer volume as $N_p 4\pi R_g^3/3$, with $N_p$ the number of polymers and $R_g$ the radius of gyration of the polymer chains. Einstein showed that for colloidal suspensions of hard spheres $[\eta] = 2.50$. For polymer chains, which we can consider to be “soft” spheres, the behaviour is analogous but $[\eta]$ is smaller. The pre-average Zimm model predicts the intrinsic viscosity of an ideal chain to be 1.49. More sophisticated theories predict values between 1.29 and 1.65.

With increasing $\phi$, the influence of the hydrodynamic interactions between the different polymer chains becomes significant. It is for this reason that
5.1 Introduction

Eq. 5.1 is only applicable in the (infinitely) dilute limit. At higher polymer volume fraction the viscosity can be written as a “virial” expansion:

\[
\frac{\eta}{\eta_s} = 1 + [\eta]\phi + k_H[\eta]^2\phi^2 + ...
\]  

(5.2)

where \(k_H\) is termed the Huggins coefficient.\textsuperscript{129} For polymeric systems without strong excluded volume interactions (for instance a polymer solution around the theta temperature) the theoretical predictions for \(k_H\) range from \(\sim 0.5\) to \(\sim 0.8\).\textsuperscript{128,130–132}

The flow profile of a pressure-driven Newtonian fluid inside a tube at low Reynolds numbers is known. The equation describing the (radially symmetric) solvent velocity at a distance \(r\) from the tube centre is given by:\textsuperscript{102}

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

(5.3)

Here \(\tilde{F}\) is the force density acting on the fluid, and \(R\) is the radius of the capillary. The maximum solvent velocity is reached at the centre of the tube \((r = 0)\) and has a value of \(V_{\text{max}} = \tilde{F}R^2/4\eta\). Because the presence of solvated polymers increases the viscosity (see above), at the very least we expect a lower flow rate for a polymer solution, for a given force density. If the polymer solution is Newtonian, the actual form of the velocity profile remains the same. If this is not the case, the shape of the velocity profile will not be parabolic for pressure-driven (semi-)dilute polymer solutions. In the literature, various models have been proposed to take this into account and describe the true shape of the flow profile. These models can be classified into three different approaches, which we will discuss in the proceeding paragraphs.

Above some value of the shear rate, all polymer solutions are non-Newtonian. The viscosity in the non-Newtonian regime then itself depends on the shear rate \(\dot{\gamma}\). One way of describing non-Newtonian fluids is the Ostwald-de Waele model.\textsuperscript{102} This model treats the relation between the shear and the viscosity using a power-law, \(\eta \propto \dot{\gamma}^{n-1}\). If the dimensionless quantity \(n = 1\), the fluid is Newtonian, for \(n > 1\) the fluid is shear-thickening and for \(n < 1\) it is shear-thinning.\textsuperscript{133} Rewriting Eq. 5.3 according to this power-law, we find:

\[
\frac{V_s(r)}{\bar{V}_s} = \frac{n + 3}{n + 1} \left[ 1 - \left( \frac{r}{R} \right)^{1+\frac{n}{1}} \right]
\]  

(5.4)

where \(\bar{V}_s\) denotes the average solvent velocity. For \(n = 1\), this equation is equal to Eq. 5.3. In the limit \(n \to \infty\) the profile becomes plug flow.\textsuperscript{102} In the systems we consider in this chapter, the Reynolds number and, con-
sequently, the shear rate is very low, so we do not expect $n$ to be large. Moreover, the polymer segment concentration is not radially constant, as is implicitly assumed in the Ostwald-de Waele model. Due to steric hindrance the polymer is depleted from the boundary, resulting in a lower viscosity near the boundary than in the centre of the capillary.

To address this point, one can take the polymer segment distribution into account to determine the shape of the velocity profile. For ideal polymer chains this distribution, as a function of the distance from a flat wall at position $r = 0$, is given to a good approximation by:

$$\frac{\rho_s(r)}{\rho_s(\infty)} = \tanh^2\left(\frac{r}{\delta}\right)$$

One can define the local polymer volume fraction at a distance $r$ from the wall as $\phi(r) = \phi \rho_s(r)/\rho_s(\infty)$. By inserting this expression in the first part of Eq. 5.2, the following relation between the viscosity and the distance from the wall $r$ is obtained:

$$\frac{\eta(r)}{\eta_s} = 1 + [\eta] \phi(r) = 1 + [\eta] \phi \tanh^2\left(\frac{r}{\delta}\right)$$

The flow profile of a shearing polymer solution near a single wall is then given by:

$$V_s(r) = \dot{\gamma}\left(\delta \sqrt{[\eta] \phi \arctan\left(\sqrt{[\eta] \phi \tanh\left(\frac{r}{\delta}\right)}\right)} + r\right)$$

Here $\dot{\gamma}$ is the shear rate in the bulk (defined as $\dot{\gamma} = dV_s/dr$) and $\delta$ is the thickness of the depletion layer which is close to $R_g$. In principle one can also derive a polymer segment dependent expression for the flow profile of a pressure-driven polymer solution inside a capillary. This is more appropriate when the volume fraction of the polymers exceeds unity. Either way, the crucial prediction of theories of this type is that it is a depletion boundary region, of width of the order of $R_g$, that causes deviations from normal Newtonian behaviour. Because this phenomenon does not depend on the shear rate (that is, non-Newtonian behaviour of the bulk polymer solution per se) it is an effect that will be present in the microfluidic regime we consider here. However, as we will show, we have been unable to describe the shape of the flow profile in our problem in terms of such a depletion layer.

A philosophically similar approach is successfully used to describe the flow of blood in a vessel. In the centre of the vessel the viscosity is higher than near the wall because the relatively big red blood cells are hindered by the wall. The flow profile of blood in a vessel is now estimated using a “two-fluid model”. Inside the vessel there is a tubular region of higher vis-
viscosity, whereas the viscosity of the depletion layer has a lower viscosity. In
between these regions there is an interface where the viscosity changes dis-
continuously. For a capillary with radius $R$ and with an outer boundary layer
of width $\delta$ (such that the model parameter $\zeta = (R - \delta) / R$), the velocity profile
as a function of $r / R$ is given by:

$$V_{s,c}(r / R) = V_s(0) \left[ 1 - \frac{\eta_c}{\eta_o} (\zeta^2 - (r / R)^2) \right], 0 \leq r / R \leq \zeta$$  \hspace{1cm} (5.8)

$$V_{s,o}(r / R) = V_s(0) \left[ 1 - (r / R)^2 \right], \zeta \leq r / R \leq R$$  \hspace{1cm} (5.9)

where $V_{s,c}$ and $V_{s,o}$ are the velocities of the core region and the outside re-
gion respectively, $\eta_c$ and $\eta_o$ are the viscosities of these two regions and $V_s(0)$
is the maximum solvent velocity of a pressure-driven flow of a solvent with
viscosity $\eta_o$. Unfortunately, it is doubtful if this model will work for poly-
mer chains because polymer chains are not impenetrable, whereas red blood
cells are. Solvent particles can move in and out the polymer region, making
the polymer chains more like a porous medium. Based on this observation,
one could conceive of a different approach based on the Brinkman model for
flow through porous media. The Brinkman model proceeds by modifying the empirical Darcy equation such that the force the porous medium
exerts on the fluid is taken into account.

It is difficult to perform simulations on concentrated polymer system with
all hydrodynamic couplings included. One relatively simple method for do-
ing so is Brownian dynamics (BD). Here the solvent is modelled as a con-
tinuous medium and all hydrodynamic interactions are accounted for via
the configurationally dependent mobility matrix. Unfortunately, the long-
ranged hydrodynamic interactions between the polymer chains make the
method computationally expensive with increasing number of chains. To
counter this problem, complex algorithms have been proposed to speed up
the BD method. Furthermore, it is not straightforward to incorporate a
solid boundary within the framework of BD. One way of accounting for such
an interface is correcting the mobility matrix by a pre-processing step. A
more promising route for this problem is therefore to use particle methods
which do not suffer from these drawbacks (admittedly at the disadvantage
that they require an explicit, albeit simplified, solvent). Possible methods
are for instance Stochastic Rotational Dynamics (SRD), where the system
is partitioned into cells and particles exchange momentum by rotating their
velocity around the centre-of-mass velocity, or Lattice-Boltzmann (LB)
where solvent densities move on a grid according to given collision rules.
Here we choose to employ the Lowe-Andersen (LA) thermostat, a method
that is similar in spirit to Dissipative Particle Dynamics (DPD). Mesoscopic particles move in continuous space and the interactions are
dealt with via thermostating collisions. The method is Galilean invariant and conserves momentum, two features that are essential for correct hydrodynamic behaviour. Compared to DPD the repulsive interactions are abandoned, turning the solvent into a dissipative ideal gas.\textsuperscript{116} However, by tuning the parameters of the model in a feasible manner we are able to recover correct hydrodynamic behaviour on long enough time- and lengthscales.\textsuperscript{7,81} We demonstrated the procedure for single polymer chains in chapter 4. With the methodology developed in chapter 3 we also know that we can model the solid/liquid interface accurately, even in the computationally convenient limit of a sparse solvent. Further, we argued that our methodology was particularly suited for concentrated solutions containing more than a single polymer. Here we will show that the methodology is easily extendable to multiple polymer systems and that this is indeed the case.

We begin this chapter with a short overview of the computational techniques we employ in this chapter. Subsequently, we examine the shape of the velocity profile of pressure-driven polymer solutions inside capillaries. We show that the three theories outlined above are unable to explain our results. We propose a novel “slight slip” model that accurately describes the shape of the flow profiles we observe. Furthermore, we can make a comparison between our results and experimental data on the shape of the solvent flow profile and on the volumetric flow rate. Finally, we return to the problem of hydrodynamic chromatography and consider the accelerated drift velocity of the polymer chains. Compared to chapter 4, where only very dilute polymer solutions were considered, here we examine the influence of increasing polymer concentration on the drift velocity. In addition, we consider the more practical case of polymer solutions consisting of chains of different sizes.

5.2 SIMULATION DETAILS

The model polymer chains consist of $N_b$ beads, connected to each other via a harmonic potential:

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

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 (the root mean squared distance between connected beads) and $\vec{r}_i$ the position of particle $i$. As a measure of the size of the polymer chains we take the mean radius of gyration, $R_g$, of the ideal chain. The mean squared radius of an ideal chain
is

\[ <R_g^2> = \frac{(N_b + 1)(N_b - 1)}{6N_b} b^2 \]  \hspace{1cm} (5.11)

The mean radius of gyration is then \( R_g = \sqrt{<R_g^2>} \). The centre-of-mass diffusion coefficient \( D \) of a polymer chain in the dilute limit is given by:

\[ \frac{D}{D_0} = \frac{1}{N_b} + \frac{a}{N_b^2} \left( \sum_i \sum_{j \neq i} \frac{1}{\|\vec{r}_i - \vec{r}_j\|} \right) \]  \hspace{1cm} (5.12)

where \( D_0 \) is the diffusion coefficient of a single bead and \( a \) is the hydrodynamic radius:

\[ a = \frac{k_B T}{6\pi \eta D_0} \]  \hspace{1cm} (5.13)

As we discussed before in more detail, it is possible to mimic long polymer diffusive behaviour using only a small number of beads. To do so, we must set the ratio of \( a \) over \( b \) such that \( a/b = 4.04 \). We performed simulations on systems with chains of 32, 16 and 4 beads at varying solvent densities such that the ratio \( R_g/R \), where \( R \) is the capillary radius, varies. Values range from 0.462 and 0.366 for the chains with \( N_b = 32 \), 0.366 and 0.158 for \( N_b = 16 \), and 0.158 and 0.126 for \( N_b = 4 \).

To model the solvent we use an LA thermostat, a technique similar in spirit to DPD, although it does not involve dissipative and random forces as in “classical” DPD. The bath collisions of the thermostat take over the role of the dissipative forces in DPD, while the distance dependent random force is not present. The LA thermostat satisfies the same conservation laws DPD does, while being computationally simpler. It also conserves momentum and is Galilean-invariant. The thermostating procedure is as follows. Every time step pairs of particles have a certain probability of undergoing a bath collision. Each time a collision is at hand a new relative velocity along the line of centres is drawn from the Maxwell-Boltzmann distribution. Because the method acts locally we are allowed to use a neighbour-list to speed up the calculations. This means that the computational work required scales in proportion to the number of solvent particles. Since the LA thermostat collisions transport momentum they enhance the viscosity. This is important for recovering realistic liquid-like behaviour from an otherwise gas-like solvent. One requirement for this is that the Schmidt number (which is the ratio of the kinematic viscosity to the diffusion coefficient) is significantly greater than unity. By choosing the cut-off radius \( r_c \) and the collision probability \( \Gamma \) in a sensible way, we are able to work at a high (fluid-like) value for this ratio. Here we should also point out that thermostat collision are only allowed between polymer beads and solvent, and between solvent particles.
There are no bead-bead interactions (other than the bonding potential). This procedure ensures that all momentum transport takes place via the solvent, consistent with a hydrodynamic description of the problem.

Next we turn to the solid boundary. From a mesoscopic point of view the boundary should not distort the density and temperature profile of the solvent, and the average solvent velocity at the position of the interface should be zero. One would expect that it is relatively easy to implement a solid boundary in a mesoscopic particle method, since the particles are allowed to move continuously in space. However, the opposite is true. One elegant method that works particularly good for planar walls is developed by Visser et al. Here we use a method where the boundary is implemented using a wall region of width $r_c$, filled with particles that are identical to the solvent particles. Interactions between the particles in the two regions proceed in the normal manner. The regions are separated by a no-slip boundary: a simple bounce-back is performed whenever a particle impinges on this interface. We confine the particles in the wall region using a slip-boundary. The flow is driven by a uniform force density over the system particles. Finally, we apply a uniform force on the wall particles opposite to the flow direction such that no nett momentum is introduced in the system. Because no momentum is introduced into the system as a whole, the force on the actual interface is, by definition, equal (but opposite) on both sides. Therefore, the stress over the interface is continuous, ensuring that also the velocity profile is continuous over the interface. If we now return to the three requirements the boundary model should fulfill we see that, because the stress over the interface is continuous, the density and temperature profiles are not distorted. Finally, the no-slip boundary ensures the average solvent velocity at the interface will be zero. This method works for any axi-symmetric geometry.

Because we will be looking at changes in the properties of the polymer solution relative to the pure solvent, it is necessary that we accurately know the properties of the former. Notably, that we know its viscosity. Even though the model solvent is relatively simple, theoretical estimates of this quantity are not accurate enough. We therefore need to “calibrate” the model by calculating it numerically. Commonly, the viscosity of mesoscopic particle solvents is determined using the Lees-Edwards boundary method. However, here we choose to use the much simpler periodic Poiseuille flow method. The simulation box (with periodic boundaries on all sides) is divided into two volumes of identical size. Over the particles in each volume a uniform force density is applied, in one region in the positive direction, in the other in the negative direction. As long as the flow velocities are kept relatively low, the result is a two-dimensional parabolic velocity profile in each region. Finally, the viscosity is calculated by using the relation between the average solvent
5.3 Calculated hydrodynamic properties of concentrated model polymer solutions

We begin with a brief examination of the change in viscosity of the model polymer solution with increasing concentration. Using the periodic Poiseuille flow method outlined above, we studied a system subject to periodic boundary conditions. This mimics the “infinite” unbounded case. The external force we applied was minimal to ensure that the shear rates were insufficient to generate any non-Newtonian behaviour. The calculations extend up to concentrations $\phi \sim 1$, where polymers begin to significantly overlap each other.

The definition of the polymer volume fraction is not unique, but here we define it as $\phi = (4\pi R_b^3)/3$. Fig. 5.1 shows the increase in the solution viscosity relative to that of the pure solvent. There are two things to note from the figure. First, the results for model chains with 32 beads and 16 beads coincide to within the errors. From this we can conclude that the 16 bead model adequately captures the intra and inter-polymer hydrodynamic interactions adequately (at least for these values of $\phi$). Second, we can use the data to estimate the intrinsic viscosity and the Huggins coefficient. The values we obtain are $[\eta] = 1.6 \pm 0.1$ and $k_H = 0.77 \pm 0.05$ respectively. These results are

**Figure 5.1:** The relative additional solvent viscosity $\eta/\eta_s - 1$ as a function of the relative polymer volume fraction $\phi$. The circles represent polymers with $N_b = 32$, the filled diamonds polymers with $N_b = 16$. The dashed line is a fit of $\eta/\eta_s - 1 = [\eta]\phi + k_H[\eta]^2\phi^2$, where $[\eta] = 1.6 \pm 0.1$ and $k_H = 0.77 \pm 0.05$. Flow velocity and the ratio of the applied force density to the viscosity.
not particularly accurate but they lie within the accepted range predicted by
theory and calculated from experimental results. The reason for
the lack of accuracy is that we used an extremely low maximum shear rate to
ensure that we could neglect any non-Newtonian effects. This could probably
be increased to give more accurate results without violating this condition.
However, in this chapter we are more interested in the flow of confined poly-
mer solutions than in accurate values of these coefficients. It is sufficient to
say that, in terms of the viscosity of the unbounded solution, our method is
adequate.

5.4 CALCULATED FLOW PROFILES FOR CONCENTRATED
POLYMER SOLUTIONS IN A CAPILLARY

In our model system the values of several of the parameters are fixed by
the requirement that both the fluid behaviour and the coupling between the
fluid and the polymer motion is correct. This leaves us with three parameters
that we can vary. Namely, the number of beads in each polymer chain \( N_b \),
the polymer volume fraction \( \phi \) and the polymer size relative to the radius
of the capillary \( R_g/R \). In this section we will carefully examine the influence
of changing these three parameters on the resulting solvent flow profile. We
begin by looking at the influence of the number of beads in the chains on
the results of the simulations for a given value of \( \phi \). Remember, in reality a
polymer is made up of considerably more monomers. These results should
be independent of the number of beads, if these chains are representative of
“real” polymer chains of a given size (i.e. a given value for \( R_g/R \)). If this is not
the case we must increase the number of beads, until we reach a value where
the results do not depend on the number of beads anymore. In Fig. 5.2 (A)
we demonstrate that the flow profile is indeed independent of the number of
beads. If we look at the chains consisting of 32 and 16 beads, we observe
that the flow profiles for both chain lengths are identical. This means that
we can reproduce the behaviour of a chain of length \( N_b = 32 \) using only
16 beads. Moreover, if we look at chains consisting of 16 and 4 beads, it is
remarkable to observe that a solution of chains with only 4 beads already
behaves identically to solutions with a much higher resolution. This does
not necessarily mean that the individual small chains behave in exactly the
same manner as the bigger ones do. However, it does at least mean that a
polymer solution with a certain polymer volume fraction consisting of chains
of 4 beads behaves identically to a solution with the same volume fraction
consisting of chains with \( N_b = 16 \) and with the same size. From this we can
conclude that at least up the moderate volume fractions plotted, the method
we are using works.

Next we consider the situation where the volume fraction is changed, while keeping the number of beads and the ratio of polymer size to the tube radius constant (in this case \( N_b = 32 \) and \( R_g/R = 0.183 \)). In real life this corresponds to increasing the concentration of a solution of a polymer with a given molecular weight. The results are plotted in Fig. 5.2 (B). As the figure shows, with increasing polymer volume fraction the maximum velocity decreases relative to that of the pure solvent. This is unsurprising because the viscosity of the solution increasingly exceeds that of the pure solvent. The striking thing is that, with increasing concentration, the form of the profile changes significantly from the hyperbolic form characteristic of the pure solvent. Specifically, the profile gets blunted and appears to approach something more like plug-flow at volume fractions \( \phi \gg 1 \). This is in qualitative agreement with experimental results.\(^{144-146}\) In addition, we note that we do recover the normal (pure solvent) profile in the vicinity of the boundary. However, the region for which this is true shrinks with increasing \( \phi \). We should stress that these results all have the same polymer size, so this length is not determined by any depletion effect because the depletion length is the same in each case.

Finally, we consider the case where we keep the polymer volume fraction \( \phi \) constant, but this time change \( R_g/R \) (through \( N_b \)). In Fig. 5.2 (C) we plot the flow profile for three different systems, all with a volume fraction of \( \phi = 0.2 \). However, the relative polymer size \( R_g/R \) differs significantly (by a factor of almost four) between them. Despite this, the curves superimpose on top of each other to a high degree of accuracy. Based on this figure we can conclude that the only thing that matters in determining the form of the profile is the polymer concentration. Whereas from the above we concluded that the relative size of the polymer did not determine the width of the boundary layer, we can now go further and conclude that it is in fact completely irrelevant. Theories based on a slip layer of width \( \sim R_g \) can never be consistent with this observation. A successful theory should be based on the volume fraction instead of on a depletion layer dependent on the polymer size. As we are not aware of one, at this point we construct our own.

### 5.5 SLIGHT SLIP MODEL

Given the observation that the velocity profile for the polymer solution is not a function of \( R_g/R \), models that consider a depleted viscosity layer cannot explain our results. Furthermore, we also know that we are in the regime

Figure 5.2: The relative flow velocity profile for various systems. The total driving force is constant for all systems, all profiles are corrected for the difference in the viscosity of the pure solvent, the error bars are smaller than the symbol size.

Figure A shows results from simulations with polymer chains of 16 and 32 beads with $R_g/R = 0.366$ and $\phi = 0.328$ (filled circles and squares respectively), and of polymer chains of 16 and 4 beads with $R_g/R = 0.158$ and $\phi = 0.632$ (open circles and squares respectively).

Figure B shows results from simulations with polymer chains all consisting of chains of 32 beads with $R_g/R = 0.183$: the circles represent a system with a polymer volume fraction $\phi = 0.03$; the diamonds represent a system with a polymer volume fraction $\phi = 0.33$; the triangles represent a system with a polymer volume fraction $\phi = 1.64$.

Figure C shows results from simulations of systems with a volume fraction of $\phi = 0.2$: the circles represent chains of 4 beads and $R_g/R = 0.079$; the squares represent chains of 16 beads, $R_g/R = 0.063$; the diamond represent chains of 32 beads, $R_g/R = 0.231$. 
where the polymer solution is Newtonian. To verify this we calculated the
viscosity as a function of dimensionless shear rate. The results for low to
moderate shear rates are shown in Fig. 5.3. Notice that the viscosity of the
solvent is independent of shear rate, it is Newtonian. As the plot shows,
at high enough shear rates the polymer solution is, in contrast to the pure
solvent behaviour, shear thickening. This is in agreement with other simula-
tions of ideal chains. For the simulations reported here the maximum shear
rate always satisfies $\tau \dot{\gamma} \ll 1$.

Although we are now considering concentrated rather than dilute solutions,
it seems highly unlikely that this is the explanation for the form of the profile.
Further, we are again in the regime where the Péclet number for the polymers
is low, so we do not expect that the distribution of polymers and monomers
in the system differs significantly from their equilibrium form. Again we
have verified this. In Fig. 5.4 we plot the relative density distribution of
the polymer centre-of-mass for a typical simulation of the flowing polymer
solution. As the figure shows, the distribution is of the equilibrium form.142

From the above we can conclude that the deviation of the flow profile from
the hyperbolic form in the dilute limit is purely an effect of the hydrodynamic
interactions. To see how this might be the case, we turn to a theory that has
proved to be an extremely useful tool for modelling flow in spatially inho-
ogeneous porous media:147,148 the Brinkman theory.139,140 This proceeds as
follows. As long as the Reynolds number is low, for a fixed porous medium
the relation between the steady-state flow velocity $\bar{V}$ through the medium
and the applied force density $\bar{F}$ is given by Darcy’s law:

$$\bar{V} = -\frac{\kappa \bar{F}}{\eta}$$  \hspace{1cm} (5.14)

where $\kappa$ is a constant (the permeability) that depends on the properties of
the porous medium but not on those of the fluid. The Brinkman equation
considers the balance of forces acting on a volume element of fluid, i.e. the
driving force, the divergence of the viscous stress tensor and the friction force
exerted by the porous medium on the fluid.
Figure 5.3: The viscosity as a function of the dimensionless shear rate $\tau \dot{\gamma}$, where $\tau$ is defined as $R_g^2/D_0$ and $\dot{\gamma} = 4V_{\text{max}}/L$. The viscosity is measured using the periodic Poiseuille flow method.$^{101}$ The simulations are performed with chains of length $N_b = 32$ at a polymer volume fraction of $\phi = 0.5$ (circles). Also plotted is the pure solvent result ($\phi = 0$, diamonds).

Figure 5.4: The relative distribution of the polymer centre-of-mass as a function of the tube radius. The simulations are performed with chains of length $N_b = 32$, $R_g/R = 0.462$ for polymer volume fraction of $\phi = 0.328$ (circles), 0.656 (squares) and 1.312 (diamonds). Also plotted is the equilibrium results (straight line).
The assumption now is that the latter can be replaced locally by the force term in Darcy’s law (Eq. 5.14). That is, one considers the porous medium as a continuum that exerts a friction on the fluid at every point. This being the case, we arrive at the Brinkman equation:

$$\eta \nabla^2 v - \bar{F} - \frac{\eta}{\kappa} v = 0$$

In spite of its approximate nature, Brinkman’s theory describes flow in spatially inhomogeneous porous media surprisingly accurately.\textsuperscript{147,148} Notably, it predicts that the Brinkman length $\lambda (= \sqrt{\kappa})$ acts as a screening length for the hydrodynamic interactions. For example, for the axial flow of a fluid through a tube of radius $R$, packed with a porous medium of permeability $1/\lambda^2$, the solution for the flow velocity, a distance $r$ from the centre, satisfying the stick boundary condition, is

$$v(r) = A \left[ 1 - \frac{\cosh \left( \frac{r}{\lambda} \right)}{\cosh \left( \frac{R}{\lambda} \right)} \right]$$

The constant $A$ is fixed by the condition that there is no net force on the fluid, giving

$$A = \frac{\lambda^2 \bar{F}}{\eta}$$

For $\lambda \gg R$ Eq. 5.16 reduces to normal Poiseuille flow, for $\lambda \ll R$ the velocity profile reduces to plug flow ($v(r)$ is constant) outside a region of the order of $\lambda$ from the tube wall. This is qualitatively similar to the behaviour we observe for the polymer solution. However, it seems unreasonable to consider this system as a fixed rigid porous medium.

What we can more reasonably conjecture is that the polymers in solution have some “slight slip”. That is, they travel at a velocity $V_p$ that is slightly less than the local flow velocity. Assuming this slip is independent of $r$, then $V_p = v(r) - \alpha v(r)$, where $\alpha$ is a constant that is less than unity (otherwise the polymer would be accelerating the fluid). In this case, the Brinkman equation becomes:

$$\eta \nabla^2 v - \bar{F} - \frac{\eta}{\kappa} (1 - \alpha) v = 0$$

where $\kappa$ is the “rigid” polymer solution permeability (the permeability of a porous medium composed of polymers that are fixed in space). If we now define an effective polymer solution permeability $k_s$, that takes into account that the polymers are not fixed,

$$k_s = \frac{\kappa}{(1 - \alpha)}$$
then Eq. 5.18 has an identical form to the normal Brinkman equation (Eq. 5.15) with a modified Brinkman length $\lambda_s = \sqrt{\kappa s}$.

To make further progress we need to know the rigid solution permeability $\kappa$. A porous medium composed of a density $\rho$ of points that exert friction, (while having negligible spacial extension) has a permeability

$$\kappa = \frac{1}{(6\pi \rho a)} \quad (5.20)$$

when the points have a friction coefficient equal to $6\pi \eta a$. Here $a$ defines a hydrodynamic radius. Porous media that physically occupy a negligible volume of space are a rarity, but the ideal polymer chains we are considering here are one such case (the monomers exert friction on the fluid but do not otherwise interact with each other). We can now consider two limits for the polymer solution. The first is the dilute limit, where the polymers themselves can be regarded as the points that exert friction. That is the polymer volume fraction (neglecting the factor $4/3\pi$), $\phi_p = \rho_p R^3_g$, is negligibly small. In this case we have

$$\kappa(\phi_p \to 0) = \frac{1}{(6\pi \rho_p a_p)} \quad (5.21)$$

where $\rho_p$ and $a_p$ are the polymer density and polymer hydrodynamic radius respectively. The latter is to a good approximation the radius of gyration $R^3_g$. In terms of the volume fraction, we therefore have

$$\kappa(\phi_p \to 0) = \frac{R^2_g}{(6\pi \phi_p)} \quad (5.22)$$

The second limit is that of high polymer volume fractions, $\phi_p \gg 1$, for which we recover a monomeric porous medium and we have,

$$\kappa(\phi_p \gg 1) = \frac{1}{(6\pi \rho_m a_m)} \quad (5.23)$$

where $\rho_m$ and $a_m$ are the monomer density and hydrodynamic radius respectively. The polymer density, $\rho_p$, in terms of the monomer density, is simply $\rho_p = \rho_m/n$, where $n$ is the number of monomers in the chain. Eq. 5.23 now reduces to

$$\kappa(\phi \gg 1) = \frac{R^3_g}{(6\pi \phi_p n a_m)} = \frac{R_g b^2}{(6\pi a_m \phi_p)} \quad (5.24)$$

Examining the behaviour in these two limits (Eq. 5.22 and 5.24) suggests
that more generally we can write

\[ \kappa(\phi) = \frac{L(R, b, a_m)}{(6\pi\phi_p)} \]  

(5.25)

where \( L(R, b, a_m) \) is a function that is known in the limits \( \phi_p \to 0 \) and \( \phi_p \gg 1 \).

We now know that the effective permeability of the slipping polymers and so the corresponding Brinkman length is given by:

\[ \lambda_s = \sqrt{\kappa_s} = \sqrt{\frac{L(R, b, a_m)}{(6\pi\phi_p)(1 - \alpha)}} \]  

(5.26)

To determine the degree of slip, we require that the solution to this Brinkman-like equation satisfies the scaling observed in the simulations. That is, we require that \( \lambda = Rf(\phi_p) \), where \( f(\phi_p) \) is some unknown function. Comparing with Eq. 5.26, this is only true if

\[ (1 - \alpha) \sim \frac{L(R, b, a_m)}{R^2} \]  

(5.27)

in which case we have

\[ \lambda_s \sim R \sqrt{\left(\frac{1}{6\pi\phi_p}\right)} \]  

(5.28)

Because this is a scaling argument, it is not possible to predict constant pre-factors but here we maintain the factor \( 6\pi \) because it is not small (the remaining constant factor we then hope is close to unity). At this point it useful to look at what the model predicts for this slip. In the low volume fraction limit, it follows from Eq. 5.27 that,

\[ (1 - \alpha) \sim \left(\frac{R}{R}\right)^2 \]  

(5.29)

Consequently, so long as \( R \ll R \), \( \alpha \) is slightly less than unity. The polymers almost follow the ambient velocity. In the concentrated (\( \phi_p \gg 1 \)) limit, given that the hydrodynamic radius is the order of the Kuhn length \( b \), Eq. 5.27 can be re-written as

\[ (1 - \alpha) \sim \left(\frac{R}{R}\right) \left(\frac{b}{R}\right) \]  

(5.30)

The first term on the right hand side is small if the polymer is small compared to the tube radius. However, the second term on the right hand side is always small as long as the polymer is long. Consequently \( (1 - \alpha) \) is always small, meaning that \( \alpha \) is close to unity. So, according to the model, in both limits the
polymer almost follows the velocity of the solvent but not quite. A reasonable term to describe it is thus a “slight slip” model. It is reassuring that we recover this result because one would not expect the polymers to move at a completely different velocity than the ambient fluid. The reason that this slight slip still modifies the flow is because the polymer solution is relatively impermeable. This means that although the slip is slight, it is enough to cause a non-negligible force on the solvent.

Finally, using the solution of the Brinkman equation for the tubular geometry we consider here (Eq. 5.16), we have a prediction for the velocity profile of the form

\[
v(r) = A(\phi_p) \left[ 1 - \frac{\cosh \left( \frac{r \sqrt{6\pi \phi_p}}{k} \right)}{\cosh \left( \sqrt{6\pi \phi_p} \right)} \right]
\]  

(5.31)

Considering the pre-factor \( A(\phi) \), we know that in the dilute limit it must go to the usual Brinkman value, otherwise Poiseuille flow is not recovered in this limit. So we have

\[
A(\phi \rightarrow 0) = \frac{\tilde{F} \lambda_s^2}{\eta} \quad (5.32)
\]

On the other hand, in the limit \( \phi \gg 1 \), it is not obvious that the pre-factor takes the usual Brinkman form because we have a porous medium that is flowing, not fixed. This makes it difficult to work out what the pre-factor should be based on momentum balance arguments. What we can say is that the dimensionless velocity, \( v(r) \eta/(\tilde{F} R^2) \) must only be a function of \( \phi_p \). That is, we have

\[
A(\phi_p) = \frac{\tilde{F} R^2}{\eta} f(\phi_p) \quad (5.33)
\]

where \( f(\phi_p) \) is some generally unknown function (although in the limit \( \phi_p \rightarrow 0 \), we know that \( f(\phi_p \rightarrow 0) \sim (6\pi \phi_p)^{-1} \)). What we can conjecture is that in this limit, where the monomers are relatively homogeneously distributed in the system, for a given \( R_g/R \) only the concentration of polymer is relevant. Satisfying this condition requires that

\[
A(\phi \gg 1) \sim \frac{\tilde{F} R^2}{\eta} \phi_p^{-2/3} \sim \frac{\tilde{F} R^2}{\eta R_g^2} \rho_p^{-2/3}
\]  

(5.34)

Note here that \( \eta \) is still the pure solvent viscosity. We concede here that this is currently a much less satisfactory argument than the one we used to determine \( \lambda \). However, we can always test it, which we proceed to do so now.
5.6 COMPARISON OF THE SLIGHT SLIP THEORY WITH SIMULATION AND EXPERIMENT

To test the slight slip theory we fitted a function with the form of Eq. 5.31 to the simulation data. In Fig. 5.5 we compare the fit with the profiles obtained from simulations for volume fractions up to $\phi = 1.7$. At first sight the agreement is excellent. Since the only relevant quantity in the slight slip theory is the polymer volume fraction, we can further speculate that the theory also describes mixtures. To test this assumption we carried out the same fitting procedure for flow profiles calculated from simulations of bi-disperse mixtures. Specifically, we repeated the simulations for a mixture of polymer chains of length $N_b = 4$ and $N_b = 32$ (at a ratio of 8 : 1). The results are shown in Fig. 5.6. As the figure shows, again the fit accurately describes the profiles, even up to volume fractions as high as $\phi \sim 4$. In fact, at an equivalent volume fraction (illustrated for $\phi = 0.2$), the equivalence is exact.

To rule out the possibility that the theory just gets lucky we can now check to what extent the values of $\lambda$ and $A(\phi)$ given by the fit agree with the predictions of the theory. Beginning with the apparent Brinkman length, $\lambda_s$, in Fig. 5.7 we show the calculated values, relative to the value predicted by Eq. 5.28, as a function of polymer volume fraction. The fitted data includes both mono and bi-disperse systems and polymer sizes of $N_b = 4, 16, 32$. As the figure shows, there is no systematic variation of this quantity with volume fraction. It is actually constant to within the error in the fitted values (not shown). This means that it does indeed scale in the way the slight slip theory predicts. Further, the constant of proportionality is close to unity, our best estimate is that $\lambda/\lambda_s = 0.85$. Turning to the pre-factor, $A(\phi)$, in Fig. 5.8 we have plotted the relative pre-factor $A(\phi)/A(\phi \to 0)$ as a function of $\phi^{1/3}$ for the simulations with polymer chains of 32, 16 and 4 beads. The quantity $A(\phi)$ is calculated from the same fit to the velocity profiles (Eq. 5.31) that we used to calculate $\lambda$. According to the theory (Eq. 5.34) this plot should be linear (because $A(\phi) \sim \phi^{-2/3}$, whereas $A(\phi \to 0) \sim \phi^{-1}$). Examining the results for the simulations with $N_b = 16$ we observe that in this case the value of $A(\phi)/A_0$ agrees with the $N_b = 32$ results.
Figure 5.5: The relative solvent velocity profiles of three different systems and the accompanying fits according to Eq. 5.31. The results from top to bottom represent the following systems: (1) \( N_b = 16, \phi = 0.10, R_g/R = 0.158 \), (2) \( N_b = 4, \phi = 0.53, R_g/R = 0.126 \), (3) \( N_b = 32, \phi = 1.68, R_g/R = 0.366 \).

Figure 5.6: The relative solvent velocity profiles of polydisperse polymer solutions simulations. The squares represent simulation results of a mixture with a volume fraction of \( \phi = 0.2 \), the crosses are results from simulations of solutions of single polymer species (as also shown in Fig. 5.2 (C)). Next, from top to bottom, the circles represent mixtures with a volume fraction of \( \phi = 0.43, 0.87, 2.17 \) and 4.334 respectively. We also show the corresponding fits according to Eq. 5.31.
5.6 Comparison of the slight slip theory with simulation and experiment

![Figure 5.7: The Brinkman length $\lambda_s$ relative to the predicted Brinkman length (Eq. 5.28) as a function of polymer volume fraction $\phi$. We determine $\lambda_s$ by fitting the flow profiles from simulations to Eq. 5.31. The squares represent results of simulations with chains of length $N_b = 32$, the triangles with $N_b = 16$ and the circles with $N_b = 4$, respectively.](image)

![Figure 5.8: The relative pre-factor $A(\phi)/A_0$ as a function of $\phi^{1/3}$ for polymer solutions with chains consisting of 32 (squares), 16 (diamonds) and 4 beads (circles).](image)
This suggests that the results are independent of the number of beads in the chains at least for \( N_b > 16 \), and should hold for all longer chains. It is plausible that the plot is linear, as the theory predicts, but the errors (not shown) are rather high so it is difficult to absolutely conclude that this is the case. One unambiguous observation is that the ratio is not constant, that is the pre-factor is (unsurprisingly) modified compared with the usual Brinkman result. From the figure we also see that for model chains with \( N_b = 4 \) we find \( A(\phi)/A(\phi \to 0) \) is significantly lower than for \( N_b \geq 16 \). This is probably not a physical effect, but an artifact. We believe the small number of beads in the model does not adequately capture the hydrodynamics in the concentrated regime. This is in contrast with the results for \( \lambda \), where the \( N_b = 4 \) results agreed with those for longer chains.

Clearly, the agreement between the slight slip model and the simulation results for concentrated solutions of both mono and bi-disperse polymers is remarkable. The crucial question now is, does it describe reality? We have already pointed out that it is in qualitative agreement with what is known experimentally. Can we be more quantitative? Polymer solutions are usually polydisperse. However, comparison with simulations suggests that the theory is valid for bi-disperse system so there seems no reason to believe that this does not generalize to the polydisperse case (again, because our theory
5.7 VOLUMETRIC FLOW RATE

A quantity that is more easily measured experimentally than the actual flow profile is the volumetric flow rate. Comparison between the experimental values and the volumetric flow rates found in the simulations would be a useful method to relate the computer simulations to experiments. The volumetric flow rate \( Q \) is defined as the fluid volume passing a given cross section in the tube per unit time. For a solvent flowing with a uniform velocity \( V \)

![Figure 5.10](image-url)  
**Figure 5.10:** The volumetric flow rate of the polymer solutions relative to the value it would be for Poiseuille flow as a function of volume fraction. We calculated the volumetric flow rate for the Poiseuille flow based on the viscosity of the polymer solutions. The squares represent the polymers with \( N_b = 4 \) (for the open symbols \( R_g/R = 0.126 \), for the filled symbols \( R_g/R = 0.158 \)), the circles represent polymers with \( N_b = 32 \) (for the open symbols \( R_g/R = 0.366 \), for the filled symbols \( R_g/R = 0.462 \)) and the diamonds represent a mixture of the two types.

only depends on the total volume fraction \( \phi \)). In Fig. 5.9 we compare our prediction of the solvent flow profile with experimental results on the flow profile of polydisperse solutions of polyethyleneoxide in water through a 700 μm capillary. Because we do not have information on the exact composition of the solution, the volume fraction is unknown. Consequently, the comparison is only semi-quantitative. The modified Brinkman length is a free parameter and we only consider the normalized flow profile. However, we can still conclude that Eq. 5.31 is able to describe the shape of these experimental profiles to a high degree of accuracy.
through a tube of radius $R$ we have $Q = \pi R^2 V$. In the case of a flowing solvent in a tube with a non-uniform flow profile the volumetric flow rate is given by the following integral over the cross section of the tube:

$$Q = \int_0^R V(r) 2\pi r dr$$

Solving this integral, for Poiseuille flow (defined in Eq. 5.3) we find:

$$Q = \frac{\pi \xi R^4}{8 \eta}$$

Because we determined the viscosity as a function of the polymer volume fraction (see Fig. 5.1) we can predict the volumetric flow rate of a polymer solution assuming the flow profile is that of Poiseuille flow of a Newtonian fluid with the polymer solution viscosity. This we denote $Q_{\text{poli}}$. On the other hand, we can numerically determine the volumetric flow rate of the simulated systems because we know exactly what the accompanying flow profile of these systems is. If we calculate the ratio of the two, we can quantify how much the flow rate of the polymer solution differs relative to that of the equivalent Newtonian fluid. There will be two effects contributing to this. First, we know that the shape of the profile changes and this will have an effect (see Eq. 5.35). Second, the magnitude of the flow velocity will change but, according to the slight slip theory, not obviously in a way that is inversely proportional to the solution viscosity (see Eq. 5.34). In Fig. 5.10 we have plotted the volumetric flow rate relative to $Q_{\text{poli}}$, calculated numerically from the simulation results, as a function of volume fraction. The data has a relatively large error because of the accumulation of errors in the flow profiles, numerical integration of the profiles and the solution viscosity. Nonetheless, with increasing polymer volume fraction $\phi$, the relative volumetric flow rate $(Q/Q_{\text{poli}})$ clearly increases. That is, the polymer solution flows at a rate notably higher than a Newtonian fluid with the same viscosity. The magnitude of the effect appears to increase roughly linearly and for $\phi = 3$ the polymer solution flows at four times the rate of its Newtonian counterpart. This is exactly the “slip” effect observed experimentally. We do not have detailed enough experimental data (notably data at a known volume fraction, which requires that the size of the polymers is known) to make a complete comparison. What we can say is that the magnitude of the slip effect we observe is at least comparable. Values of up to 5 are reported at high concentrations, where the volume fraction is certainly greater than unity.
From an experimental point of view it is of interest to look at the accelerated drift velocity of the polymer chains. In chapter 4 we discussed this in detail for systems with volume fractions $\phi \ll 1$, here we will discuss simulations up to $\phi \sim 4.5$. Due to steric hindrance of the wall the centres-of-mass of the polymer chains get excluded from the area close to the wall. In this area of the tube, the average solvent flow velocity is typically much smaller than the flow velocity in the centre of the capillary. The polymers will spend more time in the high velocity area, resulting in an accelerated drift velocity, relative to the average flow velocity. We demonstrated that for small polymers, $R_g/R < 0.25$, the hydrodynamic interactions have little influence. With increasing $R_g/R$ the hydrodynamics will decrease the average drift velocity, relative to methods where these interactions are not taken into account.\(^{141}\)

In the simulations we describe here, the polymer chains with $N_b = 4$ are smaller than $R_g/R < 0.25$, whereas the chains with $N_b = 32$ are bigger. For an experimentalist the mixed case will be the most interesting: how well can a given capillary distinguish chains of different size, where, in this case, the bigger chains are almost three times bigger than the smaller. Furthermore, we are interested in finding out if there is a difference in drift velocity ($\Delta V$) between systems with only one type of polymer and a mixed polymer solution.

In Fig. 5.11 (A) we plot the drift velocity $V_P/V_S$ for systems with only chains of $N_b = 4$ ($R_g/R = 0.126$), for systems with chains with $N_b = 32$ ($R_g/R = 0.366$), and for a mixture of the two. Let us first look at the results of the simulations with only one type of polymer chain. A first difference between the big and the small chains is the fact that the larger chains drift faster than the smaller chains. In both systems, for small $\phi$, the results are in agreement with the results found in chapter 4. We find that with increasing $\phi$ the drift velocity decreases. This effect is stronger for the bigger chains. In Fig. 5.11 (B) we plot the difference between the two drift velocities as a function of $\phi$. For $\phi \sim 0.5$ we find $\Delta V$ is only about 75% of the value we calculated for $\phi \to 0$. We also estimated the drift velocity for three different polymer volume fractions based on the relative density distribution of the centre-of-mass inside the tube (see Fig. 5.4). If we assume that the polymer chain drifts with the average solvent velocity at the radial position of the centre-of-mass we can calculate the flow velocity of this chain using Eq. 4.2. In this case we use the flow profile we measured during the simulations, instead of the undisturbed parabolic velocity profile (i.e. the procedure we followed in chapter 4). The drift velocities calculated using this method are also plotted in Fig. 5.11 (A). These estimates are $\sim 10\%$ higher than the drift velocity found
in the simulations. The predictions do follow the same trend as found in the simulations, therefore we find the same value for $\Delta V$ as a function of $\phi$ (also plotted in Fig. 5.11 (B)). Let us now turn to the simulations with a mixture of both polymer sizes. In Fig. 5.11 (A) we do not observe a difference between $V_P/V_S$ for the chains in the mixture and for the chains in the systems with only one type. However, it is interesting to find that the drift velocity of the small polymer chains is constant, even for large values of $\phi$. For the longer chains, $V_P/V_S$ keeps decreasing with increasing $\phi$. The estimated velocity, based on the distribution of the centre-of-mass and the velocity profile, is almost identical to the results we found earlier. Interestingly, $\Delta V$ decreases with increasing $\phi$, going to only 50% of the original value for $\phi > 2$.

We repeated the simulations for a lower solvent density, resulting in polymer sizes of $R_g/R = 0.158$ and 0.462 for $N_b = 4$ and 32 respectively. As shown in Fig. 5.12 (A), for solutions with one polymer type we observe a decreasing $V_P/V_S$ with increasing $\phi$. Again, the estimated drift velocity based on the distribution of the centre-of-mass is higher than the results from the simulations (20% for the larger chains, 9% for the smaller). Fig. 5.12 (B) shows that $\Delta V$ decreases with increasing $\phi$, just as we observed for the simulations at a higher solvent density. However, despite following the same trend, here the estimated value of $\Delta V$ lies much higher than the results from the simulations. Turning to the mixture in Fig 5.12 (A), for the larger chains $V_P/V_S$ is identical to results found for the non-mixed simulations. For the small chains there is a notable difference between the drift velocity for the mixture and the single species simulations. For the mixture $V_P/V_S$ decreases $\sim 10\%$ up to $\phi \sim 2.5$, but for higher values of $\phi$ we observe an increase of the drift velocity. Contrary to this observation, the estimated drift velocity remains constant for the small polymer chains, independent from the polymer volume fraction. Again, the estimated values for both polymer lengths are higher than the values found in the simulations. In the case of the mixture we see in Fig 5.12 (B) that $\Delta V$ is almost constant up to $\phi \sim 2.5$. At even higher volume fractions $\Delta V$ decreases. The estimated values for $\Delta V$ show a continuous decrease with increasing $\phi$, going from almost a factor of two higher than found in the simulations for small volume fractions to lower values for at least $\phi > 1$. 
**Figure 5.11:** Results from simulations with chains of $N_b = 4, R_g/R = 0.126$ (circles), chains with $N_b = 32, R_g/R = 0.366$ (squares) and a mixture of these two. Figure A shows the relative polymer velocity for the single species (open symbols) and mixture (filled symbols) simulations. The symbols are results from simulations, the x (4 beads) and + (32 beads) are predictions based on the solvent flow profile and the polymer density distribution.

Figure B shows the difference in relative polymer velocity $V_P/V_S$. The lines are results extracted from the simulation (the dashed line represents the mixture, the continuous line the single species simulations), the circles are predictions based on the solvent flow profile and the polymer density distribution (open for the single species simulations, filled for the mixture). The results in this figure are extracted from Figure A.

**Figure 5.12:** Results from simulations with chains of $N_b = 4, R_g/R = 0.158$ (circles), chains with $N_b = 32, R_g/R = 0.462$ (squares) and a mixture of these two. Figure A shows the relative polymer velocity for the single species (open symbols) and mixture (filled symbols) simulations. The symbols are results from simulations, the x (4 beads) and + (32 beads) are predictions based on the solvent flow profile and the polymer density distribution.

Figure B shows the difference in relative polymer velocity $V_P/V_S$. The lines are results extracted from the simulation (the dashed line represents the mixture, the continuous line the single species simulations), the circles are predictions based on the solvent flow profile and the polymer density distribution (open for the single species simulations, filled for the mixture). The results in this figure are extracted from Figure A.
In this chapter we considered the pressure-driven flow of polymer solutions of various concentrations through microfluidic capillaries at low Reynolds numbers. We used mesoscopic computer simulations to calculate the flow profiles. The simulations were consistent, in that we could reproduce long polymer behaviour with short model chains, for fractions up to $\phi \sim 4$. This clearly demonstrates the power of the simulation techniques we employ. We should stress that simulating concentrated polymer solutions in the presence of a solid/fluid interface, while accounting for all the relevant hydrodynamic interactions, is a very complex problem. However, we demonstrated that it is possible to do so, using only a limited amount of computational resources. The flow profile of Newtonian solutions is parabolic (the Poiseuille result). However, the flow profile of a polymer solution, even in the micro fluidic regime, shows a strong deviation from the parabolic profile. The shapes and magnitudes are not described by existing theories. They are, however, accurately described by the slight slip theory we developed in this chapter.

The slight slip theory considers the polymer solution as a porous medium moving at a velocity that is not quite that of the ambient fluid. One thing we have ignored thus far is the mechanism that generates the apparent slip. At this point we should point out that the observation that polymers in solution change the flow profile on length scales very much longer than the polymer radius of gyration, $R_g$, is not true for simple shear flow. In this case the effect really is limited to a region of width $R_g$ adjacent to the surface. So whereas our model succeeds spectacularly for flow in a capillary, it fails spectacularly for simple shear flow. For this case there is no slight slip. In turn this suggests that it is the non-uniformity of the unperturbed stress over the space occupied by a polymer that is important. That is, the fact that the average over the region of space occupied by the polymer differs from the velocity at the centre of mass. To shed more light on this it would be instructive to see how the slight slip model arises from the hydrodynamics in terms of a more detailed microscopic description. Further, this could allow a theoretical calculation of the constants involved. This is beyond the capability of the theory as it stands. Nevertheless, the “slight slip” theory clearly describes the simulation results very well, not to mention experimental observations.

We should emphasize here that the slip we are talking about is a small difference between the polymer drift velocity and the ambient flow velocity. It is absolutely not a breakdown of the stick boundary conditions at the solid/fluid interface. The observation that the flow of polymer solutions is anomalously rapid is often put down to this. We should emphasize that
we observe the latter phenomenon, but our simulations rigorously enforce the stick boundary condition. Put simply, the experimentally observed “slip” effect has nothing to do with violations of the usual stick boundary condition. In our simulations this is rigorously enforced, but we see the same effects observed experimentally.

Returning to hydrodynamic chromatography, we determined the drift velocity of the polymer chains for the chains of length $N_b = 4$ and $N_b = 32$, and for the mixture of the two. From an experimental point of view this last system is of special interest because it mimics a separation technique called hydrodynamic chromatography. In chapter 4 we discuss this technique in detail. In general we do not observe a difference between the results for the mixture and for the single species simulations. Only the system with $N_b = 4$ and $R_g/R = 0.158$ behaves different compared to the mixture. Nevertheless, in all cases we observe that the polymer flow velocity relative to the average flow velocity decreases with increasing polymer volume fraction. This is not that surprising, considering the fact that the flow profile flattens with increasing volume fraction. For a completely flat flow profile, no matter what the preferred location of the polymer chains is, $V_P/V_S$ will always be one. Also, the difference between the drift velocity of the bigger and the smaller chains decreases with increasing volume fraction. Consequently, we suggest experimentalists to employ the hydrodynamic chromatography separation technique only for polymer fractions $\phi < 1$. 