Polymer Conformational Changes under Pressure Driven Compressible Flow in Nanofluidic Channels

By

Riyad Chetram Raghu

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

Department of Chemistry

University of Toronto

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Riyad Chetram Raghu

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Department of Chemistry
University of Toronto

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Abstract

A hybrid molecular dynamics/multiparticle collision dynamics algorithm was constructed to model the pressure-driven flow of a compressible fluid through a nanoscopic channel of square cross-sectional area, as well as the effect of this flow on the configuration of a polymer chain that was tethered to the surface of this nanochannel. In the process of simulating channel flow, a new adiabatic partial slip boundary condition was created as well as a modified source/sink inlet and outlet boundary condition that could maintain a specified pressure gradient across the channel without the large entrance effects typically associated with these algorithms. The results of the flow simulations were contrasted with the results from a series solution to the Navier-Stokes equation for isothermal compressible flow, and showed excellent agreement with the results from the series solution when slip-boundary conditions were applied. A finitely extendible non-linear elastic spring and bead polymer chain was used to simulate the effect of flow on the polymer chain configuration under poor solvent and θ solvent conditions. Under θ solvent conditions, the
cyclical dynamics that have been previously observed for tethered polymer chains in pure shear flows were noted, however they were restricted to the end of the polymer chain. Under poor solvent conditions, the polymer adopted a metastable helix configuration as it collapsed to a globule state. The study also examined interchain and intrachain entanglements in polymers using the granny knot and overhand knot. The mechanisms by which these tangles untied themselves were determined. At low flow rates, the tangles unravelled by the end of the chain migrating through the loops of the tangle. At high flow rates, the tangles behaved like an entrained object as they reptated towards the end of the chain.
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# Table of Contents

## Contents

Acknowledgments ................................................................................................................... iv  
Table of Contents .................................................................................................................. v  
List of Tables ........................................................................................................................ viii  
List of Figures ....................................................................................................................... ix  
List of Appendices ................................................................................................................ xiv  

### Chapter 1 Introduction

1.1 Purpose .......................................................................................................................... 1  
1.2 Applications ................................................................................................................... 3  
1.3 Structure ....................................................................................................................... 5  
1.4 Simulation Hardware ...................................................................................................... 5  

### Chapter 2 Channel Flow

2.1 Overview ......................................................................................................................... 7  
2.2 Theoretical Review ......................................................................................................... 8  
2.2.1 The Boltzmann Equation .......................................................................................... 10  
2.2.2 Direct Simulation Monte Carlo .............................................................................. 12  
2.2.3 Dissipative Particle Dynamics ................................................................................ 14  
2.2.4 Multi-Particle Collision Dynamics ....................................................................... 16  
2.2.5 Continuum Approaches ......................................................................................... 21  
2.2.6 Simulating Channel Flow ....................................................................................... 23  
2.2.7 Applications to Channel Flow ............................................................................... 25  
2.3 MPCD-Molecular Dynamics Algorithm Implementation ........................................... 28  
2.3.1 MPCD-Molecular Dynamics Algorithm ............................................................... 29
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.2</td>
<td>Boundary Conditions</td>
<td>35</td>
</tr>
<tr>
<td>2.3.3</td>
<td>Channel Flow Parameters</td>
<td>45</td>
</tr>
<tr>
<td>2.4</td>
<td>Channel Flow Results</td>
<td>47</td>
</tr>
<tr>
<td>2.4.1</td>
<td>Equilibrium Simulations</td>
<td>50</td>
</tr>
<tr>
<td>2.4.2</td>
<td>Flow Simulations</td>
<td>59</td>
</tr>
<tr>
<td>2.5</td>
<td>Conclusions</td>
<td>71</td>
</tr>
<tr>
<td>3.1</td>
<td>Overview</td>
<td>73</td>
</tr>
<tr>
<td>3.2</td>
<td>Theoretical Review</td>
<td>74</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Polymer Models</td>
<td>75</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Extension under shear flow</td>
<td>78</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Cyclical Dynamics</td>
<td>83</td>
</tr>
<tr>
<td>3.3</td>
<td>Simulation Method</td>
<td>84</td>
</tr>
<tr>
<td>3.4</td>
<td>Polymer results</td>
<td>89</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Θ solvent conditions</td>
<td>92</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Poor Solvent Conditions</td>
<td>104</td>
</tr>
<tr>
<td>3.5</td>
<td>Conclusions</td>
<td>109</td>
</tr>
<tr>
<td>4.1</td>
<td>Overview</td>
<td>111</td>
</tr>
<tr>
<td>4.2</td>
<td>Theoretical Review</td>
<td>112</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Primitive Path Analysis (PPA)</td>
<td>118</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Skein Invariants</td>
<td>119</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Entanglements Under Shear</td>
<td>122</td>
</tr>
<tr>
<td>4.3</td>
<td>Simulation Methodology</td>
<td>126</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Overhand knot formula</td>
<td>127</td>
</tr>
</tbody>
</table>
List of Tables

Table 2.2.4.1 Transport Coefficients for the 3D MPCD algorithm .................................................. 19

Table 3.2.2.1 Results for the change in the thickness of a polystyrene layer under shear flow ... 82

Table 3.3.1 Potential parameter values for simulations ................................................................. 88

Table A.1 Final Expressions from the Navier-Stokes Equation .................................................. 182
List of Figures

Figure 1.2. 1 A schematic for a pressure operated gate .......................................................... 4

Figure 2.2.4. 1 An illustration of the anisotropy of the square cell ........................................ 17

Figure 2.3.2.2. 1 Illustration for the need for a positive bias to $\mathbf{v}_{\text{flow}}$ in the boundary condition algorithm from a pneumatic spring .................................................................................. 44

Figure 2.3.3. 1 Schematic of the model channel ....................................................................... 46

Figure 2.4. 1 The inlet and outlet effects on hydrodynamic variables ...................................... 48

Figure 2.4.1. 1 An illustration of the two mechanisms by which a pressure of $P$ can be produced by the boundary condition algorithm ................................................................................ 53

Figure 2.4.1. 2 Cell density and pressure distribution functions for the inlet cells. ............... 55

Figure 2.4.1. 3 Cell number density function vs. cell coordinate ......................................... 57

Figure 2.4.1. 4 Cell pressure density function vs. cell coordinate ....................................... 58

Figure 2.4.2. 1 A plot of flow rate vs. pressure gradient .................................................... 60

Figure 2.4.2. 2 The Knudsen number as a function of flow rate and channel length ............ 61

Figure 2.4.2. 3 Pressure as a function of channel length and flow rate .................................. 62

Figure 2.4.2. 4 Temperature as a function of flow rate and channel length ......................... 63

Figure 2.4.2. 5 Density as a function of channel length and flow rate .................................. 64

Figure 2.4.2. 6 Centre channel, or maximum, velocity as a function of channel length and flow rate ........................................................................................................................................ 66

Figure 2.4.2. 7 A plot of the slip velocity as a function of the flow rate ............................... 67

Figure 2.4.2. 8 The slip velocity vs. the product of the shear rate and the mean free path length. 69
Figure 2.4.2. 9 The velocity profile across the width of the channel at the centre of the channel as a function of flow rate ................................................................. 70

Figure 3.4.1 A plot of the Radius of gyration of the polymer under equilibrium conditions vs. the parameters of the solvent-polymer Lennard-Jones potential ................................................................. 91

Figure 3.4.1.1 The radius of gyration and its three components plotted vs. time for 2 simulations ........................................................................................................................................ 93

Figure 3.4.1.2 The steady state radius of gyration and its three components vs. Wall Shear Rate at the point of adhesion .................................................................................................................. 94

Figure 3.4.1.3 Cross-correlation function between the average $x$ and $y$ velocity components of the last 50 beads of the centimer ........................................................................................................ 96

Figure 3.4.1.4 A spectral analysis of the cross-correlation function between the $x$ and $y$ velocity components ........................................................................................................................................ 97

Figure 3.4.1.5 The magnitude of the end to end vector and radius of gyration plotted vs. time. 99

Figure 3.4.1.6 Illustration of cyclical dynamics in a simulation .................................................. 102

Figure 3.4.1.7 The Cross-Correlation function between the $x$ and $z$ components of the Radius of Gyration ........................................................................................................................................ 102

Figure 3.4.1.8 A quiver plot of the deviations in the flow field before and after the addition of the polymer chain ........................................................................................................................................ 103

Figure 3.4.2.1 Equilibrium polymer configurations ................................................................. 104

Figure 3.4.2.2 Polymer configurations under flow under different solvent conditions .......... 105

Figure 3.4.2.3 The radius of gyration and its three components vs. wall shear rate .......... 106

Figure 3.4.2.4 Cross-correlation function between the $x$ and $y$ velocity components for the last 50 beads of the centimer ........................................................................................................................................ 107
Figure 3.4.2. 5 A quiver plot of the deviations in the flow field before and after the addition of the polymer chain.................................................................................................................. 108

Figure 4.2. 1 Positive and negative crossings................................................................................................................................. 113

Figure 4.2. 2 The three basic Reidemeister moves for unoriented crossings ......................... 114

Figure 4.2. 3 Two closings of the overhand knot ............................................................................................................................... 116

Figure 4.2. 4 Closing a single component knot when a direction, $x$, can be found for which the entire knot is contained between the end points ................................................................................................. 116

Figure 4.2. 5 Closing a two component tangle consisting of a single crossing ..................... 117

Figure 4.2.2. 1 The construction of the generalized knot invariant of the $2_1^2$ from the recurrence relation Eqn. 4.2.2.1 ......................................................................................................................... 120

Figure 4.2.2. 2 The conversion of the trefoil knot from an unoriented knot to a piecewise linear lattice........................................................................................................................................ 121

Figure 4.2.2. 3 Edge labelled crossing................................................................................................................................. 121

Figure 4.3.1. 1 The tying of the overhand knot in a single open component ....................... 127

Figure 4.3.2. 1 The reef knot family of six crossing tangles .................................................. 129

Figure 4.3.2. 2 The tying of the granny knot ........................................................................ 130

Figure 4.3.2. 3 The initial configurations of the granny knot in the parallel chain configuration and the channel spanning configuration. .................................................................................................................. 133

Figure 4.4.1. 1 The initial configuration of the tangle and its relaxed configuration ............. 135

Figure 4.4.1. 2 Unknotting times for 10 equilibrium runs with a tangle initially composed of 41 beads ........................................................................................................................................ 136

Figure 4.4.1. 3 Rapid unknotting of a polymer under equilibrium conditions. .................. 137

Figure 4.4.1. 4 Slower unknotting of a polymer chain under equilibrium conditions .......... 138
Figure 4.4.1. 5 The unknotting of the polymer chain under a high flow rate ........................................ 139

Figure 4.4.1. 6 Unknotting times vs. flow rate for low flow rates .................................................. 140

Figure 4.4.1. 7 The first passage time distribution from the Brownian motion model in Appendix B, vs. the tangle size, $N_{\text{tangle}}$ .................................................................................................. 142

Figure 4.4.1. 8 Simulation data of unknotting times for the polymer as a function of $N_{\text{tangle}}$ under equilibrium conditions ........................................................................................................ 143

Figure 4.4.1. 9 Unknotting time vs. $N_{\text{tangle}}$ for high flow rate simulations .............................. 144

Figure 4.4.1. 10 The number of beads in the tangle during simulation vs. the flow rate .......... 145

Figure 4.4.1. 11 Plot of the tangle position along the end to end vector vs. time .................... 146

Figure 4.4.1. 12 A plot of the tangle migration rate as a function of the fluid velocity .......... 147

Figure 4.4.2. 1 The unknotting of a granny knot tied between two parallel chains ........... 150

Figure 4.4.2. 2 The unknotting time of the six crossing granny knot and the four crossing two component overhand knot as a function of the flow rate, for the granny knot in a parallel chain configuration ............................................................................................................. 152

Figure 4.4.2. 3 The equilibrium configuration of two polymer chain in a parallel chain configuration ................................................................................................................................. 153

Figure 4.4.2. 4 The rate of tangle migration vs. the fluid velocity near the wall ................. 155

Figure 4.4.2. 5 The unknotting of a granny knot tied across the channel, for a high flow rate simulation ........................................................................................................................................... 156

Figure 4.4.2. 6 The unknotting time of the granny knot and the four crossing tangle as a function of the flow rate, for the granny knot tied in a channel spanning configuration .................. 157
Figure 4.4.2. 7 Plot of the tangle position along the end to end vector vs. time, for a high flow rate simulation

Figure 4.4.2. 8 The rate of tangle migration vs. the centre channel velocity for the granny knot tied in the channel spanning configuration

Figure B. 1 The initial position of the particle and the disk for the Brownian motion model

Figure C. 1 The first passage time distribution, displacement rate and Rousian diffusion coefficient
List of Appendices

Appendix A: Navier-Stokes Solution to Isothermal Compressible Flow .............................................. 179

Appendix B: Brownian Diffusion model of a Particle to a Disk ......................................................... 192

Appendix C: Brownian Diffusion model for knot in a Shear Field ....................................................... 195
Chapter 1
Introduction

1.1 Purpose

Scale poses a challenge not only in the fabrication of nanofluidic devices, but also in their characterization and theoretical description. Scale is at the crux of difficulties encountered when modelling the effect of the flow of a fluid through a nanoscale device on the configuration of a polymer chain that has been tethered to its surface. While the atomistic equations of motion can be written to describe the behaviour of the fluid, the polymer and their mutual effect on each other, the complete solution of the dynamics is computationally prohibitive. Alternative approaches such as the traditional continuum equations lack the nuance to capture crucial aspects of the relationship between the fluid flow field and the motion of the polymer. To address the problem of scale in nanofluidic devices, this report examines the effect of flow in a nanoscopic channel on the behaviour of a polymer chain that has been tethered to the surface of a square cross-section nanochannel by means of a mesoscopic algorithm; the multiparticle collision dynamics algorithm (MPCD) [Malevanets 1999]. In particular, the effect of flow on a single grafted polymer chain, the effect of flow on entanglements in a single polymer chain and the effect of entanglements between polymer chains inside a nanochannel is investigated through mesoscale simulations.

Flow can be generated through several processes. While gravity or magnetism (in the case of ferro-magnetic fluids) can be used to drive flow, by far the most common method is through the use of a pump to supply a pressure head. Simulating a pressure-driven flow in a nanochannel using a MPCD fluid required the creation of a new algorithm to simulate a pressure-driven flow in a nanochannel for a MPCD fluid while minimizing inlet and outlet artefacts so that small pressure gradients could be simulated; a result that existing methods are incapable of producing with a MPCD fluid. The new algorithms were developed to generate a compressible flow profile in which the fluid expands as it flows, producing both elongational and shear components in the flow. This expansion does not develop in a gravitational flow, which has been studied previously and is easier to replicate.
To model the interface between the wall and the channel, an adiabatic wall boundary condition was also developed to produce the same streamwise momentum accommodation as thermally diffusive wall collisions, thus producing an intermediate result to Bounce-Back [Allahyarov 2002] [Lamura 2001] and specular collision adiabatic boundary conditions. The new boundary conditions reproduce slip flow, which is expected in nanofluidic devices.

A molecular dynamics (MD) subsystem was introduced to allow the fluid particles to interact with the polymer model through the use of an explicit potential. Hence it was necessary to develop a hybrid MD-MPCD algorithm to manage the interface between the MD and MPCD algorithms and successfully model the effect of the flow field on the polymer.

The polymer chain was simulated under θ solvent conditions and poor solvent conditions. There are three kinds of solvent conditions for polymer chains, θ solvent conditions, good solvent conditions and poor solvent conditions. These conditions are defined by the physical size adopted by the polymer chain under equilibrium conditions in the solvent relative to its size in vacuum. If the chain adopts a larger configuration in the solvent than in a vacuum then the solvent is called a good solvent. Alternately, if the chain adopts a configuration of a similar size to its configuration under vacuum conditions then the solvent is called a θ solvent. If the polymer assumes a smaller configuration relative to its vacuum configuration then it is called a poor solvent. Due to the presence of an elongational component of flow and fluid slip, the behaviour of the polymer was modified from its behaviour in a pure shear flow. Under θ solvent conditions, the cyclical dynamics observed both experimentally [Doyle 2000] [LeDuc 1999] and theoretically [DiMarzio 1978] [Delgado-Buscalioni 2006] are restricted to the end of the chain and are found to be aperiodic. Under poor solvent conditions the polymer chain formed a metastable helix. Due to the stability of the conformation of the polymer, it is possible to visualize the perturbation created by a single polymer chain on the flow field, a result that has not previously been presented.

The simulation of intrapolymer and interpolymer entanglements was conducted using tangles (or open component knots). In particular the single component overhand knot (which when closed forms the \(3_1\), or trefoil knot) and the two component granny knot (which when closed forms the \(6_2^1\) link) were used. Special attention was focused on the unknotting of these polymers. The
Unknotting of polymer chains under flow conditions has not previously been presented, although studies on the unknotting of polymer chains under equilibrium conditions [Lai 2000] [Lai 2003] and between two chains that have been mechanically pulled apart [Kirmizialtin 2008] have been conducted.

1.2 Applications

As a theoretical model, the basic MPCD algorithm and polymer model utilized in this report is unsuitable for conducting detailed engineering calculations. However, it does provide a basic predictive model that can be employed to perform preliminary calculations and basic feasibility studies for the construction of gas phase nanofluidic devices, or possibly a fluid phase device where compressibility effects of an ideal gas equation state are acceptable. In the design of fluidic devices, the known variables are often the head created by a pump, the temperature of the device and the outlet pressure. Hence an algorithm that can perform a particle-based simulation using these quantities as sole inputs is of value for studying the properties of real nanofluidic devices.

Similarly, the adiabatic boundary conditions presented in section 2.3.2 can be used with any particle-based simulation method to simulate channel flow. This method is of value in any simulation where energy conservation is important, or for the modelling of a well-insulated device.

The results on polymers should be general enough to indicate considerations for the use of polymers in gas phase nanofluidic devices. Examples of application where grafted polymers are used in nanoscale systems include: the use of polymer coatings to reduce friction in natural gas pipelines, the flow of gases through nylon filters with nanoscopic pores, or gas phase MEMS. One such device was the original focus of this work, though it proved to be too complex to simulate. The device was a flow operated gate, see figure 1.2.1. This hypothetical device consists of a channel with polymer chains tethered to its walls. At low flow rates, the polymers form a mechanically entangled gel network that span the channel. At high flow rates, the polymers extend in the direction of the flow to create an aperture in the centre of the channel. In such a system, an aerosolized particle that is larger than the pore size of the network would be unable to pass through the channel at low flow rates, but could pass through the aperture at higher flow rates.
Figure 1.2. 1 A schematic for a pressure operated gate, consisting of polymer chains tethered to the walls of a channel. At low flow rates, left (a), the polymer forms a mechanical network. At high flow rates, right (b), the polymer extends in the direction of flow, creating an aperture in the centre of the channel.

It was not feasible to simulate the pressure driven gate with the algorithm utilized in this study due to the size of the molecular dynamics subsystem and the length of time for which the system would have needed to be simulated. The most demanding computation in the algorithm is the calculation of the forces acting on the polymer beads, which has to be performed every molecular dynamics time step. For a single centimeter, with a fluid density of 40 particles per cell, a 1 ns simulation took approximately 5 days to run on a 1.8 GHz AMD Opteron processor. A simple model of the pressure operated gate requires approximately 30 centimeters. The number of polymer-solvent contacts scales linearly with the number of chains, hence approximately 150 days would have been required to simulate a 30 centimeter gate for 1 ns (2000000 MD time steps). However this would only be sufficient to simulate the transition from the entangled state to the oriented state or from the oriented state to the entangled state. To simulate the transition from an entangled state to the orientated state and back to the entangled state would require at least 3 ns (6000000 MD time steps) of simulation. While this process could be accelerated through parallelization of the algorithm, multiple simulations would have to be conducted under various flow conditions. At the time that these simulations were conducted, there were not enough processors available to perform multiple parallel simulations in parallel and parallel processes in series are slower than serial processes in parallel.
One of the features of such a device would be the hysteresis created by the physical entanglements of the chain. As the flow rate is decreased, the network reforms at a lower flow rate than is necessary to destroy it, due primarily to the resistance offered by the physical entanglements. The work presented here on tangles may prove useful in understanding the shear response of these entanglements for sparse polymer networks.

### 1.3 Structure

The contents of this report are naturally divided into three topics, with each topic founded on the theory of the previous one: fluid mechanics in nanoscale devices, polymer dynamics under shear flow and the dynamics of tangles in polymer chains under shear flow. Hence the second chapter of this report focuses on the work done in fluid mechanics. The third chapter focuses on polymer dynamics under shear flow. The fourth chapter presents the results for entanglements under flow and the fifth chapter presents the conclusions of this report and suggests future projects that could extend the work presented here. Each of chapters 2 through to 4 are further divided into subsections of a theoretical review, algorithm development and simulation results.

In addition to the main body of this report, there are several appendices that present theoretical work conducted to support these results. The first appendix presents series solutions to the Navier-Stokes solution for flow in channels of square cross-section both with and without slip boundary conditions. The second appendix outlines a Brownian motion model for a particle diffusing towards disk as an analogue for the unknotting of an overhand knot in a polymer under equilibrium conditions. The third appendix contains a Brownian motion model for linear diffusion in a tilted potential with a decaying oscillatory component as model for the unknotting of single component tangles in shear flow.

### 1.4 Simulation Hardware

The simulations were conducted on three computers. The first was a Beowulf cluster composed of 60-Dual CPU 1.8 GHz AMD Opteron CPUs each with 2 GB of RAM, running a Linux OS x64. The second was an AMD Turion TL-60 2GHz CPU with 2 GB of RAM running Windows Vista x64. The third computer was an Intel Q9450 2.8GHz CPU with 8 GB of RAM running Window Vista x64. The algorithm was written in C++ and compiled using the Microsoft Visual
Studio C++ compiler 2005 and 2003 editions as well as GNU C++ compiler in Linux. The Mersenne Twister [Matsumoto 1998] was used for random number generation.
Chapter 2  
Channel Flow

2.1 Overview

This chapter focuses on the use of MPCD to model flow in nanofluidic devices. In particular, the simulation of a flow field created by a pressure gradient through a nanochannel of square cross-sectional area. A pressure-driven flow was chosen in part for practical reasons, as flow in these devices is most often induced through the use of a pump to create a head pressure. It was also chosen as it presents a theoretical challenge. Flows are typically classified as either elongational flows or shear flows. Shear flows are characterized by a rotation of the principle axes of strain of a fluid element as it is deformed, while elongational flows are an irrotational flow [Bird 1987]. For an incompressible fluid, channel flow is a pure shear flow, produced by the drag forces of the wall acting against the head forcing the fluid through the pipe. However, for a compressible fluid, the pressure drop across the channel causes an expansion of the fluid in the direction of flow, hence there are elongational contributions to the flow in addition to the shear components. The simulation of a pressure-driven flow with a compressible fluid allows for the effect of an elongational flow component on a polymer to be examined.

To recreate this flow within a MPCD simulation, it was necessary to create a new boundary condition algorithm that would act as a particle source or sink to maintain a pressure gradient while minimizing the entrance effects. As the polymer had to be integrated by a MD simulation method it was necessary to interface the MPCD algorithm with a MD subsystem. An adiabatic partial slip wall boundary collision operator was also developed that simulates the slip produced by thermally diffuse collisions with a rough wall.

The next section of this chapter, section 2.2, presents a review of the existing theory related to flow in nanochannels, including the competing mesoscopic algorithms and the existing experimental results for channel flow in nanoscopic devices. Section 2.3, presents the details of the MPCD algorithm as implemented in this work. Section 2.4 presents the results of the simulations of pressure-driven flow through a channel. The final section, section 2.5, presents a summary of the conclusions of this chapter.
2.2 Theoretical Review

The MPCD algorithm belongs to a general class of mesoscopic fluid algorithms. These algorithms are designed to bridge the gap between continuum equations, such as the Navier-Stokes equation, and computationally prohibitive molecular dynamics simulations. For systems where the distance over which momentum transfer occurs is small relative to the scale of the system, the corpuscular nature of the fluid can be replaced with a local average of the fluid properties and the continuum approach can be applied. However, if the distance over which momentum transfer occurs is significant relative to the scale of the system, this corpuscular nature must be considered and a particle-based approach must be used.

The distance over which momentum transfer occurs can be approximated by the mean free path, $\lambda$, which is the average distance a particle travels between collisions. The distance over which the hydrodynamic variables change significantly is called the characteristic length scale of the system, $\Lambda$. It can be taken as a limiting physical constraint of the system (such as the width of a nanochannel) or it can be calculated as,

$$\Lambda = \rho \left( \frac{d\rho}{dz} \right)^{-1},$$

Eqn. 2.2.1

where $\rho$ is the density of the system and $z$ is the direction of flow for the system. The ratio of these quantities is called the Knudsen number,

$$Kn = \frac{\lambda}{\Lambda} = \sqrt{\frac{\pi\gamma}{2}} \frac{Ma}{Re}.$$  

Eqn. 2.2.2

This number is often written in terms of the Mach number (or the speed of the fluid, relative to the speed of sound in the fluid), $Ma$, the Reynolds number (or the ratio of inertial forces to viscous forces in the fluid), $Re$, and the ratio of specific heats, $\gamma$. If $Kn < 0.001$, continuum approaches such as the Navier Stokes equation can be used. This range can be extended to $Kn < 0.1$ if slip boundary conditions are applied as well. If $Kn > 10$, then molecular dynamics must be used. While an increase in $Kn$ does lower the density of the system, reducing the computational load of a molecular dynamics approach, there remains an intermediate range of
$0.1 < Kn < 10$, where continuum approaches are no longer valid and molecular dynamics is too computationally intensive to be feasible [Roy 2003]. This is the range for which the mesoscopic algorithms were developed.

Classical molecular dynamics is based on the classical equations of motion, for a system where only binary interactions between particles are considered these can be written for the position, $q_i$, and momentum, $p_i$, of the $i^{th}$ of $N$ particles as,

$$\frac{dq_i(t)}{dt} = \frac{p_i(t)}{m_i}$$

$$\frac{dp_i(t)}{dt} = \sum_{j=1,j\neq i}^{N} F_{ij}(q_i(t), q_j(t)) + \sum_{k=1}^{N_{wall}} F_{ik}(q_i(t)) + g(q_i(t), t).$$

Eqn. 2.2.3

where $m_i$ is the mass of the $i^{th}$ particle, $F_{ij}(q_i(t), q_j(t))$ is the force acting on the $i^{th}$ particle as generated by the $j^{th}$ particle, $F_{ik}(q_i(t))$ is the force acting on the particle generated by the $k^{th}$ of $N_{wall}$ walls and $g(q_i(t), t)$ is the resultant force of a systemic force field (magnetic, gravitational, etc.). For all but the most trivial of systems, these equations can only be solved by numerical integration. The first equation is easy to integrate, but the latter equation is where the intricacy of molecular dynamics arises.

For a system of $N$ particles where only two body potentials are considered, each particle can potentially interact with $N - 1$ additional particles. For pairwise potentials depending on the relative position vector of particles $i$ and $j$, $q_{ij} = q_i - q_j$, the force exerted by particle $i$ on particle $j$ is the negative of the force exerted by particle $j$ on $i$, thus $N(N-1)/2$ potential interactions need to be considered for each numerical integration step. In practice, positional sorting and a screening range on the potential can streamline the process to reduce the calculation to scale more as order $N$. Additional complexity arises from the large second derivatives of the intermolecular potentials at close range. This typically requires that the simulation be integrated with a time step in the femtosecond range. As hydrodynamics tend to require at least a nanosecond of simulation to manifest, computational limitations restrict the use of formal molecular dynamics to small systems where the Knudsen number, $Kn$, is greater than 10.
2.2.1 The Boltzmann Equation

As the limiting computational factor is the integration of the interparticle potentials, the majority of mesoscopic algorithms attempt to simplify the collision process. The precursor to these algorithms is the Boltzmann equation, which describes the phase-space evolution of single particle probability densities and simplifies the collision process through the introduction of a collision operator that replaces the integration of the potentials. For a closed system at equilibrium, the time evolution of the phase-space probability density, \(f^{(N)}(\mathbf{q}^N, \mathbf{p}^N, t)\) is given by Liouville Equation [McQuarrie 2000] [Hansen 1986],

\[
\frac{\partial f^{(N)}}{\partial t} = \sum_{i=1}^{3N} \left( \frac{\partial H}{\partial q_i} \frac{\partial f^{(N)}}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial f^{(N)}}{\partial q_i} \right),
\]

where \(H(\mathbf{q}^N, \mathbf{p}^N)\) is the Hamiltonian of the system. For a sub-group of \(n\) particles, the phase space density function can be calculated by integrating over the position and momentum vectors of the other \(N-n\) particles in \(f^{(N)}(\mathbf{q}^N, \mathbf{p}^N, t)\),

\[
f^{(n)}(\mathbf{q}^n, \mathbf{p}^n, t) = \frac{N!}{(N-n)!} \int \cdots \int f^{(N)}(\mathbf{q}^N, \mathbf{p}^N, t) d\mathbf{q}^{(N-n)} d\mathbf{p}^{(N-n)}.
\]

The time dependence of this reduced density function is more difficult to characterize than the Liouville equation. An exact form cannot be given directly, but in general a recurrence relationship can be found that relates \(f^{(n)}\) to \(f^{(n+1)}\). For a single particle, the time evolution of \(f^{(1)}\) can be written as

\[
\left( \frac{\partial}{\partial t} + \frac{1}{m} \mathbf{p}_1 \cdot \frac{\partial}{\partial \mathbf{q}_1} + \mathbf{F}_1 \cdot \frac{\partial}{\partial \mathbf{p}_1} \right) f^{(1)}(\mathbf{q}_1, \mathbf{p}_1, t) = -\int \cdots \int \mathbf{F}_{12} \cdot \frac{\partial}{\partial \mathbf{p}_1} f^{(2)}(\mathbf{q}_1, \mathbf{p}_1, \mathbf{q}_2, \mathbf{p}_2, t) d\mathbf{q}_1 d\mathbf{p}_1 d\mathbf{q}_2 d\mathbf{p}_2,
\]

where \(m\) is the mass of the particle, \(\mathbf{F}_1\) is the force acting on particle 1 and \(\mathbf{F}_{12}\) is the force acting on particle 1 due to particle 2. Under the assumptions that collisions are uncorrelated and binary in nature, Ludwig Boltzmann obtained a formula that replaces the right hand term of the previous equation with a collisional average based on single particle distributions,
Here the collisional term is,

\[
\left( \frac{\partial f^{(i)}}{\partial t} \right)_{\text{collisions}} = \frac{1}{m} \sum_{i=2}^{N} \iiint \sigma(\Omega, |p_1 - p_2|) \int f^{(i)}(q_i, p_i', t) f^{(i)}(q_i, p_i, t) - f^{(i)}(q_i, p_i, t) f^{(i)}(q_i, p_i', t) d\Omega dp_i,
\]

where the prime notation denotes the post collisional momenta and \( \sigma(\Omega, |p_1 - p_2|) \) is the cross section for scattering into a solid angle \( \Omega \).

From the perspective of simulations, the advantage of this equation is that it replaces the explicit calculation of the forces with the pre and post collisional momenta of the particles. This simplification allows for the replacement of an explicit potential with a collision operator. While this is a reduction in complexity of the molecular dynamics approach, it is still too computationally intensive to examine systems in the \( 0.1 < Kn < 10 \) range.

In the Boltzmann equation, energy, mass and linear momentum are conserved and the resulting non-equilibrium averages of local densities of these variables generate the same first order hydrodynamics as the Navier-Stokes equation. As long as the probability of a particle being deflected by an angle \( \theta \) after a collision is the same as the probability of a particle being deflected by \( -\theta \), the algorithm is Galilean invariant. The Boltzmann equation also satisfies the second law of thermodynamics; i.e. as a closed system evolves in an irreversible process,

\[
\frac{dS(t)}{dt} \geq 0 \text{ for all } t, \text{ where } S(t) \text{ is the entropy.}
\]

Boltzmann proved this through the use of an H-theorem [Bird 1994], defining a function,

\[
H(t) = \iiint f^{(i)}(q, p, t) \ln f^{(i)}(q, p, t) dq dp,
\]

which is similar to \(-S(t)\) for the full phase space distribution. Showing that \( \frac{\partial H(t)}{\partial t} \leq 0 \text{ for all } t \), is equivalent to proving that the system evolves to a equilibrium state regardless of initial configuration.
2.2.2  Direct Simulation Monte Carlo

One of the earliest mesoscopic algorithms is the Direct Simulation Monte Carlo (DSMC) algorithm of G. A. Bird [Bird 1970]. This algorithm, or rather a collection of algorithms as there are many different models and variations on this algorithm, simplifies molecular dynamics by replacing individual particles with an aggregate that is representative of several particles. In DSMC the explicit calculation of collisions is replaced with a Boltzmann type collision operator which randomly performs collisions of particles that are spatially localized. The standard no time counter (NTC) algorithm requires the division of the system into cells. The cells should be large enough that they hold more than 20 particles to ensure molecular chaos, but they should not be so large that particles remain in the same cells over multiple time steps as this would introduce unrealistic physical correlations. Ignoring the boundary conditions for the rest of this description, the system is then numerically integrated with time step $\Delta t$. The position is advanced based on the value of the particle momenta as per standard molecular dynamics, e.g.

$$q(t + \Delta t) = q(t) + \frac{p(t + \Delta t/2)}{m} \Delta t.$$ 

The calculation of the momentum changes is where the simplification of DSMC arises. Particles sharing a cell are randomly selected for collision and are collided.

The probability of a pair of particles being collided is [Bird 1994],

$$p_{ij} = \frac{F_N \sigma_T |v_{ij}|}{V_{cell}} \Delta t,$$

where $F_N$ is the number of real fluid particles per DSMC particle, $v_{ij}$ is the relative velocity $(v_i - v_j)$ between particles $i$ and $j$, $V_{cell}$ is the volume of the cell and $\sigma_T$ is total collisional cross-section. This is effectively the volume traversed by the pair of particles relative to each other, over the volume of the cell. While the simulation can be performed by examining each pair of particles in the cell and testing against this probability to see if a collision is performed, this is not the method used in the NTC algorithm. In this algorithm, the number of pairs tested for collisions is:
\[ \frac{N\bar{N}F_N\left(\sigma_T|v_{ij}\right)_{\text{max}} \Delta t}{2V_{\text{cell}}} \],

where \( N \) is the number of DSMC particles in the cell, \( \bar{N} \) is the time averaged value of \( N \) and \( \left(\sigma_T|v_{ij}\right)_{\text{max}} \) is ideally chosen to be the highest product of \( \sigma_T \) and \( v_{ij} \) that has occurred within the cell. In practice, \( \left(\sigma_T|v_{ij}\right)_{\text{max}} \) is selected arbitrarily and is updated with a larger value if one is found during simulations. The probability of a selected pair undergoing a collision is,

\[ p_{ij} = \frac{\sigma_T|v_{ij}|}{\left(\sigma_T|v_{ij}|_{\text{max}} \right)}. \]

The definition of \( \sigma_T \) is dependent on the model being used, and can generally be written as,

\[ \sigma_T = 2\pi \int_0^\chi b_{ij} \left| \frac{db_{ij}}{d\chi} \right| d\chi, \]

where \( \chi \) is the change in direction of \( v_{ij} \) from upon collision and \( b_{ij} \) is shortest distance between particles as they pass each other. If a collision occurs, \( b_{ij} \) is obtained from a scaled uniform random variable (URV) and \( \chi \) is calculated based on that value. For the variable hard sphere (VHS) model,

\[ \sigma_T = \frac{\pi (d_i + d_j)^2}{4}, \]

\[ \chi = 2\cos^{-1}\left( \frac{2b_{ij}}{d_i + d_j} \right), \]

where \( d_i \) and \( d_j \) are the diameters of particles \( i \) and \( j \) and \( b_{ij} \) is selected from a URV that has been scaled between 0 and \( \frac{d_i + d_j}{2} \). The components of the post collisional relative velocity, \( v_{ij}^* \), are,
\[ v_{ij}^* = |v_{ij}| \cos(\chi) \]
\[ v_{ij}^* = |v_{ij}| \sin(\chi) \cos(\epsilon) \]
\[ v_{ij}^* = |v_{ij}| \sin(\chi) \sin(\epsilon), \]

where \( \epsilon \) is the angle between the collision plane and an arbitrarily chosen reference plane (for the VHS model \( \epsilon \) is drawn from a URV on the \([0,2\pi]\) interval). The post collisional velocities are thus,

\[ v_i^* = \left( \frac{m_i v_i + m_j v_j}{m_i + m_j} \right) + \frac{m_i v_{ij}^*}{m_i + m_j}, \]
\[ v_j^* = \left( \frac{m_i v_i + m_j v_j}{m_i + m_j} \right) - \frac{m_j v_{ij}^*}{m_i + m_j}, \]

where \( m_i \) and \( m_j \) are the mass of particles \( i \) and \( j \) respectively.

Like the Boltzmann equation, DSMC conserves mass, momentum and energy and satisfies the second law of thermodynamics. Whether it reproduces the correct hydrodynamics within the mesoscopic Knudsen range is uncertain, though it does reproduce the results of solutions to the Navier Stokes equation. The model does not rigidly enforce excluded volume interactions, though the VHS model has been used to replicate the phase diagram of a hard sphere fluid.

### 2.2.3 Dissipative Particle Dynamics

An alternate mesoscopic algorithm is Dissipative Particle Dynamics (DPD), which was introduced by Hoogerbrugge and Koelman [Hoogerbrugge 1992]. This model effectively modifies the molecular dynamics algorithm to introduce a soft potential between particles that allows a larger integration time step to be used. Like DSMC [Groot 1997], the particles in DPD are representative of multiple particles. The trajectories of these particles are integrated according to equations 2.1, however, the interparticle forces, \( \mathbf{F}_{ij} \) are composed of three terms,

\[ \mathbf{F}_{ij} = \mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R, \]

where \( \mathbf{F}_{ij}^C \) is the conservative force, \( \mathbf{F}_{ij}^D \) is the dissipative force and \( \mathbf{F}_{ij}^R \) is the random force. Beyond these modifications, which allow for a larger time step due to the soft
potential and reduce the number of particles, the method is unchanged from standard molecular dynamics.

The conservative force is generally given as,

$$ F^C_{ij} = \begin{cases} 
A_{ij} \left( 1 - \frac{|r_{ij}|}{r_c} \right) \frac{r_{ij}}{|r_{ij}|} & \text{for } |r_{ij}| < r_c, \\
0 & \text{for } |r_{ij}| \geq r_c
\end{cases} $$

where $r_c$ is the cut-off distance for the potential, $A_{ij}$ is the maximum value of the potential between particles $i$ and $j$. The dissipative force is given as,

$$ F^D_{ij} = \begin{cases} 
\gamma_D \left( 1 - \frac{|r_{ij}|}{r_c} \right)^2 \left( \frac{p_{ij}}{|r_{ij}|} \cdot \frac{r_{ij}}{|r_{ij}|} \right) & \text{for } |r_{ij}| < r_c, \\
0 & \text{for } |r_{ij}| \geq r_c
\end{cases} $$

where $p_{ij}$ is the relative momenta of particles $i$ and $j$, and the random force is given as,

$$ F^R_{ij} = \begin{cases} 
\sigma_D \left( 1 - \frac{|r_{ij}|}{r_c} \right) \sqrt{\Delta t} \xi_{ij} \frac{r_{ij}}{|r_{ij}|} & \text{for } |r_{ij}| < r_c, \\
0 & \text{for } |r_{ij}| \geq r_c
\end{cases} $$

where $\xi_{ij}$ is a Gaussian random variable with a mean of zero and a unit variance. The parameters $\gamma_D$ and $\sigma_D$ are related to each other through a fluctuation dissipation theorem, $\sigma_D^2 = 2 \gamma_D k_B T$.

As DPD only modifies the potentials and introduces a random force term, it does include excluded volume interactions and can simulate some local structure. Hence it can simulate more complex fluids than DSMC and perhaps even some simple liquids. However it sacrifices performance to retain this additional detail, being computationally slower than DSMC.
2.2.4 Multi-Particle Collision Dynamics

Multi-particle Collision Dynamics (MPCD) or Stochastic Rotation Dynamics (SRD) is a mesoscopic algorithm that was developed by Malevanets and Kapral [Malevanets 1999]. The algorithm is described in full in section 2.3, but a brief description of its modification to molecular dynamics is presented here. MPCD forgoes pairwise collisions; instead momentum transfer is achieved by rotating the velocities of the particles about the local average velocity at discrete intervals. Like DSMC, the particles in an MPCD simulation are grouped into cells, with an edge length of $L$. In MPCD these cells form the basis for the calculation of the local average velocity for the rotation, i.e.,

$$v_i^* = M(\pm \phi)(v_i - \bar{v}) + \bar{v}, \quad \text{Eqn. 2.2.4.1}$$

where $v_i^*$ is the post collisional velocity, $\bar{v}$ is the local cell average of the velocity and $M(\pm \phi)$ is the rotation operator for an angle $\phi$. The probability of a negative or positive rotation is equal.

The period of the rotation, $\tau_c$, is not specified in the base algorithm. Ideally it should be long enough that particles are not likely to be in the same cells during subsequent rotation steps to ensure molecular chaos. However, it should also be short enough to allow for efficient energy transfer between particles and rapid system equilibration. A good guideline for this frequency can be found by matching the mean free path length of the fluid to the edge length of a cell. The mean free path length for a MPCD fluid is $\lambda = |\bar{v}|\tau_c$, where $\bar{v}$ is the average velocity of a fluid particle. Thus at high temperatures, $\tau_c$ can be chosen such that $\lambda = L$, where $L$ is the edge length of a cell [Kapral 2008]. For a Maxwell-Boltzmann velocity distribution, $\bar{v} = \sqrt{8k_BT/(\pi m)}$, thus $\tau_c$ should be selected such that,

$$\tau_c = L\sqrt{\frac{\pi m}{8k_BT}}. \quad \text{Eqn. 2.2.4.2}$$

At low temperatures, $\tau_c$ as calculated from equation 2.2.4.2 may prove too long for effective equilibration of the fluid. If $\tau_c$ is lowered such that $\lambda < L$, then particles may remain in the same cells for multiple time steps. As each rotation step introduces a correlation between the
velocities of the particles in the cells, particles are correlated prior to collision. If the algorithm was applied to a moving frame of reference, where the particles had an average velocity of $-\mathbf{v}$, this velocity correlation would not exist in the moving frame of reference, hence the algorithm is not Galilean invariant. Galilean invariance can be restored by shifting the cells by a vector, $\mathbf{\delta}$, prior to rotation and shifting the cells by $-\mathbf{\delta}$ post rotation. $\mathbf{\delta}$ is formed by drawing uniform random variables on the $[-L/2, L/2]$ interval for the Cartesian components of the vector [Ihle 2001] [Ihle 2003]. This also smooths out a physical irregularity caused by using the cell structure to perform rotations (see figure 2.2.4.1). A particle near the boundary of a cell will not interact with a particle that is in a neighboring cell even if it is closer than a particle that is at the edge of the system.

Figure 2.2.4.1 An illustration of the anisotropy of the square cell. Along an edge a cell has a length of $L$, along the diagonal the cell has an edge length of $\sqrt{2}L$. As the rotations introduce a velocity correlation between particles in the cell, the range of these correlations are not the same in different dimensions. The cell structure also introduces a positional dependence on the interaction range in addition to the distance based dependence. The red
The discussion of the MPCD algorithm thus far has not specified the direction about which a rotation should be performed. In two dimensions the direction normal to the plane of the simulations can be selected. In three dimensions, the axis of rotation needs to be randomized to allow for momentum transfer in all dimensions. There are two variants that are used for selecting the axis of rotation for the three dimensional algorithm. The first variant is to rotate the velocities of the particles about a randomly chosen axis [Malevanets 1999], called model A in the study of Ihle, Kroll and Tüzel [Tüzel 2003]. The second is to randomly select one of the three orthogonal axes of the system and perform the rotation about that axis, called model B [Tüzel 2003]. The forms of the transport coefficients are somewhat different for the two models. These differences are summarized in table 2.2.4.1 [Tüzel 2003] [Ihle 2004] [Kikuchi 2003] [Hecht 2005]. The first model has the advantage of assuring the proper rotational symmetry for the stress tensor of the fluid, while the second model allows for faster execution.

As the algorithm does not require the calculation of interparticle potentials or the numerical integration of trajectories, the MPCD algorithm is one of the most computationally efficient mesoscopic algorithms for studying fluid motion. However, for this gain of computational efficiency, it sacrifices local structure and excluded volume interactions. As a consequence, this basic algorithm cannot accurately model a liquid or a dense fluid. The MPCD algorithm does conserve mass, momentum and energy. An MPCD system also evolves to a state of maximum entropy and reproduces hydrodynamics consistent with the Navier-Stokes equation in the low rarefaction limit [Malevanets 1999].
The MPCD algorithm can be extended to simulate multi-component fluids [Tucci 2004] and can be modified to include excluded volume interactions [Ihle 2006]. To simulate a multi-component fluid, two modifications have to be made to the basic algorithm. First, the basic rotation step has to be modified due to the presence of particles of different masses, eqn. 2.2.4.1 becomes,
\[ \mathbf{p}_i^* = M(\pm \phi) \left( \mathbf{p}_i - \frac{m}{\bar{m}} \bar{\mathbf{p}} \right) + \frac{m}{\bar{m}} \bar{\mathbf{p}} , \]

where \( \bar{m} \) is the number average particle mass in the cell. Second, an additional rotational step is conducted after the general rotation step between particles of the same molecular species. This expression is the same as eqn. 2.2.4.1 with the modification that only particles of the same species as the \( i^{th} \) particle are used for the calculation of the average momentum. Hence the post collisional momenta of the \( i^{th} \) particle is,

\[ \mathbf{p}_i^* = M(\pm \phi) \left( M(\pm \phi) \left( \mathbf{p}_i - \frac{m}{\bar{m}} \bar{\mathbf{p}} \right) + \frac{m}{\bar{m}} \bar{\mathbf{p}} - \bar{\mathbf{p}} \right) + \bar{\mathbf{p}} , \]

where \( \phi \) is the rotation angle and \( \bar{\mathbf{p}} \) is the average momentum for the particles of the species of the \( i^{th} \) particle [Tucci 2004].

The inclusion of excluded volume interactions has been performed by introducing specular collisions between cells [Ihle 2006]. An additional set of super-cells is defined with edge length \( 2L \), which connects 4 adjacent cubic cells. Due to this modification, the length of \( \mathbf{\hat{d}} \) has to be doubled. After a rotation step, a pair of cells from each super-cell is randomly selected. If the average velocity of the particles in these cells indicate that the particles are moving towards each other, \( \mathbf{\bar{v}}_i \cdot \mathbf{\hat{v}}_i < 0 \), these cells will collide with probability,

\[ p_{ij} = \tanh \left( A \left| \mathbf{\bar{v}}_i \cdot \mathbf{\hat{q}}_i \right| N_{C,j} N_{C,i} \right) \text{ for } \mathbf{\bar{v}}_i \cdot \mathbf{\hat{q}}_i < 0 , \]

where \( \bar{v}_i \) is the average velocity of the \( i^{th} \) cell, \( \bar{v}_i = \bar{v}_j - \bar{v}_i \) is the relative cell velocity, \( \mathbf{q}_i \) is the position of the geometric centre of the \( i^{th} \) cell, \( \mathbf{\hat{q}}_i = (\mathbf{q}_j - \mathbf{q}_i) / \left| \mathbf{q}_j - \mathbf{q}_i \right| \) , \( A \) is an adjustable parameter and \( N_{C,i} \) and \( N_{C,j} \) are the number of particles in cell \( i \) and \( j \), respectively. If the cells are selected to collide, they do so using a specular collision operator, \( \mathbf{\bar{v}}_i' = \mathbf{\bar{v}}_i + \mathbf{\hat{q}}_i \cdot (\mathbf{\bar{v}}_j - \mathbf{\bar{v}}_i) \). While this method does introduce excluded volume interactions, the fluid still does not possess an internal energy. In addition, the equation of state of the fluid does not match the equation of state of a hard sphere gas, though it may be possible to replicate the latter equation of state.
through modifications that relate the collision probability to the collision probabilities of the VHS model of DSMC. The equation of state for this fluid is,

\[ P = \rho k_B T \left( 1 + \frac{1}{2\sqrt{2}} + \frac{1}{4} \frac{A\rho}{2L\tau_c} \right), \]

where, \( \rho \) is the number density.

### 2.2.5 Continuum Approaches

Thus far only particle-based simulation methods have been considered. However, hydrodynamics can also be derived by examining the rate of change of the local values of the mass, momentum and energy fluxes and coupling these results with an equation of state for the fluid. For a differential cubic element of fluid, the general differential forms of the mass, momentum and energy fluxes are [Welty 1984]:

\[
\begin{align*}
\text{mass:} & \quad \nabla \cdot (\rho \mathbf{v}) + \frac{\partial \rho}{\partial t} = 0, \quad \text{Eqn. 2.2.5.1} \\
\text{momentum:} & \quad \rho \frac{Dv_i}{Dt} = \rho g_i + \sum_{j=1}^{3} \frac{\partial \tau_{ij}}{\partial t}, \quad \text{Eqn. 2.2.5.2} \\
\text{energy:} & \quad \sum_{i=1}^{3} \frac{\partial}{\partial t} \left( \kappa \frac{\partial T}{\partial t} \right) + \frac{\partial q}{\partial t} + \Lambda_{\mu} = \nabla \cdot P \mathbf{v} + \frac{\rho}{2} \frac{Dv^2}{Dt} + \rho \frac{Du}{Dt} + \rho \frac{D\Phi}{Dt}, \quad \text{Eqn. 2.2.5.3}
\end{align*}
\]

where \( i \) and \( j \) are indices representing the three Cartesian coordinates, \( \frac{D}{Dt} \) is the substantive derivative, \( \frac{d}{dt} + \sum_{i=1}^{3} v_i \frac{d}{dq_i} \), \( g_i \) is the acceleration from any local force fields, \( \tau_{ij} \) is the stress acting in the \( i \) direction on the \( j \) normal surface, \( \kappa \) is thermal conductivity of the fluid, \( \frac{\partial q}{\partial t} \) is the rate of heat generation in the fluid, \( \Lambda_{\mu} \) is the rate of viscous work per unit volume, \( u \) is the internal energy of the fluid and \( \Phi \) is the local potential energy. The first two of these equations are the general forms of the Navier-Stokes equation. Typically the Navier-Stokes equation is written as
\[
\frac{Dv}{Dt} = \rho g - \nabla P + \mu \nabla^2 v.
\]

Eqn. 2.2.5.4

However this form assumes an incompressible Newtonian fluid. This equation was developed in 1822 by Claude-Louis Navier [Navier 1822], but it did not appear in its current form until 1845, when it was revised by George Gabriel Stokes [Stokes 1845]. Since its introduction, the Navier-Stokes equation has been the dominant hydrodynamic equation used in engineering and physics.

The Navier-Stokes equation is only valid in the low rarefaction limit, \( Kn < 0.001 \), though this can be extended by the use of slip boundary conditions. In a channel flow simulation, the highest point of shear stress in the fluid is at the walls. If this stress is higher than the viscosity of the fluid, the assumption of continuous momentum transfer within the fluid breaks down and a discontinuity in the flow field emerges at the wall of the channel. While the fluid slips at this point, this slippage relaxes the stresses on the fluid, hence the continuum approximation is still valid within the channel. This extends the usefulness of the base algorithm. The slip velocity can be modeled using Maxwell’s first order slip relation given as [Jie 2000] [Maxwell 1879],

\[
v_{slip} = \alpha \lambda \left. \frac{dv_z}{dx} \right|_{wall},
\]

Eqn. 2.2.5.5

where \( z \) is the direction of flow, \( x \) is the direction normal to the wall of the channel, \( \lambda \) is the mean free path length and \( \alpha \) is the streamwise momentum accommodation, which for a thermally diffuse collision has a value of 1 [Arkillic 1997] [Renksizbulut 2006]. Physically, slip velocity is proportional to the rate at which the velocity changes in the fluid and distance over which momentum transfer occurs.

The Navier-Stokes equation can be derived by evaluating the first moment of the mass and momentum fluxes for a system in local equilibrium from particle-based models. For this reason, it is considered a first-order hydrodynamic equation. It is possible to extend the use of continuum algorithms by including corrections from higher moments of these fluxes. The most popular higher-order continuum equation is the Burnett equation, which is derived from the Chapman-Enskog approximation of the Boltzmann Equation. The equation is too complicated and tangential to this report to be included here, though it can be found in the original article.
As the Burnett equation includes thermal effects, it is primarily used to model thermal flows, though it has been used to study nanofluidic flows as well. Though the Burnett equation is assumed to be valid in the mesoscopic range, there is no proof of its accuracy beyond the range of the Navier-Stokes equation [Mackowski 1999].

### 2.2.6 Simulating Channel Flow

For a continuum approach, establishing the boundary conditions to generate shear flow is a simple matter. Specifying the temperature, the inlet pressure and either the outlet pressure or the flow rate will suffice. Within a particle-based simulation, the task is more complex. The most common methods of generating flow fields are to use sliding-brick boundary conditions [Evans 1984], gravitational flows [Allahyarov 2002] [Steiner 2009], or by maintaining a pressure gradient at the inlet and outlet by generating a positive particle flux at the inlet and a negative particle flux at the outlet [Peikos 1996] [Li 1998] [Steiner 2009]. For a compressible fluid, channel flow is a combination of shear flow and elongational flow due to the expansion of the fluid due to pressure drop. Hence sliding-brick and forced flows do not generate complete profiles.

The sliding brick algorithm of Evans and Morriss [Evans 1984] works by creating moving images at the shear surfaces of system. The top image moves with a speed of \( L\dot{\gamma} \), where \( \dot{\gamma} \) is the target shear rate and \( L \) is the length of the system in the direction normal to the plane being sheared. Likewise, the bottom image moves with a velocity of \(-L\dot{\gamma}\). The boundary conditions otherwise behave like periodic boundary conditions; i.e. if a particle exits through the top of the system, it is replaced by its image from the lower cell. Hence, ignoring other potential interactions, the equations of motion for a particle entering the system through the shear planes would be,

\[
\begin{align*}
q(t + \Delta t) &= q(t) + \left( \frac{p(t)}{m} - L\dot{\gamma} \right) \Delta t \\
p(t + \Delta t) &= p(t) - mL\dot{\gamma} \Delta t
\end{align*}
\]

for a particle entering from the bottom image and,
for a particle entering from the top image. This method provides an easy means of generating a pure shear flow. However, the limitations of this method are that it can only create a pure shear flow and, as it requires periodic boundary conditions across the surfaces that are being sheared, it is problematic to introduce a surface-tethered polymer that is being sheared by this flow.

Flow can also be induced by directly applying an external force to each of the particles in the system [Allahyarov 2002]. A common example of this is a gravitational flow where a force field of the type $F = mg$ is applied to the particles along the direction of flow. In this approach the force field simply becomes a systemic $+ mg$ term in the differential equation for the momentum. This type of boundary condition can produce a Poiseuille flow in a channel, since the gravitational force is balanced by the drag forces exerted by the wall and the familiar parabolic flow profile emerges. Unfortunately, it reproduces the flow profile for an incompressible fluid when a compressible fluid is simulated as the periodic boundary conditions across the inlet and outlet eliminate the elongation flow component. Thus it is not ideal for studying channel flow for compressible fluids.

The final method of simulating an ideal flow in a channel is to create a pressure gradient by directly controlling the particle fluxes at the inlet and outlet of the channel [Peikos 1996]. The advantage of this method is that it does generate a compressible channel flow and, as the parameters that need to be specified for this boundary condition are easily obtained by experiment, it is easy to adapt to the simulation of a real system. However, matching a target pressure gradient for the channel can be quite challenging as this method relies on highly accurate estimates of the local average velocity to determine the value of state variables such as the pressure and temperature which need to be reproduced. The addition of particles at the inlet, or removal of them at the outlet can also produce large fluctuations in these parameters that can persist well into the channel. Lastly this method requires more computational overhead than the other methods. The source/sink boundary condition algorithm is presented in full in section 2.3.2, as a modified version of this algorithm.
A variation of this particle injection method is to use selective reflections at the inlet and outlet [Li 1998]. This method involves a simple modification to standard periodic boundary conditions across the exterior surfaces of the inlet and outlet. Particles exiting the system at the inlet are replaced with their image at the outlet with probability, \( p \), and reflected back into the inlet with probability \( 1 - p \). Particles exiting the system across the outlet are always replaced with their image at the inlet as per standard periodic boundary conditions. This establishes an imbalance in the particle flux across the boundaries which manifests as an increase in inlet pressure and decrease in outlet pressure until the flux of particles entering the outlet across the boundary is the same as the flux of particles entering the inlet across the boundary. Though it produces the correct flow profile, there are some drawbacks to this method. The correlation between \( p \) and a specific pressure gradient is not a simple function of the pressure alone, but also depends on several other factors, including the total number particles in the system and the inlet and outlet temperatures, so that trial and error has to be used to calibrate the system. It is also a closed system, hence it cannot be used without modifications to study changes in pressure from a small gradient to a large gradient or to calculate a washout distribution. The reflection can also cause large fluctuations in the macroscopic observables due to the unphysical nature of the boundary condition. Finally, in long simulations of several nanoseconds, the pressure gradient appears to diminish, the temperature drops and the fluid velocity increases in the direction of flow unless there are additional thermal control mechanisms in the system (e.g. through particle wall interactions), that prevent the reflection process from sorting the velocities of the particles.

### 2.2.7 Applications to Channel Flow

There are very few existing simulations of channel flow, and most these simulations have focused on flow through slits. However there have been several studies examining fluid flow in channels using all of the algorithms discussed above. Due to the limitations of the mesoscopic algorithms to include excluded volume interactions and accurately replicate local structure, all of these studies have examined gas flows. This review will only consider the post-1996 results, for a review of the earlier results see the review of Ciafolo, et al. [Ciafolo 1996].

#### 2.2.7.1 Molecular dynamics

There have been several molecular dynamics simulations of channel flow [Song 2008] [Soong 2007] [Zhang 2007] [Mao 2000]. All of these studies utilized liquid argon with a Lennard-Jones
potential as a fluid and used a gravitational force field to generate flow, except for the study of Mao et al, where the flow of small chained alkanes through carbon nanotubes was studied. In this study the particles entering the nanotubes were artificially accelerated with a positive velocity in the direction of flow.

Song et al simulated flow in cylindrical channels and a slit. The flow field was generated using a gravitational flow. For both cylindrical and slit geometries Gaussian diffusion [Tenenbaum 1982] (see page 36) and an atomistic simple cubic (SC) wall model were utilized to simulate the boundary conditions between the wall and the fluid. The interactions between particles were modeled with a Lennard-Jones potential. This study found that the slip velocity was higher in the cylindrical pores than in the slits. It also found that while the Gaussian model did not accurately predict the molecular distribution of the fluid near the wall, it did recreate the same velocity and thermal profile as the SC model.

In the study of Soong et al, flow was simulated in slits composed of face centered cubic (FCC) atoms with different crystal planes exposed to examine the effect of wall geometry on the flow profile. The flow profile was generated using a gravitational flow and by moving one of the walls of the channel. They studied the <1 1 1>, <1 0 0> and <1 1 0> planes of the crystal and found that the roughness of the surface has a fairly large effect on the slip velocity of the channel for the same driving force. They postulated that the wall friction would be lower for a smooth surface and high packing density. In particular the <1 1 0> surface had the lowest slip velocity and the <1 1 1> surface had the highest slip velocity.

In the study of Zhang et al, the gas was modeled as liquid argon with a Lennard-Jones intermolecular potential. The walls of the channel were modeled by three layers of molecules in a FCC lattice. The flow field was generated using a gravitational force field. The simulations revealed the typical double parabola velocity field of channel flow which became flatter as the aspect ratio increased making the channel into more of a slit.

2.2.7.2 DSMC

Utilizing DSMC, there have been several simulations of flow in nanoscale devices [Peikos 1996] [Xue 2000] [Wang 2006]. All of these studies used the NTC algorithm with a variable hard
sphere fluid model (similar to a hard sphere model, but the diameter of the spheres is a monotonic increasing function of the relative velocity between colliding particles [Bird 1994]). In the first and third studies [Peikos 1996] [Wang 2006], Gaussian diffusion boundary conditions were implemented at the wall, while the study of Xue et al [Xue 2000] made use of the Cercignani-Lampis-Lord boundary conditions [Lord 1991] (a diffusive boundary condition that incorporates the incident velocity into the probability distribution for the deflected velocity of a particle) and the flow field was generated by controlling the particle fluxes. In all of these studies the pressure, temperature and transverse velocity were specified at the inlet and only the pressure was specified at the outlet.

2.2.7.3 DPD

There are a few studies that use DPD to examine channel flow [Steiner 2009] [Fedosov 2008]. The latter study focused on the use of DPD to study polymer depletion near the wall of a channel due to flow. In this study, the field was created by a gravitational flow. The boundary conditions were established by performing a DPD simulation under no flow conditions and freezing the particles in the wall during the flow experiment for use in the calculation of wall particle interactions, while the velocity of colliding particles were corrected to remove fluid slip. The study of Steiner, et al. [Steiner 2009] established the flow field through the method of periodic boundary conditions with a reflection probability of \( (1 - p) \) described in section 2.2.6 [Li 1998]. The wall boundary conditions were handled using a similar method to Fedosov et al.

2.2.7.4 MPCD

There have only been only two attempts to model channel flow with MPCD outside of this study, the model of Allahyarov and Gommper [Allahyarov 2002], and Kapral and Tao [Tao 2010]. In both studies a gravitational force field was used to create flow with bounce back wall boundary conditions, where the momentum of a particle striking a wall is completely reversed upon collision. In the former study the flow field is studied in a slit, while in the latter study the flow in studied in a channel.

2.2.7.5 Continuum Approaches

There have been several attempts to model channel flow using the Navier-Stokes equation [Arkillic 1997] [Jie 2000] [Damean 2001] [Roy 2003] [Renksizbulut 2006] and the Burnett
Equation [Xue 2001]. The work of Arkillic and Schmidt presented a partial analytical solution for isothermal flow in a rectangular channel with slip boundary conditions. A complete description of this flow profile is presented in appendix A. The remaining Navier-Stokes studies used finite element methods to generate a flow profile. Xue et al. utilized the Burnett Equation to study gaseous Couette flow in nanoscale devices with thermal effects included.

2.2.7.6 Experimental Results

While the velocity profile is generally one of the most useful sources of hydrodynamic data, as it can be used to determine residence time distributions and mixing within the channel, this data is not available for nanochannels as the traditional methods of determining velocity profiles such as tracer injection are not possible. However, there are data on pressure drops across these devices as a function of flow rate [Arkillic 1997] [Weilin 2000] [Yu 2005], which could be contrasted with theoretical predictions of the flow rate as a function of pressure drop. While these data are useful to verify the theoretical results, they are generally insufficient to confirm velocity profiles or density distributions within the channel. Instead simulation results from the Navier-Stokes equation and other mesoscopic simulations are used to verify the predictions of mesoscopic models.

2.3 MPCD-Molecular Dynamics Algorithm Implementation

The MPCD algorithm was introduced in section 2.2.4. It is a particle-based mesoscopic algorithm that was developed by Kapral and Malevanets [Malevanets 1999]. The version presented here makes use of the model B three dimensional variant presented in Ihle, Kroll and Tüzel [Tüzel 2003] and is further modified to allow certain cells within the algorithm to be integrated with full molecular dynamics in order to facilitate the addition of polymer chains. The algorithm also makes use of the random shift procedure suggested by Ihle and Kroll [Ihle 2003] to restore Galilean invariance. Although, for the simulations $\lambda$ is greater than $L$, hence the effects of the shift procedure are negligible.

The basic algorithm is presented in the next subsection (section 2.3.1). In order to implement channel flow with this algorithm, it was necessary to develop a new boundary condition algorithm at the inlet and outlet to control the channel flow through the specification of a
pressure gradient, which was stable for small pressure gradients. An adiabatic partial slip boundary condition also had to be created to simulate adiabatic boundary conditions while reproducing the same slip behavior as Gaussian diffusion boundary conditions. The details of this implementation are presented in section 2.3.2. The simulation conditions used to perform the simulations using this algorithm are presented in the final subsection 2.3.3.

2.3.1 MPCD-Molecular Dynamics Algorithm

For the MPCD algorithm, the system is divided into cubic cells of edge length \( L \). These cells form the basis for the calculation of local properties, such as the average velocity that is used to perform rotations. While the cell structure is convenient and, in these simulations, also serves as the maximum resolution for macroscopic observables in the system, it does introduce a correlation between particles in the same cell and, since cells have different lengths along different dimensions (e.g. a cubic cell with an edge length of \( L \) as a length of \( \sqrt{3}L \) along the principle diagonal), this correlation has different lengths in different dimensions (see figure 2.2.4.1). This manifests as anisotropy in the diffusion coefficient and fluid viscosity. Hence isotropic cells are preferred to minimize the effect of this geometry-based correlation.

In order to facilitate the addition of molecular dynamics, the velocity was truncated at a value of \( L/\Delta t \), where \( \Delta t \) is the length of the streaming time step for the MPCD system. This rigorously imposes the restriction that a particle cannot travel more than one cell length in a single time step. This restriction simplifies several calculations by providing a screening distance for interactions. Due to this truncation, the particle-wall interactions only need to be checked for particles in the cells adjacent to the wall, and the maximum distance from the polymer at which a fluid particle could interact with the polymer chain over \( \Delta t \) can be easily calculated. In general this truncation velocity is selected such that \( \frac{L}{\Delta t} > 4 \sqrt{\frac{k_B T}{m}} \), so that only roughly 3 out of every \( 2 \times 10^8 \) particles require velocity truncation.

The algorithm was written to follow a leap frog integration method [Frenkel 2002]. However, the use of this integration scheme is not necessary for the MPCD algorithm. The rotations and collisions with the walls are handled by instantaneous operators and otherwise the momentum of the particles is a constant. Hence, the streaming equation for the \( i^{th} \) particle,
The equation for the position is
\[ q_i(t + \Delta t) = q_i(t) + \frac{p_i(t)}{m_i} \Delta t \]
is an exact expression and the errors in the trajectories are limited to floating point rounding errors.

While the leap frog integration scheme was not necessary for the MPCD algorithm, a robust integration scheme was necessary for the molecular dynamics subsystem that was used to simulate the polymer. As was presented in section 2.2, the generalized equations of motion for a particle in a simulation, considering only binary collisions, are (equation 2.2.3),

\[
\frac{dq_i(t)}{dt} = \frac{p_i(t)}{m_i}, \\
\frac{dp_i(t)}{dt} = \sum_{j=1,j\neq i}^{N} F_y(q_i(t), q_j(t)).
\]

For the molecular dynamics subsystem, the latter equation is non-trivial. There are explicit potentials between the solvent and the polymer, between polymer beads that are directly bound to each other, between polymer beads that are not directly bound to each other and between the polymer and the wall. These potentials are described in next chapter, which examines the polymer model explicitly; however they are all functions of the positions of particles in the system, hence the differential equations do not decouple. In the leap-frog integration scheme these equations are integrated as,

\[
q_i(t + \Delta t) = q_i(t) + \frac{p_i(t + \Delta t/2)}{m_i} \Delta t \\
p_i(t + \Delta t/2) = p_i(t - \Delta t/2) + \Delta t \sum_{j=1,j\neq i}^{N} F_y(q_i(t), q_j(t)).
\]

This formulation is equivalent to the Verlet algorithm and hence it is accurate to \(O(\Delta t^4)\) in position and \(O(\Delta t^2)\) in momenta. Computationally this equation operates as a first order integration scheme, except for an initial and final half step to initiate and terminate the stagger.

The presence of an explicit potential within the molecular dynamics sub-system of the MPCD algorithm requires that this part of the algorithm be integrated with a much smaller timestep (\(\Delta e\) ) than the MPCD algorithm in general. For the simulations presented here, \(\Delta t/\Delta e = O(10^3)\). As
long as $\Delta t/2\Delta t$ is an integer, and there are no explicit solvent-solvent interactions in the MD subsystem, it is relatively easy to interface the molecular dynamics system with the MPCD system. The MPCD algorithm is presented in sequential steps below with the exception of the boundary conditions which are discussed in section 2.3.2.

1. **The simulation space is filled with particles; the positions are drawn from a uniform distribution on the dimensions of the channel and the velocities are drawn from a Maxwell-Boltzmann distribution with a temperature, $T$ and mean velocity, $\mathbf{v} = 0$.** Due to the lack of excluded volume interactions, particle overlap does not need to be considered when selecting particle positions. The channel is filled to the inlet density so that the equilibration process follows a wash-out distribution; i.e. a high pressure to low pressure transition. The converse process can create pressure waves and takes longer to equilibrate. The disadvantage in using this procedure is that the algorithm has a higher initial footprint in the system memory, which can slow performance if memory has to be drawn from the page file.

2. **If it is time for the polymer chain to be inserted, the polymer is inserted with either a configuration that extends straight along the normal vector of the wall that the polymer is tethered to, or with one of the knotted configurations defined in section 3.4. Any fluid particles that would have a non-zero potential with the polymer chain are deleted from the system.** The momenta of the polymer beads are selected from a Maxwell-Boltzmann distribution with temperature $T$ and $\mathbf{v} = 0$.

3. **If the polymer is present in the system** (The polymer model is described in section 3.3): 
   a) **At system time, $t = c\Delta t$, where the integer $c$ is the number of timesteps, the envelope of cells containing fluid particles that could interact with the polymer chain during an interval of $\Delta t$ is calculated.** Due to the truncation of the particle velocities, a fluid particle can move at most a distance $L$ during a time step. Similarly, a polymer bead can move at most $L$. Hence, only particles within $2L + r_c$, where $r_c$ is the cut-off radius of the potential between a fluid particle and polymer bead, can interact with the polymer chain. Every cell containing particles that could be within $2L + r_c$ of the polymer chain therefore formed this envelope. The cells in this envelope form the molecular dynamics system for the next period of $\Delta t$. 
b) *The particles in the cell envelope are tagged as being integrated with a time step* $\Delta t$. This is done to prevent the system from integrating the position and momentum of the tagged particles with a time step of $\Delta t$ when the rest of the system updates during the next MPCD time step.

c) *The position and momenta of the fluid particles and polymer beads in the envelope are advanced as per the leap frog algorithm* [Frenkel 2002] *with time step* $\Delta t$ *until the system time is* $\Delta t(c + \frac{1}{2})$.

4. *If necessary, the momenta for particles in the channel that were not marked as being integrated with time step* $\Delta t$, *are integrated.* This functionality was not utilized in the simulations that comprise this work, though it was added and used for a few trial simulations with an explicit wall potential. The wall collision operator is described in section 3.3 and implemented during the step 8.

5. *Corrections are made to the inlet and outlet cells to maintain boundary conditions.* This step is described in section 2.3.2.2.

6. *If the remainder of* $c/n_c = 0$, *a rotation step is performed.* Here, $n_c$, *the number of streaming steps between rotations, is chosen such that* $n_c\Delta t \approx \tau_c$, *where* $\tau_c$ *is the mean collision time, which is taken as*

$$
\tau_c = \frac{1}{8r^2(P_{in} + P_{out})} \sqrt{\frac{mk_BT}{\pi}},
$$

*Eqn. 2.3.1.2*

where $P_{in}$ and $P_{out}$ are the inlet and outlet pressures, respectively, and $r$ is the radius of a fluid particle (which was taken as the radius of Argon). This equation is the mean collision time for an ideal gas. While $\Delta t$ could have been chosen such that $n_c = 1$, in some simulations this would have resulted in a truncation velocity that was low enough to affect a significant portion of the distribution, and the boundary condition algorithm may have made corrections too slowly to prevent the formation of flow artefacts. This rotation step can be broken into the following steps:

a) *The particles are displaced by a displacement vector* $\delta$. The vector $\delta$ is selected by drawing three uniform random variables (URVs) on the $[-L/2, L/2]$ interval. This step is performed to maintain Galilean invariance [Ihle 2001].
b) The velocities of the particles in the cells are rotated about the average velocity of the cell by an angle $\phi$ about a randomly chosen axis. Hence the post collision velocity of the $i^{th}$ particle in the cell, $v_i^*$, is,

$$v_i^* = R_k(\pm \phi)(v_i - \bar{v}) + \bar{v},$$

Eqn. 2.3.1.3

where $\bar{v}$ is the average velocity of the particles in the cell. $R_k(\phi)$ is the matrix for a rotation through an angle $\phi$, about an axis $k$. For each cell, the sign of $\phi$ is randomly selected with equal probability. Similarly, $k$ is chosen to be one of the three Cartesian axes of the system with equal probability [Tüzel 2003]. For these simulations, $\phi$ was chosen to be $\pi/4$.

c) The particles are displaced by $-\delta$ to restore the position of the particles.

7. If the polymer is present in the system:

   a) The position and momenta of the fluid particles and polymer beads in the envelope are integrated with time step $\delta t$ until the system time is $\Delta t(c+1)$. This done by the same means as in step 3 c).

8. The position of the particles that were not marked as being integrated with time step $\delta t$ are integrated with time step $\Delta t$. That is for the $i^{th}$ particle,

$$q_i((c + 1)\Delta t) = q_i(c\Delta t) + \frac{p_i((c + 1/2)\Delta t)}{m} \Delta t.$$  

Eqn. 2.3.1.4

During this step any collisions between particles and the walls are calculated. As a collision operator is used instead of an explicit potential, it is more efficient to implement this operator during this operation as opposed to step 4. As the effect of the operator is instantaneous and handled exactly by the algorithm, the operation of the MPCD algorithm is an exact integration of its equations of motions, though the integration of the molecular dynamics subsystem is a numerical integration and prone to some error.

9. The marks are removed from the particles that were tagged as being integrated with time step $\delta t$, the flow parameters of interest (pressure, density, average cell velocity and temperature) are calculated and outputted and the algorithm loops back to step 2 until the termination time for the algorithm is reached.
Although the expressions for density and average velocity are intuitive, the expressions for pressure and temperature are worth noting. The temperature is given as,

$$T = \sum_{i=1}^{N_{cel}} m_i (\mathbf{v}_i - \overline{\mathbf{v}}) \cdot (\mathbf{v}_i - \overline{\mathbf{v}}) \over 3k_B N_{cel},$$  

Eqn. 2.3.1.5

where $\mathbf{v}_i$ is the velocity of the $i^{th}$ of $N_{cel}$ particles in the cell and $\overline{\mathbf{v}}$ is the average velocity of particles in the cell. The expression for the pressure also follows an ideal gas model,

$$P = \sum_{i=1}^{N_{cel}} m_i (\mathbf{v}_i - \overline{\mathbf{v}}) \cdot (\mathbf{v}_i - \overline{\mathbf{v}}) \over 3V_{cel}$$  

Eqn. 2.3.1.6

where $V_{cel}$ is the volume of the cell. In general pressure consists of a momentum flux term (the pressure expression given above) and a collisional term, which is the sum of forces being exerted on the particles in the cell by particles outside the cell [Erpenbeck 1977]. As there is velocity transfer between particles during the collision step, there can be an instantaneous contribution to this collision flux term. However it averages to zero, as can be seen from the following calculations. For an MPCD fluid the collisional term is [Ihle 2003],

$$P_{cf} = \sum_{i=1}^{N_{cel}} \left( \xi^s_i - \xi_i \right) \cdot \left( \mathbf{p}^*_i - \mathbf{p}_i \right) \over V_{cel} n_i \Delta t$$

where $i$ is the index of the $N_{cel}$ particles that shared a cell during the collision, $\xi$ is the position vector of the cell, $\xi^s_i$ is the position vector of the cell that contained the $i^{th}$ particle during the collision and $\mathbf{p}$ and $\mathbf{p}^*$ are the pre- and post-rotation momenta of the particle $i$. Recalling that for particles of equal mass, $\mathbf{p}^*_i - \mathbf{p}_i = (\mathbf{R}_k (\phi) - \mathbf{I})(\mathbf{p}_i - \overline{\mathbf{p}})$, this term becomes,

$$P_{cf} = \sum_{i=1}^{N_{cel}} \left( \xi^s_i - \xi_i \right) \cdot (\mathbf{R}_k (\phi) - \mathbf{I})(\mathbf{p}_i - \overline{\mathbf{p}}) \over V_{cel} n_i \Delta t.$$
If a particle is in the same cell before and after shifting, $\xi_i - \xi = 0$, it will make no contribution to this term, and the probability of a particle being in a different cell before and after shifting is uncorrelated from its momentum. Hence taking the ensemble average, this term becomes,

$$\langle P_{cf} \rangle = \sum_{i=1}^{N} \frac{\langle \xi_i^S - \xi_i \rangle \cdot (R_i (\phi) - I) \langle p_i - \overline{p} \rangle}{V_{cell} n_r \Delta t},$$

and as $\langle p_i - \overline{p} \rangle = \langle p_i \rangle - \overline{p} = \overline{p} - \overline{p} = 0$ for a system in local equilibrium, this term can be taken to be zero.

### 2.3.2 Boundary Conditions

While the algorithm presented in the previous section provides a method for simulating the fluid within the channel, it is also necessary to generate flow in the channel and model the interface of the fluid and the channel. This is done through the boundary conditions for the algorithm. There are two types of boundary conditions necessary for the simulation of channel flow using the MPCD-molecular dynamics algorithm. The first is a collision operator to model the interface between the fluid and the wall and the second is a method of particle addition and removal at the inlet and outlet of the channel to produce and sustain a stable flow field.

#### 2.3.2.1 Wall Boundary Conditions

Given the coarse-grained nature of the MPCD algorithm, there would be little gain from the inclusion of an atomistic wall model with a physically accurate model. The use of such a model would result in the loss of computational efficiency, as it would require that the molecular dynamics component of the system be extended to include all of the cells that bordered the walls of the channel. Instead, a collision operator is used to simulate the effect of wall-particle interactions while maintaining computational efficiency.

When the channel is simulated, a layer of cells beyond the walls of the channel is included. At the end of the streaming step of the algorithm in section 3.2 (step 8), this layer of cells is examined. Any particles in these cells must have passed through a wall during the previous \(\Delta t\) interval.
In order to apply the collision operator, it is necessary to reverse the trajectory of the particle to
the time of collision, apply the operator and then integrate the position of the particle using the
new velocity. The time of collision, $t_{\text{Coll}}$, is,

$$t_{\text{Coll}} = t - \frac{m(q_{\text{wall}} - q \cdot \hat{n})}{p \cdot \hat{n}},$$

**Eqn. 2.3.2.1**

where $t$ is the system time, $\hat{n}$ is the normal vector of the wall, $q_{\text{wall}}$ is the projection of a point on the wall onto $\hat{n}$, and $q$ and $p$ are the position and momenta of the particle respectively. In cells bordering the intersection of two walls, it is necessary to check both walls and find the time of the first collision. The position of the particle is then reversed to this time,

$$\mathbf{q}(t_{\text{Coll}}) = \mathbf{q}(t) - (t - t_{\text{Coll}}) \frac{\mathbf{p}}{m}.$$  

**Eqn. 2.3.2.2**

Once the position of the particles has been reversed, the collision operator is applied. The normal component of the momentum is reflected as per a specular collision and the remaining two components of the momentum are rotated by a uniformly distributed random angle $\theta$ on the interval $[0, 2\pi)$. The post collision momentum, $\mathbf{p}^*$, thus becomes,

$$\mathbf{p}^* = R_{\hat{n}}(\theta)p - 2(p \cdot \hat{n})\hat{n},$$  

**Eqn. 2.3.2.3**

where $R_{\hat{n}}(\theta)$ is the rotation matrix corresponding to a rotation by an angle $\theta$ about a unit vector $\hat{n}$. The rotation of the parallel components of the momentum is done to account for wall roughness and molecular motion. In an atomistic description of a wall, the atoms of the wall will be vibrating in their lattice sites, and each wall particle will have a Lennard-Jones type interaction with the particle, hence the direction in which the particle is deflected would be dependent on the positions and momenta of the nearest wall atoms as opposed to a purely specular collision.

After the collision operator has been applied, the position of the cell is advanced to time $t$,
\[ q(t) = q(t_{\text{Coll}}) + (t - t_{\text{Coll}}) \frac{\mathbf{p}}{m}. \quad \text{Eqn. 2.3.2.4} \]

Afterwards, the position of the particle is checked to ensure it did not pass through another wall. If it did pass through another wall the process is repeated, until such time that the particle is in the system at time \( t \).

The collision operator itself is a modified version of the Gaussian diffusion collision operator [Tenenbaum 1982]. In Gaussian diffusion boundary conditions, a new velocity is drawn from the following velocity density function for the component of velocity normal to the wall, \( v_{\perp} = \mathbf{v} \cdot \mathbf{n} \),

\[ p(v_{\perp}) = \frac{mv_{\perp}}{k_B T} \exp \left( -\frac{mv_{\perp}^2}{2k_B T} \right) \quad v_{\perp} \geq 0, \]

while the tangential velocity components are drawn from a MB distribution. For a fluid in thermal equilibrium, the rotation boundary condition presented here produces the same velocity distribution. The probability density of the wall normal component of the velocity of a fluid particle, \( v_{\perp} \), would have a MB distribution within the channel. However, the probability of such a particle impacting a wall over an interval of time, \( \zeta \), is proportional to the distance a particle could be from the wall and impact the wall, i.e. \( v_{\perp} \zeta \). Hence the probability of a particle with a wall normal velocity of \( v_{\perp} \) impacting the wall is proportional to:

\[ p(v_{\perp}) \propto \begin{cases} \lim_{\zeta \to 0} \frac{v_{\perp} \zeta}{\zeta} & v_{\perp} \leq 0 \\ 0 & v_{\perp} > 0. \end{cases} \]

Normalizing this function yields,

\[ p(v_{\perp}) = \begin{cases} \frac{mv_{\perp}}{k_B T} \exp \left( -\frac{mv_{\perp}^2}{2k_B T} \right) & v_{\perp} \leq 0 \\ 0 & v_{\perp} > 0. \end{cases} \]
Hence, a specular reflection of this component, \( v_\perp^* = -v_\perp \), produces the same velocity density function as Gaussian diffusion boundary conditions. For the remaining components, the probability density of the velocity is given by a bivariate Maxwell-Boltzmann distribution,

\[
p(v_{|1}, v_{|2}) = \frac{2\pi m}{k_BT} \exp\left(-\frac{m(v_{|1}^2 + v_{|2}^2)}{2k_BT}\right).
\]

Letting \( v_{|1} = v_1 \cos(\phi) \) and \( v_{|2} = v_1 \sin(\phi) \), the density can be written as,

\[
p(v_1, \phi) = \frac{2\pi m v_1}{k_BT} \exp\left(-\frac{mv_1^2}{2k_BT}\right).
\]

Hence the distribution is invariant to a random rotation by an uniformly distributed angle on the \([0,2\pi)\) interval. Thus this collision operator will produce the same reflected particle density function as Gaussian diffusion boundary conditions.

Unlike Gaussian diffusion, the magnitude of the momentum of the colliding particle is unchanged and there is no energy transfer between the wall and the particle. The reflection-rotation boundary condition is therefore an adiabatic boundary condition. Other types of adiabatic boundary conditions include bounce-back [Allahyarov 2002] [Lamura 2001] boundary conditions, where \( \mathbf{p}^* = -\mathbf{p} \), and a specular collision, where \( \mathbf{p}^* = \mathbf{p} - 2(\mathbf{p} \cdot \mathbf{n})\mathbf{n} \). The former is considered a sticky, or non-slip boundary condition where wall friction is at its maximum, and the latter is considered a frictionless boundary condition where there is no drag on the fluid from the walls. Bounce-back boundary conditions correspond to the case where \( \phi = \pi \) in the reflection-rotation boundary condition and specular collisions correspond to the case where \( \phi = 0 \). Hence the reflection-rotation boundary condition presented here produces intermediate results to these two conditions. The simulations performed with this boundary condition showed a streamwise momentum accommodation that is consistent with the theoretical value of 1 for diffusive collisions. This result is discussed in more detail in section 2.4.2.
2.3.2.2 Inlet and Outlet Boundary Conditions

The MPCD algorithm uses boundary conditions at the inlet and the outlet to implement a flow field. The MPCD algorithm is used to simulate a section of channel that is well-removed from entrance and exit effects. For example, consider a system composed of two reservoirs, one at a high pressure, $P_{\text{high}}$, and the other at a low pressure, $P_{\text{low}}$, with the two reservoirs connected to each other by a nanochannel of square cross-sectional area. The simulations attempt to simulate a section of this channel with an inlet pressure $P_{\text{in}} < P_{\text{high}}$ and an outlet pressure $P_{\text{out}} > P_{\text{low}}$ that is well-removed from the points where the fluid flows from the high pressure reservoir into the channel and the point where the fluid flows from the channel into the low pressure reservoir. Hence, the focus of this algorithm is to simulate the flow profile generated by a pressure gradient in a compressible fluid within a channel, and not on the entrance and exit effects for particles flowing into this system.

The boundary condition algorithm simulates the flow profile for the nanochannel by adding and removing particles from the inlet and outlet. To maintain the boundary conditions, the pressure and transverse velocity need to be specified at both the inlet and outlet and the temperature also needs to be specified at the inlet [Peikos 1996]. The difficulty in implementing the boundary conditions using only these data is that the local pressure and temperature are highly dependent on the local average velocity. Any fluctuations in the average velocity are squared in the calculation of the temperature and pressure. For high pressure gradient flows, the method is insensitive enough to these fluctuations that these basic data are sufficient. However, to produce stable flows for weak gradient flow fields, additional data are needed to stabilize the boundary conditions. In the case of the algorithm used in this report, the inlet velocity profile is specified from a series solution to the Navier-Stokes equation and the temperature is specified at the outlet.

The boundary condition algorithm works by either removing particles from the system or adding them to the system with a velocity drawn from a Maxwell-Boltzmann distribution with temperature $T$ and mean velocity, $\bar{v}$, to maintain a pressure gradient. The Maxwell-Boltzmann distribution provides the thermal control. The specification of a velocity profile and the number of particles in the cell provide control of the pressure, though these corrections require accurate calculations of $\bar{v}$, $T$, and $P$ in the inlet cells. Due to the effect of particles leaving the system at the inlet and outlet on the calculation of local average quantities, the use of only the outlet and
inlet layers of cells to establish the boundary region proved to be insufficient. Corrections have to be made to multiple layers of cells in the inlet and outlet regions. For the simulations presented here, 4 layers of cells were used in the inlet and outlet.

The average velocity in an inlet cell, \( \bar{v} \), is difficult to obtain as the instantaneous population of particles is too small for an accurate measurement. Furthermore, time averages have a memory that cause errors to persist for a period equal to the number of time steps used in the kernel for the average. As corrections to the pressure and temperature based on an incorrect value of \( \bar{v} \) can alter the established flow field, this potential source of error was eliminated from the algorithm by using a fixed velocity profile. Due to the use of adiabatic boundary conditions for the wall instead of isothermal boundary conditions which would have had a thermostat effect on the fluid, and the sensitivity of \( \bar{v} \), the temperature was specified at the outlet as well to eliminate the high correlation between the pressure and temperature.

The boundary condition algorithm functions differently within an entrance/exit layer of cells (the cells exposed to the system boundary) and bulk layers of cells (the buffer cells between the boundary and the system as a whole). For both the inlet and outlet boundary condition, the same algorithm is used for particles in the bulk layers. This procedure is explained in detail below:

1. The algorithm calculates a number weighed average of the cell velocity,

\[
\bar{v} = \frac{\sum_{j=c-T+1}^{c} N_c(j) \bar{v}_{inst}(j)}{\sum_{k=-c_T+1}^{c} N_c(k)},
\]

\text{Eqn. 2.3.2.2.1}

where \( n \) is the number of time steps that have passed for the system, \( c_T \) is the number of time step used to calculate the time average, \( N_c(t) \) is the number of particles in the cell at time \( t \) and \( \bar{v}_{inst}(t) = \frac{1}{N_{cl}(t)} \sum_{i=1}^{N_c(t)} v_i(t) \) is the instantaneous time average of the cell velocity. If fewer than \( c_T \) time steps had passed in the system, it was assumed that \( \bar{v} = 0 \). The components of \( \bar{v} \) that were normal to the walls of the channel were also taken to be zero due to symmetry constraints.

2. Based on \( \bar{v} \), the pressure of each cell is calculated,
\[ P(c\Delta t) = \frac{1}{3V} \sum_{i=1}^{N_{cell}(c\Delta t)} m_i (v_i - \bar{v}) \cdot (v_i - \bar{v}) \]  

\text{Eqn. 2.3.2.2}

3. The pressure is corrected:

a. If the pressure is higher than \( \bar{P} \), the target pressure, then particles are randomly removed until removing the next particle would increase the magnitude of the difference between the pressure and \( \bar{P} \). That is, particles are removed from the cell until \( |P_{N-1}(c\Delta t) - \bar{P}| > |P(c\Delta t) - \bar{P}| \), where \( P_{N-1}(c\Delta t) \) is the pressure without particle \( j \).

\[ P_{N-1}(c\Delta t) = \frac{1}{3V} \sum_{i=1, i \neq j}^{N_{cell}(c\Delta t)} m_i (v_i - \bar{v}_{N-1}) \cdot (v_i - \bar{v}_{N-1}) \]  

\text{Eqn. 2.3.2.3}

where,

\[ \bar{v}_{N-1} = \left( \frac{\sum_{k=c-c_{c+1}}^{c} N_{Cell}(k\Delta t)}{\sum_{k=c-c_{c+1}}^{c} N_{Cell}(k\Delta t)} - 1 \right) \]  

\text{Eqn. 2.3.2.4}

Particle \( j \) is randomly selected from the particles in the cell and if a particle is removed \( P(c\Delta t) = P_{N-1}(c\Delta t) \), \( \bar{v} = \bar{v}_{N-1} \) and \( N_{Cell}(c\Delta t) = N_{Cell}(c\Delta t) - 1 \).

b. If the pressure is lower than \( \bar{P} \), then particles are added to the cell until the addition of the next particle would increase the magnitude of the difference between the pressure and \( \bar{P} \). That is, particles are added to the cell until \( |P_{N+1}(c\Delta t) - \bar{P}| > |P(c\Delta t) - \bar{P}| \), where \( P_{N+1}(c\Delta t) \) is the pressure with the addition of particle \( j \).

\[ P_{N+1}(c\Delta t) = \frac{1}{3V} \left( m_j (v_j - \bar{v}_{N+1}) \cdot (v_j - \bar{v}_{N+1}) + \sum_{i=1, i \neq j}^{N_{cell}(c\Delta t)} m_i (v_i - \bar{v}_{N+1}) \cdot (v_i - \bar{v}_{N+1}) \right) \]  

\text{Eqn. 2.3.2.5}

where,
\[
\bar{v}_{N+1} = \frac{\sum_{k=-c}^{c} N_{Cell}(k\Delta t) + v_j}{\sum_{k=-c}^{c} N_{Cell}(k\Delta t) + 1}
\]

Eqn. 2.3.2.2.6

The position of particle \( j \) is randomly drawn from a uniform distribution of the cell volume. The velocity of particle \( j \) is drawn from a Maxwell-Boltzmann distribution with temperature \( T \) and mean velocity \( \bar{v} \). If a particle is added to the cell \( P(c\Delta t) = P_{N+1}(c\Delta t), \bar{v} = \bar{v}_{N+1} \) and \( N_{Cell}(c\Delta t) = N_{Cell}(c\Delta t) + 1 \). 

4. The updated values of \( \bar{v}_{inst}(c\Delta t) \) and \( N_{Cell}(c\Delta t) \) from step 3 are stored in memory for step 1 at \( t = (c + 1)\Delta t \).

The entrance/exit cell layers are the crux of the boundary condition algorithm. The bulk cells serve to moderate the transition between these cells and the remainder of the system. The essential difficulty with making corrections to these cells is that the corrections cannot be made until \( \bar{v} \) and the local pressure have been calculated. Unlike the other cells in the system, these cells each have a face, with normal vector \( \hat{n}_{Ext} \), through which there is no positive particle flux. Hence, while the cell has not gained particles with \( \bar{v} \cdot \hat{n}_{Ext} < 0 \), it has lost particles through all the faces and gained particles through all of the other faces. Thus the average velocity of the cell will tend to be biased towards a negative velocity in the inlet and a positive velocity in the outlet. Due to this bias, these cells cannot be handled in the same fashion as the other cells in the system. For cells that are in the entrance or exit layers of the channel the boundary condition algorithm functions as follows:

1. The algorithm calculates \( \bar{v} \) for the cell.
   - In the inlet, the velocity profile from the Navier-Stokes equation without slip boundary conditions (Appendix A, eqn. A.23), is used for the flow component of \( \bar{v} \), the other two components are taken to be zero due to symmetry constraints.
   - In the outlet, \( \bar{v} \) is taken from a cell one layer into the system. That is \( \bar{v} \) for the cell with coordinates \((x, y, z - L)\) is used as \( \bar{v} \) for the cell with coordinates \((x, y, z)\) where \( z \) component of the position vector in the direction of flow.
2. All of the particles in the boundary cells have their velocity and position randomized. Their position is randomly drawn from a uniform distribution of the cell volume. Their velocity is drawn from a Maxwell-Boltzmann distribution with temperature $T$ and velocity $\mathbf{v}$. The inlet temperature is used at the outlet to increase the back flow into the system, the reason for this is discussed below.

3. Using $\mathbf{v}$, the pressure of the cell is calculated using equation 2.3.2.2.2.

4. The pressure is corrected. This is similar to step 3 for the bulk layer algorithm, however as $\mathbf{v}$ is not a function of the velocity of the particles in the cell, the formulae are modified accordingly:

a. If the pressure is higher than $\overline{P}$, the target pressure, then particles are randomly removed until removing the next particle would increase the magnitude of the difference between the pressure and $\overline{P}$. That is particles are removed from the cell until $|P_{N-1}(c\Delta t) - \overline{P}| > |P(c\Delta t) - \overline{P}|$, where $P_{N-1}(c\Delta t)$ is the pressure without particle $j$,

$$P_{N-1}(c\Delta t) = \frac{1}{3V} \sum_{i \neq j} m_i (\mathbf{v}_i - \overline{\mathbf{v}}) \cdot (\mathbf{v}_i - \overline{\mathbf{v}}), \quad \text{Eqn. 2.3.2.3'}$$

particle $j$ is randomly selected from the particles in the cell and if a particle is removed $P(c\Delta t) = P_{N-1}(c\Delta t)$ and $N_{Cell}(c\Delta t) = N_{Cell}(c\Delta t) - 1$.

a. If the pressure is lower than $\overline{P}$, then particles are added to the cell until the addition of the next particle would increase the magnitude of the difference between the pressure and $\overline{P}$. That is particles are added to the cell until $|P_{N+1}(c\Delta t) - \overline{P}| > |P(c\Delta t) - \overline{P}|$, where $P_{N+1}(c\Delta t)$ is the pressure with the addition of particle $j$,

$$P_{N+1}(c\Delta t) = \frac{m_j (\mathbf{v}_j - \overline{\mathbf{v}}_{N+1}) \cdot (\mathbf{v}_j - \overline{\mathbf{v}}_{N+1})}{3V} + P(c\Delta t), \quad \text{Eqn. 2.3.2.5'}$$

The position of particle $j$ is randomly drawn from a uniform distribution of the cell volume. The velocity of particle $j$ is drawn from a Maxwell-Boltzmann
distribution with temperature $T$ and mean velocity $\bar{v}$. If a particle is added to the cell $P(n\Delta t) = P_{N+1}(n\Delta t)$ and $N_{Cell}(n\Delta t) = N_{Cell}(n\Delta t)+1$.

The period at which the boundary condition algorithm should be applied to the inlet and outlet should be commensurate with the time it takes a particle to travel the length of the cell $L$. Although the algorithm could be applied more frequently than this period, most of these corrections would be inconsequential and a waste of computational resources (this algorithm is a moderately expensive calculation). The corrections should not be made with a longer period than this as the pressure drop at the inlet and outlet would have time to increase between corrections and a pulsatile flow would form in the channel.

The inlet temperature was used at the outlet, although this temperature should be lower due to the isentropic expansion of the fluid. The reason for this decision was to expand the velocity distribution at the outlet, and thereby increase the flow of particles into the system from the outlet. As $\bar{v}$ is calculated using a local average, its value is sensitive to fluctuations unlike the inlet that uses a static value of $\bar{v}$. While the system is robust against fluctuations that increase flow into the system, it depends strongly on fluctuations that increase flow out of the system.

Figure 2.3.2.2. 1 Illustration for the need for a positive bias to $\bar{v}_{flow}$ in the boundary condition algorithm from a pneumatic spring. If particles are added from a Maxwell-Boltzmann distribution with $\bar{v}_{flow} = 0$ to maintain the pressure at $P$, the system will remain at $P$. If there is a fluctuation $\bar{v}_{flow}$ that increases its value, the system pressure will
increase, which will cause an increased flux of particles with a negative velocity in the
direction of flow which will damp out the fluctuation in $\mathbf{v}_{\text{flow}}$. However if there is a
fluctuation in $\mathbf{v}_{\text{flow}}$ that decreases its value, the system pressure will drop and there is no
external flux to dampen this fluctuation. Essentially, while one can push on a gas, one
cannot pull on a gas.

To illustrate the need for this bias, consider the physical response of the system to fluctuations in
the average velocity in the direction of flow, $\mathbf{v}_{\text{flow}}$. To reduce the number of variables simplify
the system by sealing one end of the channel, with this modification the boundary condition
algorithm acts to maintain the MPCD fluid in equilibrium within this vessel at a pressure $P$ (see
figure 2.3.2.2.1). For this simplified system, $\mathbf{v}_{\text{flow}} = 0$. If fluctuations cause an increase in this
velocity, $\mathbf{v}_{\text{flow}} > 0$, there will be increase in the particle flux into the channel. This will increase
in the pressure of the MPCD fluid, and this increase in pressure will result in an increase in the
efflux of particles from the channel which will decrease $\mathbf{v}_{\text{flow}}$. However if fluctuations cause a
decrease in this velocity, $\mathbf{v}_{\text{flow}} < 0$, there is no similar response from the vacuum outside of the
system, leading to a decrease in the particle influx and the pressure of the fluid will decrease
until the particle efflux is the same as the particle influx with the new lower $\mathbf{v}_{\text{flow}} < 0$.

Essentially, the MPCD fluid behaves as a compressed spring with no elastic modulus under
tension. If the fluctuations push into the system, the spring pushes back negating this fluctuation.
If the fluctuations pull the fluid out of the system, the spring expands with no resisting force.
Hence it is necessary to include a flow bias to stabilize the system. This bias may partially be
responsible for a decrease in the fluid temperature in the system relative to the temperature
specified by the boundary condition.

2.3.3 Channel Flow Parameters

The simulations conducted in this report were performed in a model $20 \times 20 \times 100$ nm square
cross-section channel, shown in figure 2.3.3.1. The walls are normal to the $x$ and $y$
dimensions, and flow occurs along the $z$-axis of the system. The origins of the axes $x = 0$ and
$y = 0$ were chosen the centre of the channel, while the zero point of the $z$-axis is the inlet of the channel. The system is divided into 1 nm$^3$ cells. The inlet and outlet regions are composed of 4 layers of the cells, an entrance/exit layer and 3 layers of bulk cells. The fluid particles had a mass of $m = 39.974$ AMU. $\Delta t$ for the system was 0.5 ps, hence the truncation velocity ($L/\Delta t$) was 2000 m/s. $\delta t$ was 0.5 fs for the MD subsystem.

Figure 2.3.3. 1 Schematic of the model channel. The simulations conducted in this article were performed in a model $20 \times 20 \times 100$ nm square cross-section channel. The walls are normal to the $x$ and $y$ dimensions and flow occurs along the $z$-axis of the system. $x = 0$ and $y = 0$ were chosen the centre of the channel while the zero point of the $z$-axis is the inlet of the channel. This point is indicated by the intersection of the red, blue and green lines. The system is divided into 1 nm$^3$ cells. The inlet and outlet regions are composed of 4 layers of the cells, an entrance/exit layer (highlighted in lavender) and 3 layers of bulk cells (highlighted in red).
The rotational period of the MPCD fluid is tied to the pressure gradient of the fluid through the mean collision time,

\[ \tau_c = \frac{1}{8r^2(P_{in} + P_{out})} \sqrt{\frac{mk_bT}{\pi}}. \]  

Eqn. 2.3.1.2

The particles had a radius of \( r = 0.0415 \) nm. This formula is based on the mean collision time for an ideal gas [McQuarrie 2000], \( \tau_c = \frac{\lambda}{|V|} = \frac{k_B T}{\sqrt{32\pi r^2 P}} \sqrt{\frac{8k_B T}{\pi m}} = \frac{1}{16r^2 P} \sqrt{\frac{mk_B T}{\pi}}, \) using the mid channel pressure \( P = \frac{(P_{in} + P_{out})}{2}. \) Hence \( n_r \) was calculated as \( \tau_c/\Delta t \) rounded to the nearest integer. During the rotation step, the particle velocities were rotated by an angle of \( \pi/4. \)

The outlet pressure was set to 49577872 Pa, which corresponds to a particle density of 20 particles per cell at 298.15 K. The inlet pressure was increased from that value to create a pressure gradient. The inlet velocity profile used in the entrance/exit layer of the first cell was calculated using equation A.23, where the viscosity was calculated from Tüzel’s formula for the viscosity of a MPCD fluid [Hecht 2005] [Ihle 2005] [Tüzel 2003],

\[ \mu = \frac{\rho k_B \tau_c}{2} \left( \frac{3\rho^2L^6 + 2\rho\ell^3 + 1 + \sqrt{2(\rho^2L^6 + \sqrt{2^3 - 2})}}{3\rho^2L^6 - 2\rho\ell^3 - 1 - \sqrt{2(\rho^2L^6 + \sqrt{2^3 - 2})}} \right) + \frac{\rho L^2(\rho L^3 - 1 + e^{-\rho L})}{18\tau_c\rho L^3}. \]  

Eqn. 2.3.3.1

2.4 Channel Flow Results

The results of the simulations conducted using the MPCD algorithm to simulate flow in nanoscale channels are presented in this section. For these simulations, the first ten inlet and outlet layers of cells were omitted from the analysis of the simulations as the boundary condition algorithm introduced some fluctuations in the parameters (figure 2.4.1). While there are no fluctuations in the pressure data, there is an increase in the density which corresponds to a drop in the temperature within the system. There is also an increase in the fluid velocity as the fluid clears the inlet.
Figure 2.4. 1 The inlet and outlet effects on the hydrodynamic variables for a simulation with a flow rate of $7.78 \pm 0.26 \times 10^7$ particles/ns. Figure a), top left, shows the pressure profile which does not have any entrance effects. The density and temperature are shown in figures b), top right, and c), bottom left, respectively, the temperature shows a decrease as the fluid enters the channel and the density shows a corresponding increase. Figure d), bottom right, shows the velocity profile of the fluid along the channel, the velocity is lower in the inlet region and higher in the outlet region, but this effect does not persist into the system. Due to these entrance effects, the first and last 10 cells are neglected for the purposes of analysis.

For the global fits, the velocity data were fit to the following function:

$$v_z(x, y, z) = \left( \sum_{i=0}^{6} \alpha_i z^i \right) \left( 1 + \sum_{j=1}^{3} \beta_j x^{2j} + y^{2j} \right) + \sum_{k=1}^{3} \sum_{l=k}^{3} \gamma_{kl} \left( x^{2k} y^{2l} + x^{2l} y^{2k} \right),$$

Eqn. 2.4.1

where $\alpha_i$, $\beta_j$, and $\gamma_{kl}$ are the adjustable parameters. Due to the symmetry of the flow profile about the central axis, the odd components of the polynomial could be eliminated and, as
\[ v_z(x, y, z) = v_z(y, x, z), \quad \gamma_{jk} = \gamma_{kj}. \]
The data and the momentum balance equation also indicated that the \( z \)-dependence of \( v_z(x, y, z) \) was independent of the \( x \) and \( y \) dependence. Thus the general tri-hexic equation could be reduced to 16 parameters from the standard 343. As the pressure and density data were axially homogenous, they could be fit to a 6\(^{th}\) degree polynomial that only varied along the length of the channel:

\[ P(z) = \sum_{i=0}^{6} \delta_i z^i, \quad \text{Eqn. 2.4.2} \]

\[ \rho(z) = \sum_{i=0}^{6} \epsilon_i z^i, \quad \text{Eqn. 2.4.3} \]

with adjustable parameters \( \delta_i \) and \( \epsilon_i \).

For the fit of data to a specific point, a cubic equation was used for one dimensional data and a modified tri-cubic equation was used in three dimensions. Furthermore, the contribution of residuals to the norm was scaled to \( 1/(1+\omega) \), where \( \omega \) is the distance from the point being fit to the data point. To accelerate the calculation, data points that were more than 10 nm from the point being fit in either the \( x \), \( y \) or \( z \) dimensions were omitted from the kernel. For the velocity data the following equation was used:

\[ v_z(x, y, z) = \left( \sum_{i=0}^{3} \alpha_i z^i \right) \left( 1 + \sum_{i=0}^{3} \sum_{j=0}^{\min(3, 4-i)} \beta_{jk} x^j y^k \right), \quad \text{Eqn. 2.4.4} \]

where \( \alpha_i \) and \( \beta_{jk} \) are adjustable parameters. For the average velocity, density and pressure the following equation was used:

\[ \tau(z) = \sum_{i=0}^{3} \delta_i z^i, \quad \text{Eqn. 2.4.5} \]

where \( \tau(z) \) is the parameter being modeled and \( \delta_i \) are the adjustable parameters. The data was averaged over 1 ns of simulation time, (2000 measurements for each datum).
2.4.1 Equilibrium Simulations

Equilibrium conditions provide a system with known statistics where the probability densities of the pressure and density within the cells can be examined. Under equilibrium conditions, the cells should behave as grand canonical ensembles, hence the number density should follow a Poisson distribution,

\[ p_{eq}(N) = \frac{1}{N!} \left( \frac{L^3 \bar{P}}{k_B T} \right)^N \exp \left( - \frac{L^3 \bar{P}}{k_B T} \right), \]

Eqn. 2.4.1.1

where \( \bar{P} \) is the mean pressure of the system. The pressure density can be calculated as the weighted average of the probability density for finding a pressure, \( P \), with \( N \) particles.

As the pressure is a function of the velocity (eqn. 2.3.1.6), and the velocity should have a MB-distribution, the probability of finding a pressure \( P \) with \( N \) particles is,

\[ p_n(N,P) = \int \frac{m}{2\pi k_B T} \left( \frac{3N}{m} \right)^{3N/2} \exp \left( - \frac{m}{2k_B T} \left( \sum v_i \cdot v_i \right) \right) \prod_{i=1}^{N} dv_{ix} dv_{iy} dv_{iz}, \]

which is an integral over the surface of a \( 3N \) dimensional hypersphere. Performing this integral yields the intermediate result,

\[ p_n(N,P) = \frac{1}{P} \Gamma \left( \frac{3N}{2} \right)^{-1} \left( \frac{3L^3 P}{2k_B T} \right)^{3N/2} \exp \left( - \frac{3L^3 P}{2k_B T} \right). \]

Eqn. 2.4.1.2

Thus the pressure distribution is,

\[ p_{eq}(P) = \sum_{N=1}^{\infty} \frac{1}{N!} \left( \frac{L^3 \bar{P}}{k_B T} \right)^N \exp \left( - \frac{L^3 \bar{P}}{k_B T} \right) \frac{1}{P} \Gamma \left( \frac{3N}{2} \right)^{-1} \left( \frac{3L^3 P}{2k_B T} \right)^{3N/2} \exp \left( - \frac{3L^3 P}{2k_B T} \right), \]

which simplifies to,
The boundary condition algorithm does not reproduce these distributions. At each time step, the velocity of each particle is redrawn from a Maxwell-Boltzmann distribution and the particle number is adjusted to get as close to $\bar{P}$ as possible. Under the simplifying assumption that the pressure after adjustment is $\bar{P}$, then the probability of there being $N$ particles should be proportional to the probability that $N$ particles would have a pressure $\bar{P}$. This is the expression of equation 2.4.1.2. Normalizing this probability distribution by summing over all $N$, yields the following expression for the density distribution,

$$p_{eq}(P) = \frac{1}{P} \exp \left( -\frac{L^3}{k_B T} \left( \frac{3}{2} P + \bar{P} \right) \right) \sum_{N=1}^{\infty} \frac{\bar{P}^N (3P/2)^{3N/2}}{N! \Gamma(3N/2)} \left( \frac{L^3}{k_B T} \right)^{5N/2}.$$  \hspace{1cm} \text{Eqn. 2.4.1.3}

This assumption of a constant pressure is justified, as the pressure distribution, which is derived below, is very narrow. While the correct pressure distribution could be used, it would not lead to a compact solution and eqn. 2.4.1.4 matches the data very well.

The expression for pressure density is significantly more complex. Essentially, this is the probability of a pressure $P$ occurring during the operation of the algorithm multiplied by the probability of the algorithm stopping at that pressure. This process is illustrated in figure 2.4.1.1. For a pressure $P < \bar{P}$, $P$ can be attained by two mechanisms:

1. If the initial pressure, $P_o$, was less than $P$, then particles were added until the pressure was $P$ and the algorithm terminated at this pressure because adding another particle would have made the pressure greater than $2\bar{P} - P$. The probability of this process may be expressed as,
\[
\left( p_0(P) + \int_0^P p_0(P') \sum_{N=1}^{\infty} p_n(N, P - P') dP' \right) \left( \int_{2(P-P')}^{\infty} p_n(1, \Delta P) d\Delta P \right),
\]

where \( p_0(P) \) is the initial pressure distribution and \( p_n(N, P) \) is the distribution given by equation 2.4.1.2.

2. If the initial pressure was greater than \( 2P - P \), then \( P \) was produced by the removal of particles until the removal of the final particle took the pressure from a pressure greater than \( 2P - P \) to \( P \). The probability of measuring a pressure, \( P'' \), which is greater than \( 2P - P \), is
\[
\int_{2P-P}^{\infty} \left( p_0(P'') + \int_{P'}^{\infty} p_0(P''') \sum_{N=1}^{\infty} p_n(N, P''' - P'') dP''' \right) \left( p_n(1, P'' - P) \right) dP''.
\]

Thus for \( P < P \), the probability density for \( P \), subject to renormalization is,
\[
p(P) = \left( p_0(P) + \int_0^P p_0(P') \sum_{N=1}^{\infty} p_n(N, P - P') dP' \right) \left( \int_{2(P-P')}^{\infty} p_n(1, \Delta P) d\Delta P \right) + \int_{2P-P}^{\infty} \left( p_0(P'') + \int_{P'}^{\infty} p_0(P''') \sum_{N=1}^{\infty} p_n(N, P''' - P'') dP''' \right) \left( p_n(1, P'' - P) \right) dP''.
\]

Performing a similar analysis for \( 2P > P > P \) yields the expression,
\[
p(P) = \left( p_0(P) + \int_0^P p_0(P') \sum_{N=1}^{\infty} p_n(N, P' - P) dP' \right) \left( \int_{2(P-P)}^{\infty} p_n(1, \Delta P) d\Delta P \right) + \int_0^{2P-P} \left( p_0(P'') + \int_{P'}^{\infty} p_0(P''') \sum_{N=1}^{\infty} p_n(N, P''' - P'') dP''' \right) \left( p_n(1, P - P') \right) dP'.
\]
Figure 2.4.1. 1 An illustration of the two mechanisms by which a pressure of $P$ can be produced by the boundary condition algorithm, for $P < \bar{P}$. In the top diagram, the initial pressure is in the red interval and through the addition of particles it transitions to the pressure $P$, if the addition of the next particle would cause the pressure to transition to the blue interval then the algorithm would terminate at $P$. In the bottom diagram, the initial pressure is in the red interval, if the removal of one particle from a cell with a pressure in this interval causes the pressure to transition to $P$, then $P$ would be the terminal pressure.

With the simplifying expression that $p_0(P)$ is uniform on the $[0,2\bar{P}]$ interval, which has the added advantage of making the distribution symmetric, these expressions simplify to the formula
\[
p_{bc}(P) = \begin{cases} 
\frac{1}{2\overline{P}} + \frac{1}{2\overline{P}} \int_0^\infty p_n(N, P - P') dP' \left( \int_{2\overline{P}}^{2P-P} p_a(1, \Delta P) d\Delta P \right) & \text{for } P < \overline{P} \\
\frac{1}{2\overline{P}} + \frac{1}{2\overline{P}} \int_0^\infty p_n(N, P'' - P') dP' \left( \int_{2\overline{P}}^{2P-P} p_a(1, \Delta P) d\Delta P \right) & \text{for } P = \overline{P} \\
\frac{1}{2\overline{P}} + \frac{1}{2\overline{P}} \int_0^\infty p_n(N, \overline{P} - P') dP' \left( \int_{2\overline{P}}^{2P-P} p_a(1, \Delta P) d\Delta P \right) & \text{for } \overline{P} < P < 2\overline{P} \\
\frac{1}{2\overline{P}} + \frac{1}{2\overline{P}} \int_0^\infty p_n(N, P'' - P') dP' \left( \int_{2\overline{P}}^{2P-P} p_a(1, \Delta P) d\Delta P \right) & \text{for } P \geq 2\overline{P} 
\end{cases}
\]

Since the termination criterion seems to be the governing factor for the structure of the distribution, the choice of initial distribution has little effect on the form of the final distribution as long as the distribution is broader than the pressure contribution of a single particle. Eqn. 2.4.1.5 fits the data from both equilibrium simulations, as well as the results from running the boundary condition algorithm repeatedly on an empty cell, \( p_0(P) = \delta(P - 0) \), quite well. This distribution, shown in figure 2.4.1.2, is significantly narrower than the equilibrium pressure distribution, though the system relaxes to the equilibrium distribution within 15 cell lengths.
Figure 2.4.1. 2 Cell density (top) and pressure distribution functions (bottom) for the inlet cells with coordinates (10.5 nm, 10.5 nm, 0.5 nm). The simulation results are represented by the solid black line. The heavy dashed line is the boundary condition distribution Eqn. 2.4.1.4 for the density and Eqn. 2.4.1.5 for the pressure. The light dotted line is the equilibrium distribution Eqn. 2.4.1.1 for the density and Eqn. 2.4.1.3 for the pressure.
This transition from the boundary condition distributions to the equilibrium distributions is illustrated in figure 2.4.1.3 for the number distribution, and in figure 2.4.1.4 for the pressure distribution. As these figures illustrate, there are only minor differences in how the pressure and number distributions transition from the boundary condition distributions to the equilibrium distributions for the inlet and outlet. Also note that the number distribution equilibrates faster than the pressure distribution. This is to be expected as the difference between the boundary condition and equilibrium distributions are far more significant for the pressure than for the density.
Figure 2.4.1. 3 Cell number density function vs. cell coordinate. The top graph, a), shows the number distribution for the inlet cells with $x$ and $y$ coordinates of 10.5 nm. The middle graph, b), shows the number distribution for the outlet cells with $x$ and $y$ coordinates of 10.5 nm. The lowest figure, c), shows the number distribution for the inlet cells with coordinates (10.5 nm, 10.5 nm, 10.5 nm). The simulation data are represented by the solid black line. The boundary condition distribution, Eqn. 2.4.1.5, is represented by
the heavy dashed line. The equilibrium distribution, Eqn. 2.4.1.3, is represented by the light dotted line.

Figure 2.4.1. 4 Cell pressure density function vs. cell coordinate. The top graph, a), shows the pressure distribution for the inlet cells with \( x \) and \( y \) coordinates of 10.5 nm. The middle graph, b), shows the pressure distribution for the outlet cells with \( x \) and \( y \) coordinates of 10.5 nm. The lowest figure, c), shows the pressure distribution for the inlet
cells with coordinates (10.5 nm, 10.5 nm, 10.5 nm). The simulation data are represented by the solid black line. The boundary condition distribution, Eqn. 2.4.1.4, is represented by the heavy dashed line. The equilibrium distribution, Eqn. 2.4.1.1, is represented by the light dotted line.

The other discrepancy between the anticipated distribution and the simulation results is a decrease in the system temperature as particles enter the system from the boundary region, shown in figure 2.4.1 and figure 2.4.2.4. With the use of periodic boundary conditions, this temperature drop is not observed. Hence, this temperature drop is an artefact of the boundary condition algorithm. The narrow pressure distribution manifests as the injection of a relatively constant flux of particles into the system at the same location with the same velocity distribution. Thus particles with low velocities have a longer residence time in cells near the inlet while particles with high velocities travel farther into the system. As the particles travel into the system, their velocities diffuse resulting in the broader pressure distribution, but this process has a slight velocity sorting effect which reduces the local variance of the particle velocity and hence the temperature.

2.4.2 Flow Simulations

The continuity equation (equation 2.2.5.1) indicates the mass flow rate should be constant across the length of the channel. In addition, within the simulations the pressure gradient is constant across the channel. Hence these variables are suitable for differentiating between simulation conditions for the various runs that were simulated. As the pressure gradient is not constant within the Navier-Stokes solutions, the flow rate is used for demarcation purposes. The functional relationship between pressure and flow rate is shown in figure 2.4.2.1. As equation A.23 suggests (viscosity is proportional to pressure), the relationship between flow rate and the pressure gradient is a roughly linear one. Linear regression of the data in figure 2.4.2.1 indicates such a relationship with a slope of $208.2 \pm 2.4$ particles·nm/ns/Pa and an intercept of $-2.8 \pm 1.0 \times 10^6$ particles/ns.
Figure 2.4.2. A plot of flow rate vs. pressure gradient. The black line represents a linear regression fit of the data, the line has a slope of $208.2 \pm 2.4 \text{ particles\-nm/ns/Pa}$ and an intercept of $-2.8 \pm 1.0 \times 10^6 \text{ particles/ns}$.

The distributions of the state variables under flow conditions are not well known theoretically. Hence under flow conditions the focus shifts from the distributions of these variables to their steady state values. As long as the Knudsen number is small, $Kn < 0.001$, the flow can be modeled by the Navier Stokes equation and the use of slip boundary conditions extend this range to $Kn < 0.1$. $Kn$ is plotted against the flow rate and $z$-axis of the channel in figure 2.4.2.2. As the highest $Kn$ measured during the simulations was $0.0208 \pm 0.0003$, the solutions to the Navier-Stokes equation presented in Appendix A were used for comparison purposes. $Kn$ increases along the $z$-axis of the channel due to an increase in the mean free path length, $\lambda$, and a decrease of the characteristic length scale, $\Lambda$, due to the drop in pressure. As the flow rate increases, the pressure gradient increases, which decreases $\Lambda$. However, the pressure also
increases, which decreases $\lambda$. Thus, there exists a weaker dependence of $Kn$ on flow rate as opposed to position along the channel $z$-axis, although $Kn$ increases with both parameters.

![Kn as a function of Flow Rate and Channel Length](image)

**Figure 2.4.2.** The Knudsen number as a function of flow rate and channel length. As the flow rate increases the Knudsen number shows a less than linear increase. Along the length of the channel the Knudsen number has a greater than linear increase.

The pressure drop across the length channel is shown as a function of flow rate and $z$-axis coordinate for the simulations and the Navier-Stokes solutions in figure 2.4.2.3. The pressure is uniform across the channel cross-section as would be expected. There is perfect agreement between the solutions and the simulations at $z = 10\, \text{nm}$ and $z = 90\, \text{nm}$ as the regression values for the pressure at these points were used to calculate the series solution profiles. The simulations show a linear decrease in the pressure from the inlet to the outlet, while the series solutions have a curved profile with a strong $\sqrt{z}$ component (equations A.12 and A.22). This deviation is likely caused by the neglect of the pressure dependence of the viscosity in the derivation of the pressure equations. The pressure dependence of the viscosity is complex and can be seen in equation 2.3.3.1, by replacing $\rho$ with $P/(k_BT)$.
Figure 2.4.2. 3 Pressure as a function of channel length and flow rate. The top graph (a) is a surface graph of the raw data as function of the channel length and flow rate. The middle graph (b) is the pressure as a function of the channel length for various flow rates. The top set of lines is for a simulation with a flow rate of $2.77 \pm 0.08 \times 10^8$ particles/ns, the middle set is for a simulation with a flow rate of $7.78 \pm 0.26 \times 10^7$ particles/ns and the bottom set is for a simulation with a flow rate of $1.78 \pm 0.21 \times 10^7$ particles/ns. The bottom graph (c) is the pressure as a function of flow rate in the centre of the channel $z = 50.5$ nm. The solid
lines in graph b) and c) correspond to the simulation data, the heavy dashed lines correspond to the Navier-Stokes solution with slip boundary conditions (Eqn. A.12) and the light dashed lines correspond to the Navier-Stokes solution without slip boundary conditions (Eqn. A.22).

![Temperature as a function of Flow Rate and Channel Length](image)

**Figure 2.4.2.** Temperature as a function of flow rate and channel length. The temperature decreases along the length of the channel and the inlet temperature increases as the flow rate increases.

The temperature profile of the channel is shown as a function of flow rate in figure 2.4.2.4. For the Navier-Stokes solutions, the profile was assumed to be isothermal. As was mentioned in section 2.4.1, there is a decrease in the temperature of the fluid as it transitions from the boundary condition region to the rest of the channel. The effect of this decrease is less pronounced at higher flow rates where the velocity profile within the channel is no longer a Maxwell-Boltzmann distribution. There is an additional temperature drop across the channel due to the expansion of the fluid. Note that the specification of the temperature at the outlet does decrease this effect, though it is still present. The highest temperature drop from \( z = 10 \text{ nm} \) to \( z = 90 \text{ nm} \) was 10 K for the highest flow rate simulation, hence the isothermal assumption for the Navier-Stokes solutions seems justified.
Figure 2.4.2. Density as a function of channel length and flow rate. The top graph (a) is a surface graph of the raw data as a function of the channel length and flow rate. The middle graph (b) is the density as a function of the channel length for various flow rates. The top set of lines is for a simulation with a flow rate of $2.77 \pm 0.08 \times 10^8$ particles/ns, the middle set is for a simulation with a flow rate of $7.78 \pm 0.26 \times 10^7$ particles/ns and the bottom set is for a simulation with a flow rate of $1.78 \pm 0.21 \times 10^7$ particles/ns. The bottom graph (c) is the density as a function of flow rate in the centre of the channel $z = 50.5$ nm. The solid
lines in graph b) and c) correspond to the simulation data, the heavy dashed lines correspond to the Navier-Stokes solution with slip boundary conditions (Eqn. A.12 substituted into the ideal gas law) and the light dashed lines correspond to the Navier-Stokes solution without slip boundary conditions (Eqn. A.22 substituted into the ideal gas law).

The decrease in the fluid temperature causes a corresponding increase in the density of the fluid. The density profile of the fluid is shown as a function of the flow rate in figure 2.4.2.5. Like the pressure, the density is uniform across the channel cross section. However, while the thermal effect described above causes the simulation density to be higher than the density predicted by the Navier-Stokes equation, the inlet density is lower for simulations where the flow rate is less than $7.6 \times 10^7$ particles/ns. This appears to be caused by a slight particle backflow that occurs at low flow rates. This back-flow is also seen in the velocity profiles from these low flow rate simulations, where regressed values of the slip velocity and centre channel velocity for these low flow runs indicate a negative velocity near the inlet for these simulations. The maximum velocity in the channel, which occurs in the centre of the channel, is plotted vs. the flow rate and the channel $z$-axis in figure 2.4.2.6. The velocity profile from the simulations is consistent with the results from the Navier-Stokes solutions.
Figure 2.4.2. Centre channel, or maximum, velocity as a function of channel length and flow rate. The top graph (a) is a surface graph of the raw data as a function of the channel length and flow rate. The middle graph (b) is the velocity as a function of the channel length for various flow rates. The top set of lines is for a simulation with a flow rate of $2.77 \pm 0.08 \times 10^8$ particles/ns, the middle set is for a simulation with a flow rate of $7.78 \pm 0.26 \times 10^7$ particles/ns and the bottom set is for a simulation with a flow rate of $1.78 \pm 0.21 \times 10^7$ particles/ns. The bottom graph (c) is the velocity as a function of flow rate
in the centre of the channel $z = 50.5 \text{ nm}$. The solid lines in graph b) and c) correspond to the simulation data, the heavy dashed lines correspond to the Navier-Stokes solution with slip boundary conditions (Eqn. A.16) and the light dashed lines correspond to the Navier-Stokes solution without slip boundary conditions (Eqn. A.26).

Figure 2.4.2. 7 A plot of the slip velocity as a function of the flow rate. The dashed line is the prediction of the Navier-Stokes solution with slip boundary conditions (Eqn. A.16). The simulation results are consistent with the equation.

The slip velocity at the centre of the wall at the centre of the channel ($x = 10 \text{ nm}$, $y = 0 \text{ nm}$, $z = 50 \text{ nm}$) is plotted against the flow rate in figure 2.4.2.7. The error bars are larger for these data points than the other data presented as they are extrapolated data as opposed to interpolated data. The simulation results are marginally higher than the predictions of the Navier-Stokes equation, although they are well within error bars and have the same morphology. It is apparent that the velocity profiles seem to follow the slip solution of the Navier-Stokes equation as opposed to the
non-slip solution, even at low flow rates. This phenomenon of slip under low flow conditions has been observed in several simulations based on mesoscopic simulations [Allahyarov 2002] [Winkler 2009]. The slip model used in the Navier-Stokes solution was Maxwell’s slip relation [Maxwell 1879] [Arkillic 1997],

\[ v_{\text{slip}} = \alpha \frac{dy}{dx} \bigg|_{\text{wall}} \]

\[
\text{Eqn. 2.2.5.5}
\]

where \( \alpha \) is the streamwise momentum accommodation, which has a value of 1 for diffusive collisions. If the wall boundary condition developed in section 2.3.2.1 simulates diffusive boundary conditions, then a plot of \( v_{\text{slip}} \) vs. \( \lambda \frac{dy}{dx} \bigg|_{\text{wall}} \) should have a slope of 1. This plot is shown in figure 2.4.2.8. and shows a streamwise momentum accommodation of 0.96 with standard error 0.04, which confirms that this boundary condition does replicate the slip behavior of diffusive boundary conditions.
Figure 2.4.2. 8 The slip velocity vs. the product of the shear rate and the mean free path length. The slope of this graph should be the streamwise momentum accommodation. The dashed red line is the theoretical model with a slope of 1 and an intercept of 0. The solid black line is the regressed fit to the data which has a slope of $0.96 \pm 0.04$ and an intercept of $0.6 \pm 0.2$.

The velocity profile across the width of the channel ($y=0$ nm, $z=50$ nm) is plotted as a function of flow rate in figure 2.4.2.8. For the low flow rate simulations there is too much noise in the data to indicate which of the Navier-Stokes solutions models the profile better, though the fit to equation 2.4.1 does match the slip solution better. The quality of this fit is difficult to assess. The form of equation 2.4.1 favors a form that is similar to the Navier-Stokes solutions, as the asymmetric components of the nonspecific equation were removed. At high flow rates, this equation does model the data accurately, (the average distance from data to the curve is 1.94 m/s). While the low flow rate data are harder to judge, the error is roughly commensurate with the high gradient data (the average distance from data to the curve is 2.10 m/s) and the residual
surfaces do not indicate any systematic errors. At higher flow rates it becomes apparent that the flow profile is better fit by the slip solution and the velocity profile also clearly indicates the moderating effect that slip has on the solution.

Figure 2.4.2. The velocity profile across the width of the channel at the centre of the channel (\( y = 0.5 \text{ nm}, z = 50.5 \text{ nm} \)) as a function of flow rate. The top left graph, a), is a surface plot of the raw data for all flow rates. The top right graph, b), shows the velocity profile at flow rate of \( 1.78 \pm 0.21 \times 10^6 \text{ particles/\text{ns}} \). The bottom left graph, c), shows the velocity profile at flow rate of \( 7.78 \pm 0.26 \times 10^7 \text{ particles/\text{ns}} \). The bottom right graph, d), shows the velocity profile at flow rate of \( 2.77 \pm 0.08 \times 10^8 \text{ particles/\text{ns}} \). The solid lines in graphs b), c) and d) correspond to the simulation data, the heavy dashed lines correspond to the Navier-Stokes solution with slip boundary conditions (Eqn. A.16) and the light dashed lines correspond to the Navier-Stokes solution without slip boundary conditions (Eqn. A.26). The simulations reveal slip at the wall of the channel.
2.5 Conclusions

Flow was simulated in a nanoscale channel with a square cross-section using a MPCD algorithm. The algorithm required the creation of a boundary condition algorithm that could simulate small gradient pressure-driven flows by treating the system boundary as a particle source or sink as was required to maintain a pressure gradient. This algorithm required the specification of the inlet and outlet pressure and temperature as well as the inlet velocity profile to reduce the entrance effects typically associated with boundary conditions that operate as sources/sinks. The inlet velocity profile was constructed from a series solution to the Navier-Stokes equation without slip boundary conditions. While the boundary condition algorithm still produced artefacts in the flow profile, the perturbations to the flow field were greatly reduced by this new model. Under equilibrium conditions, the algorithm produced a much narrower probability density function for the pressure than would be found under equilibrium conditions. This manifested as a decrease in the temperature through the system. This temperature drop was also noted for flow simulations. These artefacts are acceptable, as the temperature drop could be accounted for by increasing the inlet temperature and the intent of the simulations was to capture the behaviour of the fluid in the channel and not the entrance and exit regions.

The inlet and outlet boundary condition algorithm presented in this chapter could be adapted for use with other particle-based simulation methods such as molecular dynamics, DSMC or DPD. As these models have a higher computational overhead than MPCD, the boundary condition algorithm presented in this chapter is perhaps more useful for these algorithms as it requires fewer buffer cells between the boundary and the system to establish dynamics than existing methods. While a series solution to the Navier-Stokes equation was used to produce the target inlet distribution, the energy balance equation and finite element methods could be used to generate a more accurate distribution for a more complex fluid.

To simulate the effect of collisions of the fluid with the wall, a reflection-rotation collision operator was developed that preserved energy and simulated collisions that produced slip consistent with thermally diffusive collisions. The simulations showed that this model reproduced a streamwise momentum accommodation of 0.96 ± 0.04, which is consistent with the value of 1 that is produced by diffusive collisions. This boundary condition is intermediate to bounce-back and specular collision adiabatic boundary conditions, and provides a new partial-slip
boundary condition to examine through simulation. As most nanofluidic devices operate with some fluid slip, these boundary conditions should prove to be a useful tool for future hydrodynamic investigations.

The results of the simulations were consistent with the results of the Navier-Stokes solution with slip boundary conditions; however, the simulations indicated a linear decrease in the pressure profile while the solutions to the Navier-Stokes equation showed a significant $\sqrt{\varepsilon}$ contribution to the pressure profile. This component was also visible in the density profile.

The model and results presented in this chapter are the basis for the remaining two chapters. These chapters explore the interaction of a polymer with the flow field that was simulated here. The examination of polymers is not the only use for the algorithms presented in this chapter. It could also be used to study changes in channel morphology on the flow field, the use of these devices as chemical reactors, or other systems. The MPCD algorithm presented in this chapter is hybridized with a molecular dynamics subsystem to incorporate the polymer model. The ease with which this could be accomplished illustrates the versatility of this mesoscopic algorithm.
Chapter 3
Isolated Untangled Oligomers in Channel Flow

3.1 Overview

The influence of flow on the configuration of polymer chains is an important factor in the development and function of many technologies. Surface immobilized polymers are used in several flow-based applications. These applications include: enzyme-linked immunosorbent assay (ELISA) [Henares 2010], a biochemical analysis technique where a surface linked antigen binds an antibody entrained in the fluid which flows through the device; the reduction of fouling of surfaces in fluidic devices by coating them with poly(ethylene glycol) [Kim 1996], in which the high conformational entropy of this polymer prevents the surface deposition of colloids that are entrained in the fluid phase of these devices; weeping lubrication [McCutchen 1962] [Klein 2006], where a surface coating of tethered polymers (or a gel network) releases a pool of adsorbed solvent at the point of contact between two articulating surfaces and replaces a frictional contact with a viscous contact, and the effect of flow rate on the pore morphology in sub-micron nylon filters [Bagassi 1989] [Gramain 1981].

Unfortunately, there are few studies on the effects of flow on the configuration of the polymers in these devices, perhaps due to a lack of experimental results with consistent methodology in a device with well-defined geometry and effective sensory probes. While it has been possible to visualize fluorescently labeled DNA strands under flow conditions [LeDuc 1999] [Doyle 2000], the resolution of the data is frequently too poor to draw quantitative conclusions and, as a rigid molecule with large side groups that can hydrogen bond with each other, DNA is not an ideal model for drawing general conclusions. A plethora of simulation techniques and differing polymer models have also caused divergence in the theoretical results. Consequently, there are very few generalizations that can be made about the behavior of a polymer chain under flow conditions, other than the observations that tethered polymer chains can exhibit cyclical dynamics [DiMarzio 1978] under pure shear flow instead of a static steady state configuration (section 3.2.3), and that they tend to adopt an extended configuration in the direction of flow.

However, as noted in the previous chapter, the flow of a compressible fluid in a channel has an elongational component that is missing in a pure shear flow. The effect of this mixed
elongational and shear flow on the configuration of a polymer that has been tethered to the surface of a nanochannel is the focus of this chapter. The influence of pressure-driven flow on the configuration of a grafted polymer is studied through mesoscale simulation methods. In particular, the channel flow algorithm in the context of a MPCD simulation is used to drive a steady flux of fluid particles past a tethered polymer. The simulations are used to investigate the modification of the cyclical dynamics found for pure shear flow, and to identify how the extension of the polymer chain in the direction of flow depends on the flow profile. Additionally, under solvent conditions where the polymer adopted a collapsed configuration (poor solvent conditions), a flow stabilized helix configuration is identified. Metastable helices have been found for homopolymer collapse from a stretched initial configuration in a poor solvent under equilibrium conditions at low temperatures [Sabeur 2008], but this is first study in which flow is shown to stabilize this structure. As the flow profiles were well known from chapter 2, the changes in the flow field caused by the interaction of the polymer and the solvent can be visualized. The effect of a grafted polymer on the flow field in a nanoscopic channel has not been examined previously.

The next section of this chapter, section 3.2, reviews the theoretical and practical approaches taken to analyze polymer dynamics under flow in a channel. Section 3.3, presents the details of the polymer model. The penultimate section of this chapter, section 3.4 contains the results of the simulations performed with a single polymer chain under flow for both a θ solvent and a poor solvent. Section 3.5 concludes the chapter with a summary of the work presented here.

3.2 Theoretical Review

Although tethered polymer chains have been simulated under flow conditions before, previous studies have focused on polymers in a pure shear flow or elongational flow as opposed to the flow profile established by pressure gradients in channels for a compressible fluid, which contains both elongational and compressible components. The majority of these simulations have examined the behavior of the polymer under shear flow. Prior to an exposition of the extant theoretical and experimental results, it is useful to survey the existing polymer models and simulation techniques. The latter was the focus of section 2.2.
The polymer chain simulated in this work is a bead and spring representation of a real polymer chain. As the MPCD model (section 2.2.4) is a coarse-grained fluid model that sacrifices local order for computational efficiency, there would be no appreciable improvement in the accuracy of the simulation results if an atomistic description of a real polymer was used, and the additional computational resources required to simulate such a model negates the computational gain from the MPCD model. Furthermore, by utilizing a simple model, several variables that could influence the results of the simulations can be eliminated, such as steric interactions between polymer side groups and polar attractions, thereby isolating the results to the effect of flow on the configuration of the backbone of the polymer.

For the purpose of the present study, the polymer is represented by series of beads, each of which is representative of a backbone carbon and its side groups. Although this chain would not be a good model for a polymer with large side chains such as polystyrene, it is a good model for a polymer such as polyethylene or poly(tetrafluoroethylene) where each repeat unit for the chain can be reduced to each backbone carbon (e.g. CH$_2$, CF$_2$), and possibly even a polymer such as poly(ethylene oxide) which has a O-CH$_2$-CH$_2$ backbone. Instead of using a rigid backbone, a flexible bond potential was used, which allows for a larger integration time-step to be used in MD simulations, though it does increase the degrees of freedom for the beads in the chain.

3.2.1 Polymer Models

There are several models that have been used to simulate polymer chains and further variations of these models are created by the myriad of potentials that are used to simulate intermolecular and intramolecular interactions for the macromers that they represent. The models can be divided into two groups, ball and stick models and ball and spring models. The potentials used for the model polymer in this article are described in more detail in section 3.3. There are far more variations than are relevant to this work, hence only the models that have been used to simulate tethered polymers under flow conditions are presented here.

The polymer model of Kramers [Kramers 1944] is the earliest mechanical ball and stick polymer model. In this model, the polymer chain is divided into $N$ beads separated by $N-1$ rigid rods with unconstrained bond angles. In more modern algorithms, restrictions are placed on bond angle and bond torsional motions. The united atom model of polyethylene [Smith 1994]
[Mondello 1995] is one example of a modern ball and stick model. In the united atom model, the bond angle potential is modelled as,

$$\Psi_b(\theta) = -\frac{k_b}{2}(\theta - \theta_o)^2,$$

where $k_b$ is the Hookean spring constant of the potential and $\theta_o$ is the optimal bond angle ($114^\circ$). The torsional potential is modelled as,

$$\Psi_t(\phi) = a_u \cos(\phi_u),$$

where $a_u$ is the energy constant of the potential, $\phi_u$ is the torsion angle (for the bond between beads $i$ and $i + 1$, defined as the angle between the plane formed by the bonds between beads $i - 1$, $i$ and $i + 1$ and the plane formed by beads $i$, $i + 1$ and $i + 2$). One advantage of these potentials is that they reduce the number of degrees of freedom of the chain from the three perpendicular coordinates of each bead to a set of three chain coordinates, $N - 2$ bond angles and $N - 2$ torsion angles, but they also tend to require smaller integration time steps than spring potentials.

The earliest ball and spring model is generally considered to be the Zimm-Rouse model [Rouse 1953] [Zimm 1956]. In this model, nearest neighbour beads $i$ and $j$ interact with the harmonic potential,

$$\Psi_{ij} = \frac{k_h}{2}|\mathbf{q}_{ij}|^2,$$

where $\mathbf{q}_{ij}$ is the separation between beads $i$ and $j$ and $k_h$ is the Hookean spring constant. This model has the advantage of a simple form that is amenable to analytical treatments, as the polymer chain is reduced to a series of coupled harmonic oscillators. However, in the absence of external forces and in the presence of viscous energy dissipation, the polymer chain collapses onto its centre of mass as the minima of the potential occurs at zero bond length.
A variation of the Zimm-Rouse model that possesses an equilibrium bond length was introduced by Fraenkel [Fraenkel 1951], and predates the Zimm-Rouse model. It is characterized by a bond potential between neighboring monomers $i$ and $j$ of the form,

$$
\psi_{ij} = \frac{k_f}{2} \left( |q_{ij}| - a \right)^2,
$$

where $k_f$ is the force constant of the potential and $a$ is the equilibrium bond length. While this variation introduces a non-zero equilibrium bond length, the polymer chain remains infinitely extendible. Specifically, given the linear stress-strain relationship of a Hookean spring, the polymer chain extends infinitely if subjected to a constant uniaxial tension. The simplest ball and spring model that limits the bond extension is the finitely extendible non-linear elastic (FENE) spring potential [Warner 1972],

$$
\psi_{ij} = -\frac{1}{2} K_{FENE} a^2 \ln \left[ 1 - \left( \frac{|q_{ij}|}{a} \right)^2 \right], \quad |q_{ij}| < a,
$$

where $K_{FENE}$ is the force constant of the spring and $a$ is the maximum extension of the spring, where the potential becomes infinite.

The 6-12 Lennard-Jones potential [Lennard-Jones 1924] has been used to model the interaction between particles $i$ and $j$ that are not connected by a bond in the majority of studies. The potential for non-adjacent beads is written in the form,

$$
\psi_{ij} = 4\varepsilon_{LJ} \left( \frac{\sigma_{LJ}}{|q_{ij}|} \right)^{12} - \left( \frac{\sigma_{LJ}}{|q_{ij}|} \right)^{6},
$$

where $\varepsilon_{LJ}$ is the depth of the potential well and $\sigma_{LJ}$ is the point at which the potential is zero. The Lennard-Jones potential is also frequently written as,

$$
\psi_{ij} = E_{min} \left( \frac{r_{min}}{|q_{ij}|} \right)^{12} - 2 \left( \frac{r_{min}}{|q_{ij}|} \right)^{6},
$$
where $E_{\text{min}}$ is the energy at the minimum of the potential well and $r_{\text{min}}$ is the particle separation at the minimum. The 6\textsuperscript{th} power attractive term is representative of the Van der Waals forces and the 12\textsuperscript{th} power repulsive term is representative of the Pauli repulsion forces.

### 3.2.2 Extension under shear flow

Although it is expected that a polymer chain will extend its conformation into the direction of flow, the exact functional relationship between the strength of the flow field and the extension is not necessarily simple or easily computed. Thus, this relationship is examined through the simulations presented in this chapter. As a first approximation, the time average force on a polymer bead is proportional to the momentum flux of the fluid impacting the effective surface area of the bead or [Welty 1984],

$$F \propto \left( \rho_m |v_r|^2 \right) \hat{v}_r r^2,$$

where $\rho_m$ is the mass density of the fluid, $v_r$ is the relative velocity between the polymer bead and the fluid, $\hat{v}_r$ is a unit direction vector along $v_r$ and $r$ is radius of the bead. In theory, $r$ should be the hydrodynamic radius of the bead instead of the thermodynamic hard sphere radius, but the relationship between the thermodynamic radius of the bead and the hydrodynamic radius of the bead can be accounted for in the proportionality constant [Young 1991]. For the ball/spring and ball/stick polymer chains described in section 3.2.1 where there are no strong attractive potentials between polymer beads that are not bound to each other, the primary resistance to extension is given by the loss of conformational entropy of the polymer chain when it is extended by the force field. For such a model, the entropic theory of polymer elasticity can be used to provide an estimate of how the polymer should react to an extensional force. The entropic theory predicts that the work to deform an elastomer is given entirely by the entropic loss of the polymer chains composing the sample under deformation. Although the theory assumes an isothermal and isochoric process and is only true for small deformations, it describes the low stress, stress/strain relationship of synthetic and natural rubber quite well. For a Gaussian distribution of the end to end separation of a polymer chain (which is true for a random walk polymer), the entropic change on deformation is [Young 1991],
\[
\Delta S = -\frac{k_B}{2} \left( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right),
\]

where \( \lambda_1, \lambda_2 \) and \( \lambda_3 \), are the elongation ratios of the chain (the ratio of the deformed dimensions of the polymer along the principle axes of strain to the undeformed dimensions), with the isochoric constraint \( \lambda_1 \lambda_2 \lambda_3 = 1 \). Hence the reversible isothermal work of deformation is \( -T \Delta S \) or,

\[
w = \frac{k_B T}{2} \left( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right).
\]

Under uniaxial extension, \( \lambda_2 \lambda_3 = 1/\lambda_1 \rightarrow \lambda_1 = \lambda_1, \quad \lambda_2 = \lambda_3 = 1/\sqrt{\lambda_1} \), and this work expression simplifies to,

\[
w = \frac{k_B T}{2} \left( \lambda_1^2 + \frac{2}{\lambda_1^2} - 3 \right).
\]

The resistance to deformation from the extension should be proportional to,

\[
\sigma \propto \frac{dW}{d\lambda_1} = k_B T \left( \lambda_1^2 - \frac{1}{\lambda_1^2} \right), \quad \text{Eqn. 3.2.2.1}
\]

which is the approximate stress-strain relationship for an entropic spring. Equating this stress to the force on the polymer bead described at the beginning of this section, yields the result,

\[
\left( \rho_m |\mathbf{v}_t|^2 \right)^{\frac{1}{2}} \propto T \left( \lambda_1 - \frac{1}{\lambda_1^2} \right), \quad \text{Eqn. 3.2.2.2}
\]

This result has been derived for a very basic model, and neglects the effects of a finite bond length, excluded volume interactions and bead-bead potentials, but for low flow rates with a constant plug flow velocity it should give the approximate relationship, \( \lambda_1 \propto |\mathbf{v}|^2 \) between the fluid velocity and the elongation of the polymer chain. As a constant velocity flow field was not simulated in the simulations presented here, this equation was not tested in this study but the
analysis above should elucidate the primary forces that determine the effect of the flow field on the polymer.

Note that equation 3.2.2.2 does not hold for an elongational flow where the fluid accelerates along the length of the channel, or for a shear flow where the velocity of the fluid varies with distance from the wall of the channel. As the force on each bead of the chain is no longer constant for these flows, the corpuscular nature of the chain must be considered. However, the interplay between the force exerted by the fluid on the polymer and the loss of conformational entropy for the polymer as it is deformed are governing factors for determining the response of the polymer to the flow field.

There have been previous studies done on the behaviour of tethered polymers under shear flow, both for a single bead and a polymer layer. Among single polymer chains, a linear relationship between the extension of the polymer chain and the shear rate of the fluid was predicted by the study of Dubbeldam and Redig [Dubbeldam 2006]. This study made use of a random walk process with height-dependent drift in the flow direction to simulate the steady state conformation of a Markov chain with a Hookean potential in which the position of the next bead in the chain is only dependent on the position of the current bead in the chain. Hooke’s law predicts a linear relationship between the shear force and the extension. However with the lack of an extensibility limit, excluded volume interactions, hydrodynamics and an equilibrium bond length, the applications of these results to the dynamics of a real polymer must be questioned. A molecular dynamics simulation of DNA in shear flow [Wang 2007] also predicted an extension of the polymer chain though, with only 4 data points, the exact functional relationship could not be determined. However as DNA has bulky side groups which interact strongly with each other, its behaviour would not be expected to be similar to simple homopolymer such as the polymers simulated in this work. Other recent studies of polymer dynamics under shear flow for single chains focused on cyclical dynamics.

There are more results available for polymer layers. A decrease in the layer thickness, and increase in chain extension in the direction of flow was found by a study using a lattice Monte Carlo algorithm to study a polymer layer under shear flow [Lai 1993]. These results were consistent with another study where the effect of a linear shear field on a FENE polymer brush
was simulated via Brownian dynamics [Neelov 1995]. The results of these simulations suggest a linear relationship between chain extension and flow rate. It should be noted that the response of a polymer in a polymer layer to a flow field should be different from the response of an isolated polymer chain. In a polymer layer there are physical entanglements between polymer chains that do not exist for an isolated chain. In addition to this effect, the velocity of the fluid near a single chain in a polymer layer is screened by adjacent polymers and the volume occupied by surrounding chains limits the configurational space available to each chain in that layer relative to an isolated chain. As a result of these considerations, the environment surrounding an isolated chain is very different from the environment surrounding a polymer in a polymer layer.

These results can be contrasted with the Brownian dynamics simulations of a Kramers chain in a linear shear field by Parnas and Cohen [Parnas 1991], which showed an increase in the component of the radius of gyration in the direction of flow until the chain neared its contour length. When plotted against the log of the shear rate, the data had a sigmoidal shape. Nonetheless, there were too few data points within the range of shear rates where the polymer had not completely extended to draw a definitive conclusion.

Unfortunately, there are no experimental data that can be used to confirm the theoretical findings for a single chain. There are some experimental results for tethered DNA oligomers in aqueous solution [LeDuc 1999] [Doyle 2000]. However, the quality of the data is too poor to comment on, beyond noting that the polymer extends in the direction of flow. For polymer layers there are more data, but these results are inconsistent due the use of different experimental apparati, polymers, solvents and measurement techniques. The techniques utilized include flow birefringence [Bossart 1997], small angle neutron scattering (SANS) [Lidner 1989], wide angle x-ray scattering and nuclear magnetic resonance, elipsometry [Lee 1984] and using the pressure drop to calculate the effective hydrodynamic thickness (EHT) [Cohen 1988] [Bagassi 1989] [Parnas 1991] [Gramain 1981]. The results of the studies for polystyrene are summarized in table 3.2.2.1, and illustrate the inconsistency of these results.
Table 3.2.2.1 Results for the change in the thickness of a polystyrene layer under shear flow

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solvent Quality</th>
<th>Measurement Technique</th>
<th>Change in layer thickness with increasing flow rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene-styrene</td>
<td>good</td>
<td>SANS</td>
<td>increased</td>
<td>[Lidner 1989]</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>θ</td>
<td>elipsometry</td>
<td>decreased</td>
<td>[Lee 1984]</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>θ</td>
<td>EHT</td>
<td>increased then decreased</td>
<td>[Cohen 1988]</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>θ</td>
<td>EHT</td>
<td>decreased then increased</td>
<td>[Gramain 1981]</td>
</tr>
</tbody>
</table>

As table 3.2.2.1 illustrates, solvent quality seemed to have little effect in determining which behaviour was observed. The major source of these inconsistencies can be attributed to the differences in experimental apparatus. In some of the studies where effective hydrodynamic thickness was used to model layer thickness [Gramain 1981] [Bagassi 1989], a nylon filter with nanoscale pores was used as the system. The narrow width of the filter leads to large entrance and exit effects which, coupled with a lack of monodisperse pore size and geometry, invalidate the assumption of laminar flow used in the effective hydrodynamics thickness model. Similarly, in the study of Cohen et al [Cohen 1988] the polymers were physically adsorbed instead of chemically bonded to the channel. Hence a strong flow field can break some of the weaker physical connections and cause an expansion of the polymer layer.

When considering an adsorbed polymer layer from a theoretical standpoint, it is more appropriate to consider the adhered layer of polymer chains as a physically entangled gel network [Klein 2006] [Guenet 1992], for which the percolation theory models of gels are appropriate analogues [Stauffer 1982]. Though the flow through the network will be insignificant, there will be a shear force exerted on the surface of the layer that will break the primary load bearing entanglements, or “red bonds”, of the network [Sahimi 1994]. In a randomly assembled network where the bond density is just beyond the percolation threshold, there will be sections of the network that are only connected by one or two entanglements. These entanglements will be under the highest stress as the network is mechanically deformed.
As these entanglements are broken, the chains will be able to align themselves better in the flow field.

The flow-induced alignment could explain the swelling of the network in a good solvent through enhanced solvation. As a result of chain alignment, more of the polymer is exposed to the solvent. Hence the activity of the fluid in the polymer layer will increase relative to the activity of the bulk fluid phase and fluid will flow into the gel layer to swell the polymer layer.

In a poor solvent, the alignment of the polymer chains due to the shear field allows the polymer chains to pack more tightly. Thus the gel network will collapse, reducing the thickness of the polymer layer as the shear rate increases. This flattening of the polymer layer is balanced by the loss of conformational entropy due to elongation of the chain as it is forced into a more compact configuration.

### 3.2.3 Cyclical Dynamics

Cyclical dynamics in tethered polymer chains under shear flow has been observed experimentally using DNA oligomers in aqueous solution [Doyle 2000] [LeDuc 1999]. Cyclical dynamics was first predicted by Brownian motion simulations of a single bead connected to a surface by a Hookean spring in a linear shear field by DiMarzio and Rubin [DiMarzio 1978]. In the study of DiMarzio and Rubin, the tethered bead was found to undergo a rotary motion within the plane formed by the direction of flow and the normal vector of the surface to which the spring was tethered. This process was described by a 4 part cycle:

1. **Entrainment.** The bead is entrained in the flow field and the polymer chain is stretched in the direction of flow.
2. **Rotation.** The force on the bead is balanced by force constant of the spring, which corresponds to the force associated with the entropic loss of the chain if the system is representative of a polymer under shear flow. However, as the adhesion point is below the plane of the bead, the bead is rotated towards the wall of the channel.
3. **Contraction.** As the bead is against the wall where there is no shear field, the bead retracts towards the adhesion point.
4. **Extension.** As the bead nears its adhesion point and the force exerted by the spring diminishes, the thermal motion of the bead carries it away from the wall where it becomes entrained in the flow field again and the cycle repeats.

These results have been confirmed by several other groups [Delgado-Buscalioni 2006] [Dubbeldam 2006] [Holzer 2006]. In a Brownian dynamics simulation of a FENE chain, the
dynamics were found to be periodic with a period roughly equal to $10\tau_R$, where $\tau_R$ is the relaxation time of the polymer chain [Delgado-Buscalioni 2006]. This periodicity was identified from the correlation function of the chain extension in the flow and flow components normal to the wall.

It has also been suggested that these dynamics may be periodic for some shear rates and aperiodic for others [Holzer 2006]. The study of Holzer et al used a model of three beads in a flow field that were anchored to the three vertices of an equilateral triangle by Hookean springs. In this study, the beads were not bound to each other and the hydrodynamic effect of the beads on each other was calculated. By examining the stationary solution of the dynamics of the beads for this model, a Hopf bifurcation emerged, where the parameters of this bifurcation were the height of the beads from the anchor point and the strength of the flow field. At low shear rates the polymer extended into the direction of flow, while at intermediate shear rates periodic cyclical dynamics were observed. At higher shear rates non-periodic cyclical dynamics were observed.

It should be noted that cyclical dynamics were not observed for simulations that made use of Kramers model, e.g. [Parnas 1991]. This suggests that bond elasticity and hence bond stretching forces may play a role in these dynamics, although very few rigid bond simulations of tethered polymers in shear flow have been conducted.

### 3.3 Simulation Method

MPCD-based simulations of pressure-driven flow were performed on grafted polymers in nanochannels. The focus of the simulations was the effect of shear flow on the configuration of the polymer chain. This was done by tethering the polymer in a linear configuration that was normal to the wall of a channel and performing a series of simulations with increasing flow rates. These simulations were conducted for both $\theta$ solvent and poor solvent conditions. The polymer was simulated within the $20 \times 20 \times 100$ nm channel described in 2.3.3. It was anchored to the centre of the $x$-normal wall at the $(−10,0,50)$ point. The polymer beads had a mass of 14.027 AMU and a radius of 0.50 Å. For all of the results described in this chapter, the polymer had a length of 100 beads. Due to the use of explicit potentials between the polymer and the MPCD
solvent, it was necessary to introduce a molecular dynamics subsystem to simulate the polymer and its interactions with the solvent. The hybrid MPCD-MD system was described in section 2.3.1, however, as the MD subsystem was not utilized in that chapter, it merits some further elucidation.

Since the MPCD algorithm is a particle-based method, the introduction of an MD subsystem effectively reduced to the integration a subset of that system with a smaller time step, $\delta t$, which allowed for the use of explicit potentials. Subject to the constraint that $\Delta t/2\delta t$ is an integer (which ensures that at each interval of $\Delta t/2$ the MPCD system and MD subsystem are synchronised), at each time step $\Delta t$, the MD subsystem was chosen to consist of the particles that could interact with polymer over an interval of $\Delta t$. As velocity truncation was used to ensure that no fluid particle or polymer bead could travel more than one cell length, $L$, in a single time step, the subsystem had to encompass the polymer and any particles within $2L + r_c$ of the polymer chain, where $r_c$ is the cut-off radius of the polymer-fluid potential. The cells used by the MPCD algorithm provide a natural subdivision within the system; hence the cells containing the polymer and the fluid particles within $2L + r_c$ were used to form the basis for the MD system.

The bond potential between beads in the polymer chain was modelled as a finitely extendable non-linear elastic (FENE) spring [Warner 1972] with a modification to allow for an equilibrium bond length,

$$\Psi_{i,j+1} = K_{\text{FENE}} \left[ a - |q_{i,j+1}| \right] + \frac{a}{2} \ln \left( \frac{|q_{i,j+1}|}{2a - |q_{i,j+1}|} \right), \quad \text{Eqn. 3.3.1}$$

where $q_{i,j+1} = q_i - q_{i+1}$ is the separation vector between the position of bead $i$ and $i+1$, $a$ is equilibrium bond length, and $K_{\text{FENE}}$ is the spring constant for the bond. This potential is generally better recognised by the force created by the potential:

$$F_{i,j+1} = \text{sgn}(q_{i,j+1} - a) \frac{q_{i,j+1}}{|q_{i,j+1}|} K_{\text{FENE}} \left( \frac{1}{1 - (q_{i,j+1} - a)^2/a^2} - 1 \right), \quad \text{Eqn. 3.3.2}$$
From this form it becomes clear that the extensibility limits of the potential are 0 and 2a.

The interactions between the polymer beads and the solvent particles were modelled by a Lennard-Jones 6-12 potential of the form:

\[ \Psi_{i,j} = E_{\text{min}} \left( \frac{R_{\text{min}}}{|q_{i,j}|} \right)^{12} - 2 \left( \frac{R_{\text{min}}}{|q_{i,j}|} \right)^6 \],

Eqn. 3.3.3

where \( E_{\text{min}} \) is the energy at the minimum of the potential well and \( R_{\text{min}} \) is the particle separation of minimum energy. The force exerted on this polymer by bead \( j \) on bead \( i \) is:

\[ F_{i,j} = \frac{q_{i,j}}{|q_{i,j}|} 12 \frac{E_{\text{min}}}{R_{\text{min}}} \left( \frac{R_{\text{min}}}{|q_{i,j}|} \right)^{13} - \left( \frac{R_{\text{min}}}{|q_{i,j}|} \right)^7 \],

Eqn. 3.3.4

There are some potential dangers associated with using a potential with an attractive component to model a polymer-solvent potential in the absence of an explicit solvent-solvent potential. The attractive component of this potential contributes to the drag force on the polymer chain, increasing the effective hydrodynamic radius of the beads, and the Lennard-Jones potential is more representative of the real potential that would exist between the atoms in the polymer and the solvent. However, there are no repulsive forces between solvent particles to prevent multiple solvent particles from occupying the same volume. Thus the potential could bind multiple solvent particles to the same part of the polymer and these solvent particles can serve to cross-link the polymer chain. Effectively, the attractive portion of the potential could create a magnified primary solvation shell with no secondary structure. Within the parameter range chosen for these interaction, this phenomena did not appear to occur as there was no increase in solvent density in the vicinity of the polymer chain.

The interactions between polymer beads which were not directly bonded to each other were modelled by a harmonic potential:
\[ \Psi_{i,j} = \begin{cases} K_h \frac{q_c}{2} \left( 1 - \frac{|q_{i,j}|}{q_c} \right)^2, & |q_{i,j}| < q_c, \\ 0, & |q_{i,j}| \geq q_c \end{cases} \] \hspace{1cm} \text{Eqn. 3.3.5}

where \( K_h \) is the spring constant of the potential and \( q_c \) is the cut off radius of the potential. The force exerted by bead \( i \) on bead \( j \) is,

\[ F_{i,j} = \begin{cases} \frac{q_{i,j}}{|q_{i,j}|} K_h \left( 1 - \frac{|q_{i,j}|}{q_c} \right), & |q_{i,j}| < q_c, \\ 0, & |q_{i,j}| \geq q_c \end{cases} \] \hspace{1cm} \text{Eqn. 3.3.6}

This potential was chosen to avoid the attractive portion of a more realistic potential between polymer-beads. Without excluded volume interactions, the use of an attractive potential favors a collapsed configuration of the chain. This consideration coupled with the ease of integration of the potential and its clean cut-off led to its selection.

The interactions between the walls and the polymer were modelled using an exponential repulsive potential:

\[ \Psi_{i,\text{wall}} = \alpha_w e^{-\beta_w w} - w \beta_w \alpha_w e^{-\beta_w w_c}, \quad 0 \leq w \leq w_c \] \hspace{1cm} \text{Eqn. 3.3.7}

where \( w \) is distance between the particle and the nearest point on the wall, \( \alpha_w \) is the maximum potential between bead \( i \) and the wall, \( \beta_w \) is the decay constant of the potential and \( w_c \) is the cut off radius of the potential. The force exerted by the wall on a polymer bead is,

\[ F_{i,\text{wall}} = \hat{n}_{\text{wall}} \beta_w \alpha_w \left( e^{-\beta_w w} - e^{-\beta_w w_c} \right), \quad 0 \leq w \leq w_c \] \hspace{1cm} \text{Eqn. 3.3.8}

where \( \hat{n}_{\text{wall}} \) is the normal vector of the wall. As the focus of this work is the effect of the flow field on the polymer chain, the exponential potential was chosen to minimize the effect of the wall on the conformation of the polymer chain.
### Table 3.3.1 Potential parameter values for simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{FENE}}$</td>
<td>11.6 nN</td>
</tr>
<tr>
<td>$a$</td>
<td>1.54 Å</td>
</tr>
<tr>
<td>$E_{\min}$ (θ Solvent)</td>
<td>478.041 J/mol of interactions</td>
</tr>
<tr>
<td>$E_{\min}$ (Poor Solvent)</td>
<td>1.75 kJ/mol of interactions</td>
</tr>
<tr>
<td>$R_{\min}$</td>
<td>2.073 Å</td>
</tr>
<tr>
<td>$K_h$</td>
<td>6.64 nN</td>
</tr>
<tr>
<td>$q_c$</td>
<td>3.08 Å</td>
</tr>
<tr>
<td>$\alpha_w$</td>
<td>$3.49 \times 10^{-17}$ J</td>
</tr>
<tr>
<td>$\beta_w$</td>
<td>3.0 Å$^{-1}$</td>
</tr>
<tr>
<td>$w_c$</td>
<td>10 Å</td>
</tr>
</tbody>
</table>

The values for the parameters for the potentials previously listed in this chapter are given in table 3.3.1. The parameters were kept constant over all of the simulations, with the $E_{\min}$ for the Lennard-Jones potential given by equation 3.3.3 between the solvent and the polymer. Two values were chosen for $E_{\min}$: one which allowed for the simulation of a θ solvent and the other which allowed for the simulation of a poor solvent.

During these simulations, the polymer was inserted into the channel after the MPCD algorithm had been given sufficient time to equilibrate (1 ns). The initial configuration of the polymer consisted of a linear projection from the point at which it was anchored along the $x$-axis, with each bead separated by $a$, the equilibrium bond length from the FENE potential.
3.4 Polymer results

Two solvent conditions were examined during the simulations, a poor solvent condition and a θ solvent condition. While it would have been of interest to simulate good solvent conditions, without the inclusion of fluid-fluid potentials, or modification of the internal potentials of the polymer, a set of potential values that expanded the chain relative to in vacuo conditions could not be found. Rather the best solvent conditions that could be found were the neutral θ solvent conditions. While the study of Lee and Kapral [Lee 2006], simulated a polymer in an expanded good solvent configuration and collapsed poor solvent configuration, this study modified the bead-bead potential, which would have changed the θ configuration. The parameter of principle inquiry during the simulations was the fluid flow rate through the channel and its effect on the conformation of the polymer was probed.

The solvent conditions were calculated by comparing equilibrium simulation conditions to values taken from runs with no solvent. The radius of gyration for a polymer can be written as,

\[
R_{\text{gyr}} = \sqrt{\frac{1}{N} \left( \sum_{i=1}^{N} \mathbf{q}_i \cdot \mathbf{q}_i \right) - \left( \sum_{i=1}^{N} \mathbf{q}_i \right)^2} = \sqrt{R_{\text{gyr,x}}^2 + R_{\text{gyr,y}}^2 + R_{\text{gyr,z}}^2},
\]

Eqn. 3.4.1

where \(N\) is the number of beads in the polymer chain, \(\mathbf{q}_i\) is the position vector of the \(i^{th}\) bead in the polymer chain and \(R_{\text{gyr,x}}, R_{\text{gyr,y}}\) and \(R_{\text{gyr,z}}\) are the \(x\), \(y\) and \(z\) components of the radius of gyration. These components are analogous to the radius of gyration formed using the \(x\), \(y\) or \(z\) component of \(\mathbf{q}_i\), i.e.

\[
R_{\text{gyr,x}} = \sqrt{\frac{1}{N} \left( \sum_{i=1}^{N} q_{xi}^2 \right) - \left( \sum_{i=1}^{N} q_{xi} \right)^2}.
\]

In runs with no solvent, the radius of gyration for the centimeter was found to be \(1.85 \pm 0.32\,\text{nm}\). Theoretically, the radius of gyration of a tethered polymer is expected to have the same dimensions as a polymer in free solution [Aksimentiev 1999]. However, for short chained oligomers, the polymer will behave as a self avoiding chain due to excluded volume interactions.
in the core of the chain [Ladd 1992] thus the radius of the polymer chain is approximately [Doi 1986] [Ladd 1992],

\[ R_{gyr} \propto N^{0.59}, \]  \hspace{1cm} \textbf{Eqn. 3.4.2}

where \( N \) is the number of beads in the polymer chain, where the proportionality constant is specific to the polymer being examined. Based on the calculated value of 1.85 ± 0.32 nm the proportionality constant is 0.1222 ± 0.021 nm. For the Lennard-Jones potential used to model the interactions between the polymer and the fluid, eqn. 3.3.3, the simulation values of \( R_{gyr} \) are plotted vs. \( E_{min} \) and \( R_{min} \) in figure 3.4.1. The value of \( R_{min} \), the separation between particles at the minima of the potential, did not have a significant effect on the solvation of the polymer. For \( E_{min} > 1.25 \text{ kJ/mol} \), the solvent conditions began to deteriorate for the polymer chain, while above this value the solvent conditions did not appear to improve beyond \( \theta \) conditions. The absence of good solvent conditions is to be expected as there is no impetus for chain expansion without solvent-solvent interactions that influence the packing of solvent particles bound to the polymer. The values for \( E_{min} \) and \( R_{min} \) used in the simulations are presented in table 3.3.1.
Figure 3.4. 1 A plot of the Radius of gyration of the polymer under equilibrium conditions vs. the parameters of the solvent-polymer Lennard-Jones potential. Plot a) (top) is a sweep of the $R_{\text{gyr}}$ vs. $E_{\text{min}}$ for $R_{\text{min}} = 2.173\, \text{Å}$. Plot b) (bottom) is a sweep of $R_{\text{gyr}}$ vs. $R_{\text{min}}$ for $E_{\text{min}} = -0.5\, \text{kJ/mol of bonds}$. The solid black line represents the no solvent value of 1.85 nm.

During the simulations, the polymer is initially absent from the channel which was left to equilibrate for 1 ns. At this time, the polymer is inserted into the channel with a straight
configuration that is extended along the $x$ axis, where each bead is separated from the previous bead by the equilibrium bond length $a$. Each bead is given an initial velocity drawn from a Maxwell-Boltzmann distribution at the same temperature as the fluid. Any fluid particles that have a non-zero potential with the polymer chain are deleted when the chain is inserted into the system.

3.4.1 Θ solvent conditions

During the simulations there are two competing responses to solvent interaction from the polymer. The first response is the damping of an entropy-driven retraction of the chain from its initial configuration towards a random coil configuration. The second response is a rotation of the polymer about the $y$-axis into the direction of flow and extension of the polymer due to the interaction between the polymer beads and the flow field. Within a weak flow field, $Q < 4.7 \pm 0.2 \times 10^7 \text{ particles/ns}$, the retraction of the chain is the dominant feature of the evolution of the conformation of the chain. For a stronger flow field, the flow field prevents the chain from retracting, hence the rotation of the polymer into flow field and its extension along the $z$-axis governs the evolution of the conformation of the chain.

The extension of the chain at high flow rates is reflected as a general increase in the radius of gyration $R_{\text{gyr}}$. More specifically, the flow component of the radius of gyration in the direction of flow, $R_{\text{gyr},z}$, increases while the other two components, $R_{\text{gyr},x}$ and $R_{\text{gyr},y}$, decrease. $R_{\text{gyr}}$ and its 3 components are shown as a function of time under conditions of weak and strong flow in figure 3.4.1.1, and as a function of the shear rate at the adhesion point of the polymer to the channel in figure 3.4.1.2. There appears to be a minimum velocity below which the polymer does not extend in the direction of flow. Above this velocity, the polymer rapidly extends to a value that is approximately 80% of its extension length. Without any attractive interactions between the polymer beads, the primary resistance to the extension of the polymer is the loss of conformational entropy of the chain as it is drawn into a long narrow configuration. From the stress strain relationship for an entropic spring in eqn 3.2.2.1, and Newton’s viscosity relation, the shear stress should be proportional to the shear rate. Equating the relations, yields the relationship,
\[ \dot{\gamma} \propto \left( \lambda_s - \frac{1}{\lambda_f} \right) \]  

Eqn. 3.4.1.1

However, the shear force is not the only source of stress on the polymer. The flow field has a constant component from the slip velocity (the resulting relationship given by equation 3.2.2.2) and an elongational component from the pressure drop. Thus, for low shear rates, a greater than linear relationship between the shear rate and the polymer extension should be found rather than the linear behaviour predicted by eqn. 3.4.1.1. As the polymer reaches its elastic limit and bond stretching forces become dominant, the polymer extension attains a limiting value at high flow rates. Thus a sigmoidal curve is expected. This is consistent with the results seen in figure 3.4.1.2.

![Radius of Gyration Vs. Time](image)

Figure 3.4.1. 1 The radius of gyration and its three components plotted vs. time for 2 simulations, a low flow, LF (Red), simulation and a high flow, HF (Black), simulation. The LF simulation corresponds to a flow rate of \(6.52 \pm 0.20 \times 10^7\) particles/ns, which corresponds to a wall shear rate of \(4.6 \pm 1.5 \text{ns}^{-1}\) and slip velocity of \(5.7 \pm 1.6\) m/s. The HF simulation corresponds to flow rate of \(2.41 \pm 0.01 \times 10^8\) particles/ns, which corresponds to a wall shear rate of \(16.6 \pm 2.7\ \text{ns}^{-1}\) and slip velocity of \(15.2 \pm 2.4\) m/s.
Figure 3.4.1. 2 The steady state radius of gyration and its three components vs. Wall Shear Rate at the point of adhesion (-10, 0, 50). As the shear rate increases the radius of gyration increases. This increase is caused by the increase in the flow, $z$ (blue) component as the shear rate increases. The $x$ (red) and $y$ (green) components decrease as the extension of the polymer decreases the conformational freedom of the polymer in those dimensions.

The dynamics of the polymer appears to be composed of two types of motion; a fast reptation of the individual beads of the chain, primarily torsional, that produces little effect in the radius of gyration, and a slower bulk movement of the chain that creates larger fluctuations in the radius of gyration. The faster mode appears as the finer noise in the data from figure 3.4.1.1. The periodicity of the torsional rotations can be examined through the cross-correlation function of components of the polymer velocity in the plane of the rotations. The cross-correlation function for velocity components $v_x$ and $v_y$ is,
\[
\langle v_x \cdot v_y(t) \rangle = \frac{1}{(t_s - t)\sigma_{v_x} \sigma_{v_y}} \int_{0}^{t_s} (v_x(\tau) - \bar{v}_x)(v_y(t + \tau) - \bar{v}_y) d\tau
\]

where \( t_s \) is the length of the simulation, \( \bar{v}_x \) and \( \bar{v}_y \) are the temporal mean values of \( v_x \) and \( v_y \), and \( \sigma_{v_x} \) and \( \sigma_{v_y} \) are the standard deviations of \( v_x \) and \( v_y \). Periodic oscillations within the \( x - y \) plane will appear as a sinusoidal wave within this function. From the cross-correlation function of the velocity components in the direction normal to the direction of flow, the faster mode does appear to be periodic, in particular they seem to be composed of rotations with a frequency range of 35-65 GHz. Figure 3.4.1.3 shows this cross-correlation function for the data sets shown in figure 3.4.1.1. The oscillations are not dependent on flow rate, and are not composed of consistent frequencies across simulations. A window-smoothed spectral analysis of the transverse components of the polymer velocity is shown in figure 3.4.1.4 a). The spectral analysis of this correlation function reveals a large amount of noise, though the bulk of the function can be found in three frequency ranges: the 0 to 200 GHz range (typically around 35 to 65 GHz or twice that value), a wide peak or cluster of peaks around 2.3 THz and another peak around 8 THz. The peaks associated with the frequencies in the THz range corresponds to the normal modes of the polymer chain in the absence of fluid interactions. The THz range peaks also vanish when the velocity of a segment of the chain is used instead of the velocity of a single bead (figure 3.4.1.4 b). Hence the THz range modes do not seem to contribute to the torsional reptation of the chain.
Figure 3.4.1. 3 Cross-correlation function between the average $x$ and $y$ velocity components of the last 50 beads of the centimer. The dashed red line corresponds to a single simulation with a flow rate of $6.52 \pm 0.20 \times 10^7$ particles/ns, which corresponds to a wall shear rate of $4.6 \pm 1.5$ ns$^{-1}$ and slip velocity of $5.7 \pm 1.6$ m/s. The solid black line corresponds to a single simulation with a flow rate of $2.41 \pm 0.01 \times 10^8$ particles/ns, which corresponds to a wall shear rate of $16.6 \pm 2.7$ ns$^{-1}$ and slip velocity of $15.2 \pm 2.4$ m/s.
Figure 3.4.1. 4 A spectral analysis of the cross-correlation function between the \( x \) and \( y \) velocity components. The top graph is the function for bead 90 and the bottom graph is averaged over the last 50 beads. Both of these graphs were calculated for the run with a flow rate of \( 6.52 \pm 0.20 \times 10^7 \) particles/ns in figure 3.4.1.1.

The slower bulk motion of the chain was aperiodic and uncorrelated, and is likely associated with local fluctuations in the fluid velocity. Figure 3.4.1.1 illustrates the effect of this slow
movement between $t = 1.67$ and $t = 1.75\text{ns}$ where there was a reduction in $R_{\text{gyr}}$ for the low flow rate simulation. As the shear rate increases, these slower bulk movements are restricted to the end of the chain. The restriction of this motion can be seen in figure 3.4.1.5, which shows the end to end vector to have fluctuations of similar magnitude despite the fluctuations of the radius of gyration being smaller for the high flow rate simulation than the low flow rate simulation in figure 3.4.1.1. The likely cause for the motion to be restricted to the end of the chain is the increased configurational freedom of the untethered end of the polymer chain relative to the tethered end. As will be seen below, the deviations in the flow field created by the polymer chain persist to the end of the chain, hence it is possible that the bulk motion at the end of the chain is enhanced by the shielding effect of the polymer wake.
Figure 3.4.1. 5 The magnitude of the end to end vector and radius of gyration plotted vs. time for the $2.41 \pm 0.01 \times 10^6$ particles/ns (upper graph) and $6.52 \pm 0.20 \times 10^7$ particles/ns (lower graph) flow rate simulations shown in figure 3.4.1.1.
In section 3.2.3, it was noted that cyclical dynamics are often observed for simulations of tethered polymer chains in shear flow. For simulations with a flow rate of more than $1.20 \pm 0.04 \times 10^8$ particles/ns, cyclical dynamics were found, although they only seem to involve the latter quarter of the chain instead of the entire chain. These dynamics are illustrated in figure 3.4.1.6. These dynamics do not appear to be periodic. As was noted by Delgado-Buscalioni et al [Delgado-Buscalioni 2006], there should be periodic oscillations in the cross-correlation function of the $x$ and $z$ components of the radius of gyration if the dynamics were periodic. However, the cross-correlation function is unremarkable (figure 3.4.1.7). It is unexpected that cyclical dynamics should persist in the presence of slip flow, which should hamper the retraction of the polymer chain. However, the slip flow is likely the reason why the effect is limited to the end of the chain and perhaps also the reason why the dynamics are aperiodic.
Figure 3.4.1. 6 Illustration of cyclical dynamics in a simulation with a flow rate of $2.28 \pm 0.02 \times 10^8$ particles/ns, which corresponds to a wall shear rate of $13.4 \pm 3.0$ ns$^{-1}$ and slip velocity of $16.3 \pm 3.3$ m/s. The cyclical dynamics seem to be confined to the latter quarter of the chain. At $t = 1.7055$ ns the polymer is extended into the flow field. At $t = 1.7285$ ns the end of the chain has drifted towards the wall of the channel. At $t = 1.7385$ ns the end of the chain has retracted. At $t = 1.7695$ ns the end of the chain has drifted back into the flow field. At $t = 1.7985$ ns the flow field has extended the chain again.

![Cross-Correlation Function](image)

$\langle R_{Gyr,x}(t) \cdot R_{Gyr,z}(t) \rangle$ Cross-Correlation Function

Time [ns]

Figure 3.4.1. 7 The Cross-Correlation function between the $x$ and $z$ components of the Radius of Gyration for the simulation conditions in figure 3.4.1.6.

In figure 3.4.1.8, a quiver plot of the deviations from the normal flow field created by the polymer chain is shown. The plot was created by comparing the flow profile to a fit of the equilibrium flow without the polymer chain to the function 2.4.1. The deviations were constructed by subtracting the fit from the time averaged data. These deviations were further filtered by removing any deviations that had a magnitude of less than 8 m/s, which excluded most of the standard noise from the data. The time averaging of the data is necessary due to the
presence of thermal noise, since thermal fluctuations are on the order of 240 m/s at any instant. At least 0.2 ns of time-averaging is required to diminish the noise to filterable levels. The velocity data were calculated based on the average particle velocities for the MPCD cells. The MPCD cells are 1nm³ in volume, which defines the maximum resolution of the velocity data. As the polymer itself is not in a static configuration, this resolution is quite reasonable. The deviations reveal a modification of the flow field around the polymer that begins before the flow contacts the polymer. The flow deviates in both the x and y directions, with the form of a semi-circular dome before the polymer, and a decrease in the z component of the velocity is also observed. The deviations persist for the entire length of the polymer chain, including an acceleration of the fluid after it has passed the chain, possibly indicating a low pressure area at the end of the chain, though pressure is poorly-defined for a fluid on this length scale. For a non-ideal fluid, the disruption to flow created by a single polymer chain is expected to be larger than observed in these simulations. While the MPCD collision scheme allows for momentum transfer between particles, it does not include excluded volume interactions, which are expected to be significant as the fluid is driven against polymer chain and diverted.

Figure 3.4.1.8 A quiver plot of the deviations in the flow field before and after the addition of the polymer chain for the simulation with flow rate of \( 2.41 \pm 0.01 \times 10^8 \) particles/ns in figure 3.4.1.1. The data has been time averaged for 0.2 ns and any deviations with a
magnitude less than 8 m/s are not shown in the plot. The deviations at the end of the channel are due to the error in the fit to the flow field which tend to be larger at the end of the channel than at the beginning.

3.4.2 Poor Solvent Conditions

The difference in qualitative behavior of polymers under flow between poor solvent conditions and θ solvent conditions is quite stark. A θ solvent is often considered a poor solvent. However, a θ solvent is the threshold between poor solvent and a good solvent and is in essence a neutral solvent. Examples of equilibrium configurations of a solvated polymer in a poor solvent and a θ solvent are contrasted in figure 3.4.2.1. Under poor solvent conditions, the polymer chain has an extended helix state or collapsed globule configuration, as opposed to a random coil conformation that extends into the direction of flow that was observed for the θ solvent simulation conditions (figure 3.4.2.2).

Figure 3.4.2. 1 Equilibrium polymer configurations, a) θ solvent b) poor solvent.
Figure 3.4.2. 2 Polymer configurations under flow under different solvent conditions. Top: θ solvent conditions simulation with a flow rate of $2.41 \pm 0.01 \times 10^8$ particles/ns, which corresponds to a wall shear rate of $17.2 \pm 2.5 \text{ns}^{-1}$ and slip velocity of $18.1 \pm 2.7 \text{ m/s}$. 
Bottom: simulation under poor solvent conditions at a flow rate of $3.12 \pm 0.02 \times 10^8$ particles/ns, which corresponds to a wall shear rate of $20.2 \pm 2.8 \text{ ns}^{-1}$ and slip velocity of $23.6 \pm 3.2 \text{ m/s}$.

At low flow rates, the configuration of the polymer evolves from the extended initial configuration directly to a collapsed state. As the flow rate increases, the polymer adopts a metastable helix conformation which extends into the direction of flow. However, this configuration collapses to a globule state over time (2 or 3 ns of simulation in some cases). At higher flow rates, the polymer chain adopts a stable helical configuration that persists for the lifetime of the simulations. The radius of gyration of the polymer and its three components are plotted vs. the wall shear rate at the point of adhesion in figure 3.4.2.3.
Figure 3.4.2. The radius of gyration and its three components vs. wall shear rate at the point of adhesion (0, 10, 50).

No preference was observed in the simulations for left-handed or right-handed helices. Typically, 9 monomers per turn of the helix are observed, while the helix itself grows from the end of the chain. Although the number of turns in the helix observed during the simulations varies from 3 to 6 turns, the helices formed consistently from the initial configuration. A plot of the cross-correlation function of the x and y velocity component of the end of the chain during helix formation shows a cyclical pattern consistent with the wrapping of the coil (figure 3.4.2.4). The rate of helix formation was consistent across all simulations where the polymer chain adopted a helical conformation. This cyclical turning was consistent with the rapid torsional mode described in section 3.4.1. For these simulations there were no cyclical dynamics observed for the end of the polymer chain.

The formation of a metastable helix during the collapse of an initially stretched homopolymer under low temperature equilibrium simulations has previously been observed [Sabeur 2008]. In
the study of Sabeur et al, beads in a Hookean polymer chain interact with each other through a Lennard-Jones potential. Hence, there was an attractive interaction between the polymer beads that was capable of stabilizing a helical structure. The formation of a helix in the simulations presented here are remarkable given the absence of an attractive potential between polymer beads. Surprisingly, the density of the solvent particles in the vicinity of the polymer chain does not increase and there is no evidence of solvent bridging leading to the stabilization of the helical configuration.

![Cross-Correlation Function](image)

**Figure 3.4.2.** 4 Cross-correlation function between the $x$ and $y$ velocity components for the last 50 beads of the centimer. The simulation was conducted with a flow rate of $3.12 \pm 0.02 \times 10^8$ particles/ns, which corresponds to a wall shear rate of $20.2 \pm 2.8$ ns$^{-1}$ and slip velocity of $23.6 \pm 3.2$ m/s.

The deviations in the flow field created by the polymer are consistent with the deviations under good solvent conditions, figure 3.4.2.5. The only different qualitative feature is that the largest deviations are located at the end as opposed to the beginning of the chain. The deviations are likely larger at the end due to the helix conformation that the chain adopts. It presents a larger cross-section against the flow than the chain at the adhesion point and hence a larger disruption to the flow profile.
Figure 3.4.2. A quiver plot of the deviations in the flow field before and after the addition of the polymer chain for the simulation in figure 3.4.2.4. The data have been time averaged for 0.2 ns and any deviations with a magnitude less than 8 m/s are not shown in the plot. The deviations at the end of the channel are due to the error in the fit to the flow field which tend to be larger at the end of the channel than at the beginning.

The helical structures are most likely a result of the collapse of the chain from an extended initial condition to a globule, being countered by drag exerted by the flow field on the polymer. The chain begins in an extended configuration and attempts to collapse to the globule state. However, the flow field orients the chain and exerts a force that keeps the chain extended. As the flow field adapts itself to the polymer, the end of the chain is caught in its wake and it can begin to collapse. However, it can only collapse within the wake of the chain, which is a narrow cone along the axis of the extended chain. The torsional reptation of the chain, coupled with the linear path along which the chain can contract, causes a local collapse of the end of the chain into a helix, essentially leading to a dynamically-stabilized structure. This mechanism for the formation of the helix is supported by three observations. First, in the intermediate flow rate simulations, the helix collapses to the globule state over time, which suggests that the helix is a metastable state that is stabilized by the flow field. Secondly, the helix does not form if a collapsed initial configuration was used instead of an extended configuration, which indicates
that the stretched initial configuration is necessary to create the helical structure. Finally, the solvent does not appear to be cross-linking the chain and hence there are no attractive interactions between polymer beads to stabilize the structure.

3.5 Conclusions

A simple polymer model was used to study the effect of pressure-driven channel flow of a compressible fluid on the dynamics of a tethered polymer. The simulations were conducted in a square cross-section channel using the hybrid MPCD-MD algorithm described in section 2.3. The polymer consisted of a linear string of beads connected by a FENE spring potential, while the interaction between the polymer and the fluid was modeled by a 6-12 Lennard-Jones potential, and the interaction between the polymer beads that were not connected by the FENE potential was modeled with a harmonic potential. While this polymer model lacks the complexity of a real polymer, it eliminates the variables introduced by the presence of side groups and focuses the results on the effect of the flow field on the polymer backbone conformation.

As the simulations incorporated explicit fluid-polymer interactions and, through the MPCD rotation step, momentum transfer between fluid particles, it was possible to examine not only the effects of the flow field on the polymer chain, but also the effect of the polymer chain on the flow field. Though the wake generated by the polymer was limited by the lack of excluded volume interactions, it still gave an indication of the effect that the polymer chain had on the fluid. The results indicated that the fluid velocity decreased at the point where the flow field interacted with the polymer and increased at the end of the chain, implying that there is an area of low density at the end of the chain where it is most mobile.

The simulations were conducted under two solvent conditions, a θ solvent condition and a poor solvent condition. While the response of the fluid to the polymer was consistent under the two solvent conditions, the response of the polymer to the fluid was quite different. Under θ solvent conditions, the polymer behaved in a manner consistent with the observations of previous studies. The polymer extended into the direction of flow to a value approximately equal to 80 % of its extension length. The relationship between the extension of the polymer chain and the flow rate was roughly sigmoidal. Aperiodic cyclical dynamics were also observed at the higher flow rates, as the polymer extended into the flow field then retracted. As the flow has an
elongational and a slip component, it is surprising that these dynamics persist as it is the variation of the shear force as a function of distance from the wall that is believed to give rise to these dynamics. It is likely that the variational component is large enough relative to the constant component of flow to allow these dynamics to persist.

Under poor solvent conditions, the flow field prompted a transition between a collapsed globule configuration for the polymer and an extended helix state. Due to the choice of initial configuration for the polymer in which the polymer is initially completely extended into the flow field, there were some simulations where the polymer assumed a transient helical conformation and then collapsed into the globule state. At higher flow rates the polymer remained extended in a helix state. This helix is believed to be stabilized by the flow field restricting the conformational freedom of the polymer so that it is forced to collapse along one dimension.

These results, in particular under poor solvent conditions, indicate that the effect of flow rate on the conformation of macromers could be a design consideration for lab on a chip devices. In particular, the flow-induced denaturation of proteins or surface active molecules could dictate practical limitations on flow rates in some of these devices. However, there are also potential advantages to flow induced conformational changes. Polymerization of monomers under high shear solvent conditions could result in the creation of highly crystalline aligned polymers and it may even be possible to create varying layers of crystalline and amorphous polymer in the same material through flow modulation during polymerization.
Chapter 4
Tangles

4.1 Overview

Within polymer networks, entanglements are often an important factor in determining the mechanical properties of the network. Even among single chains the presence of an entanglement will form a point of mechanical weakness in the chain as it is tightened and will likely be the point of chain scission as the chain is stressed to breaking. These entanglements are commonly referred to as knots, though in the mathematical language of knots they are tangles. A mathematical knot requires that the entanglements be embedded within a closed loop, so that the knot cannot be untied. A tangle is a knot in an open loop. A link is a knot that consists of multiple components. While a good deal of work has been done on mathematical knots, far less work has been performed on tangles. In particular, the mechanism by which the polymer untangles itself and the speed at which this process occurs under shear flow conditions have not been examined.

The process by which the polymer unknots itself is the focus of this chapter. This process is simulated by tying tangles in the FENE polymer chains from section 3.3, that are anchored to the wall of the $20 \times 20 \times 100$ nm channel containing the MPCD fluid described in section 2.3. Particular attention is given to the mechanisms by which the tangle unravels itself and how these mechanisms change as the flow rate is increased within the channel and initial tightness of the knot is varied. The conformation of the tangle during the unknotting process and the time it takes for this process to complete itself is also examined. As entanglements can exist wholly within a polymer chain and between polymer chains, a single component tangle (tangle tied with only one chain) and a two component tangle were simulated. The two component tangle was tied in two configurations: a configuration where the two chains were anchored next to one another on the same wall, and a configuration where the chains were anchored on opposing walls so that the entangled chains spanned the channel. The former configuration, henceforth referred to as the parallel configuration, ties the tangle between the chains such that it does not prevent the configuration of the polymer chains from evolving in the flow field as it did without a tangle. However, the latter configuration, the spanning configuration, places the tangle in the centre of
the channel and prevents the polymer chains from rotating towards the walls of the channel and extending into the flow field.

There are no existing data in the literature to directly compare to the data or the models used to describe the unknotting events used in this chapter. As such, simple tangles were chosen for this study, the overhand knot or half-hitch, was used as a representative single component tangle, while the granny knot was tied to examine the tangles between two components. There are some numerical studies of polymers unknotting under equilibrium conditions [Lai 2000] [Lai 2003] and under uniaxial strain for open links [Kirmizialtin 2008], which suggest untangling mechanisms that could be observed for the unknotting of the polymer and provide some points to contrast with the present study. It appears that tangles can be divided into two classes; strong tangles, tangles which tighten as the tension increases, and weak tangles, tangles which slip as the tension increases [Kirmizialtin 2008]. Strong tangles tend to be more complex than weak tangles and, as the mechanisms by which even simple tangles (such as the Granny knot) untie are not known, the behavior of strong tangles under flow in a channel was not examined.

The next section of this report, section 4.2, presents the background theory on knots, links and tangles in polymer chains. Section 4.3 presents the algorithms used to tie the tangles in the simulation. The subsequent section of this chapter, Section 4.4, presents the simulation results for single component and multicomponent tangles. Finally section 4.5, presents a summary of the results from this chapter.

4.2 Theoretical Review

Mathematically, a knot is defined as the embedding of a circle or non-intersecting loop in three dimensional space. Generally, a knot is found by collapsing the circle onto a two dimensional plane and examining the order and directionality of the crossings. Each individual loop in the knot is called a component, i.e. a knot tied using one loop is a single component knot and a knot tied with two loops is a two component link.

Knots can be either oriented or unoriented. An oriented knot is one in which the direction that the components are traversed is specified and this specification is used to identify the crossings
and properties of the knot. An unoriented knot is one in which the direction of traverse is not specified and the coordinates of the system are used to identify the crossings. This division is largely one of nomenclature, as all knots are unoriented. In general, there are $2^n$ oriented representations for an unoriented link with $n$ components. The need for oriented representations arises from the oriented knot being easier to identify than an unoriented knot. Crossings within a knot can be further differentiated by whether one component passes over another component or under it. There are two types of crossings, positive and negative. There crossings are shown in figure 4-2-1.

![Diagram of positive and negative crossings](image)

**Figure 4.2.** 1 Positive and negative crossings. The oriented crossings are shown in the top diagrams and the unoriented crossings are shown in the bottom diagram. In the positive crossings the component traversing from the lower left to the upper right crosses over the component traversing from the lower right to the upper left. In the negative crossings the component traversing from the lower right to the upper left crosses over the component traversing from the lower left to the upper right.

Not every crossing contributes to the knot, since any crossings that can be removed by moving or twisting the components without breaking the loops do not contribute to the number of crossings used to classify knots. The movements that remove these extra crossings are called Reidemeister moves [Reidemeister 1948]. There are three Reidemeister moves which are illustrated in figure 4-2-2. The first Reidemeister move is the untwisting of a loop in a chain,
thus eliminating a single crossing. The second and third moves are effectively the same motion, though the second move eliminates two crossings, while the third move changes the order of the crossings. These moves involve sliding one section of chain over another section.

Figure 4.2. 2 The three basic Reidemeister moves for unoriented crossings. The type I move (top) involves the untwisting of a loop to remove a crossing. The type II move (middle) involves sliding a part of one component over another to eliminate two crossings.
The type III move (bottom) changes the order of crossings by sliding a part of one component over a crossing.

The Reidemeister moves introduce the inherent difficulty in the use of tangles as opposed to the use of knots. Through the use of Reidemeister moves any tangle can be unraveled; hence the tangle has to be closed to form a knot before applying the Reidemeister moves to simplify the structure. However, the method used to close the loop could add or remove crossings from the resulting knot. For example, consider the overhand knot shown in figure 4.2.3, the first closing passes through the loop of the knot creating an unknot, while the second closing creates a trefoil knot. If there is a direction, \( x \), for which \( x_i \leq x \leq x_n \), where \( x_i \) is the \( x \)–coordinate of the \( i \)th of \( n \) members of the component, then the task is somewhat simplified [Janse van Rensburg 1992]. By collapsing the tangle onto a plane that contains \( x \)–direction, extending the end of the component in a direction normal to the plane and then closing the loop, it is possible to convert the tangle to a knot in such a way that conserves the structure of the original tangle (see figure 4.2.4). For a tangle oriented under a flow field, the \( x \)–direction can almost always be chosen as the direction of flow. If a direction such as \( x \) cannot be found, the process of closing the loop is more complex, the simplest solution to this is to choose an arbitrary direction and extend the end points in parallel rays that meet at infinity. Unfortunately, the choice of direction can add or eliminate crossings, hence this process has to be repeated for enough multiple directions and the maximum-likelihood knot in the resulting ensemble is taken as the actual structure. The process is even more complex with multicomponent tangles. Consider the example of a single crossing between two components in figure 4.2.5, there is an equal number of closings that form two separate loops and that form a two crossing link. For the knots examined in this chapter the problem of closing tangles is largely avoided by the use of well defined initial conditions for the tangles that allow for visual tracking.
Figure 4.2. 3 Two closings of the overhand knot. The closing on the left passes through the loop of the knot creating an unknot while the closing on the right creates a trefoil knot.

Figure 4.2. 4 Closing a single component knot when a direction $x$ can be found for which the entire knot is contained between the end points. A plane is constructed that contains $x$ and the knot is collapsed on to this plane. The end points are then extended in a direction that is normal to the plane and the loop is closed along the $x$ direction.
Figure 4.2. 5 Closing a two component tangle consisting of a single crossing. The closing on the left creates two independent loops, while the closing on the right constructs a two crossing link.

In general, knots are represented using $X^j_i$ nomenclature, where $X$ is the minimum number of crossings in the knot, $j$ is the number of components and $i$ is variant of the knot (if there is more than one variant). For single component knots, the 1 superscript is generally omitted. The simplest knot is the $0^1_i$ knot, or unknot. This knot is a simple circle. The next knot is the $3^1_i$, consisting of $(+,+,+)$ crossings, or trefoil knot. In common vernacular, when this knot is tied in an open component it is called the overhand knot or the half-hitch.

For the two component links, the simplest link is the $0^2_i$, or two unknots. The next simplest link after that is formed by two intersecting loops like two links in a chain or the $2^2_i$ knot consisting of $(+,+)$ crossings. Obviously this link is not ideal for simulating tangles as, with open components, it is simply two chains crossing once. When working with tangles, a tangle used for entanglements between two polymer chains should be a functional bend (a knot used to bind two ropes together). The inherent problem with real world knots is that many of them reduce to simpler mathematical knots under the Reidemeister moves, e.g. when the components used to tie the reef knot are closed to form a link, the link reduces to the $0^2_1$ link and similarly the Sheet Bend reduces to the $2^2_1$ link. The simplest bend that retains its form when the components are
closed under the Reidemeister moves is the granny knot which is the tangle that represents the $6_1^2$ link.

The identification of knots can either be done by reducing the knots through application of the Reidemeister moves to its most basic form, which can then be identified by inspection, or by calculation of the skein invariant (or polynomial). This former process can be performed using primitive path analysis algorithms. It is also possible to combine these techniques as it is easier to find the skein invariant for a simplified knot than a complex knot.

4.2.1 Primitive Path Analysis (PPA)

The primitive path is defined as the shortest path connecting two ends of a polymer chain to each other while preserving the topology of the chain relative to the obstacles around it. In the case where the other obstacles are another polymer chain, the primitive path is the simplest link between the two chains. PPA is typically used to define a central axis in Rousian tube models of polymer diffusion. These models, initially developed by Doi and Edwards [Edwards 1967] [Edwards 1968] [Doi 1986], reduce the system containing the polymer to the environment containing its nearest points of contact (obstacles, other chains and self-contacts) and study its motion in this environment. Within a polymer network, the movement of a polymer chain is hampered by the motion of other polymer chains. If one freezes the other chains and considers a single chain in this environment, the contact points of the mobile chain with the other chains mark out the boundaries of a volume in which the chain can move. This volume can be modelled as a tube with a central axis that is defined as the shortest path that connects the two ends of the chain while preserving the topology of the system. The central axis of this tube is the primitive path.

Primitive Path Analysis is the name given to algorithms that are used to calculate the central axis of the Rousian tube. PPA algorithms tend to operate by either conducting a molecular dynamics simulation of the chain with an increasing potential between the chain (essentially tightening the chain until the primitive path reveals itself) [Sukumaran 2005], or by applying the Reidemeister moves directly to the chain to untangle it [Kröger 2005]. Applying this process to a knot (or link) can reduce it to a form where the knot can be visually identified, or simplify the calculation of the skein invariant of the knot that can be used to identify it.
4.2.2 Skein Invariants

The skein invariants are polynomial expressions that are representative of knots or links. For oriented knots, the invariants obey a recurrence relationship of the general form,

\[ xP_+(x, y, z) + yP_-(x, y, z) = zP_o(x, y, z) \]

\[ P_o = 1, \]

Eqn. 4.2.2.1

where \( P_o \) is the polynomial of the base knot, \( P_+ \) is the polynomial of the base knot with an additional positive crossing, \( P_- \) is the polynomial of the base knot with an additional negative crossing, \( P_o \) is the polynomial of the unknot and \( x, y \) and \( z \) are parameters of the polynomial that are unique to each invariant. For example, in the Jones polynomial the values of \( x, y \) and \( z \) are \( \left( x = \frac{1}{t}, \ y = -t, \ z = t^{1/2} - t^{-1/2} \right) \) and for the Alexander-Conway polynomial \( \left( x = 1, \ y = -1, \ z = t^{1/2} - t^{-1/2} \right) \). Using the recurrence relation it is possible to construct a library of polynomial invariants of various knots as is illustrated in figure 4.2.2.1. For unoriented knots a recurrence relationship similar to equation 4.2.2.1 can also be found, though it is significantly different and not as general as the recurrence relationship for oriented knots. The Kauffman polynomial [Kauffman 1990] is a good example of an unoriented skein invariant.
Figure 4.2.2. 1 The construction of the generalized knot invariant of the $2_1^2$ from the recurrence relation Eqn. 4.2.2.1. In the top half of the diagram, the invariant of the $0_1^2$ is calculated from the invariant of the $0_1$, which is by definition 1 (the shown knot with one crossing reduces to the $0_1$ under a type 1 Reidemeister move). In the bottom half of the diagram, the invariant for the $2_1^2$ is calculated by adding a + crossing to the $0_1$ knot which already contains a + crossing, adding a negative crossing to the $0_1$ knot produces a $0_1^2$ knot.

The usefulness of the polynomial invariants is that they can be calculated from the partition function of a lattice model based on the configuration of the knot. The construction of the lattice requires collapsing the polymer onto a two dimensional plane, forming an oriented representation of the knot, and finally replacing that oriented representation with a piecewise linear lattice. This process is illustrated for the trefoil knot $3_1$ in figure 4.2.2.2. The specific lattice model that is used to calculate the partition function is dependent on the skein invariant being used. For the Jones polynomial, the invariant is calculated from the partition function of the two-state non-intersecting string model, where each crossing is a vertex of the lattice, each line segment is an edge of the lattice and each edge can have two colours. This model has the
additional constraint that pairs of neighboring edges must have the same colour. For the example crossing shown in figure 4.2.2.3, this is the requirement that either the colour of $a = b$ and $c = d$ or the colour $a = c$ and $b = d$. Hence the partition function for this model is calculated as,

$$Z = \sum_{\text{EdgeStates}} q^p \prod \omega_z \left( \begin{array}{cc} c & d \\ a & b \end{array} \right),$$

where $p$ is the number of loops in the lattice, $q = e^\eta + e^{-\eta}$, $\omega_z \left( \begin{array}{cc} c & d \\ a & b \end{array} \right) = e^{2\eta} \delta_{ac} \delta_{ad} - e^{2\eta} \delta_{ab} \delta_{cd}$ is the weight function associated with a positive or negative crossing vertex. The Jones polynomial is retrieved by substituting $-\sqrt{t} = e^{\eta}$ in the expression for $Z / q$.

Figure 4.2.2. 2 The conversion of the trefoil knot from an unoriented knot to a piecewise linear lattice. The first step is to specify a direction of traverse to examine the crossings and identify them as positive or negative. The knot is then simplified to a linear representation.

Figure 4.2.2. 3 Edge labelled crossing.
In a similar fashion, the Alexander-Conway invariant can be calculated from a spin conserving two state vertex model [Wu 1992]. There are several other knot invariants that have not been discussed including, the Homfly [Freyd 1985] and the Akutsu-Wadati [Akutsu 1987]. For more information on knot theory in general see [Wu 1992].

4.2.3 Entanglements Under Shear

There have been studies done on the effects of entanglements on the mechanical properties of bulk polymers under shear. The earliest of these models is the Rouse polymer model, which describes the mechanical properties of short chained polymer melts quite well. However, the Rouse model does not address the effect of the entanglements in polymer networks where entanglements are almost surely present. For example, a knot introduces a point of mechanical weakness in the chain at the entrance bonds (the bonds in the chain where the polymer first begins to twist into the conformation of the knot) to the knot, due to increased bond stress [Yu 2005]. There have been models that have attempted to address this effect, ranging from simulations to the Rousian tube models that gave rise to the PPA described above. There have also been molecular dynamics studies that looked at the persistence of interactions between chains in polymer melts [Yamato 2004] [Padding 2003] [Everaers 1996], though these interactions are not the same as knots or links. The molecular dynamics simulations of Kremer and Everaers suggested that the difference in Young’s modulus between the polymer network with entanglements and without was $0.85 \rho_{ent} k_B T$, where $\rho_{ent}$ is the entanglement density.

The great difficulty with simulating knots in dense molecular dynamics systems is that their occurrence by random processes in short chains is low and artificially introducing them to a dense system can be difficult. The probability of the unknot existing in a cyclic polymer can be expressed as $p_0 = Ce^{-N/N_0}$, where $C$ and $N_0$ are fitting parameters based on the polymer/model being used and $N$ is the number of Kuhn segments [Shimamura 2001]. For an FCC lattice [Janse van Rensburg 1990], the parameters are $C = 1.0011 \pm 0.003$ and $N_0 = (1.3 \pm 0.2) \times 10^5$, hence the probability of a centimeter having a knot in it is negligible and one would not expect 50% of polymers to have a knot until $N \approx 90000$. Among proteins the occurrence of knots is also lower than the theory would predict [Kardar 2008].
The results for polymer melts should not be extrapolated to a layer of polymers that have been bound to the wall of a channel. Melt polymers, unlike tethered polymers, are not bound to a wall at one end of the chain. Tethering a polymer limits the conformational entropy of the chain and places a physical constraint on the possible deformations of the layer. The application of the results of melt polymers to the behavior of an isolated chain is an even worse comparison as the intermolecular interactions that are the dominant restriction on entanglements within a polymer melt are absent in the latter system.

There is very little available experimental work or theory on the dynamics of knots and tangles. The majority of the data that do exist relates to the relaxation time of a knot or the diffusion coefficient of a knot along a chain. Unfortunately, this diffusion model does not lend itself well to tangles in tethered polymers subjected to channel flow. A polymer under these conditions is under increasing stress towards the tethered end of the chain and there is a directed force on the tangle leading it to unknot. While the mechanisms presented in these models may be relevant, the results for tangle diffusion rates and relaxation times would not be similar to these values for knots. There is also some data on the unknotting times of tangles. While none of it relates to tangles under flow conditions, some of the studies do pertain to forced conditions.

Experimentally, there have been some studies involving the presence of knots in cyclic DNA [Stasiak 1996] and the tying of tangles with optical tweezers in DNA [Arai 1999] [Bao 2003] and actin filaments [Arai 1999]. Staziak et al, found that there was a linear relationship between the electrophoretic mobility of cyclic DNA and the number of crossings that existed in a knot in the ring. Bao et al [Bao 2003], studied the diffusion of tangles tied in DNA and the tangle was found to diffuse along the chain at a slower rate than the Rouse diffusion rate of the chain (the rate of diffusion of the centre of mass of the chain). There was no tension dependence on the diffusion coefficient over the range of stresses tested (0.1 – 2 pN), but the diffusion coefficient was highly dependent on the type of knot. The diffusion coefficient was found to decrease with the number of crossings, but there was no structural dependence observed except between the $5_1^1$ and $5_2^1$ tangles.

There are several models to describe the diffusion of a tangle. One such model is a reptation model of a tangle along the chain in a Rousian tube with a diameter equal to the tangle diameter [Bao 2003] [Orlandini 2008]. The model of Metzler et al [Metzler 2006] further suggests that
this reptation is a function of two processes, the reptation of the chain and the loosening and tightening of the tangle. However, this model also predicts that the diffusion should decrease under increasing tension and increase as the tangle nears the end of the chain. The work of Huang and Makarov [Huang 2007] suggested that there were three diffusion regimes for a tangle under a tension: a blob regime where the force was not high enough to align the chain and the tangle behaved as it would if it were unstressed, an elastic regime where the chain was aligned enough that there were no intrachain interactions other than between bonded members and the tangle tightness fluctuates with chain tension and length (the diffusion coefficient increases as the tangle enters this regime but lowers as it enters the latter regime), and finally a tight regime where the tangle attained its minimum diameter. In the tight regime, the diffusion coefficient is no longer a function of tension. In the latter two regimes, the diffusion coefficient could be modeled as $D_R \propto k_B T / N \xi_o$ where $N$ is the number of segments in the tangle and $\xi_o$ is the friction factor per monomer.

The unknotting time of broken cyclic polymers has been studied under equilibrium conditions [Lai 2000] [Lai 2003] and with a multi-component tangle under stress [Kirmizialtin 2008]. The former study primarily focused on knots in ring polymers under equilibrium conditions. However, the study of Lai et al [Lai 2000] [Lai 2003] did look at the relaxation time of the polymer chain from the knotted state to the linear state if the chain was cut. It was found that this time should be proportional to $X_L^{1+2\nu}$ where $X_L$ is the chain contour length and $\nu$ is the scaling exponent for the radius of gyration. For the trefoil knot this relaxation was also proportional to $(X_L/d)^{3/5}$, where $d$ is the diameter of the knot. The type of knot, both the number of crossings and the positional organization of the crossings, had a large influence on the relaxation time. While in general, increasing the number of crossings increased the relaxation time, it was observed that certain families of knots with similar structures existed and some of the simpler knots had a longer relaxation time than larger knots that were in different families (e.g. a $3^1$ knot took longer to relax than a $4^1$).

The study of Kirmizialtin and Makarov [Kirmizialtin 2008], created a granny knot and reef knot between two chains and applied a constant tension to the chains at either end until the tangle untied. It was observed that the tangle tightened as the force increased until it seized and then
thermal fluctuations would loosen the tangle enough for it to slip along the chain until it untied. Essentially, for the tangle to slip it had to move from local minimum to local minimum along a corrugated energy surface. This potential was modeled as $\Psi(x) = F d_k \sin(2\pi x/a) - F$, where $x$ is the position of the tangle on the chain, $F$ is the magnitude of the force pulling on the chain, $a$ is the period of the potential and $d_k$ is a tangle dependent parameter. As $a$ is the period of the potential, it is roughly equal to the backbone bond length for a simple tangle in a polymer chain since going through a maximum should be equivalent to the tangle slipping over a bead. The parameter $d_k$ is the scaling parameter for the height of the maxima and is a measure of how fast the tangle holds as it is tightened. In the model $d_k$ is expected to depend on the type of tangle and the potentials between particles. From the functional form of this potential as $F$, the magnitude of the motive force on the chains, increases, the barrier to movement along the surface also increases. This motion was described by a 1-dimensional Brownian motion simulation with the following stochastic equation:

$$\eta \frac{dx}{dt} = F - \frac{2\pi F d_k}{a} \cos\left(\frac{2\pi x}{a}\right) + \xi(t),$$

where $\eta$ is a friction factor and $\xi(t)$ is a random Gaussian force equivalent to the thermal noise of the chain. From the stationary point of this equation, two regimes of tangles emerged based on the value of $d_k$. These two tangle regimes were termed the weak and strong tangle. A weak tangle was one where $d_k < a/2\pi$, the height of the barrier increased slower than the motive force on the tangle as $F$ increased, and the unknotting time decreased as $F$ increased. A strong tangle was one where $d_k > a/2\pi$, the barrier increased faster than the motive force did, and the unknotting time increased as $F$ increased.

Under flow conditions, there appears to be only a single study on tangles in an elongational flow field [Kivotides 2009]. This study examined the rate of tangle migration towards the end of the chain with a figure 8 knot ($4_1$ in a closed component) and a granny knot. Tangled polymer chains were observed to stretch at a slower rate than untangled polymer chains, however restrictions were placed on the dynamics of the chain to rigorously prevent the unraveling of the tangle. That is the dynamics would tighten the tangle as it reached the end the of chain to the
point where the tangle could no longer slip and it would become stuck as opposed to slipping loose.

### 4.3 Simulation Methodology

The focus of the simulations was to examine the effect of channel flow on the unknotting times of the polymers containing simple single component and two component tangles. The flow was simulated using the hybrid MPCD-MD algorithm described in section 2.3, and the polymer was modelled using the FENE chain described in section 3.3. The channel was a $20 \times 20 \times 100$ nm square cross-section channel with flow along the $z$-dimension of the channel. The two component knots were tied in two configurations: a configuration where the two chains were anchored next to each other on the same wall (the parallel configuration) and a configuration where the chains were anchored on opposing walls so that the entangled chains spanned the channel (the spanning configuration.) Other than increasing the length of the polymer from 100 beads to 150 beads for the channel-spanning two-component tangle, the parameters for the polymer from section 3.3 were used for the polymer in this chapter. After the flow-field was given enough time to equilibrate, the polymer, or polymers, were inserted into the channel with a knotted initial configuration. Over the course of the simulations the flow rate was varied to examine its effect on the unraveling of the polymer and the initial tightness of the tangle was varied through the initial conditions to examine its effect on the behaviour of the tangle.

The tangles that were studied were the overhand knot (which is the $3^1$, or trefoil knot in a closed loop) and the granny knot (which is the $6_2^1$ link when tied in two closed components). These tangles were chosen to test a single component tangle and a multicomponent tangle. The trefoil knot is the simplest non-trivial single component tangle. The granny knot is the simplest functional bend that, when closed, does not form a link which can be reduced under Reidemeister moves. The initial conformations for these tangles are presented in the subsequent subsections.
4.3.1 Overhand knot formula

The overhand knot or half-hitch is the open form of the trefoil knot or $3^1$. It is tied in a rope by forming a loop and then passing one end of the rope through the loop. This process is illustrated in figure 4.3.1.1. The mathematical formula for the position $(x(i), y(i), z(i))$ of each bead in the polymer with an overhand knot tangle is quite complex.

![Diagram of overhand knot](image)

**Figure 4.3.1.1** The tying of the overhand knot in a single open component. First the ends of the component are crossed to form a loop. Next one end of the component is wrapped around the other end of the component within the loop.

The formula is divided into 5 intervals between the point of tethering, $l_1, l_2, l_3, l_4$ and $l_5$ that can be derived from 3 parameters, $l_1, l_2$ and $l_5$. These intervals are:
1. \( ia \leq l_1 \), \((l_1 / a \in I)\) is the initial vertical rise of the polymer chain, where \( a \) is the equilibrium bond length from the FENE potential in section 3.3. For \( ia \leq l_1 \), the position of the \( i^{th} \) bead is \((x(i) = x_o, y(i) = y_o, z(i) = z(i-1) + a)\) where \( z(l) = z_o + a \).

2. \( l_1 < ia \leq l_2 \), \((l_2 > l_1 | l_2 / a \in I)\) is a horizontal displacement of the chain. The position of the \( i^{th} \) bead is \((x(i) = x_o + ia - l_1, y(i) = y_o, z(i) = z_o + l_1)\).

3. \( l_2 < ia \leq l_3 \), \((l_3 = l_2 + \sqrt{9\pi^2 + 1(l_2 - l_1)/3})\) is a \(3\pi/2\) descending helix. The position of the \( i^{th} \) bead is

\[
\begin{pmatrix}
x(i) = x_o + \frac{(l_2 - l_1)}{3} + \frac{2(l_2 - l_1)}{3} \cos \left( \frac{3\pi (ia - l_2)}{2(l_3 - l_2)} \right), \\
y(i) = y_o + \frac{2(l_2 - l_1)}{3} \sin \left( \frac{3\pi (ia - l_2)}{2(l_3 - l_2)} \right), \\
z(i) = z_o + l_1 - \frac{(l_2 - l_1)}{3(l_3 - l_2)} (ia - l_2)
\end{pmatrix}
\]

4. \( l_3 < ia \leq l_4 \), \((l_4 = l_3 + l_2 - l_1)\) is another horizontal displacement. The position of the \( i^{th} \) bead is \((x(i) = x_o + (l_2 - l_1)/3, y(i) = y_o + 2(l_1 - l_2)/3 + ia - l_3, z(i) = z_o + (2l_1 - l_2)/3)\).

5. \( l_4 < ia \leq l_5 \) (\( l_5 \) is the extension length of the polymer chain) is the final vertical rise of the chain. The position of the \( i^{th} \) bead is

\[
(x(i) = x_o + (l_2 - l_1)/3, y(i) = y_o + (l_2 - l_1)/3, z(i) = z_o + (2l_1 - l_2)/3 + ia - l_4).
\]

For these simulations \( a = 0.154 \) nm and \( l_1 = 15a \). The value of \( l_2 \) was allowed to vary to examine the effect of the initial tangle tightness on the behaviour of the tangle. The configuration of the tangle produced by this formula is shown in figure 4.4.1.1 a).

### 4.3.2 Granny knot formula

As a functional bend, the granny knot belongs to the family of knots that include the reef knot, the thief knot and the grief knot. These tangles have the same basic structure of 6 crossings, but there are differences in the order that the components form the crossings. The family of tangles...
that contains the granny knot is shown in figure 4.3.2.1. When these components are closed to form a two component link the granny knot and the grief knot become the $6^2_1$ link. The $6^2_1$ is one of 3 variants of 6 crossing two component mathematical links. The Granny knot is tied as two overhand knots between two components, such that the chirality of the overhand knots is the same. Essentially, if one ties the first overhand knot by crossing the right component over the left component, the tangle is completed by tying the second overhand knot by crossing the right component over the left component, if the chirality of the second overhand knot is reversed a reef knot is tied instead of the granny knot. This process is shown in figure 4.3.2.2. Mathematically, this tangle can be represented as two $2\pi$ radian helices tied between the two components.

![Figure 4.3.2.1](image)

**Figure 4.3.2.1** The reef knot family of six crossing tangles. The reef knot (or square knot) is shown in the top left corner (a). The granny knot is shown in the top right corner (b). The thief knot is shown in the lower left corner (c). The grief knot is shown in the lower right corner (d). When the components are closed to form two component links, the reef knot and the thief knot form the same structure which reduces to the $0^2_1$ link under Reidemester moves. Similarly, the granny knot and the grief knot form the same structure when the components are closed to form two component links, however in this case the resulting structure is the $6^2_1$ link. The difference between the reef and thief knot and the granny and grief knot is the choice of load bearing ends for the bend and the method used
to tie the tangles. The reef and granny knots are the easier tangles to tie and stronger under a load than the thief and grief knots.

Figure 4.3.2. 2 The tying of the granny knot. First the left (red) component is crossed over the right (green) component and wrapped around it to form an overhand knot. This action is then repeated, crossing the left component (now the green component) over the right component (now the red component) and wrapping the left component around the right component to form another overhand knot.

When the tangle is tied with parallel anchor points (separation along the y axis such that $y_{1o} = -y_{2o}$ and the separation is greater than zero), the tangle has a reverse symmetry between the two components of the chains. The parameters used to tie the granny knot are: $L_a$, the separation between the adhesion points of the chain and the width of the helices in the tangle, $a$, the equilibrium bond length, $H$, the height to which chains rise before the tangle is tied, $R$, the radius of the helices in the tangle and $l_5$, the extension length of the polymer chain.

Like the overhand knot, the formula of the bead positions for the Granny knot is also divided into 5 intervals based on the segments between the point of adhesion, $l_1$, $l_2$, $l_3$, $l_4$ and $l_5$. For the tangle in the parallel configuration the formula for the $6_i^2$ is:
1. \( ia \leq l_1, \quad l_1 = \sqrt{H^2 + R^2} \), which is a nearly vertical rise to \( H \). The position of the \( i^{th} \) bead for the chains are,

\[
\begin{align*}
(x_1(i) &= x_{i_o} + Hl_1, y_1(i) = y_{i_o}, z_1(i) = z_{i_o} + Rl_1), \\
(x_2(i) &= x_{2_o} + Hl_1, y_2(i) = y_{2_o}, z_2(i) = z_{2_o} - Rl_1).
\end{align*}
\]

2. \( l_1 < ia \leq l_2, \quad l_2 = l_1 + l_h \), which is a \( 2\pi \) double helix of length

\[
l_h = L\pi \sqrt{R^2/L^2 + 1 + \pi R^2L^2 \ln(1 + \sqrt{R^2/L^2 + 1})}
\]

in which the two chains cross. The position of the \( i^{th} \) bead of each chain in this interval is,

\[
\begin{align*}
x_1(i) &= x_{i_o} + H + R \sin\left(\frac{2\pi(ia - l_1)}{l_h}\right), y_1(i) = y_{i_o} + L\left(\frac{ia - l_1}{l_h}\right), z_1(i) = z_{i_o} + R \cos\left(\frac{2\pi(ia - l_1)}{l_h}\right), \\
x_2(i) &= x_{2_o} + H + R \sin\left(\frac{2\pi(ia - l_1)}{l_h}\right), y_2(i) = y_{2_o} - L\left(\frac{ia - l_1}{l_h}\right), z_2(i) = z_{2_o} - R \cos\left(\frac{2\pi(ia - l_1)}{l_h}\right).
\end{align*}
\]

3. \( l_2 < ia \leq l_3, \quad l_3 = l_2 + 2\sqrt{(R+a)^2 + R^2} \) which is a second vertical rise. In this interval the position of the beads are,

\[
\begin{align*}
x_1(i) &= x_{i_o} + H + \left(\frac{R+a}(ia - l_2)\right) \sqrt{(R+a)^2 + R^2}, y_1(i) = y_{2_o}, z_1(i) = z_{i_o} + R - \frac{R(ia - l_2)}{\sqrt{(R+a)^2 + R^2}}, \\
x_2(i) &= x_{2_o} + H + \left(\frac{R+a}(ia - l_2)\right) \sqrt{(R+a)^2 + R^2}, y_2(i) = y_{i_o}, z_2(i) = z_{2_o} - R + \frac{R(ia - l_2)}{\sqrt{(R+a)^2 + R^2}}.
\end{align*}
\]

4. \( l_3 < ia \leq l_4, \quad l_4 = l_3 + l_h \), a \( 2\pi \) double helix in the opposite direction in which the two chains cross again. The position for the \( i^{th} \) bead for both chains in this interval is,
\[
\begin{align*}
\begin{cases}
    x_1(i) = x_{1o} + H + 2(R + a) + R \sin \left( \frac{2\pi (ia - l_3)}{l_h} \right), \\
y_1(i) = y_{2o} - L \frac{(ia - l_3)}{l_h}, \\
z_1(i) = z_{1o} - R \cos \left( \frac{2\pi (ia - l_3)}{l_h} \right)
\end{cases}
\end{align*}
\]

\[
\begin{align*}
\begin{cases}
    x_2(i) = x_{2o} + H + 2(R + a) + R \sin \left( \frac{2\pi (ia - l_3)}{l_h} \right), \\
y_2(i) = y_{1o} + L \frac{(ia - l_3)}{l_h}, \\
z_2(i) = z_{2o} + R \cos \left( \frac{2\pi (ia - l_3)}{l_h} \right)
\end{cases}
\end{align*}
\]

5. \( l_4 < ia \leq l_5 \), a final vertical rise for the two chains. The position of the final beads in the two chains are,

\[
\begin{align*}
\begin{cases}
    x_1(i) = x_{1o} + H + 2(R + a) + (ia - l_4), y_1(i) = y_{1o}, z_1(i) = z_{1o} - R), \\
x_2(i) = x_{2o} + H + 2(R + a) + (ia - l_4), y_2(i) = y_{2o}, z_2(i) = z_{2o} + R).
\end{cases}
\end{align*}
\]

For the channel spanning tangle, the polymer chains had to be extended to 150 beads from 100. The tangle remains divided into 5 intervals, which have the same definition as per the parallel configuration, with the exception that \( l_1 = H - R \) where \( H = W/2 \) (\( W \) is the width of the channel), while \( x_{1o} = x_{2o} \) for the parallel chains, \( x_{2o} - x_{1o} = W \) for this configuration. The formula for the two chains is:

1. For \( ia \leq l_1 \), the position of the \( i^{th} \) bead is

\[
\begin{align*}
\begin{cases}
    x_1(i) = x_{1o} + ia, y_1(i) = y_{1o}, z_1(i) = z_{1o}, \\
x_2(i) = x_{2o} - ia, y_2(i) = y_{2o}, z_2(i) = z_{2o}.
\end{cases}
\end{align*}
\]

2. For \( l_1 < ia \leq l_2 \), the position of the \( i^{th} \) bead is

\[
\begin{align*}
\begin{cases}
    x_1(i) = x_{1o} + H - R \cos \left( \frac{2\pi (ia - l_1)}{l_h} \right), y_1(i) = y_{1o} + L \frac{(ia - l_1)}{l_h}, z_1(i) = z_{1o} + R \sin \left( \frac{2\pi (ia - l_1)}{l_h} \right), \\
x_2(i) = x_{2o} - H + R \cos \left( \frac{2\pi (ia - l_1)}{l_h} \right), y_2(i) = y_{2o} - L \frac{(ia - l_1)}{l_h}, z_2(i) = z_{2o} + R \sin \left( \frac{2\pi (ia - l_1)}{l_h} \right).
\end{cases}
\end{align*}
\]
3. For \( l_2 < ia \leq l_3 \), the position of the \( i^{th} \) bead is
\[
\begin{align*}
x_1(i) &= x_{1o} + H - R + \frac{R(ia - l_2)}{\sqrt{(R + a)^2 + R^2}}, \\
y_1(i) &= y_{2o} + \frac{2\pi(ia - l_2)}{l_h}, \\
z_1(i) &= z_{1o} + \frac{(R + a)(ia - l_2)}{\sqrt{(R + a)^2 + R^2}},
\end{align*}
\]
\[
\begin{align*}
x_2(i) &= x_{2o} - H + R - \frac{R(ia - l_2)}{\sqrt{(R + a)^2 + R^2}}, \\
y_2(i) &= y_{2o} + \frac{2\pi(ia - l_2)}{l_h}, \\
z_2(i) &= z_{2o} + \frac{(R + a)(ia - l_2)}{\sqrt{(R + a)^2 + R^2}}.
\end{align*}
\]

4. For \( l_3 < ia \leq l_4 \), the position of the \( i^{th} \) bead is
\[
\begin{align*}
x_1(i) &= x_{1o} + H + R \cos \left( \frac{2\pi(ia - l_3)}{l_h} \right), \\
y_1(i) &= y_{2o} - L \left( \frac{ia - l_3}{l_h} \right), \\
z_1(i) &= z_{1o} + 2(R + a) + R \sin \left( \frac{2\pi(ia - l_3)}{l_h} \right),
\end{align*}
\]
\[
\begin{align*}
x_2(i) &= x_{2o} - H - R \cos \left( \frac{2\pi(ia - l_3)}{l_h} \right), \\
y_2(i) &= y_{1o} + L \left( \frac{ia - l_3}{l_h} \right), \\
z_2(i) &= z_{2o} + 2(R + a) + R \sin \left( \frac{2\pi(ia - l_3)}{l_h} \right).
\end{align*}
\]

5. For \( l_4 < ia \leq l_5 \), the position of the \( i^{th} \) bead is,
\[
\begin{align*}
x_1(i) &= x_{1o} + H + R, \\
y_1(i) &= y_{1o} + 2(R + a) + (ia - l_4), \\
z_1(i) &= z_{1o} + 2(R + a) + (ia - l_4),
\end{align*}
\]
\[
\begin{align*}
x_2(i) &= x_{2o} - H - R, \\
y_2(i) &= y_{2o} + 2(R + a) + (ia - l_4), \\
z_2(i) &= z_{2o} + 2(R + a) + (ia - l_4).
\end{align*}
\]

For the simulations, \( a = 0.154 \text{ nm}, \ R = 2a, \ L = 4a, \ H = 30a \) and the extension length was \( 100a \) for the parallel configuration and \( 150a \) the channel spanning configuration. The configurations of the tangle produced by these formulae are shown below in figure 4.3.2.3.

![Diagram](image-url)

**Figure 4.3.2. 3** The initial configurations of the granny knot in the parallel chain configuration, left (diagram a), and the channel spanning configuration, right (diagram b). The red axis is the \( x \) axis of the channel, the green axis is the \( y \) axis of the system and blue axis is the \( z \) axis, or direction of flow.
4.4 Tangle Simulations

The results of the simulations for the tangled polymer are divided into two sections. Single component tangles and multi-component tangles. The primary focus of these results is the unknotting times of the polymer, for which there is little existing data in the literature, and no data for unknotting under flow conditions. The unknotting times were not calculated from the simulations due to the computational load required to obtain these data. It would require hundreds of simulations to identify the unknotting time distribution for a single set of conditions and thousands for a sweep of simulations across multiple flow rates. The particular problem in performing these simulations is the automation of the required analysis. New algorithms are required to track the position of the tangle to the end of the chain and determine the unknotting time without any human involvement. This task requires the construction of an algorithm to close the tangles to form knots and links, the use of a primitive path algorithm to identify the position of the resulting knot, and another algorithm to construct the skein invariant and identify the knot from the primitive path. These algorithms would have to be run on the configuration of the polymer at every time step of the simulation. However, there are data that cannot be extracted by this automated approach, such as the mechanisms by which the polymer unravels under these flow conditions, data on the size of the tangle during the simulation or data on the behavior of the polymer in general containing a tangle. Without these data, constructing automated tangle tracking algorithms and validating their performance would not be possible. As the unknotting time distribution could not be extracted from the simulations, a Brownian dynamics simulation was performed to simulate the distribution of unknotting times for the single component tangles. The simulations were also used to examine the size of the tangle and how it was affected by the flow rate. The untying of the tangles was only studied under the θ solvent conditions described in section 3.4.1.

4.4.1 Single Component Tangles

These results focus on the overhand knot as this is the simplest non-trivial single component tangle. The initial configuration was described in Section 4.3.1. The polymer was tethered in the 20×20×100nm square cross-section channel shown in figure 2.3.3.1. The polymer was anchored to the centre of the x-normal wall (–10,0,50). For these simulations the length of the
polymer was held constant at 100 beads, while the flow rate and the diameter of the tangle were varied to examine the effects of initial tangle tightness and flow rate on the tangle dynamics. The diameter of the tangle was controlled by altering the parameter $l_2$. The tightness of the tangle was represented by the number of beads in the tangle, $N_{tangle}$. From the formula in section 4.3.1, the initial value of $N_{tangle}$ is roughly the length of polymer chain from $l_1$ to the point where the $z$ coordinate of the chain is $z(l) = z_o + l_1$ or,

$$N_{tangle} = \frac{7 + \sqrt{9\pi^2 + 1}}{3a}(l_2 - l_1)$$

Once the simulations commenced, determining the number of beads in the tangle was more complex and required visual inspection due to the relaxed configuration adopted by the tangles, the difference in these configurations is illustrated in figure 4.4.1.1.

![a) b)](image)

**Figure 4.4.1.1** The initial configuration of the tangle and its relaxed configuration. The figure on the left, a), shows the initial configuration of a knot with $N_{tangle}$ equal to 33 beads. The figure on the right, b), shows the configuration of the tangle after 0.1 ns of simulation, $N_{tangle}$ is now roughly 41 beads in length. These results were taken from a simulation with a flow rate of $(2.03 \pm 0.03) \times 10^6$ particles/ns.

Under simulation conditions where the flow rate was not strong enough to orient the polymer chain significantly, $Q < (4.7 \pm 0.2) \times 10^7$ particles/ns, the choice of initial configuration for the tangle introduced a fast mechanism for the unknotting of the looser tangles. Past the tangle, the polymer has a stretched initial configuration. The chain therefore behaves as an entropic spring
under tension and the end of the chain recoils towards the centre of the tangle. If the end of the chain passes through the loop of the tangle, then the polymer unknots very rapidly. This is highlighted in figure 4.4.1.2, which shows the unknotting times for a set of equilibrium runs with a tangle of initial tightness $N_{tangle} = 41$. Four of the ten runs unknot through this mechanism which is shown in figure 4.4.1.3.

![Unknotting Times For Equilibrium Runs with $N_{tangle} = 41$](image)

**Figure 4.4.1.2** Unknotting times for 10 equilibrium runs with a tangle initially composed of 41 beads. Two unknotting times become apparent, a rapid unknotting time of 0.07 ns and a slower unknotting time of 0.26 ns.
Figure 4.4.1. 3 Rapid unknotting of a polymer with $N_{\text{tangle}} = 41$ under equilibrium conditions. The polymer begins with an elongated configuration shown in the top left, a). The motion of the beads in the chain as the polymer relaxes causes the end of the chain to recoil towards the anchor point, shown in the top right, b). The end of the chain passes through the loop of the half hitch unknotting the chain, shown in the bottom left, c). Finally the polymer assumes a relaxed random coil state, shown in the bottom right, d).

If the polymer does not unknot through this fast mechanism at low flow rates, $Q < (4.7 \pm 0.2) \times 10^7 \text{ particles/ns}$, then the tangle unties by the end of the chain drifting through the loop of the tangle, as shown in figure 4.4.1.4. At higher flow rates, the flow field limits the position of the end of the chain to a position downstream of the anchor point and the reptation of the chain carries the tangle along the chain until it slips off, figure 4.4.1.5. At intermediate flow rates, a combination of the two mechanisms occurs with some reptation of the tangle towards the end of the chain and some drift of the end of the chain towards the tangle. The unknotting times for tangles with an initial $N_{\text{tangle}}$ of 12 are shown in figure 4.5.1.6. The presence of two unknotting mechanisms is consistent with the study of Huang and Makarov [Huang 2007], which examined the Rousian diffusion of a tangle in a polymer under uniaxial tension and
predicted a blob and elastic regime for Rousian diffusion. In the blob regime, the tangle behaved as if it was unstressed, whereas in the elastic regime there was a linear diffusion of the tangle along the chain. The observed behavior of the tangle in the elastic regime seems to be consistent with the mechanism observed in the simulations of tangles presented in this section under high flow rates. And as the low flow mechanism also applies to equilibrium conditions, it appears that the concept of a blob regime and elastic regime also apply to a polymer under flow.

![Image](image-url)

Figure 4.4.1. 4 Slower unknotting of a polymer chain under equilibrium conditions with an initial knot size of $N_{\text{tangle}} = 41$ beads. From the initial configuration of the tangle, shown in the top left (a), the end of the polymer chain recoils towards the anchor point, shown in the top right (b). However, unlike Figure 4.4.1.3, the end of the chain is not located near the loop of the tangle after the initial recoil and it has to migrate towards the tangle, this is shown in bottom left (c). Finally the end of the chain passes through the loop of the tangle, shown in the bottom right (d).
Figure 4.4.1.5 The unknotting of the polymer chain with $N_{knot} = 12$ under a flow rate of $2.03 \times 10^8$ particles/ns (slip velocity of $13.6 \pm 1.5 \text{ m/s}$, shear rate of $13.6 \pm 1.4 \text{ ns}^{-1}$). From the initial stretched configuration shown in the top left, a), the polymer becomes entrained in flow field and is extended in the direction of flow, b). The tangle then migrates along the polymer chain (center diagrams and bottom left c), d) and e)) and unknots as it reaches the end of the chain, bottom right (f).
Figure 4.4.1.6 Unknotting times vs. flow rate for a $N_{\text{tangle}}=12$ tangle. While time did not permit enough simulations to be conducted to accurately determine the mean unknotting time by simulation, the results do indicate that at lower flow rates there is a larger variance in the unknotting time than at high flow rates. This also suggests that there are two mechanisms for unknotting at low flow rates and at high flow rates.

For the former mode of unknotting, shown in figure 4.4.1.4, the unknotting of the polymer was modeled by the Brownian motion model described in appendix B, the Brownian motion of a particle to an absorbing disk. The radius of the disk, $R_d$, the initial distance between the polymer and disk, $d_d$, were calculated as $R_d = 2l_2/3$ and $d_d = l_5 - l_4$, where $l_2$, $l_4$ and $l_5$ are defined in section 4.3.1. This model is too simple to accurately model the unknotting of the polymer as it neglects the effect of the rest of polymer on the final bead of the chain. Thus it neglects reduction in the configurational space introduced by the chain and the effect of the
motion of the chain on the dynamics of the end of the chain, both of which will tend to increase the migration of the end of the chain towards the tangle. However, the Brownian model may indicate the width of the distribution of unknotting times and the effect of the initial tangle tightness on unknotting times. For the conditions similar to a tangle with $N_{\text{tangle}} = 41$, the Brownian model predicts a mean unknotting time of 3.961 ns, that has a standard deviation of 19.1746 ns and a most likely unknotting time of 0.531 ns. The distribution is shown as a function of $N_{\text{tangle}}$ in figure 4.4.1.7. As $N_{\text{tangle}}$ increases, both the maximum likelihood estimate of the unknotting time and the variance of the distribution decreases. The maximum likelihood unknotting time decreases as $0.003N_{\text{tangle}}^2 - 0.00467N_{\text{tangle}} + 1.9847$ ns and the variance of the unknotting time decreases as $-0.0056N_{\text{tangle}}^2 - 0.1152N_{\text{tangle}} + 52.224$ ns$^2$. The simulation data for the unknotting time of the polymer is shown in figure 4.5.1.8. While there are insufficient data to draw a trend for the data, the unknotting time does appear to decrease with increasing $N_{\text{tangle}}$ and the second derivative appears to be greater than zero, which is consistent with the results of the Brownian model.
Figure 4.4.1. 7 The first passage time distribution from the Brownian motion model in Appendix B, vs. the tangle size, $N_{tangle}$. The distribution has a long exponential tail, longer than would be expected for the overhand knot and predicts a higher maximum likelihood unknotting time than is seen from the simulated tangles. As $N_{tangle}$ increases, the maximum likelihood unknotting time (lower left b) and the variance of the distribution (lower right c) both decrease. The maximum likelihood unknotting time decreases as $0.003N_{tangle}^2 - 0.0047N_{tangle} + 1.9847 \text{ ns}$ and the variance of the time decreases as $-0.0056N_{tangle}^2 - 0.1152N_{tangle} + 52.224 \text{ ns}^2$. 
Figure 4.4.1. 8 Simulation data of unknotting times for the polymer as a function of $N_{\text{tangle}}$ under equilibrium conditions.

For the simulations conducted under a higher flow rate, where the tangle reptates along the chain until it slips off the end of the chain (figure 4.4.1.5), the variance of the unknotting time is smaller, as can be seen from figure 4.4.1.6. The unknotting time is shown as a function of the initial value of $N_{\text{tangle}}$ for a fixed flow rate in figure 4.4.1.9. The data do not indicate any functional dependence on the initial value of $N_{\text{tangle}}$. This occurs due to the relaxation or tightening of the tangle to a configuration where the average number of beads in the tangle during simulation, $N_{t,\text{sim}}$, is $40.1 \pm 3.5$ (except for the simulation with the longest unknotting time where $N_{t,\text{sim}} = 30 \pm 2$). While $N_{\text{tangle}}$, does not seem to have an effect on $N_{t,\text{sim}}$, $N_{t,\text{sim}}$ appears to decrease with increasing flow rate. As an increase in the flow rate increases the tension on the chain, an increase in the tightness with increasing flow rate is to be expected.
$N_{t,\text{sim}}$ is plotted as function of the flow rate in figure 4.4.1.10. Although there are insufficient data to determine the exact functional form, the data are well fit by a linear model with a slope of $-(7.4 \pm 1.1) \times 10^{-8}$ ns/particle and an intercept of $55.7 \pm 0.7$.

![Unknotting Time Vs. $N_{\text{tangle}}$ for a High Flow Rate Simulation](image)

Figure 4.4.1.9 Unknotting time vs. $N_{\text{tangle}}$ for simulations with a flow rate of $2.03 \times 10^8$ particles/ns (slip velocity of $13.6 \pm 1.5$ m/s, shear rate of $13.6 \pm 1.4$ ns$^{-1}$). The data do not appear to show any functional dependence on $N_{\text{tangle}}$. 
Figure 4.4.1. The number of beads in the tangle during simulation vs. the flow rate. There appears to be a linear decrease in $N_{t,\text{sim}}$ as the flow rate increases. Linear regression of the data revealed a slope of $-\left(7.4 \pm 1.1\right) \times 10^{-8}$ ns/particles and an intercept of $55.7 \pm 0.7$.

As the polymer is elongated within the flow field, the position of the tangle can be tracked along the end to end vector of the chain. The tangle position was found by constructing a histogram of the values of the projection of the position of the $i^{th}$ bead relative to the anchor point of the chain on to the end to end vector, $q_{i,E} = (q_i - q_1) \cdot (q_N - q_1)$, where $q_i$ is the position of the $i^{th}$ of the $N$ beads in the chain. The maximum of this histogram corresponds to the point of maximum polymer density along the end to end vector, which should be the position of the tangle (under a high enough flow field to orient the polymer). A plot of the tangle position along the end to end vector is shown in figure 4.4.1.1. As this diagram illustrates, there is an initial period of time where the tangle migrates linearly with time towards the end of the chain. This linear migration region was observed in all the simulations conducted under high flow rates. The tangle
migration rate is plotted as a function of the fluid velocity near the polymer (1.5 nm from the wall) in figure 4.4.1.12.

Figure 4.4.1.11 Plot of the tangle position along the end to end vector vs. time. This plot was constructed for a simulation with an initial $N_{tangle} = 12$ and a flow rate of $(2.40 \pm 0.01) \times 10^8$ particles/ns (slip velocity $14.9 \pm 2.7$ m/s, shear rate $15.2 \pm 2.3$ ns$^{-1}$). The tangle unties itself at 1.33 ns, however the loop of the overhand knot persists until 1.48 ns, when the polymer assumes its equilibrium untangled state. From the addition of the polymer to the system at 1 ns to the dissipation of the tangled structure at 1.48 ns, there is a linear increase in the position of the tangle along the chain.
Figure 4.4.1. A plot of the tangle migration rate as a function of the fluid velocity 1.5 nm away from the wall. The graph shows a linear trend in the data, with a slope of $0.97 \pm 0.13$ and an intercept of $-6.86 \pm 0.84$ m/s. This would suggest that the tangle behaves as if it were entrained in the fluid, though subject to a flow independent drag.

An analysis of Figure 4.4.1.12 suggests that the tangle behaves as if it were entrained in the fluid, though subject to a drag force as it slides through the polymer chain. Thus it could be represented by an equation of the form,

$$\frac{dx}{dt} = v_{\text{fluid}} - F_d,$$

where $v_{\text{fluid}}$ is the local fluid velocity and $F_d$ is the drag force. This is consistent with weak tangle behavior of the Brownian motion algorithm of Kirmizialtin and Makarov [Kirmizialtin 2008] discussed in section 4.2.3. For a weak tangle, the periodic portion of the equation can be replaced with its average and the stochastic ODE can be simplified to [Reimann 2002],
\[
\eta \frac{dx}{dt} = F + \xi(t) - \frac{1}{a} \int_0^a 2\pi F d_k \cos \left( \frac{2\pi x}{a} \right) dx
\]

As the overhand knot is known to be a tangle that slips, weak tangle behavior is to be expected. However, many tangles that behave as strong tangles when tension is applied to either end of the chain may behave as weak tangles under shear flow. There are several factors that facilitate the untwisting of a tangle under shear flow: the flow field applies force directly to the tangle instead of the chain, the tangle acts as a weir creating a low pressure area in front of the tangle that decreases the tension in the chain that is immediately in the path of the tangle and (as the flow field applies force to each bead in the polymer chain) the tension on the end of the chain holding the tangle taught diminishes as the tangle moves towards the end of the chain. It seems that a damped oscillatory potential as opposed to the constant potential used in the Kirmizialtín and Makarov [Kirmizialtín 2008] model is more appropriate. This model is discussed in Appendix C.

4.4.2 Multicomponent Tangles

While the overhand knot was selected to examine single component tangles and the effect of the flow field on intramolecular entanglements, the granny knot (which reduces to the $6_2$ when represented as a closed link) was used to examine the multicomponent knots and the effect of the flow field on intermolecular entanglements. This tangle was chosen as it is the simplest bend that retains its form as a two component link under Reidemeister moves. The granny knot is a tangle that is known to slip. In fact, any reference on bends for camping or sailing does not recommend using this tangle as a bend for this reason. The reef knot or sheet bend are stronger bends of similar complexity. However, when represented as a two component link, the reef knot reduces to the $0^2$ under Reidemeister moves and the sheet bend reduces to the $2^2$ under Reidemeister moves. The granny knot was tested in two configurations, with the tangle tied between two parallel components and with the tangle spanning the channel. Hence in the former configuration the flow field would align the chains and relax the tangle, and in the second configuration the flow field applies tension to the tangle. For the granny knots tied in a channel spanning configuration, a centimeter proved to be of insufficient length to tie a tangle that would
span the channel and leave a trailing length of chain that would prove sufficient for analysis of
the migration of the tangle. Hence a polymer of 150 beads, was used for the two components of
the tangle.

Unlike the overhand knot in the previous section which unknots completely in one step, the
granny knot tends to unknot in stages, a pair of crossings at a time. The granny knot is tied as
two $2\pi$ helices on top of each other, at the beginning of the simulation, the two helices rebound
off of each other and the helix at the end of the chain unravels quickly reducing the six crossing
tangle to a 4 crossing tangle (in reality a two component overhand knot, which when closed
introduces a fourth crossing and forms a $4_1^2$ link). This 4 crossing tangle then reptates towards
the end of the chain and then either unknots completely or reduces to a two crossing tangle
(when closed a $2_1^2$ link) prior to unknotting. This process is shown in figure 4.4.2.1.
Figure 4.4.2. 1 The unknotting of a granny knot tied between two parallel chains. The red axis is the $x$ axis of the channel (the polymer is anchored at $x = 0$), the green axis is the $y$-axis of the system and blue axis is the $z$-axis, or direction of flow. The data shown here are from a simulation with a flow rate of $2.03 \times 10^8$ particles/ns (slip velocity of $13.6 \pm 1.5$ m/s, shear rate of $13.6 \pm 1.4$ ns$^{-1}$). From the initial configuration, shown in top left (a), the two helices of crossings rebound off of each other very soon into the simulation, top right (b), for this simulation within 14.5 ps of simulation time. This rebound causes the two helices of crossings to separate, and the first set of crossings unravels before the polymer chains are fully extended in the flow field leaving a four crossing tangle, middle left (c). Under the flow field the remains of the tangle diffuse to the end of the chain and unravel, middle right (d), this process takes considerably longer than the unraveling of the first set of two crossings.
crossings. After the unraveling the polymer chains sometimes remain crossed leaving a two crossing tangle, though this often unravels at the same time as the four crossing tangle, bottom left (e). The tangle fully unravels after some time and the two chains fully disengage, bottom right (f).

Since the granny knot unknots in stages, there are multiple unknotting times associated with the tangle. In particular, there are well-defined unknotting times for the granny knot and the four crossing tangle it reduces to. These unknotting times are plotted in figure 4.4.2.2. For \( Q > 10^8 \) particles/ns, the unknotting time of the granny knot was \((1.72 \pm 0.14) \times 10^{-1}\) ns. However, within the same range of flow rates, the unknotting of the four crossing tangle seemed to follow an exponential decay, \( \alpha u e^{-\beta u Q} \), with a decay constant, \( \beta u \), of \((3.02 \pm 0.33) \times 10^{-9}\) ns/particle and a prefactor, \( \alpha u \), of \((6.50 \pm 0.14) \times 10^{-1}\) ns. A rapid unknotting time that increases with flow rate is consistent with weak knot behavior, and the unknotting of the four crossing tangle seems to follow the same mechanism as the high flow rate unknotting mechanism of the single component overhand knot in the previous section 4.4.1. As figure 2.4.2.7 indicates, the shear force, which should be proportional to the slip velocity, can be roughly modeled by a logarithmic fit. Hence the linear decrease unknotting time with increasing force, which would constitute weak tangle behavior, would appear similar to an exponential decrease when the unknotting time is plotted against the flow rate.
Figure 4.4.2. The unknotting time of the six crossing granny knot, red, and the four crossing two component overhand knot, black, as a function of the flow rate, for the granny knot in a parallel chain configuration. The unknotting time of the granny knot is constant and seems to be driven by the initial collision of the two double helices. For \( Q > 10^8 \) particles per ns, linear regression of the unknotting time of the granny knot revealed a line with a slope \((0.5 \pm 2.5) \times 10^{-10} \text{ns}^2/\text{particle}\) and an intercept of \((1.72 \pm 0.14) \times 10^{-1} \text{ns}\). The unknotting time of the four crossing tangle appears to be a decaying exponential function \(e^{-\beta Q}\), with a decay constant, \(\beta_u\), of \((3.02 \pm 0.33) \times 10^{-9} \text{ns/particle}\) and a prefactor, \(\alpha_u\), of \((6.50 \pm 0.14) \times 10^{-1} \text{ns}\).

At lower flow rates, \( Q < 10^8 \) particles/ns, while the granny knot seemed to maintain a similar constant unknotting time of \((1.72 \pm 0.14) \times 10^{-1} \text{ns}\), there was far more variance in the unknotting time of the four crossing tangle. The granny knot unknotted before the polymer had relaxed.
from its initial extended configuration. However, the polymer did relax from this configuration during the unknotting of the four crossing tangle. With a separation between the anchor points of the chains of quadruple the bond length (0.616 nm), the polymer coils freely interpenetrated each other (figure 4.4.2.3) and without a strong enough flow field to orient the polymer chains, there was not a large driving force for the unknotting of the four crossing tangle. Hence, there was a large variance in the unknotting times of the four crossing tangle under low flow conditions, similar to the unknotting of the single component overhand knot under low flow conditions.

Figure 4.4.2. 3 The equilibrium configuration of two polymer chain in a parallel chain configuration. The red axis is the $x$ axis of the channel (the polymer is anchored at $x = 0$), the green axis is the $y$-axis of the system and blue axis is the $z$-axis. The two polymer chains freely interpenetrate each other.

As the polymer chains are extended in the direction of flow for high flow rate simulations, $Q > 10^8$ particles/ns, it was possible to examine the location of the knot through the same methods used to create figure 4.4.1.11. The plots of tangle location showed a region of linear migration for the tangle along the end to end vector of the chain, similar to the previously mentioned figure. This migration is shown as a function of the channel velocity 1.5 nm from the
wall in figure 4.4.2.4. As for the single component overhand knot, the data show a linear trend with a slope of $1.06 \pm 0.28$ which is consistent with the single component data. Hence, the tangle behaves as an entrained object in the flow field. However, while the single component overhand knot had a negative intercept, the parallel chains have a positive intercept of $4.2 \pm 1.8$ m/s; i.e. the two component overhand knot has a higher migration rate than the single component overhand knot at the same flow rate. The reason for this is, in part, that the parallel chains are further from the wall of the channel than the single chain, likely due to the additional modification to the flow field from the second polymer chain. While the single chain had an average separation between the end of chain and the wall of $1.34 \pm 0.62$ nm for a run with a flow rate of $(2.91 \pm 0.01) \times 10^8$ particles/ns, the parallel chains had an average separation of $1.73 \pm 0.56$ nm for the same flow rate. Hence, the tangles in the parallel chains were subjected to a higher fluid velocity than the single component tangles. In addition, the single component overhand knot may be more resistant to reptation along the chain than the two component overhand knot. Physically this would be expected, since it is easier to move a loop along an independent chain than it is to move a loop along the chain when that chain itself is used to form the loop.
Figure 4.4.2. The rate of tangle migration vs. the fluid velocity near the wall. The data seem to follow a linear trend with a slope of $1.06 \pm 0.28$ and an intercept of $4.2 \pm 1.8$ m/s.

For high flow rate simulations, $Q > 8 \times 10^7$ particles/ns, the granny knot untied through a slightly different mechanism from an initial configuration that spanned the channel, as opposed to the parallel chain configuration. As the flow field was exerting force on both the chains, the maximum force was on the double helix nearest to the anchor point of the chains. Thus the two helices did not separate and the time between the unknotting of the granny knot and the unknotting of the four crossing tangle was shorter than for the parallel chain configuration despite the chain being longer. This mechanism is shown in figure 4.4.2.5.
Figure 4.4.2. The unknotting of a granny knot tied across the channel, for a simulation with a flow rate of $2.03 \times 10^8$ particles/ns (slip velocity of 13.6 ± 1.5 m/s, shear rate of 13.6 ± 1.4 ns$^{-1}$). The red axis is the $x$-axis of the channel (the polymer is anchored at $x = \pm 10$ nm), the green axis is the $y$-axis of the system and blue axis is the $z$-axis, or direction of flow. From the initial configuration, shown in top left (a), the two helices of crossings rebound off of each other very soon into the simulation, top right (b), for this simulation within 70 ps of simulation time. However, the two helices do not separate and the $6_1^2$ reptates towards the end of the chain. The first set of crossings unravels, leaving a $4_1^2$ knot, bottom left (c). Soon after the $4_1^2$ unravels, bottom right (d).

The unknotting times for the granny knot and the four crossing tangle for the chain in the channel spanning configuration are shown in figure 4.4.2.6. The distance from the second helix to the end of the chain is 6.9 nm for the tangle in the channel spanning configuration and 4.6 nm for the chains in the parallel configuration, hence the rates have to be adjusted for length to compare the results. Unlike the parallel chains, for $Q$ greater than $10^8$ particles/ns, the unknotting time of the granny knot appears to decrease linearly with a slope of
\((-4.28 \pm 0.88) \times 10^{-10}\) ns\(^2\)/particle and an intercept of \((2.66 \pm 0.05) \times 10^{-1}\) ns. When this is adjusted for length, the intercept has a value of \((3.86 \pm 0.07) \times 10^{-2}\) s/m which is consistent with the rate of \((3.74 \pm 0.30) \times 10^{-2}\) s/m found for the parallel chains. The force of the fluid pushing the first helix against the second helix coupled with the higher fluid velocity in the centre of the channel as opposed to near the wall must cause this faster decrease in the rate of the unknotting of the granny knot.

![Unknotting Time Vs. Flow Rate](image)

Figure 4.4.2. 6 The unknotting time of the granny knot, red, and the four crossing tangle, black, as a function of the flow rate, for the granny knot tied in a channel spanning configuration. The unknotting time of the granny knot indicates a decrease of the unknotting time with increasing flow rate. For \(Q > 10^8\) particles per ns, linear regression of the unknotting time of the granny knot revealed a line with a slope \((-4.28 \pm 0.88) \times 10^{-10}\) ns\(^2\)/particle and an intercept of \((2.66 \pm 0.05) \times 10^{-1}\) ns. The unknotting time of the four
crossing tangle appears to be a decaying exponential function $\alpha_u e^{-\beta_u Q}$, with a decay constant, $\beta_u$, of $(4.12 \pm 0.11) \times 10^{-9}$ ns/particle and a prefactor, $\alpha_u$, of $(5.70 \pm 0.04) \times 10^{-1}$ ns.

Similar to the results for the tangle in the parallel configuration, the rate of unknotting for the four crossing tangle in the channel spanning configuration shows a decaying exponential relationship with the flow rate, with a decay constant of $(4.12 \pm 0.11) \times 10^{-9}$ ns/particle and a prefactor of $(5.70 \pm 0.04) \times 10^{-1}$ ns. When the prefactor is normalized for the length of the chain, the prefactor for the parallel configuration becomes $(1.41 \pm 0.03) \times 10^{-1}$ s/m, while the prefactor for the spanning configuration is $(8.26 \pm 0.06) \times 10^{-2}$ s/m, which has a ratio of $1.71 \pm 0.13$.

Demonstrating that a tangle in the spanning configuration should unknot nearly twice as fast as a tangle in the parallel configuration in the absence of flow. The ratio between the decay constant for the parallel configuration and the spanning configuration is $0.733 \pm 0.082$. Thus the unknotting time for a tangle in the spanning configuration has a stronger flow rate dependence than a tangle in the parallel configuration. Both of these results are expected. The granny knot configuration that spans the channel holds the chains in an entropically unfavorable configuration, thus the tangle would be expected to unravel faster under no flow conditions. As the tangle is located in the centre of the channel, it is subject to the maximum velocity of the fluid, thus the unknotting time of the tangle would be expected to have a stronger flow rate dependence as well.

The plots of the tangle position vs. time constructed in the same manner as figure 4.4.1.11 show a linear region, figure 4.4.2.7. This is unexpected as the chain is not in an extended configuration due to the presence of the tangle which introduces a bend in the chain. A plot of the migration rate of the tangle vs. the centre channel velocity is shown in figure 4.4.2.8. The migration rate seems to have a linear dependence on the centre channel velocity with a slope of $1.37 \pm 0.17$ and an intercept of $-27.5 \pm 1.7$ m/s. Although the slope of the plot is greater than unity, which suggests that the tangle migration rate increases faster than the velocity of the fluid increases, the negative value of the intercept ensures that the migration rate of the tangle is lower than the fluid velocity over the range of flow rates examined by these simulations. It would appear that due to the two helices remaining close to each other, there is an additional impediment to the motion of the tangle. However, as the flow rate increases, the slippage of the
tangle increases and the migration rate approaches the fluid velocity. Thus the tangle shows weak tangle behavior in the channel spanning configuration, just as it did in the parallel configuration.

![Plot of Tangle Position Along End to End Vector Vs. Time](image)

**Figure 4.4.2.** 7 Plot of the tangle position along the end to end vector vs. time, for a simulation with a flow rate of $2.03 \times 10^8$ particles/ns (slip velocity of $13.6 \pm 1.5$ m/s, shear rate of $13.6 \pm 1.4$ ns$^{-1}$). The granny knot unties itself at 1.2 ns and the four crossing tangle is untied at 1.25 ns.
Figure 4.4.2. 8 The rate of tangle migration vs. the centre channel velocity for the granny knot tied in the channel spanning configuration. The data seem to follow a linear trend with a slope of $1.37 \pm 0.17$ and an intercept of $-27.5 \pm 1.7$ m/s.

4.5 Conclusions

The results presented in this chapter are the first studies of the effect of channel flow on the unknotting of polymer chains. Simulations were conducted on the overhand knot (which when tied in a closed component is the $3_1$, or trefoil, knot) and the granny knot (which when tied as a two component link is the $6_1^2$ link) that were tethered to the wall of a $20 \times 20 \times 100$nm square cross-section nanochannels to examine the effect of a pressure-driven channel flow on the process of untangling for these knots. The former was used to study the dynamics of entanglements within polymer chains, while the latter was used to study the dynamics of
entanglements between polymer chains. The granny knot was used in two configurations between two parallel chains and between two chains that span the channel. These tangles were chosen as they had the simplest representations as single component and multicomponent mathematical knots and links while still being functional knots.

The results for the overhand knot indicated that there were two mechanisms by which this single component tangle unties. At low flow rates, \( Q < (4.7 \pm 0.2) \times 10^7 \) particles/ns, where the flow field was too weak to orient the polymer chain, the polymer unties by the end of the chain migrating through the loop of the tangle. At higher flow rates the tangle behaves like an object entrained in the flow field and slips off of the end of the chain.

Increasing the initial size of the overhand knot decreases the time it takes for the tangle to unravel and the variance of the unknotting time for the low flow rate simulations (\( Q < 4.7 \pm 0.2 \times 10^7 \) particles/ns.) At high flow rates, the initial diameter of the tangle does not appear to have any effect on the unknotting time, as the tangle adopts a size that is dependent on the flow rate as opposed to the initial condition. For the overhand knots under high flow rate, the size of the tangle decreases linearly with the flow rate. These results for the overhand knot are consistent with the weak tangle behaviour of the Brownian motion model of Kirmizialtin and Makarov [Kirmizialtin 2008]. However, this is not an endorsement of that model as the weak tangle behaviour could be predicted by several models. The overhand knot is known to be a tangle that slips and therefore this behaviour is to be expected.

The unknotting of the granny knot was more complex because the tangle does not unknot directly to the unknot, but tends to untie one pair of crossings at a time to the four crossing two component overhand knot (when closed the \( 4_1^2 \) link) and a two crossing tangle. The granny knot was tied as two double helices on top of each other, and this structure governed the unknotting of the granny knot in the parallel chain configuration. The helices collide with each other at the beginning of the simulation and the momentum of the collision carries the helix nearest to the free end of the chain, the exterior helix, to the end of chain. Hence, starting the tangle in the parallel chain configuration, the granny knot showed a flow rate independent unknotting time. The remaining four crossing tangle unknots by mechanisms similar to its three crossing single component analogue.
For the channel spanning tangle configuration of the granny knot, the helix that was nearest to the anchor points of the chains, the interior helix, was under the greater degree of stress from the flow field, hence the interior helix did not separate from the exterior helix and the knot travelled to the end of the chain as a single structure. Unlike the parallel chain configuration, the unknotting time of the granny knot in the spanning configuration showed a linear decrease in unknotting time as the flow rate increased. For both the parallel and channel spanning tangle configurations, the unknotting time of the four crossing tangle showed a decaying exponential functional relationship, with a larger rate constant the relationship was stronger for the spanning configuration. This is unsurprising as the flow field is strongest in the centre of the channel where the tangle is located for the spanning configuration.

All of the tangles showed a linear migration of the tangle along the end to end vector of the chain. For the single component overhand knot and the granny knot in the parallel configuration this rate was consistent with the velocity of the fluid near the tangle. For the granny knot in the channel spanning configuration, the rate linearly increases towards this value as the fluid velocity increases, but it is lower for low velocity simulations. It would appear that this additional impediment to the migration of the tangle is due to the two helices of the tangle not separating during simulations, so that the tangle remains tight. This result is consistent with weak tangle behaviour. The granny knot and the intermediate tangles that it reduces to as it unravels are also known to be tangles that slip, and so weak tangle behaviour was expected for these tangles.

There was a fairly broad distribution of unknotting times for the low flow simulations and the distribution of unknotting times could not be discerned due to the computational cost. However, a model for this process has been proposed in the appendices for both the low flow rate and high flow rate unknotting mechanisms. While these are simple models and cannot be validated without many more simulations, they do provide a starting point for a more thorough exposition of the subject.

Entanglements and tangles between polymer chains are responsible for the storage modulus of mechanically entangled polymer networks and polymer layers. It is therefore vital to understand how these entanglements resolve themselves under flow conditions as polymeric networks and gels are utilized in nanoscale and microscale fluidic devices. They also act as points of
mechanical weakness in single chains and can disrupt the packing of polymer chains within a polymer melt, hence the application of these results to polymerizations in sheared or flowing solutions may provide a mechanism for limiting the formation of these entanglements. This study has taken a few tentative steps into the greater abyss of this fascinating subject. Hopefully this work will provide a suitable foundation for further exploration of the unknotting of polymers under flow conditions.
Chapter 5
Conclusions

5.1 Summary

This work has examined the effects of a pressure-driven channel flow on the configuration of a tethered polymer in a shear field through the use of a MPCD fluid. The polymer was represented by a serial string of beads connected by a FENE potential. While this polymer chain lacked the specificity of a particular polymer, it was useful for the study of the effect of the flow field on the backbone of a polymer. To study the effects of entanglements within polymers the overhand knot (the tangle equivalent of the trefoil knot or $3_1$ knot) was examined as a single component tangle and the granny knot (the tangle equivalent of the $6_2^1$ link), was used to test multicomponent tangle. The multicomponent tangles were tested in both a parallel configuration and a channel spanning configuration.

In order to simulate flow in this channel it was necessary to modify the extant DSMC source/sink algorithm to reproduce small gradient flows through the specification of the pressure. This method required the specification of the inlet velocity profile using an isothermal solution to the Navier-Stokes equation, in addition to the transverse velocity, pressure and temperature. The algorithm did prove capable of simulating small pressure gradient flows, however it required a very narrow pressure distribution at the inlet which resulted in a decrease in the system temperature and an increase in the system density.

The simulations also made use of a new adiabatic boundary condition that simulates thermally diffuse boundary conditions. It was shown that under equilibrium conditions the algorithm produces the same results as Gaussian diffusion boundary conditions and it has the same streamwise momentum accommodation as that algorithm.

The simulations revealed than under $\theta$ solvent conditions, the polymer chain extended into the direction of flow to approximately 80% of its contour length. The end of the chain also underwent aperiodic cyclic dynamics. Cyclical dynamics have been found previously for polymers in pure shear flows, and typically involve the whole chain. The combination of elongational flow and slip flow more than likely restricted the motion to the end of the chain. It
was also possible to visualize the wake produced by the polymer chain. The deviations seem to indicate that there was an area of low particle density at the end of the chain. This effect, coupled with the increased configurational space available to the end of the chain relative to the rest of chain, are the likely cause of the cyclical dynamics being restricted to this portion of the chain.

In the poor solvent simulations a different result was observed. At high flow rates the polymer assumed a metastable helix state. This state appears to be caused in part by the choice of initial condition as well as the flow field. Otherwise, the behaviour of the polymer under the poor solvent conditions is similar to the θ solvent conditions, except that the polymer assumes a collapsed globule configuration as opposed to a random coil configuration under low flow and equilibrium configurations.

The untying of polymer tangles under channel flow conditions, or shear flow conditions, have never been examined prior to this work. Due to the lack of a frame of reference, the simplest non-trivial single component tangle, the overhand knot, and functional bend, the granny knot, were chosen for simulation purposes. Unfortunately, there was a fairly broad distribution of unknotting times for the low flow simulations and the distribution of unknotting times could not be discerned. However, a model for this process has been proposed in the appendices for both the low flow rate and high flow rate unknotting mechanisms. While these are simple models and cannot be validated without many more simulations, and the inclusion of additional types of knots, they do provide a starting point for a more thorough exploration of the subject.

The single component tangles showed two mechanisms for unknotting. At low flow rates the tangle seemed to untie itself by the end of the chain diffusing through the loop of the tangle, while at high flow rates the tangle seems to reptate towards the end of the chain. Surprisingly, the rate of this reptation was consistent with the velocity of the fluid, and the tangle behaves as an object entrained in the flow field at high flow rates.

The untying of the granny knot was more complex as the tangle seemed to unravel two crossings at a time, to a four crossing tangle (the two component overhand knot) and then a two crossing tangle before completely unravelling. There were different mechanisms at work for the two configurations of the granny knot that were tested. When the tangle was tied in the parallel configuration, the granny knot would untie very quickly as the two helices that composed the
tangle separated. The remaining two component overhand knot behaved similarly to its single component counterpart and reptated towards the end of the chain. In contrast, the flow field prevented the helices from separating and the tangle reptated as a whole to the end of the chain in the channel spanning configuration.

In as much as this work has been an examination of the effect of compressible fluid flow in a nanochannel on the configuration of a tethered polymer, it has also tested the ability of the MPCD algorithm to implement this fluid and interface with the MD subsystem that formed the basis for the polymer-fluid interface. That the algorithm was capable of operating on two timescales with a MD system that changed size and shape over the course of the simulations with only minor modifications is a testament to its versatility. Hopefully this study will prove the basis for future forays into increasingly complex systems.

5.2 Future Recommendations

The primary extension of this project involves the continued examination of tangles in polymer chains. In particular, enough simulations need to be performed to determine distribution of unknotting time and the tangle migration rates. This would require thousands of simulations to be performed. The essential difficulty of this task is not computational, but rather one of human involvement in the analysis of the data. The analysis of the data sets would have to be automated to the point where no human involvement is necessary. This is a considerable undertaking, as it requires the identification of linear regions in noisy data, tangle identification based solely on algorithms, outlier detection and regression analysis on rough parameter surfaces.

Further complicating this task is the need to study strong tangles to grasp the full complexity of the effect of channel flow on tangles. The overhand knot was chosen due to its simple structure and the granny knot was chosen because it is the simplest bend that does not reduce under Reidemeister moves. However, both of these are weak tangles. As the unknotting of the granny knot indicated, more complex tangles unknot through simpler tangles; thus complicating the analysis. It would be ideal to study tangles of similar complexity to the granny knot that were stronger tangles. Physically, the reef knot and the sheet bend are considered stronger tangles than the granny knot and have a similar degree of complexity. However, in its closed form the two component reef knot reduces to the $0^2_1$ link under a series of type II Reidemeister moves and
the two component sheet bend reduces to the $2\tau^2$ under Reidemeister moves. Hence, they would not be identified by a tangle identification algorithm that uses Reidemeister moves to reduce tangle complexity prior to analysis. It may be possible to construct an algorithm that would identify these tangles, however it is more likely that more complex tangles would have to be simulated.

Another extension would be the introduction of explicit fluid-fluid interactions to the hybrid MD-MPCD algorithm within interaction range of the polymer. This would allow for the inclusion of some solvation effects and the simulation of good solvent conditions for the polymer model, without modifying the polymer bond or bead-bead potentials. This would also require that the strength of the potential between fluid particles be a function of the distance from the particle to the polymer, such that a particle transitioning from the MPCD system to the MD system would not experience a sudden strong potential. With a more complete description of the hydrodynamics, the behaviour of the polymer under $\theta$ and poor solvent conditions may be modified as well.

Finally, the work here could be extended to systems containing more than one or two polymer chains. Ideally polymer brushes and small patches of densely packed tethered polymers, could be examined to simulate the effect of multiple chains on the flow profile and the effect of flow on these chains as well.
Chapter 6
References


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Appendix A
Navier-Stokes Solution to Isothermal Compressible Flow

The Navier-Stokes equation is an effective predictor of the hydrodynamic behavior of fluids for $Kn < 0.001$ and with the use of slip boundary conditions the validity of this equation can be extended to $Kn < 0.1$. Hence, the equation provides a suitable model to contrast with the results of the MPCD simulations for channel flow and an appropriate model for the inlet velocity distribution. As the MPCD fluid has similar equilibrium properties to an ideal gas, the solution to the Navier-Stokes equation must take into account the compressibility of the fluid. In general, the Navier-Stokes equation is written in terms of the mass and momentum balance equations, but the introduction of fluid compressibility introduces the need for an equation of state and an energy balance equation.

The square channel system used in chapter 2 consists of a square channel, with the z axis serving as the direction of flow with x and y normal walls with intercepts at $x, y = \pm H/2$. The flow is driven by a head pressure. Thus the flow control parameters are the system temperature, $T$, the inlet and outlet pressure, $P_{in}$ and $P_{out}$, and the wall boundary conditions. In the absence of slip, the wall boundary condition is,

$$v_z\left(\pm \frac{H}{2}, y, z\right) = v_z\left(x, \pm \frac{H}{2}, z\right) = 0.$$

In the presence of slip, the boundary condition is given by Maxwell’s first order solution to the slip velocity [Maxwell 1879] [Arkillic 1997],

$$v_z\left(\pm \frac{H}{2}, y, z\right) = -\alpha \lambda \left| \frac{dv_z(x, y, z)}{dx} \right|_{x=\pm H/2},$$

$$v_z\left(x, \pm \frac{H}{2}, z\right) = -\alpha \lambda \left| \frac{dv_z(x, y, z)}{dy} \right|_{y=\pm H/2}.$$
where $\alpha$ is the streamwise momentum accommodation, and $\lambda$ is the mean free path length. This expression is often written in terms of the tangential momentum accommodation, $\sigma_m$, where $\alpha = (2 - \sigma_m)/\sigma_m$.

The governing equations for this system are presented below. The mass balance equation is given in its closed form as,

\[
Q = \frac{P(z)\bar{v}_z(z)H^2}{k_bT},
\]

Eqn. A.1

where $Q$ is the mass flow rate and $\bar{v}_z$ is the average fluid velocity for the channel cross-section at $z$. The momentum balance equation for a differential element of this fluid is,

\[
\tau_{zx+\Delta x} - \tau_{zx} \Delta y \Delta z + \tau_{zy+\Delta y} \Delta x \Delta z - \tau_{zy} \Delta x \Delta z - \tau_{z\bar{x}} \Delta x \Delta y + \tau_{z\bar{x}+\Delta x} \Delta x \Delta y = 0,
\]

where $\tau_{zx}$ is the shear stress acting in the $z$ direction on the $x$-normal surface (at $x = x$) of the control volume and $\tau_{zx+\Delta x}$ is the shear stress acting in the $z$ direction on the $x$-normal surface (at $x = x + \Delta x$) of the control volume. Dividing through by $\Delta x \Delta y \Delta z$ and taking the limit as $\Delta x \Delta y \Delta z \to 0$, this equation simplifies to,

\[
\frac{\partial \tau_{zx}}{\partial x} + \frac{\partial \tau_{zy}}{\partial y} + \frac{\partial P}{\partial z} = 0.
\]

Inserting Newton’s viscosity relation, $\tau_{zx} = \mu \frac{\partial \bar{v}_z}{\partial x}$, where $\mu$ is the shear viscosity, the momentum balance equation reduces to,

\[
\frac{\partial^2 \bar{v}_z}{\partial x^2} + \frac{\partial^2 \bar{v}_z}{\partial y^2} = -\frac{1}{\mu} \frac{\partial P}{\partial z} = C.
\]

Eqn. A.2
The equation of state for this fluid can be taken as the ideal gas law \( P = \rho k_B T \), where \( \rho \) is the number density of the fluid. The energy balance for this equation is,

\[
\frac{\partial}{\partial z} \left( \kappa \frac{\partial T}{\partial z} \right) + \left( \mu v_x^2 \right) \left( \frac{\partial^2 v_z}{\partial z^2} \right) + 2\mu \left( \frac{\partial v_z}{\partial z} \right)^2 + \mu \left( \frac{\partial v_z}{\partial x} \right)^2 + \mu \left( \frac{\partial v_z}{\partial y} \right)^2 = \]

\[
\frac{\partial v_z}{\partial z} \left( \rho_m h + \frac{3\rho v_z^2}{2} \right) + \rho_m v_z \frac{\partial h}{\partial z}.
\]

where \( h \) is the enthalpy of the fluid, and \( \kappa \) the thermal conductivity. This latter equation can be eliminated by an isothermal flow assumption. With this assumption, the temperature of the fluid is constant and any pressure loss within the system is converted into an expansion of fluid. As long as the channel length is relatively short there should not be a significant decrease in the fluid temperature due to isentropic expansion.

The derivation of a series solution from equations A.1, A.2 and the equation of state subject to boundary conditions is presented subsequently. It follows the solution of Shah and London [Shah 1978] for the flow of an incompressible fluid in a square channel and the partial solution of Arkilic et al [Arkillic 1997]. The goal of this derivation is to determine expressions for the pressure distribution, the fluid velocity profile as well as the Reynolds’ number, \( Re \) and the Knudsen number, \( Kn \). In the process of deriving these formulae, expressions for the flow rate, \( Q \) and the Poiseuille number, \( Po \), will also be derived. For ease of reference, the final formulae from the derivation are summarized in table A.1, where the symbols \( W = H + 2\lambda \), \( \alpha_{NS} = 256 - \pi^4 \), \( \beta_{NS} = 192 - \pi^4 \) and \( \gamma_{NS}(j) = (2j - 1)\pi/W \). The series solution converges rapidly, due to the \( (2j - 1)^3 \) term in the denominator, and, while the first 100 terms of the series were used to calculate the profiles shown in chapter 2, the solution is accurate enough for most purposes with the use of 10 terms.
Table A.1 Final Expressions from the Navier-Stokes Equation

\[
P(z) = \left( \frac{\alpha_{NS}}{\beta_{NS}} \right) \frac{6k_B T}{\sqrt{2}H\pi r^2} + \sqrt{\left( \frac{\alpha_{NS}}{\beta_{NS}} \right)^2 \frac{18k_B^2 T^2}{H^2 \pi^2 r^4} + \left( \frac{24\pi^5}{\beta_{NS}} \right) \frac{Qk_B T \mu \epsilon}{H^4} + P_m^2 + \left( \frac{\alpha_{NS}}{\beta_{NS}} \right) \frac{12k_B T P_{in}}{\sqrt{2}H\pi r^2}}
\]

Slip Eqn. A.12

\[
\sqrt{P_m - \frac{2P_0 \mu k_B T Q}{H^4}}_z
\]

No-slip Eqn. A.22

\[
V_r(x,y,z) = \frac{2W^2 P_0}{\mu \pi^5 H z} \left( \frac{P_m}{P(z)} - 1 \right) \left( \frac{\beta_{NS}}{12} \right) H \left( P(z) + P_m \right) + \alpha_{NS} \frac{k_B T}{\sqrt{2}\pi r^2}\times
\]

\[
\sum_{j=1}^{\infty} \frac{(-1)^{j-1}}{(2j-1)^3} \left( 1 - \frac{\cosh(\gamma_{NS}(j)y)}{\cosh(\gamma_{NS}(j)H/2) + \gamma_{NS}(j)\sinh(\gamma_{NS}(j)H/2)} \right) \cos(\gamma_{NS}(j)x)
\]

Slip Eqn. A.16

\[
\frac{2H^2 (P_m + P(z))}{\mu \pi^5 z} \left( \frac{P_m}{P(z)} - 1 \right) \sum_{j=1}^{\infty} \frac{(-1)^{j-1}}{(2j-1)^3} \left( 1 - \frac{\cosh((2j-1)\pi y/H)}{\cosh((2j-1)\pi y/2)} \right) \cos \left( \frac{(2j-1)\pi x}{H} \right)
\]

No-Slip Eqn. A.26

\[
Q = \frac{H^3 (P_{out} - P_m)}{2\mu \pi^5 L} \left( \frac{\beta_{NS}}{12} \right) H \left( P_{out} + P_m \right) + \frac{\alpha_{NS}}{k_B T} \right)
\]

Slip Eqn. A.13

\[
\frac{H^4 (P_m^2 - P_{out}^2)}{2P_0 \mu k_B T L}
\]

No-Slip Eqn. A.23

\[
Po = \left( \frac{W^3}{12H^3} - \frac{16W^5}{\pi^5 H^4 (W + \pi \lambda)} \right)^{-1}
\]

Slip Eqn. A.10

28.4542

Slip Eqn. A.21

\[
Re = \frac{H^2 (P(z) - P_m) - P_m H \left( P(z) + P_m \right) + \alpha_{NS}}{12k_B T \sqrt{2}\pi r^2}
\]

Slip Eqn. A.18

\[
\frac{H^3 (P_m^2 - P(z)^2)}{2P_0 \mu k_B T z}
\]

No-Slip Eqn. A.27
Due to symmetry constraints, the flow profile has to be even about the central axis of the channel in both the \( x \) and \( y \) dimensions. Hence equation A.2 can be solved using a cosine Fourier series.

\[
v_z(x, y) = \sum_{n=1,3,5,...}^{\infty} a_n(y) \cos \left( \frac{n\pi x}{W} \right).
\]

Eqn. A.3

Substituting equation A.3 into equation A.2 yields,

\[
\sum_{n=1,3,5,...}^{\infty} \left( \frac{\partial^2 a_n(y)}{\partial y^2} - \frac{n^2\pi^2}{W^2} a_n(y) \right) \cos \left( \frac{n\pi x}{W} \right) = C.
\]

Eqn. A.4

Since,

\[
\int_{-\frac{H}{2}}^{\frac{H}{2}} v_z(x, y) \cos \left( \frac{m\pi x}{W} \right) dx = \int_{-\frac{H}{2}}^{\frac{H}{2}} \sum_{n=1,3,5,...}^{\infty} a_n(y) \cos \left( \frac{n\pi x}{W} \right) \cos \left( \frac{m\pi x}{W} \right) dx = \frac{W}{2} a_m(y),
\]

equation A.4 can be simplified to,

\[
\int_{-\frac{H}{2}}^{\frac{H}{2}} \sum_{n=1,3,5,...}^{\infty} \left( \frac{\partial^2 a_n(y)}{\partial y^2} - \frac{n^2\pi^2}{W^2} a_n(y) \right) \cos \left( \frac{n\pi x}{W} \right) \cos \left( \frac{m\pi x}{W} \right) dx = C \int_{-\frac{H}{2}}^{\frac{H}{2}} \cos \left( \frac{m\pi x}{W} \right) dx
\]

\[
\frac{\partial^2 a_m(y)}{\partial y^2} - \frac{m^2\pi^2}{W^2} a_m(y) = 4C \left( \frac{m\pi}{W} \right)^{m-1}.
\]

The general solution to this equation:
\[ a_m(y) = c_1 \cosh\left(\frac{m\pi y}{W}\right) + c_2 \sinh\left(\frac{m\pi y}{W}\right) - \frac{4CW^2}{m^3 \pi^3} (-1)^{\frac{m-1}{2}}, \]  
Eqn. A.5

where \( c_1 \) and \( c_2 \) are the constants of integration. Since \( a_m(y) \) is even about \( y = 0 \), \( c_2 = 0 \). The solution of \( c_1 \) is dependent on the choice of wall boundary conditions. At this point the derivation of the solution must be handled separately for the choice of boundary condition.

### A.1 Slip solution

The second integration constant, \( c_1 \), in equation A.5, is solved using the slip boundary condition, which reduces to,

\[ a_m\left(\frac{H}{2}\right) = \alpha \left| \frac{da_m(y)}{dy} \right|_{y=H/2}, \]

as \( \alpha = 1 \) for diffusive collisions. Thus \( c_1 \) can be solved to yield,

\[ c_1 = \frac{4CW^2}{m^3 \pi^3} \left( \cosh\left(\frac{m\pi H}{2W}\right) + \frac{m\pi\lambda}{W} \right) \left( \sinh\left(\frac{m\pi H}{2W}\right) \right)^{-1}. \]

With this value of \( c_1 \), equation A.5, reduces to,

\[ a_m(y) = \frac{4CW^2}{m^3 \pi^3} \left( \cosh\left(\frac{m\pi y}{W}\right) \right) \left( \cosh\left(\frac{m\pi H}{2W}\right) + \frac{m\pi\lambda}{W} \right)^{-1} \left( \sinh\left(\frac{m\pi H}{2W}\right) \right) - 1. \]  
Eqn. A.6

Substituting equation A.6 back into equation A.3 and recalling the value of \( C \),
\[ v_z(x, y) = -\frac{4W^2}{\mu\pi^2} \left( \frac{dP}{dz} \right) \times \]

\[
\sum_{j=1}^{\infty} \left( \frac{(-1)^{j-1}}{(2j-1)^3} \right) \left\{ 1 - \frac{\cosh((2j-1)\pi y/W)}{\cosh((2j-1)\pi H/2W) + \frac{(2j-1)\pi \lambda}{W} |\sinh((2j-1)\pi H/2W)|} \right\} \cos \left( \frac{(2j-1)\pi x}{W} \right). \text{ Eqn A.7} \]

Thus far, the derivation has ignored the definition of \( W \). This is defined by the slip boundary condition, \( v \left( \frac{H}{2}, y \right) = -\alpha \frac{\mu \lambda}{\pi} \frac{d v_z(x, y)}{dx} \bigg|_{x=H/2} \), or,

\[
\sum_{j=1}^{\infty} \left( \frac{(-1)^{j-1}}{(2j-1)^3} \right) \left\{ 1 - \frac{\cosh((2j-1)\pi y/W)}{\cosh((2j-1)\pi H/2W) + \frac{(2j-1)\pi \lambda}{W} |\sinh((2j-1)\pi H/2W)|} \right\} \cos \left( \frac{(2j-1)\pi H}{2W} \right) =
\]

\[
\frac{\pi \lambda}{W} \sum_{j=1}^{\infty} \left( \frac{(-1)^{j-1}}{(2j-1)^3} \right) \left\{ 1 - \frac{\cosh((2j-1)\pi y/W)}{\cosh((2j-1)\pi H/2W) + \frac{(2j-1)\pi \lambda}{W} |\sinh((2j-1)\pi H/2W)|} \right\} \sin \left( \frac{(2j-1)\pi H}{2W} \right). \]

Solving this equation for only the first term yields,

\[ W \cot \left( \frac{\pi H}{2W} \right) = \pi \lambda, \]

Expanding the cotangent around \( \pi/2 \),

\[ W \left( \frac{W - H}{W} \right) \frac{\pi}{2} + \frac{1}{3} \left( \frac{W - H}{W} \right)^3 \left( \frac{\pi}{2} \right)^3 + \ldots = \pi \lambda. \]

Hence for \( W - H << W, W \approx H + 2\lambda \).

Using equation A.7, the average velocity is:

\[ \bar{v} = \frac{1}{H^2} \int_{-H/2}^{H/2} \int_{-H/2}^{H/2} v_z(x, y) \, dx \, dy, \]

\[ \bar{v} = -\frac{8W^3}{\mu\pi^3 H^2} \left( \frac{dP}{dz} \right) \sum_{j=1}^{\infty} \left( \frac{(-1)^{j-1}}{(2j-1)^3} \right) \left\{ H - \frac{2W}{(2j-1)\pi} \right\} \frac{1}{\cosh((2j-1)\pi H/2W) + \frac{(2j-1)\pi \lambda}{W}} \sin \left( \frac{(2j-1)\pi H}{2W} \right). \text{ Eqn A.8} \]

From equation A.8 the Poiseuille number is:
\[ P_0 = -\frac{H^2}{\bar{v} \mu} \left( \frac{dP}{dz} \right) \]

\[ = \frac{\pi^4 H^4}{8W^3} \left( \sum_{j=1}^{\infty} \frac{1}{(2j-1)^4} \left( H - \frac{2W}{(2j-1)\pi} \right) \frac{1}{\cosh((2j-1)\pi H/W) + (2j-1)\pi \lambda/W} \sin\left( (2j-1)\pi H/2W \right) \right)^{-1} \text{. Eqn. A.9} \]

To simplify this expression further assume, that \( H >> 2\lambda \), such that \( H \approx W \) and the transcendental functions can be eliminated and the summation performed.

\[ P_0 = \frac{\pi^4 H^4}{8W^3} \left( \sum_{j=1}^{\infty} \frac{1}{(2j-1)^4} \left( H - \frac{2W}{(2j-1)\pi} \right) \frac{1}{1 + (2j-1)\pi \lambda/W} \right)^{-1} \]

\[ = \frac{\pi^4 H^4}{8W^3} \left( H \sum_{j=1}^{\infty} \frac{1}{(2j-1)^4} \cdot \frac{2W}{\pi} \sum_{j=1}^{\infty} \frac{1}{(2j-1)^3} \left( \frac{1}{1 + (2j-1)\pi \lambda/W} \right) \right)^{-1} \text{.} \]

This first summation term, \( \sum_{j=1}^{\infty} \frac{1}{(2j-1)^4} = \frac{\pi^4}{96} \), and the second term converges so rapidly that it can be approximated by its first term (accurate to 2 decimal places). Hence,

\[ P_0 = \frac{\pi^4 H^4}{8W^3} \left( H \frac{\pi^4}{96} \cdot \frac{2W^2}{\pi} \left( \frac{1}{H + (2 + \pi) \lambda} \right) \right)^{-1} \]

\[ = \left( \frac{W^3}{12H^3} - \frac{16W^5}{\pi^5 H^4} \left( \frac{1}{H + (2 + \pi) \lambda} \right) \right)^{-1} \text{. Eqn. A.10} \]

Substituting this definition of \( P_0 \) back into equation A.1 yields the differential equation,

\[ \bar{v} c = -\frac{H^2}{P_0 \mu} \left( \frac{dP}{dz} \right) = \frac{k_b TQ}{PH^2} \text{. Eqn. A.11} \]

Inserting the definition of \( P_0 \), yields,

\[ \left( \frac{16(H + 2\lambda)^5 P}{H^2 \pi^5 \mu} \left( \frac{1}{H + (2 + \pi) \lambda} \right) - \frac{(H + 2\lambda)^3 P}{12\mu H} \right) \left( \frac{dP}{dz} \right) = \frac{k_b TQ}{H^2} \text{.} \]
Expanding this expression up to terms of \( \lambda \) and, assuming \( \frac{H + 2\lambda}{H + (2 + \pi)\lambda} \approx 1 \), this equation reduces to,

\[
\left( \frac{16H^3 + 8\lambda H}{\pi^5 \mu} \right) P - \left( \frac{H^2 + 6\lambda H}{12 \mu} \right) \left( \frac{dP}{dz} \right) = \frac{k_B T Q}{H^2}.
\]

Inserting the definition \( \lambda = \frac{k_B T}{\sqrt{2\pi^3} \mu} \),

\[
\left( \frac{192 - \pi^5}{12\pi^2} \right) H^4 P + \left( \frac{256 - \pi^5}{2\pi^5} \right) \frac{H^3 P}{\sqrt{2\mu \pi^2}} \left( \frac{dP}{dz} \right) = Q.
\]

Solving this equation for the pressure yields,

\[
\left( \frac{192 - \pi^5}{24\pi^5} \right) H^4 P^2 + \left( \frac{256 - \pi^5}{2\pi^5} \right) \frac{H^3 P}{\mu \pi \sqrt{2\pi^2}} = Q
\]

\[
P(z)^3 + \left( \frac{256 - \pi^5}{192 - \pi^5} \right) 12k_B TP(z) = \left( \frac{24\pi^5}{192 - \pi^5} \right) \frac{Qk_B T \mu \varepsilon}{H^4} + P^2 + \left( \frac{256 - \pi^5}{192 - \pi^5} \right) \frac{12k_BT P_{in}}{\sqrt{2\pi^2}}.
\]

Thus,

\[
P(z) = -\left( \frac{256 - \pi^5}{192 - \pi^5} \right) \frac{6k_B T}{\sqrt{2\pi^2}} \frac{12k_B TP(z)}{192 - \pi^5}
\]

\[
+ \sqrt{\left( \frac{256 - \pi^5}{192 - \pi^5} \right)^2 \frac{18k_B^2 T^2}{H^2 \pi^2 \mu^4} + \left( \frac{24\pi^5}{192 - \pi^5} \right) \frac{Qk_B T \mu \varepsilon}{H^4} + P^2 + \left( \frac{256 - \pi^5}{192 - \pi^5} \right) \frac{12k_B TP_{in}}{\sqrt{2\pi^2}}}. \tag{Eqn. A.12}
\]

Utilizing this expression, the flow rate and average velocity can also be solved to yield,

\[
Q = \frac{H^3 (P_{in} - P_{out})}{2\mu \pi^5 L} \left( \frac{\pi^5 - 192}{12} \right) \frac{H(P_{out} + P_{in})}{k_B T} + \frac{\pi^5 - 256}{\sqrt{2\pi^2}} \right), \tag{Eqn. A.13}
\]

and
\[ \bar{v}_z = \frac{H}{2\mu \pi^3 z} \left( \frac{P_{in}}{P(z)} - 1 \right) \left( \frac{\pi^5 - 192}{12} \right) H(P(z) + P_{in}) + \left( \frac{\pi^5}{12} - 256 \right) \frac{k_B T}{\sqrt{2\pi r^2}} \]  
\text{Eqn. A.14}

Hence,

\[ \left( \frac{dP}{dz} \right) = -\frac{P_o}{2H\pi^5 z} \left( \frac{P_{in}}{P(z)} - 1 \right) \left( \frac{\pi^5 - 192}{12} \right) H(P(z) + P_{in}) + \left( \frac{\pi^5}{12} - 256 \right) \frac{k_B T}{\sqrt{2\pi r^2}} \]  
\text{Eqn. A.15}

Putting this definition back into equation A.9, yields this final expression for the velocity profile,

\[ v_x(x, y, z) = \frac{2(H + 2\lambda)^2}{\mu \pi^3 H z} \left( \frac{P_{in}}{P(z)} - 1 \right) \left( \frac{\pi^5 - 192}{12} \right) H(P(z) + P_{in}) + \left( \frac{\pi^5}{12} - 256 \right) \frac{k_B T}{\sqrt{2\pi r^2}} \times \]

\[ \sum_{j=1}^{\infty} \left( \frac{-1}{2(j - 1)} \right)^j \left( 1 - \frac{\cosh((2j - 1)\pi y / (H + 2\lambda))}{\cosh((2j - 1)\pi H / (H + 2\lambda)) + \frac{(2j - 1)\pi H}{(H + 2\lambda)} \sinh((2j - 1)\pi H / (H + 2\lambda))} \right) \cos \left( \frac{(2j - 1)\pi x}{H + 2\lambda} \right) \text{Eqn A.16} \]

The Reynolds number can be written as,

\[ Re = \rho \bar{v}_z D = \frac{Q}{H \mu} \]  
\text{Eqn. A.17}

Utilizing the results of equation A.13, the Reynolds number can be written as

\[ Re(z) = \frac{H^2}{2\mu^2 \pi^5 z} \left( P_{in} - P(z) \right) \left( \frac{\pi^5 - 192}{12} \right) H(P(z) + P_{in}) + \frac{\pi^5}{12} - 256 \right) \frac{k_B T}{\sqrt{2\pi r^2}} \]  
\text{Eqn. A.18}

The characteristic length for the system for the Knudsen number,

\[ D(z) = \rho \left( \frac{\partial \rho}{\partial z} \right)^{-1} = \frac{P}{k_B T} \left( \frac{1}{k_B T} \frac{\partial P}{\partial z} \right)^{-1} = \left( \frac{1}{P} \frac{\partial P}{\partial z} \right)^{-1} \]

\[ D(z) = \frac{2\pi^5 z H P(z)^2}{Po} \left( \frac{1}{P(z) - P_{in}} \right) \left( \frac{\pi^5 - 192}{12} \right) H(P(z) + P_{in}) + \left( \frac{\pi^5}{12} - 256 \right) \frac{k_B T}{\sqrt{2\pi r^2}} \]  

\text{Eqn. A.16}
Hence, the Knudsen Number can be written as,

$$\text{Kn}(z) = \frac{\lambda}{D} = \frac{k_B T \rho_0}{2\sqrt{2} H \pi^\frac{3}{2} r^2 z P(z)} \left( \frac{P_z}{P(z)} - 1 \right) \left( \frac{\pi^3 - 192}{12} \right) \left( 1 + \frac{P_m}{P(z)} \right) + \left( \pi^3 - 256 \right) \frac{k_B T}{\sqrt{2} \pi r^2 P(z)}, \quad \text{Eqn. A.19}$$

A.2 Non-Slip Solution

Application of the non-slip boundary condition, \( v_z(\pm \frac{H}{2}, y) = 0 \), to equation A.3, dictates that \( W = H \). Similarly the second integration constant, \( c_1 \), in equation A.5, is solved using the boundary condition,

$$a_m \left( \pm \frac{H}{2} \right) = 0,$$

Thus \( c_1 \) can be solved to yield,

$$c_1 = \frac{4CH^2}{m^3 \pi^3} \left( -1 \right)^{\frac{m-1}{2}} \text{COSH} \left( \frac{m\pi}{2} \right).$$

With this value for \( c_1 \) equation A.5, reduces to,

$$a_m(y) = \frac{4CH^2}{m^3 \pi^3} \left( -1 \right)^{\frac{m-1}{2}} \left( \frac{\text{cosh}(m\pi y/H)}{\text{cosh}(m\pi/2)} - 1 \right).$$

Substituting this equation back into equation A.3 and recalling the value of \( C \),

$$v_z(x, y) = -\frac{4H^2}{\mu \pi^3} \left( \frac{dP}{dz} \right) \sum_{j=1}^\infty \left( -1 \right)^{j-1} \left( 1 - \frac{\text{cosh}\left( (2j-1)\pi y / H \right)}{\text{cosh}\left( (2j-1)\pi / 2 \right)} \right) \cos \left( \frac{(2j-1)\pi x}{H} \right). \quad \text{Eqn. A.20}$$

Using this equation, the average velocity is:
\[ \bar{v} = \frac{1}{H^2} \int_{-H/2}^{H/2} \int_{-H/2}^{H/2} v_x(x, y) dx dy. \]  

\[ \bar{v} = -\frac{16H^3}{\mu \pi^5} \left( \frac{dP}{dz} \right) \left( \frac{\pi}{2} \sum_{j=1}^{\infty} \frac{1}{(2j-1)^2} - \sum_{j=1}^{\infty} \frac{\tanh((2j-1)\pi/2)}{(2j-1)^2} \right). \]

From this equation the Poiseuille number is:

\[ P_o = \frac{\pi^5}{16} \left( \frac{\pi}{2} \sum_{j=1}^{\infty} \frac{1}{(2j-1)^2} - \sum_{j=1}^{\infty} \frac{\tanh((2j-1)\pi/2)}{(2j-1)^2} \right)^4 \approx 28.4542. \quad \text{Eqn. A.21} \]

As \( P_o \) is a constant, equation A.11 becomes,

\[ P \left( \frac{dP}{dz} \right) = -\frac{P_o \mu k_b T Q}{H^4}. \]

Thus,

\[ P(z) = \sqrt{P_{in}^2 - \frac{2P_o \mu k_b T Q}{H^4} z}. \quad \text{Eqn. A.22} \]

Utilizing this expression the flow rate and average velocity can also be solved to yield,

\[ Q = \frac{H^4 \left( P_{in}^2 - P_{out}^2 \right)}{2P_o \mu k_b T L}, \quad \text{Eqn. A.23} \]

and

\[ \bar{v}_z = \frac{H^2 (P_{in} + P(z))}{2P_o \mu \varepsilon} \left( \frac{P_{in}}{P(z)} - 1 \right). \quad \text{Eqn. A.24} \]

Finally the pressure gradient becomes,

\[ \left( \frac{dP}{dz} \right) = \frac{(P_{in} + P(z))}{2z} \left( 1 - \frac{P_{in}}{P(z)} \right). \quad \text{Eqn. A.25} \]
Putting this definition back into equation A.20, yields this final expression for the velocity profile,

\[
v_z(x, y, z) = \frac{2H^2(P_m + P(z))}{\mu \pi^2 z} \left( \frac{P_m}{P(z)} - 1 \right) \sum_{j=1}^{\infty} \left( \frac{1}{2j-1} \right) \left( -1 \right)^{j-1} \left( 1 - \frac{\cosh((2j-1)\pi y/H)}{\cosh((2j-1)\pi y/2)} \right) \cos \left( \frac{(2j-1)\pi x}{H} \right). \tag{Eqn A.26}
\]

Utilizing the results of equation A.23 in equation A.17 the Reynolds number is,

\[
Re(z) = \frac{H^3(P_m^2 - P(z)^2)}{2P_0 \mu^2 k_b T z}.
\tag{Eqn. A.27}
\]

The characteristic length for the system for the Knudsen number,

\[
D(z) = \frac{2z P(z)^2}{(P_m^2 - P(z)^2)}.
\]

Hence, the Knudsen Number can be written as,

\[
Kn(z) = \frac{k_b T (P_m^2 - P(z)^2)}{2\sqrt{2\pi \varepsilon} r^2 P(z)^3}.
\tag{Eqn A.28}
\]
Appendix B
Brownian Diffusion model of a Particle to a Disk

A simple Brownian model for the free diffusion of a particle to a disk was used to simulate the unknotting of the overhand knot under simulations where \( Q < 4.7 \pm 0.2 \times 10^7 \) particles/ns. The flow field was too weak in these simulations to orient the tangle and the polymer unknotted itself by the diffusion of the end of the chain through the loop of the tangle. Abstracting the aperture of the loop to a planar disk and replacing the end of the chain with a single particle, the unknotting process can be approximated by the free diffusion of the particle to the disk. This system is shown schematically below in figure B.1

![Diagram of initial position of particle and disk](image)

**Figure B. 1** The initial position of the particle and the disk for the Brownian motion model. 

\( R_d \) is the radius of the disk and \( d_d \) is the distance from the disk to the particle.

The stochastic differential equation for the velocity, \( \mathbf{v} \), of the particle in the diffusion model can be written as,
\[
\frac{dv}{dt} = -\zeta \mu v + A(t), \quad \text{Eqn. B.1}
\]

where \( \zeta \mu = \frac{6\pi \mu r}{m} \) is the dissipative (viscous) force, \( r \) is the radius of the particle, \( m \) is the mass of the particle and \( \mu \) is the viscosity of the surrounding fluid and \( A(t) \) is a Gaussian random force with zero mean and \( \int_{-\infty}^{\infty} \langle A(t) \cdot A(0) \rangle dt = \frac{6k_BT \zeta \mu}{m} \). For the stochastic ODE given in equation B.1, the probability distribution of a particle being at position \( q \) at time \( t \), given that it was at position \( q_0 \) and \( v_o \) at \( t = 0 \) is [McQuarrie 2000],

\[
W(q,t;q_0,v_0) = \left( \frac{m\zeta^2}{2\pi k_BT(2\zeta t + 3 + 4e^{-\zeta t} - e^{-2\zeta t})} \right)^{3/2} \exp \left( -\frac{m\zeta^2}{2k_BT(2\zeta t + 3 + 4e^{-\zeta t} - e^{-2\zeta t})} |q - q_0 - \zeta^{-1}v_0(1 - e^{-\zeta t})|^2 \right). \quad \text{Eqn. B.2}
\]

Letting \( q_0 = (0,0,0) \) and assuming that \( v_0 \) has a Maxwell-Boltzmann distribution, the effect of the initial velocity can be averaged out of eqn. B 2 to yield an expression that is only a function of \( q \) and \( t \),

\[
W(q,t) = \int_{-\infty}^{\infty} \left( \frac{m\zeta^2}{2\pi k_BT(2\zeta t + 3 + 4e^{-\zeta t} - e^{-2\zeta t})} \right)^{3/2} \exp \left( -\frac{m\zeta^2}{2k_BT(2\zeta t + 3 + 4e^{-\zeta t} - e^{-2\zeta t})} |q - q_0 - \zeta^{-1}v_0(1 - e^{-\zeta t})|^2 \right) \exp \left( -\frac{mv_o^2}{2k_BT} \right) dv_0 dv_o dv_o.
\]

This equation reduces to,

\[
W(q,t) = \left( \frac{m\zeta^2}{4\pi k_BT(2\zeta_t - 1 + e^{-2\zeta t})} \right)^{3/2} \exp \left( -\frac{m\zeta^2}{4k_BT(2\zeta t + 3 + 4e^{-\zeta t} - e^{-2\zeta t})} q^2 \right).
\]

Converting \( q \) to cylindrical coordinates and integrating it over the planar disk, yields a distribution for the particle being in the disk at time \( t \), subject to renormalization,

\[
W(t) = \left( \frac{m\zeta^2}{4\pi k_BT(2\zeta_t - 1 + e^{-2\zeta t})} \right)^{3/2} \left( \frac{2\zeta_t - 3 + 4e^{-\zeta t} - e^{-2\zeta t}}{2\zeta_t - 3 + 2e^{-\zeta t}} \right) \exp \left( -\gamma_b d^2 \left[ 1 - \exp \left( -\gamma_b R_d^2 \right) \right] \right). \quad \text{Eqn. B.3}
\]
Equation B.3 is the probability density of the particle being at the disk at time $t$. The first passage time probability density, $W_f(t)$, can be calculated from this distribution by subtracting the probability that a particle that diffused to the disk at some time $\tau < t$, is still in the disk at time $t$, 

$$W_f(t) = W(t) - \int_0^t W(\tau) U(t-\tau) d\tau,$$

**Eqn. B.4**

where $U(\tau)$ is the probability that the particle is in the disk at $t = \tau$, given that it was also in the disk at time $t = 0$. This can be calculated from Eqn. B.2, 

$$U(\tau) = \left( \frac{m \zeta^2}{4 \pi k_B T (\zeta^2 \tau - 1 + e^{-\zeta \tau})} \right)^{\frac{1}{2}} \times \int \int \int \int \exp \left( -\gamma_B \left( (q_x - q_{x_0})^2 + (q_y - q_{y_0})^2 \right) \right) dq_x dq_{x_0} dq_y dq_{y_0}.$$

**Eqn. B.5**

While two of these integrals can be performed, the expression for $U(\tau)$ has to be solved numerically. The distribution calculated from equation B.4 is very similar to equation B.3.

It should be noted that this distribution does not consider the direction from which the particle contacts the disk. For short times, most of the crossings should be in the direction which would untie the knot. However, at long times the particle would have an equal chance of passing from above as from below. This model also does not consider the effect of the rest of the chain on the diffusion of the bead. The rest of the chain would restrict the phase space available to the chain and accelerate the unknotting process. Hence, this model will over predict the unknotting time and have a longer tail than the real unknotting distribution. The first passage time distribution from eqn. B.4 is shown in figure 4.4.1.7, where it is used to predict the effect of initial tangle size on the unknotting of a overhand knot under low flow rate simulations.
Appendix C  
Brownian Diffusion model for tangle in a Shear Field

In section 4.2.3 the model of Kirmizialtin and Makarov [Kirmizialtin 2008] was introduced to describe the unknotting of a tangle under uniaxial tension. In this model the process of unknotting was modeled as a particle within a constant force field moving along a corrugated potential. Starting with a 1-dimensional stochastic differential equation of the form,

$$\eta \frac{dx}{dt} = -\frac{dV(x)}{dx} + \xi(t).$$  \hspace{1cm} \text{Eqn. C.1}$$

where $x$ is the location of the tangle on the chain, $\eta$ is intrinsic viscosity of the medium and $\xi(t)$ is a random Brownian force, with

$$\langle \xi(t) \rangle = 0$$
$$\langle \xi(t) \cdot \xi(\tau) \rangle = 2\eta k_B T \delta(t - \tau).$$

and $V(x)$ is the potential surface that the tangle has to travel along as it unties. For the Kirmizialtin model the potential has the form of $V(x) = F d_k \sin(2\pi x/a) - Fx$, where $a$ is the bond length of the polymer and $d_k$ is a scaling parameter for this model. The force, $F$, on the end of the chain provides the motive force for the tangle hence the potential should contain a $-Fx$ term for the work done to move the chain. However, the force should also tighten the tangle providing resistance to the movement of the chain. As the tightened tangle moves along the surface of the chain, it encounters resistance similar to sliding a rubber washer along a string of beads; as the bead moves through the tightest part of the washer the potential increases to a maximum and as the bead passes and the string sits in the centre of the washer the potential reaches a minimum. Hence a corrugated potential was chosen to model this resistance to movement.

Analyzing this model, it becomes apparent that two kinds of behavior can be expected from this model depending on whether there were stationary points for the distribution or not; i.e. if
\[ d \geq a/(2\pi) \text{ or } d < a/(2\pi). \] If there are stationary points, then as the force is increased the tangle tightens until it cannot move and the unknotting time increases with increasing force. Such behavior is termed strong tangle behavior. If there are no stationary points, the tangle behaves as if there is no retarding potential as the force is increased and the unknotting time decreases with increasing force, this is termed weak tangle behavior.

For a tangle in a shear field this model must be modified. While the potential giving rise to the work done to move the tangle along the chain, the \(-Fx\) term, remains, the form of the corrugated potential must be changed. If the tightness of the tangle is a linear function of the force exerted on the segment of chain between the tangle and the end of the chain, then, as the shear field exerts a force on each bead in the chain, the strength of the corrugated potential should be dependent on the number of beads between the tangle and the end of the chain. Thus, the potential should have the form,

\[ V(x) = F\alpha_k \left(1 - \frac{x}{L}\right) \sin\left(\frac{2\pi x}{a}\right) - Fx, \quad \text{Eqn. C.2} \]

where \(\alpha_k\) is an adjustable parameter and \(L\) is the length of the chain. This potential has a derivative of,

\[ \frac{dV(x)}{dx} = \frac{2\pi Fa\alpha_k}{a} \left(1 - \frac{x}{L}\right) \cos\left(\frac{2\pi x}{a}\right) - \frac{F\alpha_k}{L} \sin\left(\frac{2\pi x}{a}\right) - F. \quad \text{Eqn. C.3} \]

Hence equation B.1, becomes,

\[ \eta \frac{dx}{dt} = \frac{Fa\alpha_k}{L} \left( \frac{L}{\alpha_k} - \frac{2\pi}{a} (L - x) \cos\left(\frac{2\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right) \right) + \xi(t). \quad \text{Eqn. C.4} \]

If the stochastic component of this ODE is neglected then the solution can be found by a series expansion of the solution about its stationary points. The stationary points of the equation are the points where:

\[ \frac{L}{\alpha_k} = \frac{2\pi}{a} (L - x) \cos\left(\frac{2\pi x}{a}\right) - \sin\left(\frac{2\pi x}{a}\right). \]
This expression reduces to,

\[ \cos \left( \frac{2\pi x}{a} \right) = \frac{2\pi L}{a\alpha_k} \left( \frac{2\pi}{a} \right) \left( L - x \right)^2 + 1 - \frac{L^2}{\alpha_k^2} \left( \frac{2\pi}{a} \right)^2 + 1. \]  

Eqn. C.5

For \( x << L \), equation C.5 simplifies to.

\[ x = \frac{a}{2\pi} \arccos \left( \frac{2\pi L^2}{a\alpha_k} \pm \left( \frac{2\pi}{a} \right)^2 + 1 - \frac{L^2}{\alpha_k^2} \left( \frac{2\pi}{a} \right)^2 + 1 \right). \]

From this equation it becomes apparent that for the stationary points of the system to be real,

\[ \alpha_k > L \left( \frac{2\pi}{a} \right)^2 \left( L - x \right)^2 + 1 \]

Eqn. C.6

Thus as the tangle reaches the end of the chain, the probability of a stationary point occurring decreases and a tangle that exhibits strong tangle behavior under uniaxial tension would be expected to slip. If there are no stationary points, the corrugated portion of the potential has little effect on the simulation and the Brownian motion can be roughly modeled by [Reimann 2002],

\[ \eta \frac{dx}{dt} = -\frac{1}{a} \int_0^a dV(x) dx + \xi(t) \]

\[ = F + \xi(t), \]

with the solution,

\[ x - x_o = \frac{F}{\eta} t + \frac{1}{\eta} \int_0^t \xi(t). \]

The \( i^{th} \) moment of the first passage time distribution for a 1 dimensional Brownian motion model is [Reimann 2001],
\[
f_i(x_0, x_1) = \frac{i\eta}{k_B T} \left( \frac{\partial}{\partial x} \int_{x_0}^{x_1} e^{\frac{v(x)}{k_B T}} \left( \int_{-\infty}^{y} f_{i-1}(y, x_1) e^{\frac{v(y)}{k_B T}} dy \right) dx \right),
\]

where, \(x_0\) is the initial location of the particle, \(x_1\) is its final location and \(f_0(x_0, x_1) = 1\). Thus the first two moments of equation C.4. are:

\[
f_1(x_0, x_1) = \frac{\eta(x_1 - x_0)}{F},
\]

\[
f_2(x_0, x_1) = \left( \frac{\eta}{F} \right)^2 \left( x_1 - x_0 \left[ \frac{2k_B T}{F} + (x_1 - x_0) \right] \right).
\]

The displacement rate, \(\langle \dot{x}(t) \rangle\), and Rousian diffusion coefficient, \(D_R\), can be calculated from these moments [Reimann 2001],

\[
\langle \dot{x}(t) \rangle = \frac{L}{f_1(x_0, L + x_0)},
\]

\[
D_R = \frac{L^2 \left( f_2(x_0, L + x_0) - f_1(x_0, L + x_0)^2 \right)}{2f_1(x_0, L + x_0)^3}.
\]

Thus, for equation C.4, the displacement rate and Rousian diffusion coefficient are

\[
\langle \dot{x}(t) \rangle = \frac{F}{\eta}, \quad \text{Eqn. C.7}
\]

and

\[
D_R = \frac{k_B T}{\eta}. \quad \text{Eqn. C.8}
\]

As equation C.5 illustrates as long as \(\alpha \leq L\) there will be a point along \(x\) where there are no more stationary points and the regime described above will manifest.

When there are stationary points, the corrugated potential must be considered. The series expansion of the solution can be expressed as,
\[ x(t,x_o) = x_o + \frac{dx}{dt} \bigg|_{t=0} t + \frac{d^2x}{dt^2} \bigg|_{t=0} \frac{t^2}{2} + \frac{d^3x}{dt^3} \bigg|_{t=0} \frac{t^3}{6} + \ldots \]

\[ = a_o + a_1t + a_2 \frac{t^2}{2} + a_3 \frac{t^3}{2} + \ldots \]

As equation C.4 is a first order differential equation, the terms of the series can be evaluated by differentiating it, hence,

\[ a_o = x_o \]

\[ a_1 = F \left( 1 - \frac{2\pi \alpha_k}{a} \left( 1 - \frac{x_o}{L} \right) \cos \left( \frac{2\pi x_o}{a} \right) + \frac{\alpha_k}{L} \sin \left( \frac{2\pi x_o}{a} \right) \right) + \xi(0) \]

\[ a_2 = \frac{2\pi F \alpha_k}{a} \left( \frac{2\pi}{a} \left( 1 - \frac{x_o}{L} \right) \sin \left( \frac{2\pi x_o}{a} \right) + \frac{2}{L} \cos \left( \frac{2\pi x_o}{a} \right) \right) a_1 + \frac{d\xi(0)}{dt} \]

\[ a_3 = F \alpha_k \left( \frac{2\pi}{a} \right)^2 \left( \frac{2\pi}{a} \left( 1 - \frac{x_o}{L} \right) \cos \left( \frac{2\pi x_o}{a} \right) - \frac{3}{L} \sin \left( \frac{2\pi x_o}{a} \right) \right) a_1 \]

\[ + F \alpha_k \left( \frac{2\pi}{a} \left( 1 - \frac{x_o}{L} \right) \sin \left( \frac{2\pi x_o}{a} \right) + \frac{2}{L} \cos \left( \frac{2\pi x_o}{a} \right) \right) a_2 + \frac{d^2\xi(0)}{dt^2} \]

A piecewise solution can be constructed from this method to predict the trajectory of the tangle until it reached a value of \( x \) for which the fixed points vanished and the solution with no stationary points could be used. However, a numerical simulation is more useful for gathering information. For a simulation where \( \alpha_k = L \left( \frac{2\pi}{a} L \right)^2 + 1 \right)^{\frac{1}{2}} \), i.e. a fixed point first appears, the first passage time distribution, displacement rate and Rousian diffusion coefficient are shown as a function of the force term in figure C.1. For \( \alpha_k \) greater than this value, the simulation rapidly becomes too computationally expensive to evaluate.
Figure C.1 The first passage time distribution, a) top, displacement rate, b) middle, and Rousian diffusion coefficient, c) bottom, for a set of simulations where

\[ \alpha_k = L \left( \frac{2 \pi}{a} L \right)^2 + 1 \right)^{-\frac{1}{2}} . \]

For these simulations, \( a \) was 0.154 nm, \( L \) was 60\( a \), \( \eta \) was 1.8268 \( \times 10^7 \) amu/nm/ns and the temperature of the simulation, \( T \), was 298.15 K.
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