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# Multi-Scale Modelling Describing Thermal Behaviour of Polymeric Materials

Scalable lattice-Boltzmann models based upon the theory of Gmela towards  
refined thermal performance prediction of polymeric materials at micro and nano  
scales

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# Abstract

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Micrometer injection moulding is a type of moulding in which moulds have geometrical design features on a micrometer scale that must be transferred to the geometry of the produced part. The difficulties encountered due to very high shear and rapid heat transfer of these systems has motivated this investigation into the fundamental mathematics behind polymer heat transfer and associated processes. The aim is to derive models for polymer dynamics, especially heat dynamics, that are considerably less approximate than the ones used at present, and to translate this into simulation and optimisation algorithms and strategies, Thereby allowing for greater control of the various polymer processing methods at micrometer scales.

Keywords: Lattice-Boltzmann, Polymer, Mathematical Model, Numerical Simulation, Extrusion, Thermal, Micro, Nano.

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# Chapter 1

## Introduction

A long time ago, in a university not so far away, it was a time of great empiricism. Scientists of Bradford University's Polymer Interdisciplinary Research Centre were busy compounding, extruding and moulding plastics and recording the results with ever more involved sensors and set ups. Amidst this process the scientists of the Micromoulding Interest Group were looking for the polymers in their very small moulds to behave better. There was perhaps a feeling that the available models good though they were, were a little lacking when applied at the micro scale. Yet, at that time the Bradford branch of the IRC put little emphasis on mathematical theory. Some time a newly graduated mathematician made a speculative enquiry about the possibility of a PhD at Bradford University, and "two and two were added together" and this PhD project was conceived.

At the time it was felt that the unusual polymeric behaviour was in no small part due to the large surface to volume ratio of the mould invalidating typical assumptions about heat transport and cooling, but the possibility was raised that unusual patterns of polymer chain orientation, that might be created by virtue of the small mould geometry's, might alter the temperature dynamics of the polymer. Concerns voiced related to issues with weak points in the moulded parts and moulds that did not completely fill.

Since no existing tractable models (we are aware of) fully incorporate polymer chain orientation into its dynamics and because there seemed no obvious way to ‘tack on’ such dynamics to something familiar, the need was felt to turn to rather more exotic and less tractable models, arguably more basic models, and “build them up” into something fit for purpose.

## 1.1 Approach

The approach was to go back to basics and investigate the mathematical theories that give rise to the more tractable models from which simulations and optimisation algorithms are constructed, and seek to derive new and more applicable models that encompass the dynamics that are of concern to us.

When the research was started it was envisaged to take a very different course than it eventually did. It was the intention that a model or models would be constructed and if they did not prove amenable to analytical treatment a combination of numerical approximation and heuristics could be used to implement an optimisation process. However, the nature of the model was such that each step suggested another analytical technique that might possibly work. Consequently this research contains a lot of comparatively complex mathematics, compared to the typical engineering project. A side effect of this is that there is a greater degree of work and imagination required to apply the theories to polymer engineering but we like to think a greater breadth and depth of application will be the result of the firm analytical basis of this work when additional work is done.

The understanding of the problem grew holistically with the research. Other contributing factors, such as the dynamics of air-polymer interfaces, turned out to be easy to express in terms of the modelling framework that was chosen. Indeed, in the easiest cases this amounted to cannibalising and perhaps slightly generalising aspects of existing models.

## 1.2 Aims and Objective

The end point is to produce models that can facilitate simulations and optimisations of micro injection moulding processes and perhaps elucidate polymer behaviour in general outside of well understood industrial processes. The desirable net result so far as the empiricists and industrialists are concerned is to work towards a good computer model that can be used to adjust aspects of manufacturing processes and experiments in computer aided design, seeking optimisation prior to real-world implementation, and of course for the empiricist to also provide simulation data to compare to actual results in order to probe the limits of the models validity.

The intention is that the model may lead to a better understanding of the more esoteric behaviour of polymers in general. Perhaps in time it will prove possible to relate some existing approximations as special cases of the theory developed and presented in this thesis.

More generally we assert that the novelty of this model can make a contribution to broadening the toolbox of techniques used to model polymeric behaviour and hope others will be able to pick up the model and apply it to unconnected areas, which is itself the philosophy adopted in its construction.

## 1.3 Overview of Thesis

In this section a rough guide is provided to the component chapters in the thesis, chapter by chapter, to facilitate a quick-and-easy parsing of the text.

**Literature Review** In this chapter we critically review a body of work relating to the thermal modelling of polymers. We cover a number of models not normally used for this purpose, that we have never the less applied, or attempted to apply, to the modelling. Importantly we also attempt to introduce the reader to some key mathematics used in seeking generalisations of models and that the reader may not be

familiar with. We shall also indicate the potential importance of these mathematical tools in relation to the “nuts and bolts” progression of the research.

**Grmela’s Equation, Seeking a Solution** In this chapter we introduce a model due to Grmela and his colleagues [1, 2] that is specifically formulated for modelling polymers. We then attempt to apply a series of mathematical techniques to simplify and derive more useable models from Grmela’s model that are more like those of conventional fluid dynamics. To do this we have to appeal to some complex mathematics towards the end of the chapter as well as developing a new mathematical tool which we can contrast and compare to a old tool for reference purposes. We then show how the application of these techniques might be used to attain the results we seek. We also construct a worked example of the technique developed to illustrate it and also to demonstrate that it does have non trivial applications.

**Seeking a Thermal Lattice Boltzmann-like Method from a Linear Grmela-like Equation** Here we show how discrete models can be derived from the model described in chapter three, and how, in principal, continuous fluid dynamic like models can be recovered from the discrete models. These derived discrete models are further developed to generalise them, introducing rules for curved boundaries, interactions with other fluids, and the reintroduction of internal potential forces within the fluid.

**Miscellaneous Investigations** In this chapter we bring together several other approaches. This chapter may be instructive to those wishing to continue this area of research. We attempt to develop a generalisation based upon a model developed by Kirkwood that allowed him to derive a continuum model by applying operators to the ensemble of all particle states. This model never quite yields the momentum conservation equation we strive for. Nevertheless there seems to be a great untapped potential nascent in their further investigation.

We also investigate a very important function (typically labelled  $W$ ) in the model of chapter three that is related to the microscopic properties of the polymers and attempt to define necessary conditions and reasonable approximations upon its form based on its physical interpretation. Considerable improvements in its form are made but not sufficient to quite suggest easy simplifications in the calculations described in chapter three.

Lastly we examine a technique based upon functional differentiation in order to develop an approximate solution to the model in chapter three.

**Conclusions** Here we set out the major results and review work that is unfinished and work that might yet be investigated. We also critically assess the work presented in the thesis and make a series of recommendations.

**Appendix A Thermal Polymer LBM Pseudocode** Here we provide pseudocode for the results derived in chapter four that can be used to develop source code proper for a polymer flow modelling package.

# Chapter 2

## Literature Review

This review of the literature will be unlike that in the typical PhD thesis. Typically one reads research papers that are closely related to the application one is concerned with then, possibly bases ones next steps upon the outcomes. The approach here has been to consistently go back to first principles with the models and mathematics that underpin the basis of the field and then seek generalisations, and sometimes, entirely new approaches. As such the literature review is not so much a catalogue of related research in the state of the art in the field upon which we intend to build, but rather a brief review of not only some of the mathematics that is basic to the study of thermal polymer melts but also of the mathematical tools called upon in seeking useful results<sup>1</sup>.

### 2.1 Micro Moulding and Polymer Fluid Dynamics

When modelling the behaviour of polymers in bulk, the most conventional method is to select a stress tensor that gives the particular type of behaviour that is expected to be important in the model and then, either by referring to records or by educated

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<sup>1</sup>Therefore we hope the reader will forgive us if it seems like we are trying to teach them to ‘suck eggs’ as we are well aware the detail here will be familiar to some.

guess work, fine tune the constants until the model starts to give reasonable answers. The key property that tends to distinguish these stress tensors from those in non-polymeric fluids is that they usually contain integrals over time. If temperature is of particular importance in the model these expressions tend to grow even more complex, as do the equations describing the dynamic change in temperature (which are often approximated otherwise). So, one is typically left with a suite of three equations: one for mass conservation, which is more or less uniform across all of physics, one for the motion of the fluid, and one for its temperature dynamics. These three examples come from Ottinger's [3] and Mashelkar's [4] books

$$\begin{aligned}\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) &= 0 \\ \frac{\partial \rho \vec{v}}{\partial t} &= -\nabla (\rho \vec{v} \vec{v}) - \nabla \cdot \pi \\ \frac{dT}{dt} &= \frac{\lambda}{c\rho} \nabla^2 T + \frac{q}{c\rho} \frac{d\beta}{dt}\end{aligned}$$

$\frac{d}{dt}$  is the total derivative and  $\pi$  is a tensor related to viscosity,  $c$  is heat capacity,  $\lambda$  is thermal conductivity, and the last term in the third equation corresponds to chemical reactions occurring in a polymer melt. It should be mentioned that in this thesis we shall, in our own calculations, define units in such a way that as many constants as possible will disappear, certain in the knowledge that they can be reasonably easily reintroduced by those with a mind to do so. This dropping of constants under the assumption that they can be absorbed with a change of units may cause equations to feel unfamiliar to some readers but be assured care was taken to ensure this was valid.

What all these equations have in common is that they are instances of, or derived from, continuity equations. A continuity equation is as much a consequence of geometry as physics, and is basically the statement that “what is in something” is the sum of everything that has been put in it minus the sum of everything that has been taken out. A “sum of things” is most naturally expressed as an integral equation

but may be re-written as a differential equation using the divergence theorem giving the expression

$$\frac{\partial \bar{A}}{\partial t} + \nabla \cdot \bar{\mathbf{B}} = 0$$

$\bar{A}$  and  $\bar{\mathbf{B}}$  are generally tensors with  $\bar{\mathbf{B}}$  having one more index than  $\bar{A}$ . So, for the mass conservation equation, we have density  $\rho$  and momentum  $\rho \vec{U}$ , respectively, for  $\bar{A}$  and  $\bar{\mathbf{B}}$ . For the momentum conservation equation we have momentum  $\rho \vec{U}$  and the expression  $\rho \vec{U} \vec{U} - \sigma$  where  $\sigma$  is the stress-strain tensor. Lastly, for energy conservation, we have energy density  $\rho E$  energy per unit volume and the energy flux  $\vec{q}$ . Clearly the choices of these unknowns, such as  $\sigma$  and  $\vec{q}$ , is hugely important to the meaningfulness and validity of these equations.

## 2.2 Multi Scale Modelling

The Reader having more familiarity with research in polymer dynamics may consider the direction chosen in this research atypical. We are aware of the very good work done by colleagues in the Universities of Leeds and Bradford in multi-scale modelling of polymers. We have made a deliberate choice to go in another direction<sup>2</sup>. Nevertheless those researchers have made great progress in applying multi-scale modelling to polymer dynamics [5] and it is instructive to say a few words here about what multi-scale modelling is and how it works so we can clearly explain how the present approach differs.

Normally a multi-scale simulation seeks to take simulation based on continuum mechanics and link it to a molecular simulation. Using conventional equations for fluid dynamics one takes a number of small characteristic regions of the fluid and performs a molecular simulation of the transformation that this region has just undergone, extracting important values that are then interpolated across the fluid

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<sup>2</sup>We very much wanted to do original research rather than rehash or tack on some minor result to the work of others. Partly because that is what we feel a PhD should be but also because that is our personal preference.



and fed back into the constitutive equation to calculate the system properties and values for next time step.

This is one way of trying to include the information contained in the molecular structure of the material with in the simulation. We chose to investigate another approach, the mesoscopic approach, where a limited amount of information about the molecular structure of the medium is added to the equations as new continuum variables.

## 2.3 Mesoscopic Physics

Equations such as Navier-Stokes, and even the Burnett equation for supersonic flows, can be derived from more fundamental equations, particularly from the equations of gas kinetics. The equations of gas kinetics are a particular type of mesoscopic equation, which is a model that has only half divorced itself from the molecular nature of the fluid and is very much based in the study of statistical mechanics. Not only are distributions over the points of space taken into account but a single statistical distribution over all of phase space describes the behaviour of the typical particle in the fluid. Such a phase space may include internal variables such as orientation and spin. In gas kinetics this produces the Boltzmann equation, and techniques, specifically the Chapman-Enskog expansion, can then be used to derive equations for mass, momentum, and heat transport. The Boltzmann equation also has a discrete analogue that is efficiently parallelized to simulate the Navier-Stokes equation. In fact it has been proved [6] that this analogue can be derived *a priori* from the Boltzmann equation. Many variations on the Boltzmann equation have been derived to study a range of phenomena so diverse that it includes t-cell proliferation and, critically, polymer dynamics.

### 2.3.1 The Boltzmann Equation

In the mid to late nineteenth century a series of scientists were beginning to develop a theory regarding the way molecular dynamics lead to the fluid and heat dynamics of gasses and diffusion phenomena that was based upon statistical mechanics. [7] One of the seminal conclusions was Boltzmann's equation [3, 8]

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_x f + \vec{f} \cdot \nabla_v f = \int \int \int W(\vec{v}'_1, \vec{v}'_2, \vec{v}, \vec{v}_2) f(\vec{v}'_1) f(\vec{v}'_2) - W(\vec{v}, \vec{v}_2, \vec{v}'_1, \vec{v}'_2) f(\vec{v}) f(\vec{v}_2) d^3 \vec{v}'_1 d^3 \vec{v}'_2 d^3 \vec{v}_2 \quad (2.1)$$

Conceptually the Boltzmann equation can be divided into two parts as shown in equation (2.1). Were the right hand set to zero, we would recover the Liouville equation that describes the way a single isolated particle (the state of which is only known statistically over phase space described by the distribution  $f(\vec{x}, \vec{v}, t)$ ) moves. The left side is essentially the total derivative of the variable  $f$  being directly proportional to force. In fact, it is acceleration.  $\vec{f}$  is generally assumed to be zero in gas dynamics. Solutions of Liouville equations describe the trajectories that a particle takes through phase space if there is nothing there for it to interact with except a force field.

The Boltzmann equation has an integral on the right hand side. Conceptually this integral represents a number of particles interacting with each other through collisions. The first term in the integral represents the potential for two particles to collide, shifting one of them into a trajectory of the solutions to the Liouville equation (and when integrated gives the rate at which this is happening). The second term encodes the possibility that a collision causes a particle to leave that trajectory. In this equation  $f$  no longer represents the statistical distribution of one particle but now describes the averaged-out density in phase space of all such particles. On analysing these terms we can see several notable assumptions:

1. That all collisions are binary, occurring between two particles;

2. that the likelihood of a collision between two states is directly proportional to the product of the distribution functions for the states. This is often called molecular chaos [9, p. 58] .

Further conditions inherent to the physics of collision dynamics are encoded into  $W$ .  $W$  has several symmetry properties relating to its physical interpretation and is typically composed of a product of a function with several Dirac delta functions that represent properties that are preserved in collisions, such as momentum and energy.

As a result of the assumption of molecular chaos it is possible to prove that this system must always adhere to the second law of thermodynamics [9, p. 73]. Boltzmann defined a functional

$$H = \int f \ln f d^3\vec{v}$$

that was directly proportional to entropy, as it happens by a negative factor<sup>3</sup>. It is possible to explicitly calculate its time derivative using the Boltzmann equation and it is subject to the condition

$$\frac{dH}{dt} \leq 0,$$

thus proving that entropy tends to a maximum.

### 2.3.2 Lattice Boltzmann Method

The lattice Boltzmann method was developed independently of the Boltzmann equation, being inspired by the work on lattice gas automation (LGA). In LGA models, space and time is discretized as well as the velocities of each particle. Each node, a unit of space, may have a finite number of states relating to the absence or presence

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<sup>3</sup>So low negative values of  $H$  equate to high positive entropy.

in that node of a particle with a given velocity. Each velocity is itself wedded to a transition to some nearby node. The simulation is a two step process. Each node ‘sends’ its particles to the appropriate nearby node. Nodes then allow the particles within them to ‘collide’. That is, the node may change its state to a new state having the same total momentum and mass based on some weighted random selection rule. Initially the node geometry, which are properly termed lattices, and the rules were such that the ‘fluid’ like behaviour of the cellular automata was very anisotropic. Later transition from square to hexagonal lattices improved this.

The lattice Boltzmann model (LBM) replaces the finite states of the nodes with a set of continuous values for each discrete velocity and a collision rule which bears remarkable similarity to the linearized Boltzmann equation.

$$f_i(\vec{x} + \vec{v}_i \Delta t, \vec{v}_i, t + \Delta t) - f_i(\vec{x}, \vec{v}_i, t) = -\frac{1}{\tau} (f_i(\vec{x}, \vec{v}_i, t) - f_i^{eq}(\vec{x}, \vec{v}_i, t)).$$

The rationale is that with each collision the distribution is nudged towards the equilibrium function, that is, the function that represents the distribution with the most entropy for a given set of properties (such as density etc). The continuous equivalent of this function will be derived a little later on in equation (2.6) but the form of the discrete version is different but related. One of the great advantages of this method is that it very easily allows us to implement boundary conditions by ‘bouncing back’ the distribution in much the same way as the LGA would bounce back an individual particle, although much more sophisticated boundary methods have been devised since. In fact it is quite difficult to implement curved boundaries intuitively but several approaches have been devised to do this and often improve the accuracy of simulations over curved surfaces [10, 11]. Unlike the LGA it is possible to simulate heat transport in a lattice Boltzmann model [12–14]. However, the numerical stability and isotropy of these models often suffers (although as with the LGA a good choice of the lattice can help). It happens that the choice of

the discrete velocities in the model deeply effects stability and isotropy and that mathematically, for constancy, certain conditions must be met by these velocities to accurately replicate momentum conservation isotropically. The conditions for accurate replication of energy conservation are more stringent still [15,16].

In fact, the choice of the form of function  $f_i^{eq}$  was originally determined largely by the type of momentum conservation equation that could be reconstructed from it. The general form used is

$$f_i^{eq} = \rho \left( A_i + B_i \vec{v}_i \cdot \vec{U} + C_i \left( \vec{v}_i \cdot \vec{U} \right)^2 + D_i U^2 \right)$$

as given in several texts [16, p. 159-160] [17, p. 1816] [18, p. 2942] [12, p. 319-320] [19, p. R15].  $A_i$ ,  $B_i$  etc are constants that may be different for different magnitudes of  $\vec{v}_i$ . By selecting these in a slightly more flexible way than a strict analogue with the continuous case would suggest more general results may be obtained that are capable of modelling viscous fluids with non ideal equations of state [12, 16–19]. Further generalisations have allowed the modelling of multiple immiscible fluids by allowing components to exert a repulsive force on each other. These same generalisations also broaden the class of fluids that may be modelled by allowing a given fluid component to exert proximity forces on itself [17, 18].

Most importantly of all, since its conception, it has since been shown that the lattice Boltzmann equation can be derived from the Boltzmann equation *a priori* by invoking some techniques from numerical integration [6]. This provides a starting point for taking any generalisation or variation of the Boltzmann equation and attempting to find a lattice equivalent. As is seen normally, doing thermal simulations using the lattice Boltzmann method leads to numerical instabilities [20] and hybrid schemes have been developed to attempt to compensate for this by modelling temperature separately, either as a ‘passive scalar’ or by invoking conventional computational fluid dynamics to model temperature and link it to the lattice

Boltzmann equation (which is still used to model flow and density). Attempts have also been made to re-formulate the lattice Boltzmann equation based on consideration of molecular dynamics to increase numerical stability [12]. However, He and Luo [6] observe that the natural derivation of a non isothermal fluid in their *a priori* technique does not neatly or properly map all velocities onto an adjacent node but rather onto the spaces between the nodes. This, to them, suggests the need for an interpolation step between the nodes. They believe that this provides “an explanation of the instability of the existing LBE thermal models” and this line of thinking was most influential in the present thinking when working on lattice Boltzmann like models in this research.

### 2.3.3 Chapman-Enskog Method

Developed by Chapman and Enskog [9] in a series of papers in the early 20th century, the Chapman-Enskog method allows a ladder of progressively better approximate solutions to the Boltzmann equation to be derived, solutions that can then be used to find progressively more complex continuity equations. The integro-differential equation is broken down into a non-linear integral equation and an infinite ‘ladder’ of linear integral equations, each recycling the results of the previous approximation, produces the next approximation. Notably, at the first (or maybe we would be better to call it the zeroth step) one acquires the Euler equations. Subsequently the Navier-Stokes, Burnett, and super Burnett equations for gases are acquired. This is achieved through expansion in a small parameter that has the same dimensions as the Knudsen number, which is why the procedure is some times called an expansion in the Knudsen number and is the rationale for it being a better approximation for fluids who’s Knudsen numbers are small. We mostly follow the working presented by Harris [8] as being easier to follow but often borrowing the notation of Ottinger [3] as being less ambiguous.

The Boltzmann equation (2.1) is modified to introduce a small parameter  $\varepsilon$

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_x f = \frac{1}{\varepsilon} \int \int \int W(\vec{v}'_1, \vec{v}'_2, \vec{v}, \vec{v}_2) f(\vec{v}'_1) f(\vec{v}'_2) - W(\vec{v}, \vec{v}_2, \vec{v}'_1, \vec{v}'_2) f(\vec{v}) f(\vec{v}_2) d^3 \vec{v}'_1 d^3 \vec{v}'_2 d^3 \vec{v}_2 \quad (2.2)$$

An ansatz for  $f$  is defined in that parameter

$$\begin{aligned} f &= f_0(\vec{v}, \rho, \vec{U}, T) + \varepsilon f_1(\vec{v}, \rho, \vec{U}, T, \nabla_{\vec{x}} \rho, \nabla_{\vec{x}} \vec{U}, \nabla_{\vec{x}} T) + \dots \\ &= \sum_{i=0}^{\infty} f_i(\vec{v}, x^{\{i\}}) \end{aligned} \quad (2.3)$$

dependence of  $f$  on time is only expressed through the variation of the spatial derivatives it takes as arguments. Because of this, the time derivative in equation (2.2) must be expanded using the chain rule

$$\frac{\partial f}{\partial t} = \frac{\partial \rho_\varepsilon}{\partial t} \frac{\partial f}{\partial \rho} + \frac{\partial U_{i,\varepsilon}}{\partial t} \frac{\partial f}{\partial U_i} + \frac{\partial T_\varepsilon}{\partial t} \frac{\partial f}{\partial T}.$$

in addition, because the time variation is inherently linked conceptually to the expansion in  $\varepsilon$  the time derivatives in this chain rule are also expansions in  $\varepsilon$  obtained by inserting expansion (2.3) into the Boltzmann equation (2.1) and applying the rule.

$$\begin{pmatrix} \rho \\ \rho \vec{U} \\ \rho E \end{pmatrix} \delta_{0i} = \int \begin{pmatrix} 1 \\ \vec{v} \\ v^2 \end{pmatrix} f_i d^3 \vec{v} \quad (2.4)$$

$E = T + \frac{1}{2} U^2$ . This extra condition defines the relationship between the mesoscopic and macroscopic systems and ensures a unique solution where otherwise many equivalent solutions could be obtained by redistributing values and terms between different  $f_i$ . This gives the following expression used to obtain time derivatives in the

chain rule:

$$\begin{pmatrix} \frac{\partial \rho_\varepsilon}{\partial t} \\ \frac{\partial \rho_\varepsilon \vec{U}_\varepsilon}{\partial t} \\ \frac{\partial \rho_\varepsilon E_\varepsilon}{\partial t} \end{pmatrix} = \int \begin{pmatrix} 1 \\ \vec{v} \\ v^2 \end{pmatrix} \int \int \int W(\vec{v}'_1, \vec{v}'_2, \vec{v}, \vec{v}_2) f(\vec{v}'_1) f(\vec{v}'_2) \\ - W(\vec{v}, \vec{v}_2, \vec{v}'_1, \vec{v}'_2) f(\vec{v}) f(\vec{v}_2) d^3 \vec{v}'_1 d^3 \vec{v}'_2 d^3 \vec{v}_2 - \begin{pmatrix} 1 \\ \vec{v} \\ v^2 \end{pmatrix} \vec{v} \cdot \nabla_x f d^3 \vec{v}$$

For our purposes this can be rearranged and truncated before the first-order terms to give

$$\begin{aligned} \frac{\partial \rho_\varepsilon}{\partial t} &= -\nabla \cdot (\rho \vec{U}) \\ \frac{\partial \vec{U}_\varepsilon}{\partial t} &= -(\vec{U} \cdot \nabla) \vec{U} - \frac{1}{\rho} \nabla \frac{2\rho T}{3} + \mathcal{O}(\varepsilon) \\ \frac{\partial T_\varepsilon}{\partial t} &= -\vec{U} \cdot \nabla T - \frac{2T}{3} \nabla \cdot \vec{U} + \mathcal{O}(\varepsilon) \end{aligned} \quad (2.5)$$

On neglecting the first order terms we recover the Euler equations, which we shall use later.

Expanding equation (2.2) in terms of  $\varepsilon$  and taking the  $\frac{1}{\varepsilon}$  terms we obtain a non-linear integral equation for  $f_0$ .

$$0 = \int \int \int W(\vec{v}'_1, \vec{v}'_2, \vec{v}, \vec{v}_2) f_0(\vec{v}'_1) f_0(\vec{v}'_2) - W(\vec{v}, \vec{v}_2, \vec{v}'_1, \vec{v}'_2) f_0(\vec{v}) f_0(\vec{v}_2) d^3 \vec{v}'_1 d^3 \vec{v}'_2 d^3 \vec{v}_2$$

The solution to this equation is found by solving the related problem of the special case where entropy is constant related to Boltzmanns H theory,

$$\frac{\partial H}{\partial t} = 0 \Rightarrow f_0 = \frac{3\sqrt{3}\rho}{8\pi^{\frac{3}{2}} T^{\frac{3}{2}}} e^{-\frac{3(\vec{v}-\vec{u})^2}{4}} \quad (2.6)$$

This is known as the Maxwell distribution and happens to also be a solution for  $f_0$ . With a great many handwaving arguments it can be established that for sensible  $W$



it is the general solution [8, p. 90, Chapter 5].

By taking the constant term of the expansion of equation (2.2), for which we need the substitutions (2.5), and by invoking a symmetry property of  $W$  related to its physical meaningfulness, namely  $W(\vec{v}'_1, \vec{v}'_2, \vec{v}, \vec{v}_2) = W(\vec{v}, \vec{v}_2, \vec{v}'_1, \vec{v}'_2)$ , we obtain an expression for  $f_1$ ,

$$\begin{aligned} & \frac{3f_0}{2T} \left( (\vec{v} - \vec{U})(\vec{v} - \vec{U}) - \frac{(\vec{v} - \vec{U})^2}{3} \mathbf{I} \right) : \nabla \vec{U} + \frac{f_0}{T} \left( \frac{3(\vec{v} - \vec{U})^2}{4T} - \frac{5}{2} \right) (\vec{v} - \vec{U}) \cdot \nabla T \\ &= \int \int \int W(\vec{v}, \vec{v}_2, \vec{v}'_1, \vec{v}'_2) (f_1(\vec{v}'_1) f_0(\vec{v}'_2) - f_1(\vec{v}) f_0(\vec{v}_2) \\ & \quad + f_0(\vec{v}'_1) f_1(\vec{v}'_2) - f_0(\vec{v}) f_1(\vec{v}_2)) d^3 \vec{v}'_1 d^3 \vec{v}'_2 d^3 \vec{v}_2 \end{aligned}$$

Dyadic notation is used.

Since the left hand side is linear in the first order spatial derivatives of  $\vec{U}$  and  $T$ , and these are functions of  $\vec{x}$  which is not a variable of the integration, it then follows that the solution is linear in  $\vec{U}$  and  $T$  as well and, in fact, the solution can be shown to have the general form

$$\begin{aligned} f_1 &= f_0 \left( \frac{A(|\vec{v} - \vec{U}|)}{T} (\vec{v} - \vec{U}) \cdot \nabla T \right. \\ & \left. + \frac{3B(|\vec{v} - \vec{U}|)}{2T} \left( (\vec{v} - \vec{U})(\vec{v} - \vec{U}) - \frac{(\vec{v} - \vec{U})^2}{3} \mathbf{I} \right) : \nabla \vec{U} \right) \end{aligned}$$

$A$  and  $B$  are defined relative to  $W$  by much simpler integral equations that they must satisfy. By substituting  $f = f_0 + f_1$  into the Boltzmann equation (2.1) and making use of the conditions (2.4) we can recover the NavierStokes equation (with a fairly general term for the stress tensor) and Fourier's law (with a specific expression for conductivity given in terms of  $B$  and  $A$ , respectively). Specifically

$$\begin{aligned} \vec{q} &= \frac{\sqrt{3}\rho}{16\pi^{\frac{3}{2}}T^{\frac{5}{2}}} \int e^{-\frac{3v^2}{4}} A(|\vec{v}|) v^4 d^3 \vec{v} \nabla T \\ \sigma &= \frac{9\sqrt{3}\rho}{16\pi^{\frac{3}{2}}T^{\frac{5}{2}}} \int e^{-\frac{3v^2}{4}} B(|\vec{v}|) \vec{v}\vec{v} \left( \vec{v}\vec{v} - \frac{v^2}{3} \mathbf{I} \right) d^3 \vec{v} : \nabla \vec{U} \end{aligned}$$

We have taken the Reader through these calculations since in later chapters the Reader will have cause to refer to the specifics of such calculations in ever greater detail in the works of Ottinger [3], Harris [8], and to a lesser extent perhaps Chapman [9], who co-developed this method.

It should also be noted that a variation on the Chapman-Enskog method can be applied to the lattice Boltzmann equation [15, 16]. We can not emphasise enough how important a step we consider this process in the research. A great deal of effort was put into developing this method into something that would be useful, in terms of being as tractable as we were able to make it, upon polymers and it is well worth the time spent on familiarising the reader with it.

### 2.3.4 Collision Analysis

As previously mentioned it is possible to take the term  $W$  in the collision integral (see equation (2.1)) and derive a lot of information about it by considering the actual physics of collisions. Roughly speaking  $W(\vec{v}_1, \vec{v}_2, \vec{v}'_1, \vec{v}'_2)$  can be thought of as the probability that two particles,  $\vec{v}_1$  and  $\vec{v}_2$ , collide and leave the collisions with the new velocities,  $\vec{v}'_1$  and  $\vec{v}'_2$  respectively [8]. Clearly, because the two particles are equivalent, swapping their numbering still describes the same physical situation giving  $W(\vec{v}_1, \vec{v}_2, \vec{v}'_1, \vec{v}'_2) = W(\vec{v}_2, \vec{v}_1, \vec{v}'_2, \vec{v}'_1)$ . Also, under the assumption of time reversal symmetry, for the collision process we have  $W(\vec{v}_1, \vec{v}_2, \vec{v}'_1, \vec{v}'_2) = W(\vec{v}'_1, \vec{v}'_2, \vec{v}_1, \vec{v}_2)$ . Finally, of course, the function describes a physical process so must have rotational and Galilean invariance. We also know that the collisions preserve momentum and energy so we have  $W(\vec{v}_1, \vec{v}_2, \vec{v}'_1, \vec{v}'_2) \propto \delta(\vec{v}_1 + \vec{v}_2 - \vec{v}'_1 - \vec{v}'_2)\delta(\vec{v}_1^2 + \vec{v}_2^2 - \vec{v}'_1{}^2 - \vec{v}'_2{}^2)$ . The preservation of momentum actually proves that the values of  $\vec{v}_1$ ,  $\vec{v}_2$  etc, treated as vertices, form a parallelogram as conservation of momentum can be written as  $\vec{v}'_1 - \vec{v}_1 = \vec{v}_2 - \vec{v}'_2$  which implies two opposite sides are equal in length and direction. Using the equations for momentum and energy conservation in collisions it is also possible to derive the relation  $|\vec{v}_2 - \vec{v}_1| = |\vec{v}'_2 - \vec{v}'_1|$ , which is to say the 2 diagonals

across the parallelogram are of equal length proving that it is in fact a rectangle. Given  $\vec{v}_1$  and  $\vec{v}_2$  define two opposite corners of this rectangle, it is sufficient to define an additional unit vector  $\hat{\alpha} = \widehat{\vec{v}'_1 - \vec{v}_1}$  to give the form of the whole rectangle<sup>4</sup>.

Of some considerable use are derived equations for  $\vec{v}'_1$  and  $\vec{v}'_2$ , namely  $\vec{v}'_1 = \vec{v}_1 + a\hat{\alpha}$  and  $\vec{v}'_2 = \vec{v}_2 - a\hat{\alpha}$ . These expressions are conceptually simple: the statement that a certain amount of momentum is transferred from one particle to another and so automatically satisfies the momentum conservation equation. Insertion into the energy conservation equation gives a formula for  $a$ , namely  $a = \hat{\alpha} \cdot (\vec{v}_2 - \vec{v}_1)$ . It is quite legitimate to treat  $\vec{v}'_1$  and  $\vec{v}'_2$  as functions of  $\hat{\alpha}$  and replace the integration over  $\vec{v}_2$ ,  $\vec{v}'_1$  and  $\vec{v}'_2$  by integration over  $\vec{v}_2$ . The spherical integral over  $\hat{\alpha}$ , neglecting the Dirac delta functions for momentum and energy conservation as the substitution satisfies momentum and energy conservation automatically.

The important thing to consider is that  $W$  must have rotational and Galilean invariance, so although this substitution automatically makes  $W$  a function of  $\vec{v}_1$ ,  $\vec{v}_2$  and  $\hat{\alpha}$ , it only needs to take enough information from those variables to determine the width and height of the rectangle. The values  $|\vec{v}_2 - \vec{v}_1|$  and  $\widehat{\vec{v}_2 - \vec{v}_1} \cdot \hat{\alpha}$  would be quite sufficient, for example.

### 2.3.5 Other Models

It was extremely instructive to study many generalised Boltzmann-like models in coming to understand those relating to polymer dynamics. Of particular interest to this work were those relating to biological and sociological systems described by Bellomo [21] and his contemporaries [22–24]. It is interesting to note that biological systems are mostly composed of cells which can be modelled as point-like entities much like gas atoms and fibres (such as collagen and elastin that conceptually can be thought of as elongated strings much as polymer chains can). It is conceivable that

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<sup>4</sup>A great deal of time was spent doodling on notepads looking for generalised diagrams that might yelled useful geometric insights but to little effect.

integro-differential equations much like those of Bellomos, only more complex, might one day describe how the interplay of cells, the fibres of the extra cellular matrix, and diffusive signalling factors give rise to the complex organs and appendages of living things from much simpler structures. It might also describe how the body goes about maintaining and repairing damage to these structures. Collectively, these processes are referred to as organogenesis, morphogenesis, homeostasis, and wound remodelling, and the applications of a better mathematical understanding of these processes to regenerative medicine is obvious.

However, we refer to them here simply because they illuminate the huge range of generalisations that are possible regarding the Boltzmann equation. Sadly, there is no time to do so comprehensively but we will pick out a few themes. One obvious way is to add an extra mechanical property such as orientation (and then angular velocity must also be included). In the two dimensional case with spin perpendicular to the plain, we could write  $f = f(t, \vec{x}, y, \vec{v}, p)$  where  $y$  and  $p$  are orientation and angular velocity, respectively. These can be treated as simple extensions to the position and momentum variables and give contributions to the equation of the form  $p \frac{\partial f}{\partial y} + F_y \frac{\partial f}{\partial p}$  that mirror the contribution given by position and linear velocity  $\vec{v} \cdot \nabla_x f + \vec{F} \cdot \nabla_v f$ . In fact, in biological equations one typically considers internal properties, with no easy relationship to mechanical properties, such as the activity of a gene in a cell or the number of nucleic factors unbound and free in the cell. Nevertheless these properties, usually represented by the ‘vector’  $\vec{u}$ , give rise to terms like  $\vec{K} \cdot \nabla_{\vec{u}} f$ .

In biological systems we also tend to consider more than one particle type. For example we might consider the interaction of cancer cells with natural killer cells. This raises two issues. First, an index for different populations must be added changing  $f$  to  $f_i$  and a sum must be added to the collision integral to account for collisions between different types of particles. Also, in biological systems, the ‘particles’ (typically cells) can be both created and destroyed, as is the case with cancer cells, thus requiring far more complex collision integrals. Typically these

processes are sorted into three categories:

1. those that change a particle's state to the state of interest (the state addressed by the left, non collision, side of the equation,  $\mathbf{C}_{i+}[\vec{f}]$ , where  $\vec{f}$  is a 'vector' of all population distribution functions),
2. terms to describe conservative loss from the state of interest  $\mathbf{C}_{i-}[\vec{f}]$ , and lastly
3. terms to describe the creation and destruction of particles given by  $\mathbf{I}_i[\vec{f}]$ .

The collision term is then given by the three integrals  $\mathbf{C}_{i+}[\vec{f}] - \mathbf{C}_{i-}[\vec{f}] + \mathbf{I}_i[\vec{f}]$ . The integral  $\mathbf{I}_i$  might be non-zero in a polymer if it were modelling a polymerisation reaction in a polymer melt.

It should for example be noted that force and force-like fields such as  $\vec{F}$  and  $\vec{K}$  also often involve integrals of  $\vec{f}$ . The expression for this is typically given by equations like  $\vec{F}_i = \sum_j \int \vec{P}_{ij}(\vec{x}, \vec{v}, \vec{u}, \vec{x}', \vec{v}', \vec{u}') f_j(t, \vec{x}', \vec{v}', \vec{u}') d^3\vec{x}' d^3\vec{v}' d^3\vec{u}'$ . Here  $\vec{P}$  relates to the amount of force a particle in state  $(\vec{x}', \vec{v}', \vec{u}')$  exerts upon a particle in state  $(\vec{x}, \vec{v}, \vec{u})$ . The overall force is assumed to be the additive force from all those particles and so is proportional to  $f_j$  and is integrated over all states. Similar terms exist for  $\vec{K}$  like functions. Typically, in biological systems,  $\vec{F}$  has no dependence upon  $\vec{v}$  but  $\vec{K}$  often does have some dependence upon  $\vec{u}$  in which case it is generally more useful and correct to write  $\nabla_{\vec{u}} \cdot (\vec{K}_i f_i)$  instead of  $\vec{K}_i \cdot \nabla_{\vec{u}} f_i$ . Note that if  $\vec{K}$  has no dependence upon  $\vec{u}$ , the two are equivalent. Holding some of these generalisations in mind may be useful when we come to examine some of the more exotic models of Boltzmann-like polymer dynamics [1, 2, 25].

## 2.4 Theory of Integral Equations

The field of integral equations is wide and varied. This can be seen from their classification [26]

$$f(x) = \int_a^b K(x,t)u(t)dt, \quad u(x) = f(x) + \int_a^b K(x,t)u(t)dt$$

Equations such as those on the left are referred to as linear integral equations of the first kind, and those on the right as “second kind”. As with differential equations there is typically a homogeneous and inhomogeneous part to any solution. The equations themselves will be homogeneous if  $f(x) = 0$ . They will be Fredholm equations if  $a$  and  $b$  are constants or Volterra equations if  $a$  is a constant but  $b$  is the variable  $x$ . In fact, the Volterra equation can be thought of as a special case of the Fredholm equation as can be seen by observing that if  $K(x,t) = 0$  whenever  $t > x$  then, provided  $x < b$ , we have  $\int_a^b K(x,t)u(t)dt = \int_a^x K(x,t)u(t)dt$ . Unsurprisingly there are then techniques that apply to the solution of the Volterra equation that do not generalise to the Fredholm equation. Notice that these equations are all defined for functions of one variable. It is often taken as obvious that any dynamics of multivariable integral equations can be replicated in the one-dimensional case. Even if this is in fact true, it is our contention that it is more helpful and informative to study the multidimensional case sometimes. There are numerous methods of solving different special cases of integral equations. Volterra equations can be related to Cauchy problems on related ODE’s. Equations with kernels of the form  $K(x-t)$  may be solved by applying a Fourier Transform. However, we are concerned with the general inhomogeneous Fredholm equation of the second kind, which is the linear integral equation encountered in the Chapman-Enskog method, although in our case they are multidimensional and subject to constraints taking the form of Fredholm equations, this time homogeneous ones of the first type. The Fredholm equations we are concerned with will have improper definite integrals over all values. Therefore  $\int$

will often be used as a “short hand” for  $\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty}$  throughout this thesis. Fredholm equations with improper integrals are classed as being ‘singular’. In this case it may be less clear what class of functions will have well defined integrals with the kernel and this has a bearing on existence and uniqueness theory. However for the most part we are not concerned with such theorems beyond the methods to actually find solutions since we are looking for specific useful classes of results (the existence of unknown results intractable to access will be of little use).

There are basically three approaches typically used to solve a Fredholm equation. The first is the method developed by Fredholm [27], which may provide a single solution or a set of solutions where the homogenous parts form a finite dimensional vector space. This method involves the construction of a ratio of two infinite sums of nested integrals that tend to an infinite number of nesting towards the end of the series. We shall go into much more detail on this when we contrast Fredholm’s method with one we outline.

Another, the Hilbert-Schmidt method, only applies to symmetric kernels, that is kernels with the property  $K(s, t) = K(t, s)$ , and is based on solving the eigenvalue problem for the integral part of the equation and expressing the solution in terms of eigenvectors (and in some cases an extra finite number of constants based upon multiplicity of an eigenvalue) [26].

The final method is known as Neumann series and involves an iterative integral equation that will, under certain conditions, converge to a single answer.

Ruston has developed the theory of Fredholm equations into the equivalent theory of operators on a Hilbert space [28]. He only addresses the cases giving rise to finite dimensional solution sets, which he proves are the consequence of a certain class of operators he describes. Later we will argue that the constraints in the ad hoc method in Section 2.3.3 amounts to removing an infinite number of degrees of freedom to achieve a solution. We therefore suspect that, without constraints, the equation we consider in Section 3.3 admits an infinite dimensional space of solutions.

However, that problem may also be reformulated as a Fredholm type equation. From this we conclude that the class of kernels we are concerned with are of interesting and unusual form.

However, It is the Neumann series we will mostly draw upon in our work so it behoves us to discuss its construction.

Given the Fredholm equation

$$u(x) = f(x) + \lambda \int_a^b K(x, t)u(t)dt$$

we can construct an iterative equation of the form

$$u_{n+1}(x) = f(x) + \lambda \int_a^b K(x, t)u_n(t)dt$$

and assuming that it converges at infinity we can make the assumption  $u_0 = f$  and construct the value the iteration converges to which is given by

$$f(x_0) + \lambda \int_a^b K(x_0, x_1)f(x_1)dx_1 + \dots + \\ \lambda^n \int_a^b \dots \int_a^b K(x_0, x_1) \dots K(x_{n-1}, x_n)f(x_1)dx_1 \dots dx_n + \dots$$

Intuitively we may guess that the value converges to a fixed point of the iterative equation and hence a solution of the original Fredholm equation, and provided that a certain set of conditions is met it can be proved that the series converges and this is in fact the case. This method is grounded in the study of Hilbert space, which is independent of considerations of the number of variables in the equation or whether the limits of integration are definite or indefinite, and later we will seek to generalise this method.



## 2.5 Hilbert Spaces

Hilbert space theory is an indispensable tool much used in physics and applied mathematics. It underpins much of quantum mechanics and signal processing as well as offering a firm foundation for the study of linear differential and integral equations. Whereas integral and differential equations are formulated in a certain dimensionality of space and time, the separable infinite dimensional Hilbert spaces we consider are all isomorphic and so all theories proved for them will be applicable to any integro-differential problems we prove that can be formulated in terms of Hilbert spaces.

### 2.5.1 Hilbert Spaces

The technical definition of a Hilbert space is “any complete inner product space”. The notion of an inner product is almost certainly familiar to the Reader but we state it here for completeness. An inner product on a vector space is a mapping  $\langle \cdot, \cdot \rangle : E \times E \rightarrow \mathbb{C}$ , where  $E$  is a vector space, that has the following properties [29].

- $\langle \vec{v}, \vec{w} \rangle = \langle \vec{w}, \vec{v} \rangle^*$  where the asterisk represents conjugation.
- $\langle a\vec{u} + b\vec{v}, \vec{w} \rangle = a\langle \vec{u}, \vec{w} \rangle + b\langle \vec{v}, \vec{w} \rangle$  where  $a, b \in \mathbb{C}$ .
- $\langle \vec{v}, \vec{v} \rangle \geq 0$  and  $\langle \vec{v}, \vec{v} \rangle = 0 \Leftrightarrow \vec{v} = \vec{0}$ .

Any vector space with an inner-product is an inner-product space. Additionally, it is complete if every Cauchy sequence in it, that is every sequence  $\vec{v}_i$  such that  $\|\vec{v}_{i+1} - \vec{v}_i\| \rightarrow 0$  as  $i \rightarrow \infty$  where  $\|\vec{v}\| = \sqrt{\langle \vec{v}, \vec{v} \rangle}$ , converges to some element in the vector space. It is immediately obvious that  $\mathbb{C}^n$  is a Hilbert space. In fact, all finite dimensional Hilbert spaces are isomorphic to one of these spaces. However, there are also infinite dimensional Hilbert spaces that require more exotic representations than the finite cases, and many useful representations exist.

Examples include the space of complex-valued functions defined over a given finite interval with inner product  $\langle f, g \rangle = \int_a^b f(x)g^*(x)dx$ . The space of all complex valued functions on  $\mathbb{R}$  such that  $\int_{-\infty}^{\infty} |f(x)|^2 dx$  is well defined is a Hilbert space with the same inner product except that the integral is now over all of  $\mathbb{R}$ . Hilbert spaces may have the property of being separable, that is there exists a sequence  $\vec{x}_i \in E$  such that  $\langle \vec{x}_i, \vec{x}_j \rangle = \delta_{ij}$  and  $\langle \vec{x}_i, \vec{x} \rangle = 0 \forall i \Rightarrow \vec{x} = \vec{0}$ . This is to say the Hilbert space has a countable basis. All infinite dimensional separable Hilbert spaces are isomorphic to each other. Non-separable Hilbert spaces do exist but tend to involve functions with odd properties.

### 2.5.2 Linear Mappings

We are particularly concerned with linear mappings on Hilbert spaces, the definition being  $L : E_1 \rightarrow E_2$  where  $E_1$  and  $E_2$  are vector spaces and  $L$  has the property  $L(a\vec{v} + b\vec{w}) = aL(\vec{v}) + bL(\vec{w})$  where  $a, b \in \mathbb{C}$  and  $\vec{v}, \vec{w} \in E_1$ . Two equivalent (for linear mappings) properties are continuity (defined as  $\|\vec{v}_i - \vec{v}\| \rightarrow \|L(\vec{v}_i) - L(\vec{v})\|$  for all  $\vec{v}_i$  and  $\vec{v}$ ) and boundedness (defined as the property that  $\|L(\vec{v})\| \leq K\|\vec{v}\|$  for all  $\vec{v}$ ). The boundedness of a linear mapping can be quantified with the mappings norm  $\|L\| = \sup_{\|\vec{v}\|=1} \|L(\vec{v})\|$ , which gives us the lowest possible bound and also defines a normed vector space of all bounded linear mapping between given normed vector spaces. Another vital concept is the contraction mapping, defined as being a mapping such that  $\|L(\vec{v}) - L(\vec{w})\| \leq \alpha\|\vec{v} - \vec{w}\|$  for  $\alpha < 1$ .

### 2.5.3 Fixed Point Theorems

The Banach fixed point theorem underpins several existence and uniqueness proofs in the theory of integral equations and its generalisations. It also has a constructive proof, that is it proves the solution exists by constructing it. For this reason the proof is very instructive and will be included.

Let  $F$  be closed a subspace of a Banach space  $E$ , and let  $L$  be a contraction mapping from  $F$  into  $F$ . There exists a unique  $\vec{w} \in F$  such that  $L(\vec{w}) = \vec{w}$ . This is proved as follows. Let  $\vec{v}_{n+1} = L(\vec{v}_n)$ .  $\|\vec{v}_{n+1} - \vec{v}_n\| = \|L(\vec{v}_n) - L(\vec{v}_{n-1})\| \leq \alpha \|\vec{v}_n - \vec{v}_{n-1}\|$  for  $0 < \alpha < 1$  as  $L$  is a contraction mapping. By induction it is easily shown that  $\|\vec{v}_{n+1} - \vec{v}_n\| \leq \alpha^n \|\vec{v}_1 - \vec{v}_0\|$  and by the triangle inequality for  $m < n$  we can derive  $\|\vec{v}_n - \vec{v}_m\| \leq \sum_{i=m}^{n-1} \|\vec{v}_{i+1} - \vec{v}_i\| \leq \|\vec{v}_1 - \vec{v}_0\| \sum_{i=m}^{n-1} \alpha^i$  as  $m \rightarrow \infty$  for  $n - m$  constant  $\sum_{i=m}^{n-1} \alpha^i \rightarrow 0$ , so also  $\|\vec{v}_n - \vec{v}_m\| \rightarrow 0$ . Therefore  $\vec{v}_n$  is a Cauchy sequence and converges because  $E$  is a Banach space. Let  $\vec{v} = \lim_{n \rightarrow \infty} \vec{v}_n$ , then  $\|L(\vec{v}) - \vec{v}\| \leq \|L(\vec{v}) - \vec{v}_i\| + \|\vec{v}_i - \vec{v}\| = \|L(\vec{v}) - L(\vec{v}_{i-1})\| + \|\vec{v}_i - \vec{v}\| \leq \alpha \|\vec{v} - \vec{v}_{i-1}\| + \|\vec{v}_i - \vec{v}\|$  which tends to 0 as  $i \rightarrow \infty$  so  $L(\vec{v}) = \vec{v}$ . Suppose  $L(\vec{w}) = \vec{w}$ , then  $\|\vec{v} - \vec{w}\| = \|L(\vec{v}) - L(\vec{w})\| \leq \alpha \|\vec{v} - \vec{w}\|$  as  $\alpha < 1$  this implies  $\|\vec{v} - \vec{w}\| = 0$  and so  $\vec{v} = \vec{w}$ .

## 2.6 Functional Derivatives

A functional is a mapping of a vector space of functions to a scalar field although the term is sometimes used more loosely to indicate a mapping to another space of functions with fewer variables or a mapping to a finite dimensional vector space. Functionals typically involve integrating over the variables in a function. For example, a common form of functional is  $F[y(x)] = \int_a^b H(x, y(x)) dx$ , where  $H$  is some specified function. Functionals are important to us since in the Boltzmann equation, mass, momentum, and energy are defined using functional-like expressions and the total entropy is defined by a functional.

It is of particular concern to us as to how one differentiates a functional. Volterra adopted an interesting conceptual approach thinking about operations on functions [30]. His thinking was that a function  $y(x)$  could be approximated by a long discreet set of points at set intervals along the function  $y_x$ . That being the case, a functional  $F$  would simply be a function of the  $y_x$  and the chain rule would apply, namely  $dF = \sum_x \frac{\partial F}{\partial y_x} dy_x$ . He reasoned that he could equate parts of the discreet system

with continuous analogues.  $dy_x = \varepsilon\eta(x)$  would be an infinitesimal amount of change for the function, the infinitesimal part being  $\varepsilon$ .  $dF = F[y(x) + \varepsilon\eta(x)] - F[y(x)]$ , the infinitesimal change of the functional, and  $\frac{\partial F}{\partial y_x} = \frac{\delta F}{\delta y(x)}$ , the derivative that we are seeking. The sum is of course an inner product in a finite Hilbert space and, as we have stated for spaces of square integrable functions, the inner product is an integral. So, the analogous continuous expression is  $F[y(x) + \varepsilon\eta(x)] - F[y(x)] = \varepsilon \int \frac{\delta F}{\delta y(x)} \eta(x) dx$ . Dividing by  $\varepsilon$  and taking the limit  $\varepsilon \rightarrow 0$  we get  $\frac{d}{d\varepsilon} F[y(x) + \varepsilon\eta(x)]|_{\varepsilon=0} = \int \frac{\delta F}{\delta y(x)} \eta(x) dx$ . It will occur that the left hand side will evaluate, certainly for all functionals of the type we've described, to be a product of  $\eta(x)$  within an integral like that on the right hand side. Thus, by equating the unaccounted for expression on the left hand side with  $\frac{\delta F}{\delta y(x)}$  we may, in a sense, discover the partial differential of a functional with respect to all the possible values its input function may take at all points. This is called the Volterra functional derivative [30].

Ottinger further generalises Volterra's functional derivative by adding the capacity to consider the functional derivative subject to constraints [3]. This is achieved by noting that we have assumed  $\eta(x)$  to be arbitrary. If  $\eta(x)$  is in some way constrained, for example it is assumed that  $\delta G = 0$  (the infinitesimal change in some other functional is assumed to be zero). Assuming the functional  $G[y(x)] = \int K(x)y(x)dx$ , then  $\delta G = \varepsilon \int K(x)\eta(x)dx$ , which implies  $\int K(x)\eta(x)dx$ . We must now rewrite our expression for the functional derivative to include the expression  $-CK(x)\eta(x)$ , which will evaluate to zero under the integral on the right side. So, we have the new equation

$$\frac{d}{d\varepsilon} F[y(x) + \varepsilon\eta(x)]|_{\varepsilon=0} = \int \left( \frac{\delta' F}{\delta y(x)} - CK(x) \right) \eta(x) dx$$

where  $\frac{\delta' F}{\delta y(x)}$  is the constrained functional derivative. Thus, we have

$$\frac{\delta' F}{\delta y(x)} = \frac{\delta F}{\delta y(x)} + CK(x)$$

so contrary to our usual experience the imposition of this constraint actually gener-

ates an arbitrary constant.

## 2.7 Quadrature Methods for Numerical Integration

The derivation of lattice Boltzmann like models *a priori* is deeply tied to numerical integration and we have spent a good deal of time researching the literature on this topic. The Reader is no doubt familiar with the trapezoid rule for numerical integration. In a sense it can be thought of as the approximation of a function with piecewise line segments that is then integrated over. Generally speaking, numerical integration can be considered the process of approximating a function by considering the function only at a few input ‘points’ and then integrating this simpler approximate function [31]. This construction often involves orthogonal polynomials and polynomial interpolation to get the best approximation possible. The nature of these approximations is typically that for an integral  $\int_a^b w(x)f(x)dx$  with limits that may be definite or indefinite and where  $w(x)$  is a known as the weight function, the approximate integration defines a set of points  $x_i$  known as abscissae and constant values  $w_i$  known as weights such that the approximation is  $\int_a^b w(x)f(x)dx = \sum_i w_i f(x_i)$ . The choice of abscissae and weights is determined by the weights function and the limits of integration in order to give a good approximation. In fact, it is some times the case that one or more abscissae may be given a specified position or that the derivative of the function instead of, or as well as, its value might be considered at some point for various practical reasons. Naturally, these have trade-offs in the quality of the approximation. Also, multiple variable versions of these techniques exist and can often be constructed by simple compositions of the one dimensional case.

We are primarily concerned with the approximation of three types of integrals, namely integrals of the form  $\int_{-\infty}^{\infty} e^{-x^2} f(x)dx$  that are well approximated with Her-

mite quadrature [31], integrals of the form  $\int_{S^2} f(x)d\Omega$  (that is integration over the angular part of spherical co ordinates) which proves to necessarily have a trivial approximation provided certain conditions are imposed, and integrals of the form  $\int_0^\infty x^2 e^{-x^2} f(x)dx$ , to which we could find no reference for in literature.

## 2.8 Kirkwood's Approach to Statistical Mechanics

In our explorations of the literature we found the work of Kirkwood to be most promising. Kirkwood was able to use some novel approaches to derive equations for mass, momentum, and energy transport from a classical statistical mechanics model of molecular motion [32]. The full workings of this process are a little too verbose to include here but we shall outline the process he used along with some key techniques employed.

Kirkwood chose to consider the distribution function  $f$  over all possible states of a system of  $n$  molecules. That is  $f(\vec{R}_1, \dots, \vec{R}_n, \vec{p}_1, \dots, \vec{p}_n, t)$  where  $\vec{R}_k$  is the position of the  $k$ th molecule and  $\vec{p}_k$  is its momentum. The space of distribution functions for fixed time have an associated inner product

$$\langle g; f \rangle = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} g(\vec{R}_1, \dots, \vec{p}_n) f(\vec{R}_1, \dots, \vec{p}_n) d^3 \vec{R}_1 \dots d^3 \vec{p}_n.$$

Using this result then operators giving expectation values of the system from and for an arbitrary dynamical variable can be defined. If  $\alpha(\vec{R}_1, \dots, \vec{p}_n)$  is that dynamic variable, then  $\langle \alpha; f \rangle$  gives its expectation value.

Kirkwood's key observation was that if the distribution function was subject to time evolution under a Liouville equation

$$\frac{\partial f}{\partial t} = \sum_{k=1}^n \left( -\frac{\vec{p}_k}{m_k} \cdot \nabla_{\vec{R}_k} f + \nabla_{\vec{R}_k} U \cdot \nabla_{\vec{p}_k} f \right),$$

with some potential energy function  $U$ , then the expectation value of any non time dependant dynamical variable would be governed by the time evolution equation

$$\frac{\partial}{\partial t} \langle \alpha; f \rangle = \sum_{k=1}^N \left\langle \frac{\vec{p}_k}{m_k} \cdot \nabla_{\vec{R}_k} \alpha - \nabla_{\vec{R}_k} U \cdot \nabla_{\vec{p}_k} \alpha; f \right\rangle. \quad (2.7)$$

Kirkwood defined macroscopic variables (such as mass, momentum, and energy) from certain expectation values, specifically mass density

$$\rho(\vec{r}, t) = \sum_{k=1}^N m_k \left\langle \delta(\vec{R}_k - \vec{r}); f \right\rangle,$$

momentum density

$$\rho(\vec{r}, t) \vec{u}(\vec{r}, t) = \sum_{k=1}^N \left\langle \vec{p}_k \delta(\vec{R}_k - \vec{r}); f \right\rangle,$$

kinetic energy density

$$E_K(\vec{r}, t) = \sum_{k=1}^N \left\langle \frac{p_k^2}{2m_k} \delta(\vec{R}_k - \vec{r}); f \right\rangle,$$

potential energy density due to external fields

$$E_\psi(\vec{r}, t) = \sum_{k=1}^N \left\langle \psi_k(\vec{R}_k) \delta(\vec{R}_k - \vec{r}); f \right\rangle = \sum_{k=1}^N \psi_k(\vec{r}) \left\langle \delta(\vec{R}_k - \vec{r}); f \right\rangle,$$

and the potential energy density due to internal forces

$$E_V(\vec{r}, t) = \frac{1}{2} \sum_{j \neq k} \left\langle V_{jk} \delta(\vec{R}_k - \vec{r}); f \right\rangle.$$

The total energy density for the energy equation is defined as the sum of the three energies  $E = E_K + E_\psi + E_V$ .

Kirkwood realised that he could apply equation (2.7) to his definitions of the macroscopic variables to find time evolution equations for them. Certain aspects of the right hand sides of these new expressions would be immediately replaceable

with known macroscopic variables. Others would require extensive manipulation and subsequent approximation in order to express the whole right side in terms of macroscopic variables.

We will discuss a few key manipulations but not Kirkwood's complete workings. The first is the well known technique of replacing a term with two identical terms multiplied by  $(\frac{1}{2})$  and swapping two summation indices in the second. For example

$$\begin{aligned} & - \sum_{j \neq k} \left\langle (\nabla_{\vec{R}_k} V_{jk}) \delta(\vec{R}_k - \vec{r}); f \right\rangle \\ &= -\frac{1}{2} \sum_{j \neq k} \left\langle (\nabla_{\vec{R}_k} V_{jk}) \delta(\vec{R}_k - \vec{r}) + (\nabla_{\vec{R}_j} V_{kj}) \delta(\vec{R}_j - \vec{r}); f \right\rangle. \end{aligned}$$

Another key technique that follows on neatly from the previous example is the application of Newton's third law expressed in the equation

$$\nabla_{\vec{R}_j} V_{kj} = -\nabla_{\vec{R}_k} V_{jk}.$$

Applied to the same example this yields

$$\begin{aligned} & - \sum_{j \neq k} \left\langle (\nabla_{\vec{R}_k} V_{jk}) \delta(\vec{R}_k - \vec{r}); f \right\rangle \\ &= -\frac{1}{2} \sum_{j \neq k} \left\langle (\nabla_{\vec{R}_k} V_{jk}) \left( \delta(\vec{R}_k - \vec{r}) - \delta(\vec{R}_j - \vec{r}) \right); f \right\rangle. \end{aligned}$$

Another important identity is derived by taking the Taylor expansion of  $\delta(\vec{R}_k - \vec{r})$  giving

$$\delta(\vec{R}_k - \vec{r}) - \delta(\vec{R}_j - \vec{r}) = -\nabla_{\vec{r}} \left[ \vec{R}_{jk} \left( \sum_{i=1}^{\infty} \frac{1}{n!} (-\vec{R}_{jk} \cdot \nabla_{\vec{r}})^{n-1} \right) \delta(\vec{R}_j - \vec{r}) \right]$$

where we define  $\vec{R}_{jk} = \vec{R}_k - \vec{R}_j$ . This identity often allows most of the expression to be written in terms of  $\vec{R}_{jk}$  as opposed to  $\vec{R}_j$  or  $\vec{R}_k$ . This facilitates the next step.

When an expression, such as follows, can be written using a potentially compli-



cated operator  $P(\vec{R}_{jk})$  (that commutes with integration) and a fairly simple function  $Q(\vec{p}_j, \vec{p}_k)$ , we can formulate the following identity.

$$\begin{aligned} & \sum_{j \neq k} \left\langle P(\vec{R}_{jk}) \circ \left( Q(\vec{p}_j, \vec{p}_k) \delta(\vec{R}_j - \vec{r}) \right); f \right\rangle \\ &= \int P(\vec{R}) \circ \sum_{j \neq k} \left\langle Q(\vec{p}_j, \vec{p}_k) \delta(\vec{R}_{jk} - \vec{R}) \delta(\vec{R}_j - \vec{r}); f \right\rangle d^3 \vec{R} \\ &= \int P(\vec{R}) \circ \sum_{j \neq k} \left\langle Q(\vec{p}_j, \vec{p}_k) \delta(\vec{R}_k - \vec{r} - \vec{R}) \delta(\vec{R}_j - \vec{r}); f \right\rangle d^3 \vec{R} \end{aligned}$$

Expressions of the form  $\sum_{j \neq k} \left\langle Q(\vec{p}_j, \vec{p}_k) \delta(\vec{R}_k - \vec{r} - \vec{R}) \delta(\vec{R}_j - \vec{r}); f \right\rangle$ , if  $Q(\vec{p}_j, \vec{p}_k)$  is sufficiently simple, can be approximated as the product of two macroscopic variables, one in terms of  $\vec{r} + \vec{R}$  and the other in terms of  $\vec{R}$ , and a third function  $g(\vec{r}, \vec{R}, t)$ , a “correlation function”. In summary, Kirkwood’s general approach seems to have been to rearrange expressions he couldn’t convert directly into macroscopic variables into such forms and perform these approximations introducing “correlation functions”.

## 2.9 Summary

In examining the literature we have learned several important things that guided the research in the rest of the thesis.

- That many physical systems including polymers can be modelled using equations similar to the Boltzmann equation.
- That the Boltzmann equation and it’s analogues are more directly linked to the microscopic dynamics of physical system than fluid dynamics.
- That the Boltzmann equation has an analogue discrete in time, space, and a velocity that can be very computationally tractable.

## CHAPTER 2. LITERATURE REVIEW

- That a methodology known as the Chapman-Enskog procedure exists to facilitate attempts to derive a model similar to those of fluid dynamics from the Boltzmann equation and its discrete and continuous analogues.
- Collisions are modelled statistically by a function  $W$  that is greatly restricted to ensure that only physically possible collisions are admitted in its statistical distribution. Among other things this leads to a set of useful symmetry conditions upon  $W$  and theoretically should allow the number of variables “integrated over” in the equation to be greatly reduced.
- The Chapman-Enskog method involves solving a ‘ladder’ of Fredholm integral equations upto a certain ‘rung’.
- A series of techniques exist to solve Fredholm equations including the Neuman series where a single solution exists and a method due to Fredholm and formalised in Hilbert space theory by Ruston [28] that applies to Fredholm equations with finite dimensional ‘spaces’ of solution.
- Integral equations can be studied through the theory of Hilbert spaces.
- Certain operators on Hilbert spaces have unique fixed points to which they converge and this theory underpins the validity of the Neuman series.
- Entropy can be expressed as a functional.
- There is an analogue of partial derivatives for functionals known as functional derivatives that is useful in determining the maxima and minima of functionals.
- Functional derivatives may be generalised to include the derivative subject to constraints. This is useful in determining maxima and minima subject to constraints.
- The derivation of lattice Boltzmann like models *a priori* relates to, and is dependent upon, numerical integration.

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- The relevant forms of numerical integration are those that involve considering the integral of an approximating function that is formulated by considering the properties of the function to be integrated and a finite number of ‘points’.
- Kirkwood was able to take a simple classical statistical mechanics model of molecular interactions and use it to derive a set of fluid dynamics like transport equations from first principals.

These key points will no doubt suggest to the Reader a course upon which to proceed as it did to us, and so we shall move on to our research material directly.

## Chapter 3

# Seeking a Solution to Grmela's Equation

In dealing with polymeric fluids we often refer to their memory. The functions with which we model these fluids contain integrals over time that consider the state of the fluid over some, usually finite, time of the recent past that contributes to the behaviour of the fluid in the present. Clearly fluids don't have memory as such<sup>1</sup>. If polymeric fluids appear to have memory it is because their environment affects their internal degrees of freedom, which subsequently affects their behaviour at "later times". The internal structure of a polymer (the microscopic arrangement of its polymer chains, their branching, direction, tension and interleaving) can be expected to contribute to the behaviour of the bulk polymer.

This work seeks to include information about the distribution of polymer chain orientations and extensions in models we develop as one feature of high shear rate and micro scale mould geometries, as we can expect some degree of preferential alignment of polymer chains. It is possible that in this situation heat transfer might favour one direction over another.

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<sup>1</sup>No polymer melt ever got up in the morning and said to itself 'oh I just remembered I'm supposed to be more stretchy today.' Although give nano-technologists time and who knows, puddles of goo may be vying for dominance of planet Earth some day.

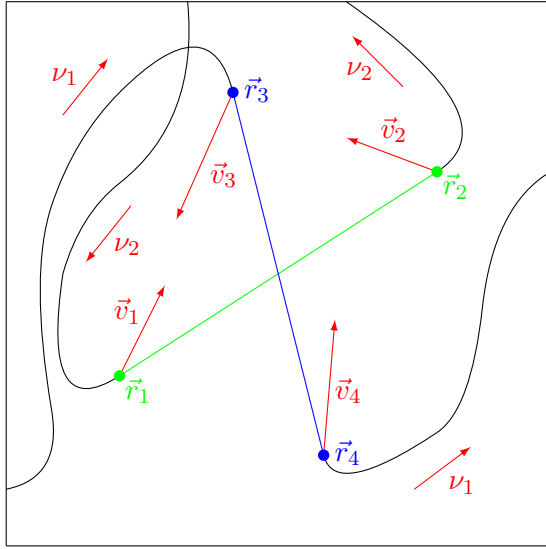


Figure 3.1: This diagram represents two sections of polymer chains potentially undergoing a collision like interaction. Immediately before and also after the interaction the position of the ‘ends’ of the ‘dumbbells’ are labelled by  $\vec{r}_i$  and the length along chain where this section rests is given by  $\sigma_i$ . These variables have associated velocity like parameters  $\vec{v}_i$  and  $\nu_i$  before the collision. These values will change post collision but  $\vec{r}_i$  and  $\sigma_i$  will experience no instantaneous change. Note  $\nu_i$ , it can be thought of as representing the ‘speed’ at which the polymer chain is being drawn through the two end points of a ‘dumbbell’.

### 3.1 Mesoscopic Kinetic Theory Approach

In gas dynamics it is possible to derive conservation equations from the kinetic theory of gasses, the so called mesoscopic domain where, instead of considering observable variables mapped over space, we consider the statistical distribution over phase space. This work was very influenced by the work of Miroslav Grmela [1, 2] who developed a kinetic theory of polymeric fluids and proved the theory’s consistency with the laws of thermodynamics. In this work we shall apply further analysis to Grmela’s equations in an effort to derive conservation equations over six dimensions, providing for three degrees of freedom for space and a further three internal degrees of freedom.

Grmela’s equation (3.1) [2] is a kinetic equation describing the time evolution of a function  $f$ , which itself describes how the material of the polymer is distributed over phase space:

$$\begin{aligned} \frac{\partial f(\mathbf{1}, t)}{\partial t} &= -v_{i\alpha} \frac{\partial}{\partial r_{i\alpha}} f(\mathbf{1}, t) - \nu_1 \frac{\partial}{\partial \sigma_1} f(\mathbf{1}, t) + \frac{\partial}{\partial v_{i\alpha}} \left( f(\mathbf{1}, t) \frac{1}{m} \frac{\partial}{\partial r_{i\alpha}} \left( \varphi^{(int)} + \varphi^{(ext)} \right) \right) \\ &+ \int \int \int \left( W(n; \mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2}) e^{-\frac{\delta S}{\delta f(\mathbf{1}', t)} - \frac{\delta S}{\delta f(\mathbf{2}', t)}} - W(n; \mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}') e^{-\frac{\delta S}{\delta f(\mathbf{1}, t)} - \frac{\delta S}{\delta f(\mathbf{2}, t)}} \right) d\mathbf{2} d\mathbf{1}' d\mathbf{2}' \end{aligned} \quad (3.1)$$

$$\mathbf{i} = (\vec{r}_{2i-1}, \vec{r}_{2i}, \vec{v}_{2i-1}, \vec{v}_{2i}, \sigma_i, \nu_i), \quad \mathcal{S}(f) = - \int f(\mathbf{1}, t) \ln f(\mathbf{1}, t) d\mathbf{1} - \mathcal{L}(n) \quad (3.2)$$

$$n(\vec{r}_1, \vec{r}_2, \sigma_1, t) = \int \int \int f(\mathbf{1}, t) d\vec{v}_1 d\vec{v}_2 d\nu_1 \quad (3.3)$$

This particular phase space as described in equation (3.2) has 14 degrees of freedom.  $\vec{r}_1$  and  $\vec{r}_2$  represent two points, at either end of an abstract dumb-bell-like entity. This could be thought of as two points reasonably close to each other on the same polymer chain.  $\vec{v}_1$  and  $\vec{v}_2$  are their associated velocities. Grmela introduced the somewhat artificial ‘feeling’  $\sigma_1$  and  $\nu_1$  as the “position co-ordinate on the line following the linear chain” and its “corresponding velocity” respectively [2].

$\mathcal{S}$  is a functional giving the entropy of  $f$ .  $n$  is a density-like functional of  $f$  that Grmela calls a “configuration space distribution function” [2].  $\varphi^{(int)}$  and  $\varphi^{(ext)}$  are potential energies, the first due to the internal tension of the polymer chain and that is purely dependent upon the length  $|\vec{r}_1 - \vec{r}_2|$ , and the second due to the external ‘crowding’ of other polymer chains dependent on  $\vec{r}_1$ ,  $\vec{r}_2$ , and  $n$ . Finally,  $\frac{\delta \mathcal{S}}{\delta f}$  is the notation we use to represent a Volterra functional derivative [30].

To give some context to the physical meaning of equation (3.1) the first three terms can be interpreted as the total derivative of  $f$ , that represent the rate of change of a ‘blob’, a volume in motion with the fluid, as opposed to a stationary volume. The fourth term can be interpreted as the effect of the force of two potential fields ( $\varphi^{(int)}$  and  $\varphi^{(ext)}$ ) upon the fluid. The fifth term represents collision-like events, typically

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short range interactions between two sections of polymer chain. The first term of this integral represents the likelihood of such and interaction between sections in states  $\mathbf{1}'$  and  $\mathbf{2}'$ , resulting in new states  $\mathbf{1}$  and  $\mathbf{2}$ . The second term describes the likelihood of 'collisions' causing states  $\mathbf{1}$  and  $\mathbf{2}$  to shift to new states  $\mathbf{1}'$  and  $\mathbf{2}'$ .

$$n(\vec{r}_1, \vec{r}_2, \sigma_1, t) \frac{\partial \varphi^{(ext)}(n; \vec{r}_1, \vec{r}_2)}{\partial r_{i\alpha}} = \int \int \int F^{(ext)}(n; \vec{r}_1, \vec{r}_2, \sigma_1, \vec{r}_3, \vec{r}_4, \sigma_2, t) \times \left( \tilde{\phi}_{i\alpha}^{(ext)}(n; \vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4) - \tilde{\phi}_{i\alpha}^{(ext)}(n; \vec{r}_3, \vec{r}_4, \vec{r}_1, \vec{r}_2) \right) d\vec{r}_3 d\vec{r}_4 d\sigma_2 \quad (3.4)$$

$$\frac{\partial}{\partial r_{i\alpha}} \frac{\delta \mathcal{L}}{\delta n(\vec{r}_1, \vec{r}_2, \sigma_1, t)} = 2 \sum_{j=3}^5 \int \int \int (r_{i\alpha} - r_{j\alpha}) \omega(n; \vec{r}_1, \vec{r}_2, \sigma_1, \vec{r}_3, \vec{r}_4, \sigma_2) \times n(\vec{r}_3, \vec{r}_4, \sigma_2, t) e^{2 + \frac{\delta \mathcal{L}}{\delta n(\vec{r}_1, \vec{r}_2, \sigma_1, t)} + \frac{\delta \mathcal{L}}{\delta n(\vec{r}_3, \vec{r}_4, \sigma_2, t)}} d\vec{r}_3 d\vec{r}_4 d\sigma_2 \quad (3.5)$$

$$\frac{\partial}{\partial \sigma_1} \frac{\delta \mathcal{L}}{\delta n(\vec{r}_1, \vec{r}_2, \sigma_1, t)} = 2 \int \int \int (\sigma_1 - \sigma_2) \omega^{rept}(n; \vec{r}_1, \vec{r}_2, \sigma_1, \vec{r}_3, \vec{r}_4, \sigma_2) \times n(\vec{r}_3, \vec{r}_4, \sigma_2, t) e^{2 + \frac{\delta \mathcal{L}}{\delta n(\vec{r}_1, \vec{r}_2, \sigma_1, t)} + \frac{\delta \mathcal{L}}{\delta n(\vec{r}_3, \vec{r}_4, \sigma_2, t)}} d\vec{r}_3 d\vec{r}_4 d\sigma_2 \quad (3.6)$$

Grmela states this set of conditions for equation (3.1) to conform to the laws of thermodynamics. To proceed with the analysis it was necessary to make some simplifications, namely that,  $\omega^{rept} = \omega = \mathcal{L} = 0$ , which automatically satisfies equations (3.5) and (3.6), and implies  $\frac{\delta \mathcal{S}}{\delta f(\mathbf{1}, t)} = -\ln f(\mathbf{1}, t)$ , which causes equation (3.1) to simplify to

$$\begin{aligned} & \frac{\partial f(\mathbf{1}, t)}{\partial t} + v_{i\alpha} \frac{\partial}{\partial r_{i\alpha}} f(\mathbf{1}, t) + \nu_1 \frac{\partial}{\partial \sigma_1} f(\mathbf{1}, t) - \frac{\partial}{\partial v_{i\alpha}} \left( f(\mathbf{1}, t) \frac{1}{m} \frac{\partial}{\partial r_{i\alpha}} \left( \varphi^{(int)} + \varphi^{(ext)} \right) \right) \\ & = \int \int \int (W(n; \mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2}) f(\mathbf{1}', t) f(\mathbf{2}', t) - W(n; \mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}') f(\mathbf{1}, t) f(\mathbf{2}, t)) d\mathbf{2} d\mathbf{1}' d\mathbf{2}' \end{aligned} \quad (3.7)$$

## 3.2 Chapman-Enskog Expansion

Non-linear integro-differential equations like (3.7) are not only computationally intensive to evaluate but they are also difficult to extract useful results from analytically. In the case of gas kinetics it is possible to derive equations for mass, momentum, and energy conservation using an analysis called the Chapman-Enskog expansion [3]. We select a number of functionals of  $f$ , much like equation (3.3), and attempt to use the expansion to construct, in some sense, an ideal form for  $f$  for the given functionals (that we shall tend to refer to as the macroscopic functions or variables) and their derivatives in the space-like co-ordinates remaining after the functional integration. This idealised  $f$  is reinserted into the original equation (3.7) to derive equations for the macroscopic variables that it is composed of.

The analysis presented in this work is a (slight) variation of the technique described in Ottinger's book [3] and is as follows.

We start with an equation of the form

$$\hat{D}_t f - \left[ \frac{\partial f}{\partial t} \right]_{coll} = 0 \quad (3.8)$$

where  $\hat{D}_t f$  represents terms relating to (effectively) long time scale forces and time evolution terms, and where  $\left[ \frac{\partial f}{\partial t} \right]_{coll}$  represents short 'collision' time scale terms. We take the equation and modify it by introducing a new variable  $\varepsilon$  like so

$$\varepsilon \hat{D}_t f - \left[ \frac{\partial f}{\partial t} \right]_{coll} = 0 \quad (3.9)$$



and define an approximation for  $f$  of the form<sup>2</sup>

$$f = \sum_{j=0}^{\infty} \varepsilon^j f^{(j)}(\vec{v}, x^{\{j\}}(\vec{r}, t)) \quad (3.10)$$

where  $x^{\{j\}}(\vec{r}, t)$  are what we shall term macroscopic variables and their spatial derivatives (in the space-like part of phase space) up to order  $j$ . These macroscopic variables are linear functionals (we shall use  $Y$  to denote one such arbitrary functional and  $y$  to denote the macroscopic variable  $Y$ 's result when applied to  $f$ ) and impose the following condition necessary to ensure uniqueness in our final result,

$$Y [f^{(i)}] = \delta_{0i} y(t, \vec{r}) \quad (3.11)$$

These macroscopic variables are fields or vector fields over the space-like co-ordinates of phase space. In gas kinetics, for example, they would be fields such as density and velocity.

We insert equation (3.10) into equation (3.8) and apply some set of functionals we simply refer to as  $Y$ , noting that

$$Y \left[ \frac{\partial f}{\partial t} \right] = \frac{\partial}{\partial t} Y [f] = \frac{\partial y}{\partial t}$$

We then generate a set of expressions for the time differentials of the macroscopic variables in terms of the  $f^{(i)}$ , and apply this technique to higher orders. We take equation (3.9) and insert equation (3.10), then apply the chain rule to occurrences of  $\frac{\partial f^{(i)}}{\partial t}$ , which introduces time derivatives of the macroscopic variables that we substitute our previously derived expressions for. The subsequent expression derived from equation (3.9) is expanded as a Taylor series, which has the form

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<sup>2</sup>conceptually each higher order of  $\varepsilon$  relates to a different 'order' of the Knudsen number and a different level of 'bumpyness' in the fluid the occurrence of higher order factors is supposed to reflect subtlety that may be unimportant when 'bumpyness' is low. For a clearer more mathematical explanation see Harris's book [8].

$$\sum_{j=0}^{\infty} \varepsilon^j \Xi^{(j)} [f^{(0)}, \dots, f^{(j)}] = 0. \quad (3.12)$$

Setting all the coefficients to 0, to satisfy the equation for all  $\varepsilon$ , gives

$$\Xi^{(j)} [f^{(0)}, \dots, f^{(j)}] = 0. \quad (3.13)$$

This generally produces a non-linear integral equation that gives  $f^{(0)}$  and linear equations thereafter. From this we can derive successive approximations for  $f$  by solving more of these equations subject to the restriction (3.11). When we have computed forms for  $f^{(0)}, \dots, f^{(j)}$  for some  $j$  we can reinsert these forms into the expressions for  $\frac{\partial y}{\partial t}$  (the time derivatives of the macroscopic variables) with the additional condition that we set  $\varepsilon = 1^3$  and thus generate time evolution equations for the macroscopic variables.

To perform this analysis on equation (3.7) we pick the following macroscopic variables:

$$\rho = n, \quad \rho \vec{U}_i = \int \vec{v}_i f d^3 \vec{v}_1 d^3 \vec{v}_2 d\nu_1, \quad \rho T = \int \left( \frac{(\vec{v}_1 - \vec{U}_1)^2 + (\vec{v}_2 - \vec{U}_2)^2}{2} + \nu_1^2 \right) f d^3 \vec{v}_1 d^3 \vec{v}_2 d\nu_1 \quad (3.14)$$

$\rho$  is a density-like variable re-labelled to reflect convention,  $\vec{U}_i$  are velocity-like variables, and  $T$  is a temperature-like variable. We also define a fourth convenient energy-like variable not independent of these three:

$$\rho \left( T + \frac{U_1^2 + U_2^2}{2} \right) = \int \left( \frac{v_1^2 + v_2^2}{2} + \nu_1^2 \right) f d^3 \vec{v}_1 d^3 \vec{v}_2 d\nu_1 = E \quad (3.15)$$

It will often be easier to work with conditions on  $E$  than conditions on  $T$ .

To perform the Chapman-Enskog expansion on equation (3.7) we define a new

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<sup>3</sup>Note this is just convenient way of recovering the original Boltzmann equation with out having to recalculate with out the presence of  $\varepsilon$ .

equation that is to equation (3.7), as equation (3.9) is to equation (3.8),

$$\begin{aligned} \varepsilon \frac{\partial f(\mathbf{1}, t)}{\partial t} &= -\varepsilon v_{i\alpha} \frac{\partial}{\partial r_{i\alpha}} f(\mathbf{1}, t) - \varepsilon \nu_1 \frac{\partial}{\partial \sigma_1} f(\mathbf{1}, t) + \varepsilon \frac{\partial}{\partial v_{i\alpha}} \left( f(\mathbf{1}, t) \frac{1}{m} \frac{\partial}{\partial r_{i\alpha}} \left( \varphi^{(int)} + \varphi^{(ext)} \right) \right) \\ &+ \int \int \int (W(n; \mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2}) f(\mathbf{1}', t) f(\mathbf{2}', t) - W(n; \mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}') f(\mathbf{1}, t) f(\mathbf{2}, t)) d\mathbf{2} d\mathbf{1}' d\mathbf{2}' \end{aligned} \quad (3.16)$$

We define an approximation for  $f$  in parallel with equation (3.10)

$$f(\mathbf{1}, t) = \sum_{i=0}^{\infty} \varepsilon^i f_i(\vec{v}_1, \vec{v}_2, \nu_1, x^{\{i\}}(\vec{r}_1, \vec{r}_2, \sigma_1)) \quad (3.17)$$

where  $x^{\{0\}}$  is  $\rho$ ,  $\vec{U}_i$  and  $T$ , collectively;  $x^{\{1\}}$  denotes  $x^{\{0\}}$  augmented by the first order spatial derivatives, and so on.

### 3.2.1 The Zeroth Order of the Expansion

We insert equation (3.17) into equation (3.16) and notice that the zero order Taylor expansion has no dependence upon the time derivatives of the macroscopic variables, so we can state the equation produced by the zero-order coefficient immediately as

$$0 = \int \int \int (W(n; \mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2}) f_0(\mathbf{1}', t) f_0(\mathbf{2}', t) - W(n; \mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}') f_0(\mathbf{1}, t) f_0(\mathbf{2}, t)) d\mathbf{2} d\mathbf{1}' d\mathbf{2}' \quad (3.18)$$

Grmela states [2] that in proving the H-theorem for the system through similarities between  $\frac{\partial H}{\partial t}$  and the right hand side of equation (3.18), a condition for the solution of equation (3.18) is given by

$$\frac{\delta \mathcal{S}}{\delta f(\mathbf{1}', t)} + \frac{\delta \mathcal{S}}{\delta f(\mathbf{2}', t)} = \frac{\delta \mathcal{S}}{\delta f(\mathbf{1}, t)} + \frac{\delta \mathcal{S}}{\delta f(\mathbf{2}, t)}. \quad (3.19)$$

Inserting the form of  $\mathcal{S}$  given in equation (3.2) subject to our simplifying assumptions on  $\mathcal{L}$ , we obtain

$$\ln f_0(\mathbf{1}', t) + \ln f_0(\mathbf{2}', t) = \ln f_0(\mathbf{1}, t) + \ln f_0(\mathbf{2}, t).$$

### CHAPTER 3. SEEKING A SOLUTION TO GRMELA'S EQUATION

Since the position co-ordinates are not changed by a collision we can expect some change in  $\vec{v}_i$ . The equation above implies that  $\ln f_0$  is composed of expressions in  $\vec{v}_i$  that are conserved in collisions, namely a constant mass that has no dependence on  $\vec{v}_i$ , energy that is given by Grmela [2] as  $\left(\frac{v_1^2+v_2^2}{2} + \nu_1^2\right)$ , and various forms of momentum that should be linear in  $\vec{v}_i$ . Thus these eight expressions should make up  $\ln f_0$ .

In truth it could be argued that  $\nu_1$ , being a velocity-like component, should also be included as a potential linear momentum component, but since its meaning is just a little ambiguous and since its inclusion makes the next step impossible as an assumption, it is left out. The only justification we have for this is the lack of a macroscopic variable to accompany the momentum associated with  $\nu_1$ . Further justification for this form will be given in Section 5.3. This gives us the form for  $\ln f_0$  as

$$\ln f_0(\mathbf{1}, t) = A + \vec{B} \cdot \vec{v}_1 + \vec{C} \cdot \vec{v}_2 + D \left( \frac{v_1^2 + v_2^2}{2} + \nu_1^2 \right) \quad (3.20)$$

$A$ ,  $\vec{B}$ ,  $\vec{C}$  and  $D$  are fields of the spatial variables  $(\vec{r}_1, \vec{r}_2, \sigma_1)$ . These fields can be set by appealing to conditions (3.14) and (3.3). This gives  $f_0$  to be.

$$f_0(\mathbf{1}) = \frac{343}{64\pi^{\frac{7}{2}}} \sqrt{\frac{7}{2}} T^{-\frac{7}{2}} \rho e^{-\frac{7}{2T} \left( \frac{1}{2}(\vec{v}_1 - \vec{U}_1)^2 + \frac{1}{2}(\vec{v}_2 - \vec{U}_2)^2 + \nu_1^2 \right)} \quad (3.21)$$

By inserting  $f_0$  for  $f$  we get

$$\frac{\partial f_0(\mathbf{1}, t)}{\partial t} + v_{i\alpha} \frac{\partial}{\partial r_{i\alpha}} f_0(\mathbf{1}, t) + \nu_1 \frac{\partial}{\partial \sigma_1} f_0(\mathbf{1}, t) - \frac{\partial}{\partial v_{i\alpha}} \left( f_0(\mathbf{1}, t) \frac{1}{m} \frac{\partial}{\partial r_{i\alpha}} \left( \varphi^{(int)} + \varphi^{(ext)} \right) \right) = 0 \quad (3.22)$$

Next, by applying density-like, momentum-like, and energy-like functionals (3.14), (3.3) to equation (3.7) we get

$$\frac{\partial \rho}{\partial t} = -\nabla_{\vec{r}_1} \cdot (\rho \vec{U}_1) - \nabla_{\vec{r}_2} \cdot (\rho \vec{U}_2) \quad (3.23)$$

$$\frac{\partial}{\partial t}(\rho U_{i\alpha}) = -\frac{\partial}{\partial r_{j\beta}}(\rho U_{i\alpha} U_{j\beta}) - \frac{\partial}{\partial r_{i\alpha}}\left(\frac{2T\rho}{7}\right) - \frac{\rho}{m} \frac{\partial}{\partial r_{i\alpha}}\left(\phi^{(int)} + \phi^{(ext)}\right) \quad (3.24)$$

$$\begin{aligned} \frac{\partial}{\partial t}\left(\rho\left(T + \frac{1}{2}(\vec{U}_1^2 + \vec{U}_2^2)\right)\right) &= -\frac{\partial}{\partial r_{i\alpha}}\left(\rho U_{i\alpha}\left(\frac{9}{7}T + \frac{1}{2}(\vec{U}_1^2 + \vec{U}_2^2)\right)\right) \\ &\quad + \frac{\rho}{m} U_{i\alpha} \frac{\partial}{\partial r_{i\alpha}}\left(\phi^{(int)} + \phi^{(ext)}\right) \end{aligned} \quad (3.25)$$

Rearranging (3.24) and (3.25) and appealing to (3.23), we get

$$\frac{\partial U_{i\alpha}}{\partial t} = -U_{j\beta} \frac{\partial U_{i\alpha}}{\partial r_{j\beta}} - \frac{1}{\rho} \frac{\partial}{\partial r_{i\alpha}}\left(\frac{2T\rho}{7}\right) - \frac{1}{m} \frac{\partial}{\partial r_{i\alpha}}\left(\phi^{(int)} + \phi^{(ext)}\right) \quad (3.26)$$

$$\frac{\partial T}{\partial t} = -U_{i\alpha} \frac{\partial T}{\partial r_{i\alpha}} - \frac{2}{7} T \frac{\partial U_{i\alpha}}{\partial r_{i\alpha}} + \frac{2}{m} U_{i\alpha} \frac{\partial}{\partial r_{i\alpha}}\left(\phi^{(int)} + \phi^{(ext)}\right) \quad (3.27)$$

By rearranging (3.23), (3.26) and (3.27), and appealing to the definition of the total derivative  $D_t$  (also known as the material derivative) we get

$$D_t \rho = -\rho \nabla_{\vec{r}} \cdot \vec{U} \quad (3.28)$$

$$D_t \vec{U} = -\frac{2}{7} \frac{1}{\rho} \nabla_{\vec{r}}(T\rho) - \frac{1}{m} \nabla_{\vec{r}}\left(\phi^{(int)} + \phi^{(ext)}\right) \quad (3.29)$$

$$D_t T = -\frac{2}{7} T \nabla_{\vec{r}} \cdot \vec{U} + \frac{2}{m} \vec{U} \cdot \nabla_{\vec{r}}\left(\phi^{(int)} + \phi^{(ext)}\right) \quad (3.30)$$

These equations are analogous to the Euler equations.

### 3.2.2 The First Order Expansion

The next set of derived equations would be akin to the Navier-Stokes equation and its accompanying mass and energy conservation equations. We take the first order term in the Taylor series of equation (3.16) to get

$$\begin{aligned}
 \frac{\partial \rho}{\partial t} \Big|_{\varepsilon=0} \frac{\partial f_0}{\partial \rho} + \frac{\partial U_{i\alpha}}{\partial t} \Big|_{\varepsilon=0} \frac{\partial f_0}{\partial U_{i\alpha}} + \frac{\partial T}{\partial t} \Big|_{\varepsilon=0} \frac{\partial f_0}{\partial T} &= -v_{i\alpha} \frac{\partial}{\partial r_{i\alpha}} f_0 - \nu_1 \frac{\partial}{\partial \sigma_1} f_0 \\
 &+ \frac{\partial}{\partial v_{i\alpha}} \left( f_0 \frac{1}{m} \frac{\partial}{\partial r_{i\alpha}} \left( \varphi^{(int)} + \varphi^{(ext)} \right) \right) \\
 &+ \int \int \int (W(n; \mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2}) (f_1(\mathbf{1}') f_0(\mathbf{2}') + f_0(\mathbf{1}') f_1(\mathbf{2}')) \\
 &- W(n; \mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}') (f_1(\mathbf{1}) f_0(\mathbf{2}) + f_0(\mathbf{1}) f_1(\mathbf{2}))) d\mathbf{2} d\mathbf{1}' d\mathbf{2}'
 \end{aligned} \tag{3.31}$$

The time derivative of macroscopic terms such as  $\frac{\partial \rho}{\partial t} \Big|_{\varepsilon=0}$  subject to the condition  $\varepsilon = 0$  are necessarily the same as the values derived in equations (3.23), (3.26) and (3.27) since the assumption used there was that only  $f_0$  contributes. Remaining conditions are given by

$$\begin{aligned}
 \frac{\partial f_0}{\partial \rho} &= \frac{f_0}{\rho}, \quad \frac{\partial f_0}{\partial U_{i\alpha}} = \frac{7(v_{i\alpha} - U_{i\alpha}) f_0}{2T} \\
 \frac{\partial f_0}{\partial T} &= \frac{7((\bar{U} - \bar{v})^2 + 2\nu_1^2 - 2T) f_0}{4T^4}, \quad \frac{\partial f_0}{\partial v_{i\alpha}} = \frac{7(U_{i\alpha} - v_{i\alpha}) f_0}{2T} \\
 \frac{\partial f_0}{\partial r_{i\alpha}} &= \left( \frac{7(\bar{v} - \bar{U})}{2T} \cdot \frac{\partial \bar{U}}{\partial r_{i\alpha}} + \frac{7((\bar{v} - \bar{U})^2 - 2T + 2\nu^2)}{4T^2} \frac{\partial T}{\partial r_{i\alpha}} + \frac{1}{\rho} \frac{\partial \rho}{\partial r_{i\alpha}} \right) f_0 \\
 \frac{\partial f_0}{\partial \sigma_1} &= \left( \frac{7(\bar{v} - \bar{U})}{2T} \cdot \frac{\partial \bar{U}}{\partial \sigma_1} + \frac{7((\bar{v} - \bar{U})^2 - 2T + 2\nu^2)}{4T^2} \frac{\partial T}{\partial \sigma_1} + \frac{1}{\rho} \frac{\partial \rho}{\partial \sigma_1} \right) f_0 \\
 \frac{\partial f_0}{\partial \rho} \frac{\partial \rho}{\partial t} &= -\frac{f_0}{\rho} \nabla_{\bar{r}} \cdot (\rho \bar{U}) \\
 \frac{\partial U_{i\alpha}}{\partial t} \frac{\partial f_0}{\partial U_{i\alpha}} &= -\frac{7(\bar{v} - \bar{U}) f_0}{2T} \left( (\bar{U} \cdot \nabla_{\bar{r}}) \bar{U} + \frac{1}{\rho} \nabla_{\bar{r}} \left( \frac{2T\rho}{7} \right) + \frac{1}{m} \nabla_{\bar{r}} \left( \phi^{(int)} + \phi^{(ext)} \right) \right) \\
 \frac{\partial T}{\partial t} \frac{\partial f_0}{\partial T} &= -\frac{7((\bar{U} - \bar{v})^2 + 2\nu_1^2 - 2T) f_0}{4T^4} \times
 \end{aligned}$$

$$\left( \bar{U} \cdot \nabla_{\bar{r}} T + \frac{2}{7} T \nabla_{\bar{r}} \cdot \bar{U} - \frac{2}{m} \bar{U} \cdot \nabla_{\bar{r}} \left( \phi^{(int)} + \phi^{(ext)} \right) \right)$$

Inserting these and equations (3.23), (3.26) and (3.27) into expansion (3.31) gives

$$\begin{aligned} & \frac{f_0}{4} \left( \frac{7K\nu_1}{T^2} \frac{\partial T}{\partial \sigma_1} + \frac{(7K-4T)(v_{i\alpha} - U_{i\alpha})}{T^2} \frac{\partial T}{\partial r_{i\alpha}} + \frac{4\nu_1}{\rho} \frac{\partial \rho}{\partial \sigma} + \frac{14KU_{i\alpha}}{mT^2} \frac{\partial}{\partial r_{i\alpha}} \left( \phi^{(int)} + \phi^{(ext)} \right) \right. \\ & \quad \left. - \frac{2(K+2T)}{T} \frac{\partial U_{i\alpha}}{\partial r_{i\alpha}} + \frac{14\nu_1(v_{i\alpha} - U_{i\alpha})}{T} \frac{\partial U_{i\alpha}}{\partial \sigma_1} + \frac{14(v_{i\alpha} - U_{i\alpha})(v_{j\beta} - U_{j\beta})}{T} \frac{\partial U_{i\alpha}}{\partial r_{j\beta}} \right) = \Lambda \\ & = \int \int \int (W(n; \mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2}) (f_1(\mathbf{1}')f_0(\mathbf{2}') + f_0(\mathbf{1}')f_1(\mathbf{2}')) \\ & \quad - W(n; \mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}') (f_1(\mathbf{1})f_0(\mathbf{2}) + f_0(\mathbf{1})f_1(\mathbf{2}))) d\mathbf{2}d\mathbf{1}'d\mathbf{2}' \end{aligned} \quad (3.32)$$

$K = 2(\nu_1^2 - T) + (\bar{v} - \bar{U})^2$  is used as a “short hand” and we introduce the simplifying notation  $\bar{U} = (\vec{U}_1, \vec{U}_2)$  and  $\bar{v} = (\vec{v}_1, \vec{v}_2)$ , the adjoining of two 3-vectors into a 6-tuple which, as it happens, also behaves as a vector. We could proceed to seek a solution of equation (3.32) directly, but a further simplification suggests itself. If we make the following substitution.

$$f_1(\mathbf{1}) = f_0(\mathbf{1})\varphi(\mathbf{1}) \quad (3.33)$$

and insert this into equation (3.32), observing that because of the conditions by which  $f_0$  was derived (namely equation (3.19)) in the collision integral, we may perform the substitution  $f_0(\mathbf{1})f_0(\mathbf{2}) = f_0(\mathbf{1}')f_0(\mathbf{2}')$  to obtain

$$\begin{aligned} \Lambda & = \int \int \int (W(n; \mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2}) f_0(\mathbf{1}')f_0(\mathbf{2}') (\varphi(\mathbf{1}') + \varphi(\mathbf{2}')) \\ & \quad - W(n; \mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}') f_0(\mathbf{1})f_0(\mathbf{2}) (\varphi(\mathbf{1}) + \varphi(\mathbf{2}))) d\mathbf{2}d\mathbf{1}'d\mathbf{2}' \\ & = f_0(\mathbf{1}) \int \int \int f_0(\mathbf{2}) (W(n; \mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2}) (\varphi(\mathbf{1}') + \varphi(\mathbf{2}')) \\ & \quad - W(n; \mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}') (\varphi(\mathbf{1}) + \varphi(\mathbf{2}))) d\mathbf{2}d\mathbf{1}'d\mathbf{2}' \end{aligned}$$

$$\begin{aligned} \frac{\Lambda}{f_0(\mathbf{1})} & = \int \int \int f_0(\mathbf{2}) (W(n; \mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2}) (\varphi(\mathbf{1}') + \varphi(\mathbf{2}')) \\ & \quad - W(n; \mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}') (\varphi(\mathbf{1}) + \varphi(\mathbf{2}))) d\mathbf{2}d\mathbf{1}'d\mathbf{2}' \end{aligned}$$

$$\begin{aligned} \frac{\Lambda}{f_0(\mathbf{1})} &= \int \int \int ((W(n; \mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2})f_0(\mathbf{2})\varphi(\mathbf{1}') + W(n; \mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2})f_0(\mathbf{2})\varphi(\mathbf{2}')) \\ &\quad - (W(n; \mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}')f_0(\mathbf{2})\varphi(\mathbf{1}) + W(n; \mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}')f_0(\mathbf{2})\varphi(\mathbf{2}))) d\mathbf{2}d\mathbf{1}'d\mathbf{2}' \end{aligned}$$

$$\begin{aligned} \frac{\Lambda}{f_0(\mathbf{1})} &= \int \int \int ((W(n; \mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2})f_0(\mathbf{2})\varphi(\mathbf{1}') + W(n; \mathbf{2}', \mathbf{1}'; \mathbf{1}, \mathbf{2})f_0(\mathbf{2})\varphi(\mathbf{1}')) \\ &\quad - (W(n; \mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}')f_0(\mathbf{2})\varphi(\mathbf{1}) + W(n; \mathbf{1}, \mathbf{1}'; \mathbf{2}, \mathbf{2}')f_0(\mathbf{1}')\varphi(\mathbf{1}')))) d\mathbf{2}d\mathbf{1}'d\mathbf{2}' \end{aligned}$$

$$\begin{aligned} \frac{\Lambda}{f_0(\mathbf{1})} &= -\varphi(\mathbf{1}) \int \int \int W(n; \mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}')f_0(\mathbf{2})d\mathbf{2}d\mathbf{1}'d\mathbf{2}' + \\ &\quad \int \int \int (W(n; \mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2})f_0(\mathbf{2}) + W(n; \mathbf{2}', \mathbf{1}'; \mathbf{1}, \mathbf{2})f_0(\mathbf{2}) \\ &\quad - W(n; \mathbf{1}, \mathbf{1}'; \mathbf{2}, \mathbf{2}')f_0(\mathbf{1}')) d\mathbf{2}d\mathbf{2}'\varphi(\mathbf{1}')d\mathbf{1}' \end{aligned} \quad (3.34)$$

This form may be re-written in terms of some appropriately defined functions  $A$ ,  $B$  and  $C$ ,

$$A(\mathbf{1}) = -B(n; \mathbf{1})\varphi(\mathbf{1}) + \int C(n; \mathbf{1}, \mathbf{1}')\varphi(\mathbf{1}')d\mathbf{1}', \quad (3.35)$$

and further rearranged to give the standard form for a multidimensional inhomogeneous Fredholm equation of the second kind,

$$\varphi(\mathbf{1}) = -\frac{A(\mathbf{1})}{B(n; \mathbf{1})} + \int \frac{C(n; \mathbf{1}, \mathbf{1}')}{B(n; \mathbf{1})}\varphi(\mathbf{1}')d\mathbf{1}' \quad (3.36)$$

### 3.3 Solving the Fredholm Equation for the First Order Expansion

The study of Fredholm equations is expediently phrased in the language of Hilbert spaces. Expressions and integrals, such as the ones we deal with here, can be expressed as operators and mappings on an infinite dimensional Hilbert space. Equa-



tion (3.36) can be rewritten as follows:

$$\varphi = \Phi + (\mathcal{A} + \mathcal{B})\varphi = \mathcal{T}\varphi. \quad (3.37)$$

$\Phi$  is the infinite dimensional vector represented by  $-\frac{A(\mathbf{1})}{B(n;\mathbf{1})}$ , and  $(\mathcal{A} + \mathcal{B})$  is the linear operator given by the integral with kernel  $\frac{C(n;\mathbf{1},\mathbf{1}')}{B(n;\mathbf{1})}$ . This is written as two operators as we expect  $C$  to contain some terms with Dirac delta functions such as  $\delta(\vec{r}_1 - \vec{r}'_1)$  due to the anticipated presence of similar terms in  $W$ . When these are simplified we shall be left with two integral operators integrating over two different sets of variables. Hence there will be times when it is necessary to consider these two operators  $\mathcal{A}$  and  $\mathcal{B}$  as separate entities.

We have drawn extensively on various proofs and theorems found in Debnath's book [29] and have added our own generalisations and modifications where appropriate. One such generalised theorem is the following.

If  $\mathcal{A}$  and  $\mathcal{B}$  are bounded linear operators with bounds  $k_A$  and  $k_B$  then  $\mathcal{T}$  is a contraction mapping if  $k_A + k_B < 1$ . The proof follows directly from the equation below,

$$\begin{aligned} \|\mathcal{T}\varphi_1 - \mathcal{T}\varphi_2\| &= \|\mathcal{A}\varphi_1 - \mathcal{A}\varphi_2 + \mathcal{B}\varphi_1 - \mathcal{B}\varphi_2\| \leq \|\mathcal{A}\varphi_1 - \mathcal{A}\varphi_2\| + \|\mathcal{B}\varphi_1 - \mathcal{B}\varphi_2\| \\ &= k_A\|\varphi_1 - \varphi_2\| + k_B\|\varphi_1 - \varphi_2\| = (k_A + k_B)\|\varphi_1 - \varphi_2\| \end{aligned} \quad (3.38)$$

It follows from the contraction mapping theorem that if  $\mathcal{T}$  is a contraction mapping then it has a unique fixed point given by

$$\varphi = \mathcal{T}\varphi \Rightarrow \varphi = \sum_{n=0}^{\infty} (\mathcal{A} + \mathcal{B})^n \Phi.$$

### 3.3.1 The Projection Operator Technique

Given a generic integral operator over a region  $\Omega$  in multiple variables  $\int_{\Omega} K(\vec{x}, \vec{y}) f(y) d\vec{y}$  a bound may be determined by observing the following inequality

$$\int_{\Omega} \left| \int_{\Omega} K(\vec{x}, \vec{y}) f(y) d\vec{y} \right|^2 d\vec{x} \leq \int_{\Omega} \int_{\Omega} |K(\vec{x}, \vec{y})|^2 d\vec{x} d\vec{y} \int_{\Omega} |f(\vec{y})|^2 d\vec{y} \quad (3.39)$$

The bound is given by  $\int_{\Omega} \int_{\Omega} |K(\vec{x}, \vec{y})|^2 d\vec{x} d\vec{y}$ . It is tempting to think we could then simply find a restriction on the form of  $\mathcal{A}$  and  $\mathcal{B}$  and use the contraction mapping theorem to solve the equation for  $\varphi$ , but sadly it is totally unreasonable to imagine that this equation has a unique solution. In the Chapman-Enskog expansion we have a restriction on  $f_1$  (see equation (3.11)) and consequently on  $\varphi$ . In the specific case of  $f_1$  and equation (3.7) and referencing our definitions for the macroscopic variables (3.14), these conditions are

$$\begin{aligned} 0 &= \int f_0 \phi d\vec{v}_1 d\vec{v}_2 d\nu_1 = \int \frac{343}{64\pi^{\frac{7}{2}}} \sqrt{\frac{7}{2}} T^{-\frac{7}{2}} \rho e^{-\frac{7}{2T} \left( \frac{1}{2}(\vec{v}_1 - \vec{U}_1)^2 + \frac{1}{2}(\vec{v}_2 - \vec{U}_2)^2 + \nu_1^2 \right)} \phi d\vec{v}_1 d\vec{v}_2 d\nu_1 \\ & \vec{0} = \int \vec{v}_i f_0 \phi d^3 \vec{v}_1 d^3 \vec{v}_2 d\nu_1 \\ &= \int \frac{343}{64\pi^{\frac{7}{2}}} \sqrt{\frac{7}{2}} T^{-\frac{7}{2}} \rho \vec{v}_i e^{-\frac{7}{2T} \left( \frac{1}{2}(\vec{v}_1 - \vec{U}_1)^2 + \frac{1}{2}(\vec{v}_2 - \vec{U}_2)^2 + \nu_1^2 \right)} \phi d^3 \vec{v}_1 d^3 \vec{v}_2 d\nu_1 \\ 0 &= \int \left( \frac{(\vec{v}_1 - \vec{U}_1)^2 + (\vec{v}_2 - \vec{U}_2)^2}{2} + \nu_1^2 \right) f_0 \phi d^3 \vec{v}_1 d^3 \vec{v}_2 d\nu_1 \\ &= \int \frac{343}{64\pi^{\frac{7}{2}}} \sqrt{\frac{7}{2}} T^{-\frac{7}{2}} \rho \left( \frac{(\vec{v}_1 - \vec{U}_1)^2 + (\vec{v}_2 - \vec{U}_2)^2}{2} + \nu_1^2 \right) \\ & \quad \times e^{-\frac{7}{2T} \left( \frac{1}{2}(\vec{v}_1 - \vec{U}_1)^2 + \frac{1}{2}(\vec{v}_2 - \vec{U}_2)^2 + \nu_1^2 \right)} \phi d^3 \vec{v}_1 d^3 \vec{v}_2 d\nu_1 \end{aligned}$$

which simplify to the conditions

$$\begin{aligned}
 0 &= \int e^{-\frac{7}{2T} \left( \frac{1}{2}(\vec{v}_1 - \vec{U}_1)^2 + \frac{1}{2}(\vec{v}_2 - \vec{U}_2)^2 + \nu_1^2 \right)} \phi d\vec{v}_1 d\vec{v}_2 d\nu_1 \\
 \vec{0} &= \int \vec{v}_i e^{-\frac{7}{2T} \left( \frac{1}{2}(\vec{v}_1 - \vec{U}_1)^2 + \frac{1}{2}(\vec{v}_2 - \vec{U}_2)^2 + \nu_1^2 \right)} \phi d^3\vec{v}_1 d^3\vec{v}_2 d\nu_1 \\
 0 &= \int \left( \frac{(\vec{v}_1 - \vec{U}_1)^2 + (\vec{v}_2 - \vec{U}_2)^2}{2} + \nu_1^2 \right) e^{-\frac{7}{2T} \left( \frac{1}{2}(\vec{v}_1 - \vec{U}_1)^2 + \frac{1}{2}(\vec{v}_2 - \vec{U}_2)^2 + \nu_1^2 \right)} \phi d^3\vec{v}_1 d^3\vec{v}_2 d\nu_1
 \end{aligned} \tag{3.40}$$

The observant reader will notice the similarity to inner-products. In fact, given that all values are real (as opposed to complex), each of the above conditions can easily be expressed as  $0 = \langle \mathbf{y}, \mathbf{x} \rangle$  where  $\mathbf{y}$  represents various kernels of the expressions above. Were this space finite, the conditions would be dot products set to zero and thus define a hyper-plane through the origin, or to put it another way a subspace of the Hilbert space. As it happens these conditions still describe a subspace in the infinite dimensional case and it is expedient<sup>4</sup> to construct a projection operator onto this space. For a given condition  $0 = \langle \mathbf{y}, \mathbf{x} \rangle$  the corresponding projection operator is

$$\mathbf{x}' = \mathbf{x} - \hat{\mathbf{y}} \langle \hat{\mathbf{y}}, \mathbf{x} \rangle \tag{3.41}$$

A hat indicates a normalised vector (that is  $\langle \hat{\mathbf{y}}, \hat{\mathbf{y}} \rangle = 1$ ). This has two important properties. First that if a vector  $\mathbf{x}$  is in the subspace ( $0 = \langle \mathbf{y}, \mathbf{x} \rangle$ ) then it acts as the identity operator  $\mathbf{x}' = \mathbf{x}$ . Secondly, that the operator maps onto the subspace as proved by the equation

$$\langle \hat{\mathbf{y}}, \mathbf{x}' \rangle = \langle \hat{\mathbf{y}}, \mathbf{x} \rangle - \langle \hat{\mathbf{y}}, \hat{\mathbf{y}} \langle \hat{\mathbf{y}}, \mathbf{x} \rangle \rangle = \langle \hat{\mathbf{y}}, \mathbf{x} \rangle - \langle \hat{\mathbf{y}}, \mathbf{x} \rangle \langle \hat{\mathbf{y}}, \hat{\mathbf{y}} \rangle = \langle \hat{\mathbf{y}}, \mathbf{x} \rangle - \langle \hat{\mathbf{y}}, \mathbf{x} \rangle = 0.$$

It is possible to define a generalised projection operator which has these properties by construction in respect to the intersection of several subspaces defined by  $\mathbf{y}_0, \dots, \mathbf{y}_n$ .

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<sup>4</sup>In the sense of being a result we will need for later work

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These will be our conditions in equation (3.40).

$$\mathbf{x}' = \mathbf{x} - \sum_{i=0}^n \alpha_i \mathbf{y}_i$$

$\alpha_i$  is fixed by the condition  $\langle \mathbf{x}', \mathbf{y}_i \rangle = 0$  which implies

$$0 = \langle \mathbf{x}, \mathbf{y}_j \rangle - \sum_{i=0}^n \alpha_i \langle \mathbf{y}_i, \mathbf{y}_j \rangle$$

$$\Rightarrow \begin{pmatrix} \alpha_0 \\ \vdots \\ \alpha_n \end{pmatrix} = \begin{pmatrix} \langle \mathbf{y}_0, \mathbf{y}_0 \rangle & \cdots & \langle \mathbf{y}_n, \mathbf{y}_0 \rangle \\ \vdots & \ddots & \vdots \\ \langle \mathbf{y}_0, \mathbf{y}_n \rangle & \cdots & \langle \mathbf{y}_n, \mathbf{y}_n \rangle \end{pmatrix}^{-1} \begin{pmatrix} \langle \mathbf{x}, \mathbf{y}_0 \rangle \\ \vdots \\ \langle \mathbf{x}, \mathbf{y}_n \rangle \end{pmatrix}$$

$$\Rightarrow \mathbf{x}' = \mathbf{x} - \begin{pmatrix} \mathbf{y}_0 \\ \vdots \\ \mathbf{y}_n \end{pmatrix}^T \begin{pmatrix} \langle \mathbf{y}_0, \mathbf{y}_0 \rangle & \cdots & \langle \mathbf{y}_n, \mathbf{y}_0 \rangle \\ \vdots & \ddots & \vdots \\ \langle \mathbf{y}_0, \mathbf{y}_n \rangle & \cdots & \langle \mathbf{y}_n, \mathbf{y}_n \rangle \end{pmatrix}^{-1} \begin{pmatrix} \langle \mathbf{x}, \mathbf{y}_0 \rangle \\ \vdots \\ \langle \mathbf{x}, \mathbf{y}_n \rangle \end{pmatrix}$$

In fact we could further generalise this by allowing skewed projections (where the null space is not perpendicular to the projected plane) by defining our projection to have the form

$$\mathbf{x}' = \mathbf{x} - \sum_{i=0}^n \mathbf{k}_i \langle \mathbf{x}, \mathbf{y}_i \rangle \quad (3.42)$$

in which  $\mathbf{k}_i$  is constrained by the condition  $\langle \mathbf{k}_i, \mathbf{y}_j \rangle = \delta_{ij}$ .

Regardless of which of these projection operators we choose it will have the form expressed in integral notation

$$\varphi' = \varphi - \int P(\mathbf{1}, \mathbf{1}') \varphi d\vec{\nu}_1 d\vec{\nu}_2 d\nu_1 \quad (3.43)$$

and in fact if we take the non-skew form equation (3.40) yield

$$\begin{aligned} & \frac{343\sqrt{7}}{8\pi^{\frac{7}{2}}T^{\frac{11}{2}}} \left( T^2 + 7T(\bar{v} - \bar{U}) \cdot (\bar{v}' - \bar{U}) + 14 \left( \frac{(\bar{v} - \bar{U})^2 - T}{2} + \nu^2 \right) \right. \\ & \left. \times \left( \frac{(\bar{v}' - \bar{U})^2 - T}{2} + \nu'^2 \right) \right) e^{-\frac{7}{2T} \left( \frac{(\bar{v} - \bar{U})^2 + (\bar{v}' - \bar{U})^2}{2} + \nu^2 + \nu'^2 \right)} = P(\mathbf{1}, \mathbf{1}') \end{aligned} \quad (3.44)$$

However, for reasons that we will explore, the skew projection will be the better choice. In that case  $P$  is

$$P = \left( k_0 + k_i v_i + k_7 \left( \frac{(\vec{v}_1 - \vec{U}_1)^2 + (\vec{v}_2 - \vec{U}_2)^2}{2} + \nu_1^2 \right) \right) e^{-\frac{7}{2T} \left( \frac{1}{2}(\vec{v}_1 - \vec{U}_1)^2 + \frac{1}{2}(\vec{v}_2 - \vec{U}_2)^2 + \nu_1^2 \right)} \quad (3.45)$$

where  $k_i$  is subject to

$$\begin{aligned} \delta_{i0} &= \int k_i e^{-\frac{7}{2T} \left( \frac{1}{2}(\vec{v}_1 - \vec{U}_1)^2 + \frac{1}{2}(\vec{v}_2 - \vec{U}_2)^2 + \nu_1^2 \right)} d\vec{v}_1 d\vec{v}_2 d\nu_1 \\ \delta_{ij} &= \int k_i \vec{v}_j e^{-\frac{7}{2T} \left( \frac{1}{2}(\vec{v}_1 - \vec{U}_1)^2 + \frac{1}{2}(\vec{v}_2 - \vec{U}_2)^2 + \nu_1^2 \right)} d^3\vec{v}_1 d^3\vec{v}_2 d\nu_1 \\ \delta_{i7} &= \int k_i \left( \frac{(\vec{v}_1 - \vec{U}_1)^2 + (\vec{v}_2 - \vec{U}_2)^2}{2} + \nu_1^2 \right) e^{-\frac{7}{2T} \left( \frac{1}{2}(\vec{v}_1 - \vec{U}_1)^2 + \frac{1}{2}(\vec{v}_2 - \vec{U}_2)^2 + \nu_1^2 \right)} d^3\vec{v}_1 d^3\vec{v}_2 d\nu_1 \end{aligned} \quad (3.46)$$

We can then define a new operator with the projection operator (let us call it  $\mathcal{P}$ ) and its complimentary projection operator ( $\mathcal{P}_\perp$ ). We derive it thus. Consider the equation that we must solve:

$$\varphi = \Phi + ((\mathcal{A} + \mathcal{B})\varphi)$$

It may be reformulated thus,  $\mathcal{I}$  being the identity operator:

$$(\mathcal{I} - \mathcal{A} - \mathcal{B})\varphi = \Phi$$

However,  $\varphi$  is constrained to be in the image of the projection operators we have defined. We may introduce a dummy variable  $\varphi'$  in the operators kernel that we will

later force to be 0:

$$(\mathcal{I} - \mathcal{A} - \mathcal{B})\varphi + \varphi' = \Phi, \varphi \in \text{im}(\mathcal{P}), \varphi' \in \text{ker}(\mathcal{P})$$

This allows us to rewrite the equation in terms of an unrestricted operator  $\phi$ :

$$((\mathcal{I} - \mathcal{A} - \mathcal{B})\mathcal{P} + \mathcal{P}_\perp)\phi = \Phi, \phi = \mathcal{P}\varphi + \mathcal{P}_\perp\varphi', \mathcal{P} + \mathcal{P}_\perp = \mathcal{I}$$

If this rewritten equation has a unique solution then we may have some hope of finding it with a Neumann series. So we rewrite the equation in the standard form of a Fredholm equation of the second kind

$$\phi = \Phi + (\mathcal{A} + \mathcal{B})\mathcal{P}\phi = \mathcal{T}'\phi$$

The solution of  $\phi$  is then given by

$$\phi = \sum_{n=0}^{\infty} ((\mathcal{A} + \mathcal{B})\mathcal{P})^n \Phi = \mathcal{T}'^{\infty} \Phi$$

subject to afore mentioned assumptions about the properties of  $\mathcal{T}'$ . A consequence of the definition of  $\phi$  is

$$\varphi = \sum_{n=0}^{\infty} ((\mathcal{A} + \mathcal{B})\mathcal{P})^n \Phi \Leftrightarrow 0 = \mathcal{P}_\perp \sum_{n=0}^{\infty} ((\mathcal{A} + \mathcal{B})\mathcal{P})^n \Phi \quad (3.47)$$

So, if a projection (probably a skew projection) operator on to the space specified by our constraints can be found that has the property that  $\mathcal{P}_\perp \sum_{n=0}^{\infty} ((\mathcal{A} + \mathcal{B})\mathcal{P})^n \Phi$  exists and is 0, we have solved our problem!

This method is analogous to that used to construct the Bott-Duffin inverse [33]. In fact if we were to approximate the kernel  $(\mathcal{A} + \mathcal{B})$  and  $\Phi$  as an arbitrary finite sum of Hermite functions then the approximated equation can be re-expressed as a matrix equation and the operator associated with the Bott-Duffin inverse (assuming

it exists) would have exactly the form:

$$\mathcal{P}((\mathcal{I} - \mathcal{A} - \mathcal{B})\mathcal{P} + \mathcal{P}_\perp)^{-1} = \mathcal{P} \sum_{n=0}^{\infty} ((\mathcal{A} + \mathcal{B})\mathcal{P})^n \quad (3.48)$$

recalling that the inverse of an invertible matrix may also be given by Neumann series.

In short, if  $T'^\infty$  is well defined and  $\mathcal{P}$  conforms to the afore mentioned conditions then we have found the solution for equation (3.36) subject to conditions in equation (3.40). The logical way to proceed would be to plug in the most general  $\mathcal{P}$  consistent with equation (3.40) then see what restrictions are necessary upon it to ensure  $T'^\infty$  exists and, lastly, ask what further restrictions are necessary to ensure  $\mathcal{P}_\perp T'^\infty = 0$  and in so doing seek a solution to the equation.

### 3.3.2 Comparison to Fredholm's Method for Multiple Solutions to Fredholm Equations

It is worth comparing the method we have outlined with other methods for solving Fredholm equations to gauge the likelihood of success when real-world functions are inserted for  $W$ . During the research we found no reference in the literature for the method used here in. It is indeed possible, although by no means certain, that the method is original. It has long been known that not all Fredholm equations have a unique solution, and that in fact many have multiple solutions. Fredholm himself described one method of finding them in his paper [27].

Fredholm considered only the equation for a single variable, integrating from 0 to 1 on the basis that this equation would generalise to a huge number of cases.

$$\varphi(x) + \int_0^1 f(x, y)\varphi(y)dy = \phi(x)$$

He defined a class of functions derived from the kernel

$$f \begin{pmatrix} x_1, x_2, \dots, x_n \\ y_1, y_2, \dots, y_n \end{pmatrix} = \begin{vmatrix} f(x_1, y_1) & f(x_1, y_2) & \dots & f(x_1, y_n) \\ f(x_2, y_1) & f(x_2, y_2) & \dots & f(x_2, y_n) \\ \dots & \dots & \dots & \dots \\ f(x_n, y_1) & f(x_n, y_2) & \dots & f(x_n, y_n) \end{vmatrix}$$

He then used this function to construct a functional of the kernel  $D_f$

$$D_f = \sum_{n=0}^{\infty} \frac{1}{n!} \int_0^1 \dots \int_0^1 f \begin{pmatrix} x_1, x_2, \dots, x_n \\ x_1, x_2, \dots, x_n \end{pmatrix} dx_1 dx_2 \dots dx_n$$

His reasoning was that a Fredholm equation could in a sense be seen as a group operation, mapping the unknown function to the inhomogeneous part of the equation, as it happens a linear operator. Therefore if the inverse can be found, then the solution can be directly stated by applying the inverse to the inhomogeneous part. In this context  $D_f$  can be seen as analogous to the determinant of a matrix since it occurs that if  $D_f$  is non zero then a unique inverse can be constructed. If not it may still be possible to construct a set of solutions. Fredholm defined a generalisation of  $D_f$

$$D_f \begin{pmatrix} \xi_1, \xi_2, \dots, \xi_n \\ \eta_1, \eta_2, \dots, \eta_m \end{pmatrix} = \sum_{\nu=0}^{\infty} \frac{1}{\nu!} \int_0^1 \dots \int_0^1 f \begin{pmatrix} \xi_1 \dots \xi_n, x_1 \dots x_\nu \\ \eta_1 \dots \eta_m, x_1 \dots x_\nu \end{pmatrix} dx_1 \dots dx_\nu$$

It occurs that if

$$D_f \begin{pmatrix} \xi_1, \dots, \xi_n \\ \eta_1, \dots, \eta_m \end{pmatrix}$$

is non zero and the lowest such function in terms of  $n$  for which it can be non zero it is possible to construct a general solution for the equation with  $n$  undetermined constants. The disadvantage of this technique is that it requires us to find the



full set of solutions when we may only desire solutions for one set of restrictions. However, it does demonstrate that Fredholm equations with multiple solutions exist and can be found through processes of infinite successive integration. Therefore we have every confidence that the proposed method will offer real and useful solutions for a reasonably wide range of forms for  $W$ .

Fredholm's methods have been generalised into a theory of operators with finite dimensional solution spaces by Ruston who proved more generally that such operators will have finite solution spaces [28] assuming that the operators are what he calls asymptotically quasi compact. We can present no proof here but our suspicion is that the operators we address will not be asymptotically quasi compact since our constraints seem sufficient to eliminate an infinite number of degrees of freedom. However, in order to give a unique solution, the new operators  $\mathcal{A}$  and  $\mathcal{B}$  derived by analogy with the constrained (Bott-Duffin) inverse have not been required to be compact but only to have sufficiently small bounds. The process of demonstrating sufficiently small boundedness would normally imply that it was a Hilbert-Schmidt operator or its multidimensional analogue, and hence compact, but our boundedness conditions fall short of that since they do not involve integration over all degrees of freedom.

### 3.3.3 Application to the First Order Expansion

The new equation we must solve,  $\varphi = \mathcal{T}'\varphi$ , has the explicit form

$$\begin{aligned} \phi(\mathbf{1}) &= -\frac{A(\mathbf{1})}{B(n; \mathbf{1})} + \int \left( \frac{C(n; \mathbf{1}, \mathbf{1}')}{B(n; \mathbf{1})} - \int \frac{C(n; \mathbf{1}, \mathbf{1}'')}{B(n; \mathbf{1})} P'(\mathbf{1}'', \mathbf{1}') d\mathbf{1}'' \right) \phi(\mathbf{1}') d\mathbf{1}' \\ &= \Phi + \int K(\mathbf{1}, \mathbf{1}') \phi(\mathbf{1}') d\mathbf{1}' \end{aligned} \tag{3.49}$$

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We have defined  $P'$  as

$$P'(\mathbf{1}, \mathbf{1}') = \delta(\vec{r}_1 - \vec{r}'_1)\delta(\vec{r}_2 - \vec{r}'_2)\delta(\sigma_1 - \sigma'_1)P(\mathbf{1}, \mathbf{1}')$$

Considering the kernel  $K$ , recall that after the elimination of terms like  $\delta(\vec{r}_1 - \vec{r}'_1)$ , we will have two integrals or more. As we have demonstrated, if these are bounded with bounds that sum to less than 1, then there is definitely a unique solution for  $\varphi$ . Defining the new kernel

$$K_n(\mathbf{1}, \mathbf{1}') = \int K(\mathbf{1}, \mathbf{2}) \cdots K(\{\mathbf{n} - \mathbf{1}\}, \mathbf{n}) d\mathbf{2} \cdots d\{\mathbf{n} - \mathbf{1}\}$$

where  $\{\mathbf{n} - \mathbf{1}\}$  represents the  $n-1$ th 14-tuple not the difference of the  $n$ th and first 14-tuple.  $\phi$  is given by the expression

$$\phi = \int \sum_{n=0}^{\infty} K_n(\mathbf{1}, \mathbf{1}') \Phi(\mathbf{1}') d\mathbf{1}' \tag{3.50}$$

Recall again that this is actually more integrals than it would initially appear.

However, this result still is still dependent on our choices of  $k_i$  which are set by requiring  $0 = \int P'(\mathbf{1}, \mathbf{1}') \phi(\mathbf{1}') d\mathbf{1}'$ . If we can do this we should have a solution  $\varphi = \phi$ .

This still leaves a great many questions unanswered. What forms of  $W$ , if any, admit such solutions and are any of them physically meaningful? And of those  $W$ , how many have forms which allow a reasonable chance of explicitly calculating  $K_n$  and the expression to which the infinite sum converges? And, finally, given the number of approximations undertaken from Grmela's original model, even with a good choice of  $W$  can this model still make useful predictions?

### 3.4 Examples of the Projection Technique

It is a non trivial matter to establish whether the methods used in section 3.3.1 actually have any non trivial applications. We are also aware the method may have confused some readers so here we demonstrate the constructions and solution of a worked example. Consider an arbitrary two variable Fredholm equation.

$$\varphi(x, y) = \phi(x, y) + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} K(x, y, x', y') \varphi(x', y') dx' dy' \quad (3.51)$$

Now suppose that this equation has no unique solution but that we have the additional constraints on any solution given by

$$0 = \int_{-\infty}^{\infty} J(y) \varphi(x, y) dy, \quad 1 = \int_{-\infty}^{\infty} J(y) L(y) dy \quad (3.52)$$

$L$  is the skewed projection kernel. The solutions of equation (3.52) can be seen as a hyperplane in the Hilbert space and a projection operator onto it is given by

$$\varphi'(x, y) = \varphi(x, y) - L(y) \int_{-\infty}^{\infty} J(y') \varphi(x, y') dy' \quad (3.53)$$

subject to the aforementioned condition on  $L$ . The analogue to the Bott-Duffin equation is made by inserting equation (3.53) into the kernel part of equation (3.51) giving

$$\begin{aligned} & \varphi(x, y) = \phi(x, y) \\ & + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left( K(x, y, x', y') - J(y') \int_{-\infty}^{\infty} L(y'') K(x, y, x', y'') dy'' \right) \varphi(x', y') dx' dy' \end{aligned}$$

This can be seen as a Fredholm equation with the new kernel

$$K'(x, y, x', y') = K(x, y, x', y') - J(y') \int_{-\infty}^{\infty} L(y'') K(x, y, x', y'') dy'' \quad (3.54)$$

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We note that because we restrict all functions to being real,  $|K|^2 = K^2$  and  $|K'|^2 = K'^2$ . It is quite useful to derive the following identity

$$K'^2(x, y, x', y') = K^2(x, y, x', y') + \left( J(y') \int_{-\infty}^{\infty} L(y'') K(x, y, x', y'') dy'' \right)^2 - 2K(x, y, x', y') J(y') \int_{-\infty}^{\infty} L(y'') K(x, y, x', y'') dy'' \quad (3.55)$$

Finally, to make the problem tractable but at the same time retain a great deal of generality, we consider the principal functions to be expansions of Hermite functions invoking the Einstein summation convention to express this:

$$K(x, y, z, w) = \kappa_{ijkl} \psi_i(x) \psi_j(y) \psi_k(z) \psi_l(w), \quad J(y) = \lambda_i \psi_i(y), \quad L(y) = \mu_i \psi_i(y) \quad (3.56)$$

Therefore, by applying equations (3.55) and (3.56), we have

$$\int_{\Omega} K'^2(x, y, z, w) d\omega = \kappa_{ijkl} \kappa_{ijkl} + \lambda_l \lambda_l \mu_m \mu_m \kappa_{ijkm} \kappa_{ijkn} - 2\lambda_l \mu_m \kappa_{ijkl} \kappa_{ijkm}$$

$d\omega$  is short hand for  $dx dy dz dw$  and  $\int_{\Omega}$  is integration over all of  $\mathbb{R}^4$ . A sufficient condition for solution via Neumann series is that this be less than one. Likewise  $\int_{\Omega} K^2 d\omega = \kappa_{ijkl} \kappa_{ijkl}$  must be greater than 1 otherwise equation (3.51) would have a unique solution. We can use this to construct a kernel and condition that only offer a solution together. One such construction is

$$K = \sqrt{2} \psi_0(x) \psi_0(y) \psi_0(x') \psi_0(y'), \quad J = 2\psi_0(y) + \psi_1(y), \quad L = \mu_0 \psi_0(y) + \dots$$

The kernel of the new equation only converges when  $\frac{4-\sqrt{6}}{10} < \mu_0 < \frac{4+\sqrt{6}}{10}$ . This shall be our worked example It's kernel given by equation (3.54)

$$K'(x, y, x', y') = \left( (\sqrt{2} - 2\sqrt{2}\mu_0) \psi_0(y') - \sqrt{2}\mu_0 \psi_1(y') \right) \psi_0(x) \psi_0(y) \psi_0(x') \quad (3.57)$$

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To calculate the Neumann series it is expedient to define

$$K'_n(x, y, x', y') = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} K'(x, y, x'', y'') K'_{n-1}(x'', y'', x', y') dx'' dy''$$

We can find the form of  $K'_n$  by appealing to proof by induction. Assume

$$K'_n(x, y, x', y') = (A_n \psi_0(y') + B_n \psi_1(y')) \psi_0(x) \psi_0(y) \psi_0(x')$$

It then follows that  $K'_{n+1}$  has the form

$$K'_{n+1}(x, y, x', y') = \int_{-\infty}^{\infty} (\sqrt{2} - 2\sqrt{2}\mu_0) (A_n \psi_0(y') + B_n \psi_1(y')) \psi_0(x) \psi_0(y) \psi_0(x')$$

However, it follows that this, and the induction step  $K'_1 = K'$ , and the above statement are satisfied if

$$A_n = (\sqrt{2} - 2\sqrt{2}\mu_0)^n, \quad B_n = -\sqrt{2} (\sqrt{2} - 2\sqrt{2}\mu_0)^{n-1}$$

giving a final form for  $K'_n$

$$K'_n(x, y, z, w) = (\sqrt{2} - 2\sqrt{2}\mu_0)^n \left( \psi_0(y') - \frac{1}{1 - 2\mu_0} \psi_1(y') \right) \psi_0(x) \psi_0(y) \psi_0(x') \quad (3.58)$$

It is useful to apply the geometric series rule to the term “to the power of  $n$ ” in equation (3.58)

$$\sum_{n=1}^{\infty} (\sqrt{2} - 2\sqrt{2}\mu_0)^n = \frac{2 - 4\mu_0}{\sqrt{2} - 2 + 4\mu_0} \quad (3.59)$$

It is likewise expedient to define a function  $R$  (sometimes called the resolvent) as the infinite sum of all  $K'_n$  and this is given by appealing to equation (3.59)

$$\begin{aligned} R(x, y, x', y') &= \sum_{n=1}^{\infty} K'_n(x, y, x', y') \\ &= \frac{2 - 4\mu_0}{\sqrt{2} - 2 + 4\mu_0} \left( \psi_0(y') - \frac{1}{1 - 2\mu_0} \psi_1(y') \right) \psi_0(x) \psi_0(y) \psi_0(x') \end{aligned} \quad (3.60)$$

### CHAPTER 3. SEEKING A SOLUTION TO GRMELA'S EQUATION

We must define the inhomogeneous part to proceed and do so:

$$\phi(x, y) = \zeta_{ij}\psi_i(x)\psi_j(y)$$

The Neumann series can then be expressed using this and equation (3.60) as

$$\begin{aligned} \varphi(x, y) &= \phi(x, y) + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} R(x, y, x', y')\phi(x', y')dx'dy' \\ &= \zeta_{ij}\psi_i(x)\psi_j(y) + \frac{2-4\mu_0}{\sqrt{2}-2+4\mu_0} \left( \zeta_{00} - \frac{\zeta_{01}}{1-2\mu_0} \right) \psi_0(x)\psi_0(y) \end{aligned}$$

This will only be a solution of the original equation if the solution is confined to the hyperplane defined by our condition (3.52)

$$\begin{aligned} 0 &= \int_{-\infty}^{\infty} J(y) \left( \zeta_{ij}\psi_i(x)\psi_j(y) + \frac{2-4\mu_0}{\sqrt{2}-2+4\mu_0} \left( \zeta_{00} - \frac{\zeta_{01}}{1-2\mu_0} \right) \psi_0(x)\psi_0(y) \right) dy \\ &= \int_{-\infty}^{\infty} (2\psi_0(y) + \psi_1(y)) \left( \zeta_{ij}\psi_i(x)\psi_j(y) + \frac{2-4\mu_0}{\sqrt{2}-2+4\mu_0} \left( \zeta_{00} - \frac{\zeta_{01}}{1-2\mu_0} \right) \psi_0(x)\psi_0(y) \right) dy \\ &= 2\zeta_{i0}\psi_i(x) + \zeta_{i1}\psi_i(x) + 2\frac{2-4\mu_0}{\sqrt{2}-2+4\mu_0} \left( \zeta_{00} - \frac{\zeta_{01}}{1-2\mu_0} \right) \psi_0(x) \end{aligned}$$

Clearly this implies  $2\zeta_{i0} = -\zeta_{i1}$  if  $i \neq 0$  leaving the condition

$$0 = 2\zeta_{00} + \zeta_{01} + 2\frac{2-4\mu_0}{\sqrt{2}-2+4\mu_0} \left( \zeta_{00} - \frac{\zeta_{01}}{1-2\mu_0} \right)$$

This may be rephrased as a quadratic equation

$$0 = (2\zeta_{00} + \zeta_{01}) \left( \sqrt{2} - 2 + 4\mu_0 \right) (1 - 2\mu_0) + 2(2 - 4\mu_0) (\zeta_{00} (1 - 2\mu_0) - \zeta_{01})$$

that has the two solutions,  $\mu_0 = \frac{1}{2}$  or  $\mu_0 = \frac{1}{4} \left( 6 - \sqrt{2} - \frac{2\sqrt{2}l_{00}}{l_{01}} \right)$ . Only the second solution is non trivial. Recalling that  $\mu_0$  has a restricted range, the second solution implies:

$$\frac{22 + 2\sqrt{6} - 5\sqrt{2}}{10\sqrt{2}} > \frac{l_{00}}{l_{01}} > \frac{22 - 2\sqrt{6} - 5\sqrt{2}}{10\sqrt{2}}$$

Recalling the condition from equation (3.52)

$$1 = \int_{-\infty}^{\infty} J(y)L(y)dy = 2\mu_0 + \mu_1 \Rightarrow 1 - 2\mu_0 = \mu_1$$

So, provided these conditions are met, a unique solution has been constructed. This may seem a some what artificial and constructed example but it demonstrates proof of concept if not perhaps usefulness.

### 3.5 Summary

In this chapter several key events have taken place.

- Grmelas equation for modelling polymers was introduced and its physical interpretation expounded.
- A simplification to Grmelas equation was introduced.
- A set of operators for deriving macroscopic variables from Grmelas model was postulated.
- A Chapman-Enskog expansion was applied to the simplified Grmelas equation in terms of the aforementioned macroscopic variables.
- Utilising results by Grmela the zeroth order of the Chapman-Enskog expansion was solved and used to derive polymer dynamics equations analogous to Euler's equations and also to create a foundation for solving the 1st order part of the expansion.
- The first order of the Chapman-Enskog expansion was calculated, previous results inserted and various manipulations were made allowing the problem to be expressed in terms of solving a linear Fredholm integral equation.

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- The Bott-Duffin inverse was generalised to infinite dimensional Hilbert spaces based on a very general 'skew projection' operator and the Neuman series method for calculating the inverse.
- The relationship between the generalised Bott-Duffin inverse and methods developed by Fredholm was explored.
- An example of a problem solvable with the generalised Bott-Duffin inverse but not conventional Neuman series was constructed.



## Chapter 4

### Seeking a Thermal Lattice

### Boltzmann-Like Method from a Linear Grmela-Like Equation

In seeking a model for the flow and behaviour of polymers we have started with the most analytically complete model that we could make reasonable progress with. However, rigour and analytical completeness will not necessarily lead to easy and useable simulations.

If one is willing to accept a degree of linearization then it is possible to derive a discreet analogue to Boltzmann-like equations, so called lattice Boltzmann equations. These lend themselves to computer simulation and are very amenable to parallelization. Code to implement these ‘lattice Boltzmann methods’ typically assumes simple cellular automaton-like actions where a time step occurs and calculations are done for each cell and then passed in a direct fashion to other cells in a neighbourhood, ready for the next time step. However, these models tend to be isothermal.

For reasons that will be explained it seemed necessary to include an interpolation step whereby results from each cell may be distributed to other cells in the

neighbourhood in a dynamic way that will vary with temperature in order to achieve good thermal simulation. Consequently, the method here is quite different and more complex than typical ‘lattice Boltzmann methods’ but still relatively straightforward to implement (and parallelise, even if necessarily more processor-hungry to run).

## 4.1 A Priori Derivation of the Lattice Boltzmann-Like Equation

In their paper, He and Lou [6] were able to find a fairly direct method to derive lattice Boltzmann equations. If we examine equation (3.7) we see that if we are willing to neglect the fourth term for potential energy on the left hand side and as just willing to linearize the right hand side collision integral, the new form of equation (3.7) is like the one given in He and Lou’s paper,

$$D_t f = -\frac{1}{\lambda} (f - f_0) \quad (4.1)$$

$D_t$  is the total derivative, in this case

$$\frac{\partial}{\partial t} + v_{i\alpha} \frac{\partial}{\partial r_{i\alpha}} + \nu_1 \frac{\partial}{\partial \sigma_1}$$

and  $f_0$  is as given in equation (3.21). It is expedient to re-express  $f_0$  with a change of variables; a change of variables that we will shortly apply to all our working notation (hopefully not confusing the Reader too much in the process).

$$f_0(\mathbf{1}) = \frac{343}{64\pi^{\frac{7}{2}}} \sqrt{\frac{7}{2}} T^{-\frac{7}{2}} \rho e^{-\frac{7}{2T} ((\vec{v}_+ - \vec{U}_+)^2 + (\vec{v}_- - \vec{U}_-)^2 + \nu_1^2)} \quad (4.2)$$

$$\begin{aligned}
 \vec{v}_+ &= \frac{\vec{v}_1 + \vec{v}_2}{2}, \quad \vec{v}_- = \frac{\vec{v}_2 - \vec{v}_1}{2} \\
 \vec{U}_+ &= \frac{\vec{U}_1 + \vec{U}_2}{2}, \quad \vec{U}_- = \frac{\vec{U}_2 - \vec{U}_1}{2} \\
 \vec{r}_+ &= \frac{\vec{r}_1 + \vec{r}_2}{2}, \quad \vec{r}_- = \frac{\vec{r}_2 - \vec{r}_1}{2}
 \end{aligned} \tag{4.3}$$

Following the course of He and Lou's work we apply a formal integration over a time interval  $\delta_t$  to acquire the following equation

$$f(\bar{r} + \bar{v}\delta_t, \bar{v}, t + \delta_t) = e^{-\frac{\delta_t}{\lambda}} f(\bar{r}, \bar{v}, t) + \frac{1}{\lambda} e^{-\frac{\delta_t}{\lambda}} \int_0^{\delta_t} e^{\frac{t'}{\lambda}} f_0(\bar{r} + \bar{v}\delta_t, \bar{v}, t + t') dt'$$

We then promptly take the Taylor expansion upto the first order in  $\delta_t$ , giving the equation

$$f(\bar{r} + \bar{v}\delta_t, \bar{v}, t + \delta_t) - f(\bar{r}, \bar{v}, t) = -\frac{1}{\tau} (f(\bar{r}, \bar{v}, t) - f_0(\bar{r}, \bar{v}, t)), \quad \tau = \frac{\lambda}{\delta_t} \tag{4.4}$$

This is the discrete time version of the equation. It is at this point that we switch our notation, and  $\bar{r}$  and  $\bar{v}$  that formally, in this chapter, represented  $(\vec{r}_1, \vec{r}_2, \sigma_1)$  and  $(\vec{v}_1, \vec{v}_2, \nu_1)$  will now represent  $(\vec{r}_+, \vec{r}_-, \sigma_1)$  and  $(\vec{v}_+, \vec{v}_-, \nu_1)$  and so on. It should be noted that this change of variables now means that the physical interpretation of  $f$  requires some care and comparison to  $f$  as expressed in the original variables.

The next step in He and Lou's method is to approximate  $f_0$  as a Taylor series for  $\bar{U}$ . He and Lou state that a second order expansion is sufficient for mass and momentum conservation, but we also require energy conservation and so perform a third order expansion (although we cannot swear that this will be sufficient for an accurate and sensible set of conservation equations via the Chapman-Enskog method). It is enough for the operator to conserve mass, momentum, and energy locally in its present form though. The expansion gives

$$\begin{aligned}
 f_0 \approx f^{(eq)} &= \frac{343}{64\pi^{\frac{7}{2}}} \sqrt{\frac{7}{2}} T^{-\frac{7}{2}} \rho e^{-\frac{7}{2T}(\vec{v}_i \cdot \vec{v}_i + \nu_1^2)} \\
 &\times \left( 1 + \frac{7}{T} \vec{U}_i \cdot \vec{v}_i + \frac{49}{2T^2} (\vec{U}_i \cdot \vec{v}_i)^2 - \frac{7}{2T} \vec{U}_i \cdot \vec{U}_i - \frac{49}{2T^2} \vec{U}_i \cdot \vec{U}_i \vec{U}_j \cdot \vec{v}_j + \frac{343}{6T^3} (\vec{U}_i \cdot \vec{v}_i)^3 \right)
 \end{aligned} \tag{4.5}$$

The latin subscripts formally index over the values + and – for the purposes of Einstein summation. Other studies have found that the function  $f^{(eq)}$  can be generalised to allow fluids with different shear and bulk viscosity to be modelled. Thus we consider a generalised form of equation (4.5) and ask what restrictions it must obey in order to conserve momentum, mass, and energy locally. First we allow each term in the brackets to have an undetermined constant

$$\begin{aligned}
 f^{(eq)} &= \frac{343}{64\pi^{\frac{7}{2}}} \sqrt{\frac{7}{2}} T^{-\frac{7}{2}} \rho e^{-\frac{7}{2T}(\vec{v}_i \cdot \vec{v}_i + \nu_1^2)} \left( a + \frac{b_{ij}}{T} \vec{U}_i \cdot \vec{v}_j + \frac{c_{ijkl}}{T^2} \vec{U}_i \cdot \vec{v}_j \vec{U}_k \cdot \vec{v}_l \right. \\
 &\quad \left. + \frac{d_{ij}}{T} \vec{U}_i \cdot \vec{U}_j + \frac{g_{ijkl}}{T^2} \vec{U}_i \cdot \vec{U}_j \vec{U}_k \cdot \vec{v}_l + \frac{h_{ijklmn}}{T^3} \vec{U}_i \cdot \vec{v}_j \vec{U}_k \cdot \vec{v}_l \vec{U}_m \cdot \vec{v}_n \right)
 \end{aligned} \tag{4.6}$$

The condition for local conservation of mass, momentum, and energy is that the right hand side of equation (4.4) is 0 when the operators that give mass, momentum, and energy are applied, or in other words that  $f^{(eq)}$  has values under those operators identical to those of  $f_0$  (our adjustment of variables in  $f_0$  serves as a guide for the physical interpretation of  $f$ ). Applying the mass operator to equation (4.6) and setting it equal to the result of the operator applied to  $f_0$  gives

$$\begin{aligned}
 \rho \left( \frac{1}{8} \left( a + \frac{d_{ij}}{T} \vec{U}_i \cdot \vec{U}_j \right) + \frac{T}{56} \frac{c_{ijkj}}{T^2} \vec{U}_i \cdot \vec{U}_k \right) &= \frac{\rho}{8} \\
 \Rightarrow \left( a + \frac{1}{T} \left( d_{ij} + \frac{c_{ikjk}}{7} \right) \vec{U}_i \cdot \vec{U}_j \right) &= 1
 \end{aligned}$$

$$\Rightarrow a = 1, d_{ij} = -\frac{c_{ikjk}}{7} \quad (4.7)$$

Repeating this procedure with the momentum operator gives

$$\begin{aligned} \rho \left( \frac{T}{56} \left( \frac{b_{ij}}{T} + \frac{g_{klj}}{T^2} \vec{U}_k \cdot \vec{U}_l \right) \vec{U}_i + \frac{3T^2}{392} \frac{h_{ijkmlm}}{T^3} \vec{U}_k \cdot \vec{U}_l \vec{U}_i \right) &= \frac{\rho}{8} \vec{U}_j \\ \Rightarrow \left( \frac{b_{ij}}{7} \vec{U}_i + \frac{1}{7T} \left( g_{klj} + \frac{3h_{ijkmlm}}{7} \right) \vec{U}_k \cdot \vec{U}_l \vec{U}_i \right) &= \vec{U}_j \\ \Rightarrow b_{ij} = 7\delta_{ij}, g_{ijkl} = -\frac{3h_{klimjm}}{7} & \end{aligned} \quad (4.8)$$

Finally, repeating this calculation with the energy operator gives

$$\begin{aligned} \rho \left( \frac{T}{8} \left( a + \frac{d_{ij}}{T} \vec{U}_i \cdot \vec{U}_j \right) + \frac{9T^2}{392} \frac{c_{ijkj}}{T^2} \vec{U}_i \cdot \vec{U}_k \right) &= \frac{\rho}{8} (T + (U_-^2 + U_+^2)) \\ \Rightarrow \left( aT + \left( d_{ij} + \frac{9}{49} c_{ijkj} \right) \vec{U}_i \cdot \vec{U}_j \right) &= (T + (U_-^2 + U_+^2)) \\ \Rightarrow \left( T + \frac{2}{49} c_{ijkj} \vec{U}_i \cdot \vec{U}_j \right) &= (T + (U_1^2 + U_2^2)) \\ \Rightarrow c_{ijkj} = \frac{49}{2} \delta_{ij} & \end{aligned} \quad (4.9)$$

We have used equation (4.7). Taking equations (4.7), (4.8) and (4.9) and substituting into equation (4.6) we get.

$$\begin{aligned} f^{(eq)} = \frac{343}{64\pi^{\frac{7}{2}}} \sqrt{\frac{7}{2}} T^{-\frac{7}{2}} \rho e^{-\frac{7}{2T}(\vec{v}_i \cdot \vec{v}_i + \nu_1^2)} & \left( 1 + \frac{7}{T} \vec{U}_i \cdot \vec{v}_i + \frac{c_{ijkl}}{T^2} \vec{U}_i \cdot \vec{v}_j \vec{U}_k \cdot \vec{v}_l \right. \\ & \left. - \frac{7}{2T} \vec{U}_i \cdot \vec{U}_i - \frac{3h_{klimjm}}{7T^2} \vec{U}_i \cdot \vec{U}_j \vec{U}_k \cdot \vec{v}_l + \frac{h_{ijklmn}}{T^3} \vec{U}_i \cdot \vec{v}_j \vec{U}_k \cdot \vec{v}_l \vec{U}_m \cdot \vec{v}_n \right) \end{aligned} \quad (4.10)$$

Whether we take this, or equation (4.5), or some higher order expression, the following steps are more or less the same.

### 4.1.1 Quadrature on Cartesian Co-ordinates

In the process of deriving an equation with discrete rather than continuous velocities we are guided by the process of quadrating integrals over velocity since our operators for converting Boltzmann-like equations to ones more typically found in fluid dynamics are all based around integrals. The equivalent operators for the discrete equations must be based on sums. Quadrature is a logical choice for discretization as it naturally converts integrals to sums. When applying these operators to  $f^{(eq)}$  and, basically, anything derived from it, we obtain expressions of the form

$$\hat{f} = \frac{343}{64\pi^{\frac{7}{2}}} \sqrt{\frac{7}{2}} T^{-\frac{7}{2}} \rho \int_{\mathbb{R}^7} e^{-\frac{7}{2T}(\bar{v}\cdot\bar{v}+\nu^2)} P(T, \bar{U}, \bar{v}, \nu) d^6\bar{v}d\nu \quad (4.11)$$

By substituting

$$\bar{v} = \sqrt{\frac{2T}{7}} \bar{v}', \nu = \sqrt{\frac{2T}{7}} \nu' \quad (4.12)$$

into equation (4.11) we get

$$\begin{aligned} \hat{f} &= \frac{343}{64\pi^{\frac{7}{2}}} \sqrt{\frac{7}{2}} T^{-\frac{7}{2}} \rho \left(\frac{2T}{7}\right)^{\frac{7}{2}} \int_{\mathbb{R}^7} e^{-(\bar{v}'\cdot\bar{v}'+\nu'^2)} P\left(T, \bar{U}, \sqrt{\frac{2T}{7}}\bar{v}', \sqrt{\frac{2T}{7}}\nu'\right) d^6\bar{v}'d\nu' \\ &= \frac{\rho}{8\pi^{\frac{7}{2}}} \int_{\mathbb{R}^6} e^{-\bar{v}'\cdot\bar{v}'} P\left(T, \bar{U}, \sqrt{\frac{2T}{7}}\bar{v}', \sqrt{\frac{2T}{7}}\nu'\right) d^6\bar{v}'d\nu' \end{aligned} \quad (4.13)$$

Treating each dimension of this integral as a single quadrature problem we immediately see that Gauss-Hermite quadrature can be applied to this form. Applied to the third order this gives

$$\hat{f} \approx \check{f} = \frac{\rho}{8\pi^{\frac{7}{2}}} \sum_{i_x, i_y, i_z, j_x, j_y, j_z, k=-1}^1 w_i w_j w_k P\left(T, \bar{U}, \sqrt{\frac{2T}{7}}\bar{v}'_{i, \vec{j}}, \sqrt{\frac{2T}{7}}\nu'_k\right)$$

The abscissae and weights are given by

$$\bar{v}'_{i, \vec{j}} = \sqrt{\frac{3}{2}}(\vec{i}, \vec{j}), \nu'_k = \sqrt{\frac{3}{2}}k, w_i = \frac{8\pi^{\frac{3}{2}}}{27(4)^{i^2}}, w_j = \frac{8\pi^{\frac{3}{2}}}{27(4)^{j^2}}, w_k = \frac{\sqrt{\pi}}{3} \frac{2}{4k^2}$$

By simple rearrangement and algebra we get

$$\check{f} = \frac{\rho}{8\pi^{\frac{7}{2}}} \sum_{i_x, i_y, i_z, j_x, j_y, j_z, k=-1}^1 W_{\vec{i}, \vec{j}, k} P(T, \bar{U}, \bar{v}_{\vec{i}, \vec{j}}, \nu_k)$$

with the modified abscissae and combined weights

$$\bar{v}_{\vec{n}} = \sqrt{\frac{3T}{7}}(\vec{i}, \vec{j}), \nu_k = \sqrt{\frac{3T}{7}}k, W_{\vec{i}, \vec{j}, k} = \frac{128\pi^{\frac{7}{2}}}{2187(4)^{i^2+j^2+k^2}}$$

Further modification, moving a constant out of the weights, achieves the final quadrature expression

$$\check{f} = \frac{16\rho}{2187} \sum_{i_x, i_y, i_z, j_x, j_y, j_z, k=-1}^1 W_{\vec{i}, \vec{j}, k} P(T, \bar{U}, \bar{v}_{\vec{i}, \vec{j}}, \nu_k) \quad (4.14)$$

with corresponding weights and abscissae.

$$\bar{v}_{\vec{n}} = \sqrt{\frac{3T}{7}}(\vec{i}, \vec{j}), \nu_k = \sqrt{\frac{3T}{7}}k, W_{\vec{i}, \vec{j}, k} = 4^{-(i^2+j^2+k^2)} \quad (4.15)$$

These abscissae give us the points we must sum over when applying the discrete equivalents of operators like those in equations (3.14), but equation (4.14) can be immediately applied to  $f^{(eq)}$  to give a discrete velocity by neglecting the sum and instead considering each term of the sum as a different discrete component that, when summed, will approximate to integration of the original expression.

It should be noted that this solution is the seven dimensional equivalent of the D3Q27 lattice which actually could be expressed as D7Q2187. In any event since it contains two D3Q27 lattices for the two velocity components we can expect order six isotropy, which has shown to be necessary for thermal modelling [9].

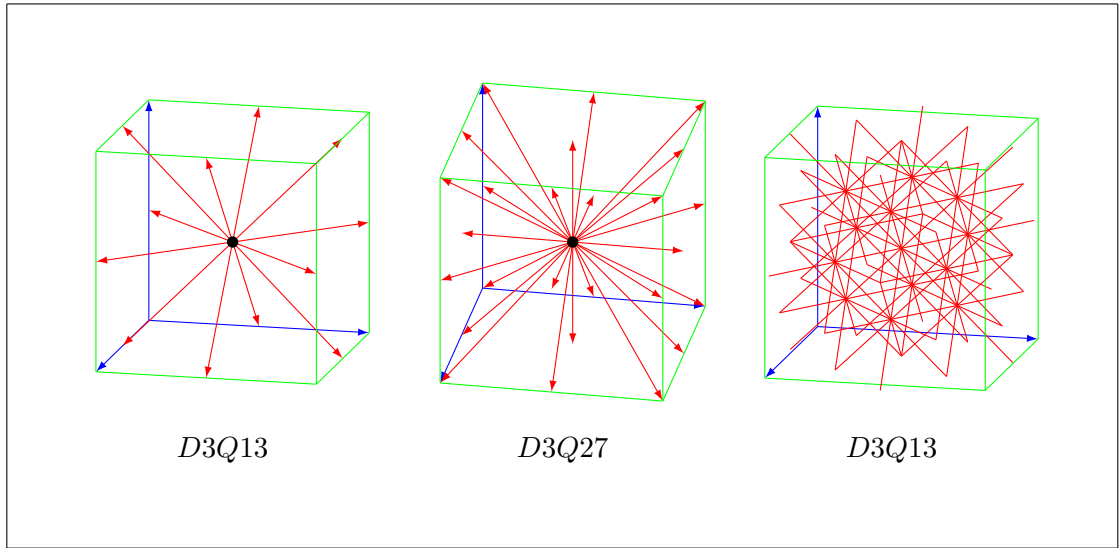


Figure 4.1: From left to right: a diagram of the velocities, subject to a scalar factor, associated with the D3Q13 lattice. A similar diagram for the D3Q27 lattice. A diagram of a section of a D3Q13 lattice with nearest neighbours connected by lines. Note the black dots represent the  $\vec{0}$  vector. Also notice the nomenclature, D $x$ Q $y$ , where  $x$  stand for the dimension of the space in which the lattice exists and  $y$  the number velocities which make up the model. Obviously the seven dimensional lattices cannot be displayed.

### 4.1.2 Quadrature on Spherical Co-ordinates

The D7Q2187 lattice drops quite neatly out of the Cartesian co-ordinate system. Partly because of this and partly because we are interested in investigating lattices that emulate sphere packing, we investigate quadrature by spherical co-ordinates. A spherical version of equation (4.13) may be obtained directly giving

$$\begin{aligned} \hat{f} = & \frac{\rho}{8\pi^{\frac{7}{2}}} \int_{-\infty}^{\infty} \int_{S^2 \times S^2} \int_0^{\infty} v_{+r}^2 \int_0^{\infty} v_{-r}^2 e^{-(v_{+r}^2 + v_{-r}^2 + \nu'^2)} \\ & \times P \left( T, \bar{U}, \sqrt{\frac{2T}{7}} \bar{v}', \sqrt{\frac{2T}{7}} \nu' \right) dv'_{-r} dv'_{+r} d\Omega_{v_+} d\Omega_{v_-} d\nu' \end{aligned} \quad (4.16)$$

$S^2$  is the whole surface of a sphere (over which we integrate) and  $d\Omega_{v_{\pm}}$  is the differential solid angle for the two velocity vectors.



#### 4.1.2.1 Methods of Radial Quadrature

The radial parts of equation (4.16) having the form  $\int_0^\infty y^2 e^{-y} g(y) dy$  do not have well publicised quadrature schemes in the literature, at least not ones we could find. It therefore fell to us to construct our own. Notice that if we perform the substitution  $x = y^2$  and define the function  $g(y) = 2f(y^2)$ , then integrals of the form considered are equivalent to the following integral

$$\int_0^\infty x^{\frac{1}{2}} e^{-x} f(x) dx = \int_0^\infty y^2 e^{-y^2} g(y) dy$$

This integral in  $x$  does have a well known quadrature, namely the Radau-Laguerre quadrature formula. Applying it we find

$$\int_0^\infty x^{\frac{1}{2}} e^{-x} f(x) dx \approx \frac{(n-1)! \Gamma(\frac{3}{2}) \Gamma(\frac{5}{2})}{\Gamma(n + \frac{3}{2})} f(0) + \sum_{k=1}^{n-1} w_k f(x_k)$$

$$w_k = \frac{\Gamma(n + \frac{1}{2})}{(n-1)! (n + \frac{1}{2}) \left[ L_{n-1}^{(\frac{1}{2})}(x_k) \right]^2}, L_{n-1}^{(\frac{3}{2})}(x_k) = 0$$

$L$  is the associated Legendre polynomial and  $\Gamma$  the gamma function. Substituting back in values for  $y$  this gives

$$\int_0^\infty y^2 e^{-y^2} g(y) dy \approx \frac{(n-1)! 3\pi}{\Gamma(n + \frac{3}{2})} \frac{g(0)}{16} + \sum_{k=1}^{n-1} w_k \frac{g(y_k)}{2} \tag{4.17}$$

$$w_k = \frac{\Gamma(n + \frac{1}{2})}{(n-1)! (n + \frac{1}{2}) \left[ L_{n-1}^{(\frac{1}{2})}(y_k^2) \right]^2}, L_{n-1}^{(\frac{3}{2})}(y_k^2) = 0$$

We take this as our radial quadrature rule. Of particular interest is equation (4.17) for  $n = 1$ ,

$$\int_0^\infty y^2 e^{-y^2} g(y) dy \approx \frac{\sqrt{\pi}}{10} g(0) + \frac{3\sqrt{\pi}}{20} g\left(\sqrt{\frac{5}{2}}\right) \tag{4.18}$$

### 4.1.2.2 Spherical Quadrature Continued

Applying equation (4.18) to the appropriate integrals in equation (4.16) we obtain the new expression

$$\begin{aligned} \hat{f} \approx \check{f} &= \frac{\rho}{8\pi^{\frac{7}{2}}} \int_{-\infty}^{\infty} e^{-\nu_1^2} \int_{S^2 \times S^2} \sum_{i,j=0}^1 w_i w_j \\ &\times P \left( T, \bar{U}, \sqrt{\frac{2T}{7}} (v'_{+ri} \hat{v}'_+, v'_{-rj} \hat{v}'_-), \sqrt{\frac{2T}{7}} \nu' \right) d\Omega_{v_+} d\Omega_{v_-} d\nu' \end{aligned} \quad (4.19)$$

The weights and abscissae are given by

$$v_{\pm ri} = \begin{cases} 0 & i = 0 \\ \sqrt{\frac{5}{2}} & i = 1 \end{cases}, \quad w_i = \begin{cases} \frac{\sqrt{\pi}}{10} & i = 0 \\ \frac{3\sqrt{\pi}}{20} & i = 1 \end{cases} = \left(\frac{3}{2}\right)^i \frac{\sqrt{\pi}}{10} \quad (4.20)$$

The issue of quadrature of the spherical integral requires some thought and appeal to symmetry conditions. One obvious method is to pick a set of points on the sphere and require that the set of rotations mapping this point set to itself will also map the respective weights in such a way that weights in the same orbit have the same value. One easy way to ensure this is to set the weights to be the surface area of the points of Voronoi cells on the space of the surface of the unit sphere. This gives consistency for quadrature of constant functions like 1, and gives a high level of rotation symmetry to the quadrature. Even without appealing to the Voronoi cells for the choice of points that gives the face centred cubic lattice sphere packaging (since every point can be mapped to any other), all weights must be the same. Consequently, for the spherical quadrature over  $\Omega_{v_{\pm}}$  our weights and abscissae are

$$\tilde{w}_i = \frac{4\pi}{12}, \quad \hat{v}'_{\pm i} = \left\{ \dots, \frac{1}{\sqrt{2}} (\pm 1, \pm 1, 0), \dots \right\}, \quad i = 1 \dots 12 \quad (4.21)$$

The abscissae are all vertices of a cuboctahedron on a unit sphere. Applying this

quadrature to equation (4.19) we obtain

$$\check{f} = \frac{\rho}{8\pi^{\frac{7}{2}}} \int_{-\infty}^{\infty} e^{-\nu'^2} \sum_{k,l=1}^{12} \sum_{i,j=0}^1 w_i w_j \tilde{w}_k \tilde{w}_l P \left( T, \bar{U}, \sqrt{\frac{2T}{7}} (v'_{+ri} \hat{v}'_{+k}, v'_{-rj} \hat{v}'_{-l}), \sqrt{\frac{2T}{7}} \nu' \right) d\nu'$$

By performing some relatively simple algebraic manipulations on this, equation (4.21), and equation (4.20), it is possible to recombine the angular and radial parts and move some constants in and out of definitions to generate the following quadrature formula for  $\vec{v}_{+i}$  and  $\vec{v}_{-j}$ !

$$\check{f} = \frac{\rho}{3200\pi^{\frac{1}{2}}} \int_{-\infty}^{\infty} e^{-\nu'^2} \sum_{i,j=0}^{13} W_{i,j} P \left( T, \bar{U}, (\vec{v}_{+i}, \vec{v}_{-j}), \sqrt{\frac{2T}{7}} \nu' \right) d\nu' \quad (4.22)$$

The new weights and abscissae are given by

$$\vec{v}_{\pm i} = \{(0, 0, 0), \dots, \sqrt{\frac{5T}{14}} (\pm 1, \pm 1, 0), \dots\}, W_{i,j} = \begin{cases} 64 & i = j = 0 \\ 8 & i = 0 \neq j \\ 8 & i \neq 0 = j \\ 1 & i \neq 0 \neq j \end{cases} \quad (4.23)$$

All that remains is to quadrature the  $\nu'$  component, which may be done by applying conventional Gauss-Hermite quadrature to the third order, giving the expression

$$\check{f} = \frac{\rho}{3200\pi^{\frac{1}{2}}} \sum_{i,j=0}^{13} W_{i,j} \sum_{k=-1}^1 \bar{w}_k P \left( T, \bar{U}, (\vec{v}_{+i}, \vec{v}_{-j}), \sqrt{\frac{2T}{7}} \nu'_k \right)$$

Associated weights and abscissae are given by

$$\nu'_k = \sqrt{\frac{3}{2}} k, \quad \bar{w}_k = \frac{\sqrt{\pi}}{3} \frac{2}{4k^2}$$

Again applying some algebraic re-arrangement to the weights and abscissae this

gives us the final form of a spherical quadrature

$$\check{f} = \frac{\rho}{4800} \sum_{i,j=0}^{13} \sum_{k=-1}^1 W_{i,j} \bar{w}_k P(T, \bar{U}, (\vec{v}_{+i}, \vec{v}_{-j}), \nu_k) \quad (4.24)$$

$W_{i,j}$  and  $\vec{v}_{\pm i}$  are given by equation (4.23) and  $\bar{w}_k$  and  $\nu_k$  by

$$\nu_k = \sqrt{\frac{3T}{7}} k, \quad \bar{w}_k = \frac{1}{4k^2} \quad (4.25)$$

In the velocity components, this lattice is comparable to the D3Q13 lattice. In fact, technically, it is a D7Q507 lattice. The D3Q13 lattice does not have order 4 isotropy, which is usually necessary for recovering the Navier-Stokes equation. Efforts were made to produce a model with a higher order isotropy by adding extra abscissae in the radial quadrature, but this was ultimately unsuccessful.

Using this technique developed in He and Lou's paper, it is possible to derive the lattice Boltzmann equation from its continuous analogue analytically, and demonstrate that for the case where temperature is inhomogeneous in space and time, an interpolation step must be used to map the post collision event population distribution to new nodes.

Regardless of which quadrature method is used, the discrete velocity equation is given by taking equation (4.4) and inserting  $f^{(eq)}$  for  $f_0$  as an approximation, then approximating  $f^{(eq)}$  with  $f_i^{(eq)}$  terms for the  $i$ th abscissa in its quadrature expression.  $f$  is approximated by  $f_i = f|_{(\bar{v})=(\bar{v}_i)}$  which gives the equation

$$f_i(\bar{r} + \bar{v}_i \delta_t, t + \delta_t) - f_i(\bar{r}, t) = -\frac{1}{\tau} \left( f_i(\bar{r}, t) - f_i^{(eq)}(\bar{r}, t) \right) \quad (4.26)$$

We define  $\bar{r}$  to include  $\sigma$  component and  $\bar{v}$  the  $\nu$  component for brevity.

## 4.2 Chapman-Enskog Expansion

The Chapman-Enskog expansion for discrete Boltzman equations is well known and understood and varies little in its application to equation (4.4) or (4.26), both of which it can be applied to without any real difference in method. Because of this and because it gets in the way of preferred notation, we omit the subscript  $i$  for these calculations. In the following calculation we employ the variation of the Chapman-Enskog expansion also employed by Lou in his thesis [15]. One begins by defining an expansion in a small parameter as in the continuous case. Only in this case the small parameter is taken to be the discrete time step. In addition a range of different time variables are introduced for different time scales.

$$f = f_0 + \delta_t f_1 + \delta_t^2 f_2 + \delta_t^3 f_3 + \dots, \quad \frac{\partial}{\partial t} = \frac{\partial}{\partial t_0} + \delta_t \frac{\partial}{\partial t_1} + \delta_t^2 \frac{\partial}{\partial t_2} + \delta_t^3 \frac{\partial}{\partial t_3} + \dots \quad (4.27)$$

$f_0$  is not the  $f_0$  defined earlier but instead is a convenient notation for  $f^{(ea)}$ . As before we seek a Taylor expansion in the small parameter. For the first term this takes the form

$$\begin{aligned} & f(\vec{r}_+ + \vec{v}_+ \delta_t, \vec{r}_- + \vec{v}_- \delta_t, \sigma_1 + \nu_1 \delta_t, \vec{v}_+, \vec{v}_-, \nu_1, t + \delta_t) \\ & \approx \sum_{i_1, \dots, i_8} \delta_t^{\sum_j i_j} \frac{v_{+x}^{i_1} v_{+y}^{i_2} v_{+z}^{i_3} v_{-x}^{i_4} v_{-y}^{i_5} v_{-z}^{i_6} \nu_1^{i_7}}{\prod_j (i_j!)} \frac{\partial^{\sum_j i_j} f(\vec{r}_+, \vec{r}_-, \sigma_1, \vec{v}_+, \vec{v}_-, \nu_1, t)}{\partial r_{+x}^{i_1} \partial r_{+y}^{i_2} \partial r_{+z}^{i_3} \partial r_{-x}^{i_4} \partial r_{-y}^{i_5} \partial r_{-z}^{i_6} \partial \sigma_1^{i_7} \partial t^{i_8}} \end{aligned} \quad (4.28)$$

For brevity and consistency with notation used in literature, we define  $\bar{e} = (\vec{v}_+, \vec{v}_-, \nu_1)$   $\bar{x} = (\vec{r}_+, \vec{r}_-, \sigma_1)$  (with which we will mostly use the Einstein notation). Using this notation, and inserting equation (4.27) into the right hand side of equation(4.4) or

(4.26) gives

$$\begin{aligned} \frac{f_0 - f}{\tau} &= \delta_t \left( e_i \frac{\partial f}{\partial x_i} + \frac{\partial f}{\partial t} \right) + \delta_t^2 \left( \frac{e_i e_j}{2} \frac{\partial^2 f}{\partial x_i \partial x_j} + e_i \frac{\partial^2 f}{\partial x_i \partial t} + \frac{1}{2} \frac{\partial^2 f}{\partial t^2} \right) \\ &+ \delta_t^3 \left( \frac{e_i e_j e_k}{6} \frac{\partial^3 f}{\partial x_i \partial x_j \partial x_k} + \frac{e_i e_j}{2} \frac{\partial^3 f}{\partial x_i \partial x_j \partial t} + \frac{e_i}{2} \frac{\partial^3 f}{\partial x_i \partial t^2} + \frac{1}{6} \frac{\partial^3 f}{\partial t^3} \right) + \dots \end{aligned} \quad (4.29)$$

Inserting equations (4.28) and (4.29) into equations (4.4) or (4.26) and equating coefficients of  $\delta_t$ , gives an infinite sequence of equations that may be used to build successively better approximations for  $f$ . The first three of them are given below:

$$-\frac{f_1}{\tau} = e_i \frac{\partial f_0}{\partial x_i} + \frac{\partial f_0}{\partial t_0} \quad (4.30)$$

$$-\frac{f_2}{\tau} = \frac{\partial f_0}{\partial t_1} + \left( 1 - \frac{1}{2\tau} \right) \left( \frac{\partial f_1}{\partial t_0} + e_i \frac{\partial f_1}{\partial x_i} \right) \quad (4.31)$$

$$-\frac{f_3}{\tau} = \left( \frac{6\tau^2 - 6\tau + 1}{3\tau(2\tau - 1)} \right) \left( e_i \frac{\partial f_2}{\partial x_i} + \frac{\partial f_2}{\partial t_0} \right) + \left( \frac{6\tau^2 - 6\tau + 2}{3\tau(2\tau - 1)} \right) \frac{\partial f_1}{\partial t_1} + \frac{\partial f_0}{\partial t_2} \quad (4.32)$$

Here, for generality, we introduce the operator  $\mathcal{O}$ . In the case of continuous velocities this would be an integration over these velocities. In the discrete case it is a sum. We define some fields with this operator,  $n$ ,  $u_i$ , and  $E$  which have well defined relationships to  $\rho$ ,  $U_i$  and  $E$  acquired by observing the effect of  $\mathcal{O}$  on equation (4.2), along with the condition, analogous to the continuous case, that only  $f_0$  contributes to the macroscopic functions which are defined by

$$\mathcal{O}[f_i] = \delta_{0i} n, \quad \mathcal{O}[e_j f_i] = \delta_{0i} n u_j, \quad \mathcal{O}[e_j e_j f_i] = \delta_{0i} n E \quad (4.33)$$

When we apply  $\mathcal{O}$  to equations (4.30), (4.31), and (4.32), and apply conditions (4.33) we get

$$0 = \frac{\partial n u_i}{\partial x_i} + \frac{\partial n}{\partial t_0}, \quad 0 = \frac{\partial n}{\partial t_1}, \quad 0 = \frac{\partial n}{\partial t_2} \quad (4.34)$$

Likewise if we repeat the same procedure but this time multiply both sides of our equations by  $e_j$ , we obtain

$$0 = \frac{\partial}{\partial x_i} \mathcal{O}[e_i e_j f_0] + \frac{\partial n u_j}{\partial t_0}, \quad 0 = \frac{\partial n u_j}{\partial t_1} + \left(1 - \frac{1}{2\tau}\right) \frac{\partial}{\partial x_i} \mathcal{O}[e_i e_j f_1], \quad (4.35)$$

$$0 = \frac{6\tau^2 - 6\tau + 1}{3\tau(2\tau - 1)} \frac{\partial}{\partial x_i} \mathcal{O}[e_i e_j f_2] + \frac{\partial n u_j}{\partial t_2}$$

If we yet again repeat the procedure but now multiply both sides by  $e_j e_j$  we obtain

$$0 = \frac{\partial}{\partial x_i} \mathcal{O}[e_i e_j e_j f_0] + \frac{\partial n E}{\partial t_0}, \quad 0 = \frac{\partial n E}{\partial t_1} + \left(1 - \frac{1}{2\tau}\right) \frac{\partial}{\partial x_i} \mathcal{O}[e_i e_j e_j f_1] \quad (4.36)$$

$$0 = \frac{6\tau^2 - 6\tau + 1}{3\tau(2\tau - 1)} \frac{\partial}{\partial x_i} \mathcal{O}[e_i e_j e_j f_2] + \frac{\partial n E}{\partial t_2}$$

At this point we set  $\delta_t = 1$  and note that this allows us to employ the relation  $\frac{\partial}{\partial t} = \sum_i \frac{\partial}{\partial t_i}$  from equation (4.27). Summing the equations (4.34), (4.35), and (4.36), respectively, and applying the aforementioned relations we get

$$\frac{\partial n u_i}{\partial x_i} + \frac{\partial n}{\partial t} = 0 \quad (4.37)$$

$$\frac{\partial n u_j}{\partial t} + \frac{\partial}{\partial x_i} \mathcal{O} \left[ e_i e_j \left( f_0 + \left(1 - \frac{1}{2\tau}\right) f_1 + \frac{6\tau^2 - 6\tau + 1}{3\tau(2\tau - 1)} f_2 \right) \right] = 0 \quad (4.38)$$

$$\frac{\partial n E}{\partial t} + \frac{\partial}{\partial x_i} \mathcal{O} \left[ e_i e_j e_j \left( f_0 + \left(1 - \frac{1}{2\tau}\right) f_1 + \frac{6\tau^2 - 6\tau + 1}{3\tau(2\tau - 1)} f_2 \right) \right] = 0 \quad (4.39)$$

These are conservation equations for the mass, momentum, and energy-like variables, respectively. The functions that would normally define the macroscopic behaviour of a fluid, the stress strain tensor for instance, are contained or related to the terms still expressed in terms of  $\mathcal{O}$  and are in terms of the functions  $f_0$ ,  $f_1$ , etc, so that the behaviour of the medium is defined in terms of  $f_0$ , which is our  $f^{(eq)}$ . These objects may be redefined in simpler terms by introducing new functions  $\chi$ ,  $\Pi$  and  $\vec{Q}$

as follows

$$\chi = f_0 + \left(1 - \frac{1}{2\tau}\right) f_1 + \frac{6\tau^2 - 6\tau + 1}{3\tau(2\tau - 1)} f_2, \quad \Pi_{ij} = \mathcal{O}[e_i e_j \chi], \quad Q_i = \mathcal{O}[e_i e_j e_j \chi] \quad (4.40)$$

The continuity equations are then given by

$$\frac{\partial n}{\partial t} + \nabla \cdot (n\vec{u}) = 0 \quad (4.41)$$

$$\frac{\partial n\vec{u}}{\partial t} + \nabla \cdot \bar{\Pi} = 0 \quad (4.42)$$

$$\frac{\partial nE}{\partial t} + \nabla \cdot \vec{Q} = 0 \quad (4.43)$$

These equations may be reformulated in a form more reminiscent of fluid dynamics, namely

$$\frac{\partial n}{\partial t} + \vec{u} \cdot \nabla n = -n \nabla \cdot (\vec{u}) \quad (4.44)$$

$$n \left( \frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u} \right) = \nabla \cdot (n\vec{u}\vec{u} - \bar{\Pi}) \quad (4.45)$$

$$n \left( \frac{\partial E}{\partial t} + \vec{u} \cdot \nabla E \right) = \nabla \cdot (n\vec{u}E - \vec{Q}) \quad (4.46)$$

By this method, macroscopic equations such as those of fluid dynamics can be recovered to aid physical interpretation of the variables with which we define the model's behaviour. For this reason and as proof of concept we endeavoured to derive  $\chi$ ,  $\Pi$ , and  $\vec{Q}$  for the continuous velocity case for  $f^{(eq)}$  given in equation (4.10). However, the calculation proved too difficult to do by hand. Finding conventional computer algebra systems unequipped to cope with the kind of tensor manipulations required we attempted to write a program using the open source GiNaC algebra manipulation library for C++ to do the computation for me but due to the partially developed nature of the library this program either failed to terminate or crashed the system. Consultation was undertaken with the GiNaC development team and several patches were applied but to no avail. A copy of this code can be found in the



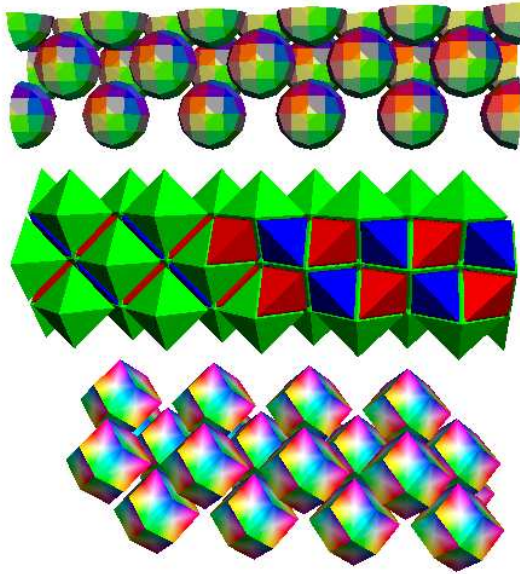


Figure 4.2: Above: A face centred cubic packing of spheres which is identical to the D3Q13 lattice in geometry. Middle: The octahedrons and tetrahedrons that represent the different cells that tessellate space interpolating values to the lattice points at the vertices. Below: The rhombic dodecahedral honeycomb tessellation that is given by the Voronoi cells of the D3Q13 lattice.

attached disk. Due to the lack of success and time constraints no attempt was made to calculate any discrete velocity Chapman-Enskog expansions. However as we will mention later algorithms for the simplification of tensor expressions exist [34] and could be implemented by a determined programmer.

### 4.3 Interpolation

Because the post collision transport of material in the lattice Boltzmann equations we have derived is no longer guaranteed to land on a well defined lattice point, it is necessary to define how this result is mapped to the lattice points. It is possible to tessellate space with octahedrons and tetrahedrons so that the vertices of these shapes are the lattice points. The values of the result of a collision can then be distributed to the vertices of the cell in which it has ‘landed’. One simple condition that ensures continuity is that the ratio of distribution between the vertices of opposite faces, in the case of an octahedron, or the vertexes a face and its opposite vertex in a tetrahedron, is the ratio of the distances of the landing point to those

places. To be specific

$$a_{i,0,0} + a_{0,j,0} + a_{0,0,k} = \frac{\vec{x} \cdot (i, j, k) + 1}{2}, \quad i, j, k = \pm 1 \quad (4.47)$$

for the octahedron where  $a_{i,j,k}$  is the proportion distributed to vertex  $(i, j, k)$

$$a_{\frac{i}{2}, \frac{j}{2}, \frac{k}{2}} = \frac{\vec{x} \cdot (i, j, k)}{2} + \frac{1}{4}, \quad i, j, k = \pm 1$$

For the tetrahedron, remembering that the tetrahedron may be oriented two ways, there are eight possible places a vertex could occur.

This leads to the immediate result for interpolating in tetrahedral cells

$$\left( (\vec{x} - \vec{q}) \cdot \vec{p} + \frac{1}{4} \right) f_a(\vec{x} + \vec{\xi}_a \delta_t) = f_a^{(contribution)}(\vec{q} + \vec{p}) \quad (4.48)$$

$\vec{q}$  is the cell centre and  $\vec{p}$  is the vector from the centre to the vertex. Using this  $f_a(\vec{x} + \vec{\xi}_a \delta_t)$  the result of our collision calculation is redistributed to  $f_a^{(contribution)}(\vec{q} + \vec{p})$  for the various permissible value of  $\vec{p}$ . Note that  $f_a^{(contribution)}(\vec{q} + \vec{p})$  is not the new pre-collision lattice value. It is merely a contribution to it. There still needs to be an adjustment to account for contributions from other collision events near by.

For the octahedron, the condition (4.47) is not enough to give conditions for  $a$  on its own.  $a$  is required to be invariant under the symmetries of the octahedron that fix its vertex and the other vertex distributions are taken to be given by symmetries that map vertices to each other. Even this is not enough to firmly fix  $a$ . If we require it must be linear and allow for the inclusion of the absolute values we do get a unique solution.

$$a_{1,0,0} = \frac{x - |x|}{2} + \frac{1 - |x| - |y| - |z|}{6}$$

We do not claim that this is in any way optimal, only that it meets the condition (4.47), is consistent with equation (4.48) on the cell boundaries, is non negative in

the cell, and has the logical property of being 1 at  $(1, 0, 0)$  and 0 on the cell faces that don't adjoin  $(1, 0, 0)$ . In short it is an expedient choice. So the general statement of this distribution for the octahedral cell is

$$\left( \frac{1 - |x - q_x| - |y - q_y| - |z - q_z|}{6} + \frac{(\vec{x} - \vec{q}) \cdot \vec{p} + |(\vec{x} - \vec{q}) \cdot \vec{p}|}{2} \right) f_a(\vec{x} + \vec{\xi}_a \delta_t) \quad (4.49)$$

$$= f_a^{(contribution)}(\vec{q} + \vec{p})$$

In all of this we have assumed a face centred cubic lattice with a distance between neighbours of  $\sqrt{2}$ . Consequently, rescaling will be necessary in applying the technique.

An alternative way to interpolate the face centred cubic lattice is to interpolate to the cubic lattice and remove the lattice points not present in the face centred cubic lattice, redistributing the contributions to their values evenly to the un-removed nearest neighbours of which there are six. Any technique for distributing values to a cubic lattice can be applied in this case. For example

$$f_a^{(contribution)}(\vec{q}) = \begin{cases} \cos^2(x - q_x) \cos^2(y - q_y) \cos^2(z - q_z) f_a(\vec{x} + \vec{\xi}_a \delta_t) & |x_i - q_i| < 1 \\ 0 & \text{otherwise} \end{cases} \quad (4.50)$$

This has the property of being not only continuous in the variation of its redistribution but also differentiable. Whether this is computationally advantageous is unclear and for ease of calculation we feel the simpler solution will suffice.

### 4.3.1 Interpolation of Contributions

Given that multiple lattice points with different lattice speeds may now make a contribution to the same population, it is necessary to have a formula for merging the contributions. That is, to produce a new combined value for two contributions that preserves the total mass, momentum, and energy of the two. Since every lattice point now has its own locally defined velocities we must interpolate for this

too. For this calculation we define  $\bar{v} = (\bar{v}_+, \bar{v}_-, \nu)$  etc. Beginning with the condition for momentum conservation.

$$\bar{v}_a f_a(\bar{r}') + \bar{v}'_a f'_a(\bar{r}') = \bar{v}''_a f''_a(\bar{r}')$$

where  $\bar{v}_a$  and  $\bar{v}'_a$  are the velocities of the two contributing lattice points and  $\bar{v}''_a$  is the new velocity of the combination, likewise  $f_a(\bar{r}')$  and  $f'_a(\bar{r}')$  are the two contributing populations and  $f''_a(\bar{r}')$  the combined one. This is for population index  $a$  for contributions at lattice point  $\bar{r}$ . Given  $\bar{v}_a \propto \bar{v}'_a$  this implies.

$$|\bar{v}_a| f_a(\bar{r}') + |\bar{v}'_a| f'_a(\bar{r}') = |\bar{v}''_a| f''_a(\bar{r}') \quad (4.51)$$

The correct expression for the energy of a pseudo particle or polymer chain segment if you prefer is, subject to some consideration of mass that will factor out,  $\frac{1}{2}\bar{v}_1^2 + \frac{1}{2}\bar{v}_2^2 + \nu^2$  which by equations (4.3) is  $\bar{v}_+^2 + \bar{v}_-^2 + \nu^2 = \bar{v}^2$ . Consequently the equation for the energy conservation of the pseudo particle is

$$\bar{v}_a^2 f_a(\bar{r}') + \bar{v}'_a{}^2 f'_a(\bar{r}') = \bar{v}''_a{}^2 f''_a(\bar{r}') \quad (4.52)$$

On dividing equations (4.52) by (4.51) we get

$$\frac{\bar{v}_a^2 f_a(\bar{r}') + \bar{v}'_a{}^2 f'_a(\bar{r}')}{|\bar{v}_a| f_a(\bar{r}') + |\bar{v}'_a| f'_a(\bar{r}')} = |\bar{v}''_a| \quad (4.53)$$

Substituting equation (4.53) into equation (4.51) we get

$$\frac{(|\bar{v}_a| f_a(\bar{r}') + |\bar{v}'_a| f'_a(\bar{r}'))^2}{\bar{v}_a^2 f_a(\bar{r}') + \bar{v}'_a{}^2 f'_a(\bar{r}')} = f''_a(\bar{r}') \quad (4.54)$$

With equations (4.53) and (4.54) we have expressions for combining contributions that respect momentum and energy. Sadly they do not conserve mass ( $f_a(\bar{r}') + f'_a(\bar{r}') \neq f''_a(\bar{r}')$ ), a small amount of mass is lost in this process. This mass deficit

can be calculated exactly and an equivalent amount of mass can be added to the 0 velocity component population that would normally receive no contribution from neighbouring lattice points. The expression for this is

$$f_a(\bar{r}') + f'_a(\bar{r}') - f''_a(\bar{r}') = \frac{(|\bar{v}_a| - |\bar{v}'_a|)^2 f_a(\bar{r}') f'_a(\bar{r}')}{\bar{v}_a^2 f_a(\bar{r}') + \bar{v}'_a{}^2 f'_a(\bar{r}')} = f_0^{(contribution)}(\bar{r}') \quad (4.55)$$

These expressions (4.53), (4.54) and (4.55) are commutative and transitive. So for each time step populations can be set to 0 and built up by a process of successive contributions.

### 4.3.2 Rescaling the Velocities

After combining contributions, each lattice point's populations have a variety of velocity magnitudes that are not in line with the velocities they are assumed to have for the purposes of the collision step, whose velocities are a function of a temperature-like field. Consequently the velocities of the population must be adjusted to those expected of the temperature in such a way that the mass, momentum, and temperature-like components remain unchanged. At the same time we want the rescaling to in some sense be minimal or optimal. Because of this we turned to the technique of Lagrange multipliers. The function chosen for minimisation was not obvious though, or rather there are at least three obvious choices:

1. minimise the redistribution of mass by taking the sum of squares of the difference in populations before and after,
2. minimisation of redistribution of momentum by looking at squares of the difference in the populations multiplied by velocities or
3. minimise the redistribution of energy by multiplying by the squares of velocities instead.

## CHAPTER 4. SEEKING A LATTICE BOLTZMANN-LIKE METHOD

In short we have three potential choices for the function for minimisation as follows.

$$M = \sum_i (f_i - f'_i)^2 \left| \sum_i (\bar{v}_i f_i - \bar{v}'_i f'_i)^2 \right| \left| \sum_i (\bar{v}_i^2 f_i - \bar{v}'_i{}^2 f'_i)^2 \right| \quad (4.56)$$

At the same time we must preserve mass, momentum, and energy-like values so we have a set of constraint functions (that give the constraints when set to 0) given by

$$C_0 = \sum_i f'_i - n, \quad \vec{C} = \sum_i \bar{v}'_i f'_i - n\bar{u}, \quad C_8 = \sum_i \bar{v}'_i{}^2 f'_i - nE \quad (4.57)$$

From expression (4.56) where we have decided to take the weighted sum (using weights  $\alpha$ ,  $\beta$ , and  $\gamma$ ) of all three possibilities and constraints (4.57) one can construct the Lagrange function

$$L = \alpha \sum_i (f_i - f'_i)^2 + \beta \sum_i (\bar{v}_i f_i - \bar{v}'_i f'_i)^2 + \gamma \sum_i (\bar{v}_i^2 f_i - \bar{v}'_i{}^2 f'_i)^2 - \lambda_0 \left( \sum_i f'_i - n \right) - \bar{\lambda} \cdot \left( \sum_i \bar{v}'_i f'_i - n\bar{u} \right) - \lambda_8 \left( \sum_i \bar{v}'_i{}^2 f'_i - nE \right) \quad (4.58)$$

The extrema of the function subject to the constraints is then given by solving the equation

$$\nabla_{\bar{\lambda}, f'_i} L = \vec{0} \quad (4.59)$$

Differentiation of the lambda components recovers the constraints

$$C_0 = 0, \quad \vec{C} = \vec{0}, \quad C_8 = 0 \quad (4.60)$$

Meanwhile differentiation of the  $f_i$  yields

$$\frac{\partial L}{\partial f'_i} = -2K_i f_i + 2J_i f'_i - \lambda_0 - \bar{\lambda} \cdot \bar{v}'_i - \lambda_8 \bar{v}'_i{}^2 = 0 \quad (4.61)$$

where we have defined symbols  $K_i$  and  $J_i$  for brevity

$$\alpha \bar{v}'_i \cdot \bar{v}_i + \beta \bar{v}'_i{}^2 \bar{v}_i^2 + \gamma = K_i, \quad \alpha \bar{v}'_i{}^2 + \beta \bar{v}_i{}^4 + \gamma = J_i \quad (4.62)$$

With this we can write an expression for  $f_i$

$$\frac{2K_i f_i + \lambda_0 + \bar{\lambda} \cdot \bar{v}'_i + \lambda_8 \bar{v}'_i{}^2}{2J_i} = f'_i \quad (4.63)$$

Inserting this into equation (4.60), recalling equation (4.57), we get a series of linear expressions for the lambdas. First, for condition 0,

$$\begin{aligned} 0 &= \sum_i \frac{2K_i f_i + \lambda_0 + \bar{\lambda} \cdot \bar{v}'_i + \lambda_8 \bar{v}'_i{}^2}{2J_i} - n \\ &= \sum_i \frac{K_i f_i}{J_i} - n + \sum_i \frac{1}{2J_i} \lambda_0 + \sum_i \frac{\bar{v}'_i}{2J_i} \cdot \bar{\lambda} + \sum_i \frac{\bar{v}'_i{}^2}{2J_i} \lambda_8 \end{aligned} \quad (4.64)$$

For conditions 1 through 7

$$\begin{aligned} \vec{0} &= \sum_i \bar{v}'_i \frac{2K_i f_i + \lambda_0 + \bar{\lambda} \cdot \bar{v}'_i + \lambda_8 \bar{v}'_i{}^2}{2J_i} - n\bar{u} \\ &= \sum_i \frac{\bar{v}'_i K_i f_i}{J_i} - n\bar{u} + \sum_i \frac{\bar{v}'_i}{2J_i} \lambda_0 + \sum_i \frac{\bar{v}'_i \bar{v}'_i}{2J_i} \cdot \bar{\lambda} + \sum_i \frac{\bar{v}'_i \bar{v}'_i{}^2}{2J_i} \lambda_8 \end{aligned} \quad (4.65)$$

Lastly, for the 8th constraint,

$$\begin{aligned} 0 &= \sum_i \bar{v}'_i{}^2 \frac{2K_i f_i + \lambda_0 + \bar{\lambda} \cdot \bar{v}'_i + \lambda_8 \bar{v}'_i{}^2}{2J_i} - nE \\ &= \sum_i \frac{\bar{v}'_i{}^2 K_i f_i}{J_i} - nE + \sum_i \frac{\bar{v}'_i{}^2}{2J_i} \lambda_0 + \sum_i \frac{\bar{v}'_i{}^2 \bar{v}'_i}{2J_i} \cdot \bar{\lambda} + \sum_i \frac{\bar{v}'_i{}^2 \bar{v}'_i{}^2}{2J_i} \lambda_8 \end{aligned} \quad (4.66)$$

By defining a new family of tensors  $A$  and  $B$  we can simplify the expressions

$$\sum_i \frac{v'_{i,j} \cdots v'_{i,k}}{2J_i} = A_{j \cdots k}, \quad \sum_i \frac{v'_{i,j} \cdots v'_{i,k} K_i f_i}{J_i} = B_{j \cdots k} \quad (4.67)$$

$v'_{i,j}$  is the  $j^{\text{th}}$  component of  $\bar{v}'_i$ . This leads to a simple set of eight linear equations in eight variables. Equations (4.64), (4.65), and (4.66) may be re-expressed as

$$\begin{aligned} 0 &= B - n + A\lambda_0 + A_i\lambda_i + A_{ii}\lambda_8 \\ 0 &= B_i - nu_i + A_i\lambda_0 + A_{ij}\lambda_j + A_{ijj}\lambda_8 \\ 0 &= B_{ii} - nE + A_{ii}\lambda_0 + A_{iij}\lambda_j + A_{iijj}\lambda_8 \end{aligned} \tag{4.68}$$

Solving this system gives values for the lambdas that can then be inserted into equation (4.63) to give the new populations. There are several questions outstanding with this method. Notably, what choices should be made for  $\alpha$ ,  $\beta$  and  $\gamma$ ? Can we guarantee that  $f'_i$  will always be non negative?

## 4.4 Reintroduction of Non Local Force and Multiple Components

Up until now our models have been bereft of the force terms dropped when considering equation (4.1). However, in their papers Shan and Chen [17, 18] devise a way of introducing a force into the model by creating a pseudo velocity used to calculate the collision step. They effectively nudge the velocity with a force field-like so

$$\rho\bar{U}' = \rho\bar{U} + \tau\frac{d\bar{p}}{dt} \tag{4.69}$$

$\frac{d\bar{p}}{dt}$  can be defined locally for each lattice point, effectively making it a force field. In physics force fields are typically described by their potentials with the force being given by the gradient  $-\nabla\phi$ . In the continuous equation there were continuous potential functions defined over  $\vec{r}_1$  and  $\vec{r}_2$ . We will now require a discreet analogue defined over  $\vec{r}_+$  and  $\vec{r}_-$  and a discreet analogue of the gradient. So, by argument of



similarity ( $\frac{d\bar{p}}{dt} \sim -\nabla\phi$ ) we take

$$\frac{d\bar{p}}{dt} = -\omega \sum_{i=1}^n \frac{\phi(\bar{r} + \bar{e}_i)\bar{e}_i}{\bar{e}_i^2} \quad (4.70)$$

This can be seen as an obvious generalisation of the discrete derivative  $\frac{\delta f}{\delta x} = \frac{f(x+h)-f(x-h)}{2h}$  but only makes sense subject to the conditions

$$I = \omega \sum_{i=1}^n \frac{\bar{e}_i\bar{e}_i}{\bar{e}_i^2}, \quad 0 = \sum_{i=1}^n \frac{\bar{e}_i}{\bar{e}_i^2} \quad (4.71)$$

$I$  is the identity matrix. Here  $\bar{e}_i$  are not velocity related vectors but vectors representing the displacement between nearby lattice points neglecting the 7th  $\sigma$  component. Considering the D7Q507 lattice with the 7th dimension neglected the conditions are met for nearest neighbour displacements with  $\omega = \frac{1}{28}$ . The Reader will recall in equation (3.7), which we are attempting to emulate, that there were two potential fields in the fourth term. The first field represents the internal potential energy of a polymer chain under some sort of tension or extension. This was dependent only upon the length of the difference of the  $\vec{r}_1$  and  $\vec{r}_2$  co-ordinates. The second field was a term for interactions with the bulk of the rest of the polymer and depended not only upon  $\vec{r}_1$  and  $\vec{r}_2$  but also upon  $n$ , the density-like field. Consequently we suggest the forms of the discrete analogues are

$$\phi^{(int)}(|\vec{r}_-|), \quad \phi^{(ext)}(\rho, \vec{r}) \quad (4.72)$$

The  $\rho$  in  $\phi^{(ext)}(\rho, \vec{r})$  is taken to mean that the function may be a value of all the values of  $\rho$  on all lattice points, although in practise it is likely only lattice points with nearby  $\vec{r}_+$  co-ordinates will be considered. Recall also that the continuous form of  $\phi^{(ext)}(\rho, \vec{r})$  was subject to a rule (3.4) and it remains to be determined just what the discrete analogue of equation (3.4) is. Also of note is the introduction of that  $\phi^{(int)}$  will tend to limit the achievable magnitude of  $\vec{r}_-$  thus making a fairly limited

array of lattice values for  $\vec{r}_-$  physically valid. Also by redefining the velocity used in the collision step we have essentially redefined  $f^{(eq)}$  to a non local function. It may be possible to generalise the Chapman-Enskog method to such equations and derive full macroscopic models from these discrete ones where the continuous equation are resistant to such analysis.

The original purpose of Shan and Chen's paper [17] was to determine how fluids with different parameters, essentially immiscible fluids, could be made to interact in a lattice Boltzmann method. It is highly desirable to generalise this method to the seven dimensional polymer lattice where interactions with air in an injection mould or water or gas in assisted injection moulding. However, such fluids are implemented with three dimensional lattices, not seven, and it is necessary to reconcile this when generalising Shan and Chen's method. It is fairly simple to define the effect of our three dimensional fluid on the polymer. We simply equate the fluid's polymer lattice to the  $\vec{r}_+$  polymer co-ordinate and with a set of displacement vectors for nearby neighbours in the 3D lattice  $\vec{e}_{+i}$ . Making the reasonably straightforward assumption that the fluid exerts no force on the orientation of polymer chains, one defines the force exerted on the polymer to be

$$\frac{d\vec{p}_p}{dt} = -\psi_p(\rho(\vec{r}, \sigma))G_{pf} \sum_{i=1}^n \psi_f(\tilde{\rho}(\vec{r}_+ + \vec{e}_{+i}))(\vec{e}_{+i}, \vec{0}) \quad (4.73)$$

The question of the force that the polymer exerts on the fluid is less straightforward. Since all the polymer lattice points with identical values of  $\vec{r}_+$  have equal proximity to given fluid lattice points it seems reasonable to sum the density-like values of those lattice points over  $\vec{r}_-$  and  $\sigma$

$$\frac{d\vec{p}_f}{dt} = -\psi_f(\tilde{\rho}(\vec{r}_+))G_{fp} \sum_{i=1}^n \psi_p \left( \sum_{\vec{r}_-, \sigma} \rho(\vec{r}_+ + \vec{e}_{+i}, \vec{r}_-, \sigma) \right) \vec{e}_{+i} \quad (4.74)$$

Here  $\tilde{\rho}$  is the density of the fluid and  $G_{fp}$  and  $G_{pf}$  are constants. Note that equation

(4.73) expresses the force of a few lattice points on many, whereas equation (4.74) expresses the effect of many on few. It would seem likely that  $G_{fp}$  will have quite different values to  $G_{pf}$  in order to compensate for this.

## 4.5 Boundaries and Dealing with the Parameter Sigma

Lastly, for this chapter, having developed a model one must consider its boundary conditions and the ranges of its variables. Assuming that a transport event crosses a boundary given by the surface  $B$ , then for some values of  $\bar{r}'$  and  $\lambda$  the following equation must be satisfied:

$$\bar{r} + \lambda \bar{v}_i \delta_t = B(\bar{r}'), \quad 0 < \lambda \leq 1 \quad (4.75)$$

A common condition for the no slip boundary method is the so called bounce back condition where every transport event that crosses to a lattice point outside the boundary is returned in the same time step to the lattice point that sent it. This is perfect for boundaries exactly between lattice points but can not represent curved surfaces in a smooth way. Since we are no longer limited to considering transport events that end on the lattice points, one simple way to implement the bounce back condition is to calculate at what point the trajectory of the event intersects the boundary and then ‘bounce back’ the remainder of the trajectory from the boundary. This new ‘landing point’ for the bounced back transport event is given by

$$\bar{r} + \lambda \bar{v}_i \delta_t - (1 - \lambda) \bar{v}_i \delta_t = \bar{r} + (2\lambda - 1) \bar{v}_i \delta_t \quad (4.76)$$

So, if  $\tilde{f}^{(contribution)}$  is some transport event that crosses the boundary, its bounced back contribution is given by

$$f^{(contribution)}(\bar{r} + (2\lambda - 1)\bar{v}_i\delta_t, -\bar{v}_i, t + \delta_t) = \tilde{f}^{(contribution)}(\bar{r} + \bar{v}_i\delta_t, \bar{v}_i, t + \delta_t) \quad (4.77)$$

Because our models of the polymer are not isothermal, it is desirable to have a mechanism where by energy can be lost through the boundary where as here it would normally be conserved. An easy way to do this is to consider a situation in which a given particle bounces back with proportionally less speed. This new landing point is easily calculated as

$$\bar{r} + \lambda\bar{v}_i\delta_t - (1 - \lambda)\mu\bar{v}_i\delta_t = \bar{r} + (\lambda - \mu + \lambda\mu)\bar{v}_i\delta_t, \quad 0 < \mu \leq 1 \quad (4.78)$$

This would give rise to a bounce back contribution of

$$f^{(contribution)}(\bar{r} + (\lambda - \mu + \lambda\mu)\bar{v}_i\delta_t, -\mu\bar{v}_i, t + \delta_t) = \tilde{f}^{(contribution)}(\bar{r} + \bar{v}_i\delta_t, \bar{v}_i, t + \delta_t) \quad (4.79)$$

The issue here is we can no longer expect the no slip condition to hold. The net momentum on the boundary is 0 only because an equal amount of momentum is bounced back every time giving no net momentum at the bounce back point. By reducing the speed we have not only lessened the returning kinetic energy but also the momentum. One way to compensate would be to increase the returning population artificially but then we must compensate for the extra mass by either taking some contribution from the original lattice points  $f_0$  population or by interpolating a hypothetical negative  $f_0$  contribution to lattice points receiving the bounce back. In our opinion the best way to approach this problem is as yet unresolved. However, if it could be resolved by varying  $\mu$  over the boundary we could simulate varied heating or cooling over the mould surface.

The final problem regarding the boundary is how it should be constructed. It

is after all an object defined in seven dimensions that represents an object in our conventional three. The obvious solution is to divide the boundary into two 3-component 2-parameter surfaces and enforce a 7th condition on the sigma coordinate. So our boundary in seven dimensions might be written as  $(\vec{B}_+(u, v), \vec{B}_-(u', v'), ?)$  where  $\vec{B}_+(u, v)$  is simply the geometry of our mould. Ideally the internal potential  $\phi^{(int)}$  will ensure that it never or rarely makes contact with  $\vec{B}_-(u', v')$ . We suggest a sphere of suitable radius would be ideal. However, it is not clear how, if at all, to bound the sigma parameter. There does not seem to be any firm break in the equations themselves that would stop large values of sigma being reached. If they are the lengths of polymer chains as suggested in Grmela and Carreau's paper [2] then we might expect them to have ends, but nothing in the continuous equations suggests this. If such ends exist we think they would have to be enforced by the collision integrals somehow. There are basically two options. Set up bounce back conditions for sigma as a pair of values. Alternatively, the method we favour is to let sigma be periodic. This gives us the option of curling sigma up till it is quite small, possibly only a single layer. No doubt such choices will dramatically affect the simulation results. We suspect that the interpretation and handling of the 7th dimension is the big challenge to be overcome in any theory derived from equation (3.1).

The question of inlets and outlets is easily resolved by defining a set of lattice points with constant post collision population outputs and no actual processing of any inputs they may receive. Unlike other inlets there is a question of considering the inlet temperature and orientation. The post collision populations can be defined using the equilibrium function  $f^{(eq)}$

A guide and illustration to the techniques described in this chapter are outlined in Appendix A which contains pseudocode for an implementation of the D7Q2187 velocities on a D7Q507 based lattice spacing.

## 4.6 Summary

In this chapter we have seen several key developments. Among them:

- A linearized analogue of Grmela's equation was postulated.
- We explored how an equation such as the linearized analogue could be used to generate a lattice Boltzmann like equation and noted that inhomogeneous temperature implied that the equation could never be naively matched to a regular lattice geometry.
- We explored numerical quadrature based on spherical geometry in the process but discover this quadrature does not offer the desired level of isometry for deriving lattice Boltzmann like equation.
- We derived an unfamiliar numerical quadrature while exploring the radial aspect of numerical quadrature with spherical coordinates.
- We explored numerical quadrature based on Cartesian coordinates, that is a grid geometry, and found it did have a good level of isometry.
- We explored how, once derived, a discrete analogue of the Chapman-Enskog method could be applied to the lattice Boltzmann like equation to derive mass, momentum, and energy transport equations comparable to the NavierStokes equation and its associated mass and energy equations.
- We explored how lattice Boltzmann like equations could be implemented on arbitrary grid geometry's using interpolation.
- We explored how internal potential energies such as those in the simplified Grmela equation could be reintroduced into the derived lattice Boltzmann like equation.

## CHAPTER 4. SEEKING A LATTICE BOLTZMANN-LIKE METHOD

- We explore how curved boundaries might be applied to the derived lattice Boltzmann like equation in a physically consistent way and speculate about conditions that could be applied to bound  $\sigma$ .

Taken collectively these studies suggest a second prong in our attempt to better understand polymer dynamics. It is a prong that is particularly applicable to creating computer simulations of polymer dynamics.

# Chapter 5

## Miscellaneous Investigations

In this section we explore several disparate approaches that have not greatly elucidated or contributed to our understanding of polymer dynamics but that may possibly be of consequence in further work.

### 5.1 The Kirkwood Approach

Early on in our research we were inspired by some of the early work on applying statistical mechanics to chemistry by Kirkwood, especially the paper by Irving and Kirkwood on deriving equations for transport processes from first principles [32]. So we attempted to construct our own transport equations for polymers by analogy, closely copying his work at most stages. We considered our basic element not to be a molecule but a polymer monomer. So the numerous polymer chains in a melt would be indexed with one variable, say  $i$ , and the individual monomers in a polymer chain with another say  $j$  in sequence from 0 to  $n_i$ . This would require considering a more complex potential energy function than Kirkwood considered, where neighbouring monomers on a chain would have potential energies different to all others to bind them together.

It was then necessary to define a set of functionals that had a reasonable chance



of relating to things we could usefully observe or guess from observations.

$$\begin{aligned}\rho(\vec{r}_1, \vec{r}_2, t) &= m \sum_{i,j} \left\langle \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\ \rho(\vec{r}_1, \vec{r}_2, t) \vec{u}_1(\vec{r}_1, \vec{r}_2, t) &= \sum_{i,j} \left\langle \vec{p}_{ij} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\ \rho(\vec{r}_1, \vec{r}_2, t) \vec{u}_2(\vec{r}_1, \vec{r}_2, t) &= \sum_{i,j} \left\langle \vec{p}_{ij+1} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\ \rho(\vec{r}_1, \vec{r}_2, t) E(\vec{r}_1, \vec{r}_2, t) &= \sum_{i,j} \left\langle (p_{ij}^2 + p_{ij+1}^2) \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle\end{aligned}$$

We typically use  $\sum_{i,j}$  as a short hand for  $\sum_i \sum_{j=0}^{n_i-1}$ . We chose  $\rho$  to be density-like,  $\vec{u}_1$  and  $\vec{u}_2$  to be velocity-like, and  $E$  to be energy-like. The total potential energy of the system we define to be

$$U = \frac{1}{2} \sum_{i,j,k,l} V_{ijkl}(\vec{R}_{ij}, \vec{R}_{kl}), \quad V_{ijij}(\vec{R}, \vec{S}) = 0$$

$V$  is the potential energy between two given particles, which is of course zero for any particle with itself. The key tool of Kirkwood's method is to consider  $f$ , the vector in the Hilbert space of probability distributions over possible states, and note that it has the property

$$\frac{\partial}{\partial t} \langle \alpha; f \rangle = \left\langle \sum_i \sum_{j=0}^{n_i} \left( \frac{\vec{p}_{ij}}{m_{ij}} \cdot \nabla_{\vec{R}_{ij}} - \nabla_{\vec{R}_{ij}} U \cdot \nabla_{\vec{p}_{ij}} \right) \alpha; f \right\rangle \quad (5.1)$$

or if preferred expressed in Einstein summation notation

$$\frac{\partial}{\partial t} \langle \alpha; f \rangle = \left\langle \frac{p_{ijk}}{m} \frac{\partial \alpha}{\partial R_{ijk}} - \frac{\partial U}{\partial R_{ijk}} \frac{\partial \alpha}{\partial p_{ijk}}; f \right\rangle$$

### 5.1.1 Mass Conservation

We adopt the convention of only applying the summation convention to Greek subscripts. That being the case we have the identity

$$\begin{aligned} & \left\langle \left( \frac{p_{\theta\phi\psi}}{m} \frac{\partial}{\partial R_{\theta\phi\psi}} - \frac{\partial U}{\partial R_{\theta\phi\psi}} \frac{\partial}{\partial p_{\theta\phi\psi}} \right) \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\ &= \left\langle \frac{p_{\theta\phi\psi}}{m} \frac{\partial}{\partial R_{\theta\phi\psi}} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\ &= \left\langle - \left( \frac{p_{ij\psi}}{m} \frac{\partial}{\partial r_{1\psi}} + \frac{p_{ij+1\psi}}{m} \frac{\partial}{\partial r_{2\psi}} \right) \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \end{aligned}$$

Applying equation (5.1) and this identity to the operator  $\alpha = \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2)$  we get

$$\begin{aligned} & \sum_{i,j} \frac{\partial}{\partial t} \left\langle \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle = \\ & \sum_{i,j} \left( - \frac{1}{m} \frac{\partial}{\partial r_{1\psi}} \left\langle p_{ij\psi} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \right. \\ & \quad \left. - \frac{1}{m} \frac{\partial}{\partial r_{2\psi}} \left\langle p_{ij+1\psi} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \right) \\ & \Rightarrow \frac{\partial \rho}{\partial t} = - \left( \frac{\partial \rho u_{1\psi}}{\partial r_{1\psi}} + \frac{\partial \rho u_{2\psi}}{\partial r_{2\psi}} \right) \end{aligned}$$

This is precisely what we would expect the mass conservation equation to be.

### 5.1.2 Momentum Conservation

As a precursor to attempting to derive the momentum conservation equation, we derived the following identities

$$\begin{aligned}
 & \left\langle \left( \frac{p_{\theta\phi\psi}}{m} \frac{\partial}{\partial R_{\theta\phi\psi}} - \frac{\partial U}{\partial R_{\theta\phi\psi}} \frac{\partial}{\partial p_{\theta\phi\psi}} \right) p_{ij+\xi k} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\
 &= - \left\langle \frac{p_{ij+\xi k}}{m} \left( p_{ij\psi} \frac{\partial}{\partial r_{1\psi}} + p_{ij+1\psi} \frac{\partial}{\partial r_{2\psi}} \right) \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\
 &\quad - \left\langle \frac{\partial U}{\partial R_{ij+\xi k}} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\
 &= - \frac{1}{m} \frac{\partial}{\partial r_{1\psi}} \left\langle p_{ij+\xi k} p_{ij\psi} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\
 &\quad - \frac{1}{m} \frac{\partial}{\partial r_{2\psi}} \left\langle p_{ij+\xi k} p_{ij+1\psi} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\
 &\quad - \left\langle \frac{\partial U}{\partial R_{ij+\xi k}} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle
 \end{aligned} \tag{5.2}$$

$$\begin{aligned}
 \frac{\partial U}{\partial R_{ijk}} &= \frac{1}{2} \sum_l \sum_{m=0}^{n_l} \left( \frac{\partial V_{ijlm}}{\partial R_{ijk}}(\vec{R}_{ij}, \vec{R}_{l,m=0}^{n_l}) + \frac{\partial V_{lmij}}{\partial R_{ijk}}(\vec{R}_{lm}, \vec{R}_{ij}) \right) \\
 &= \sum_l \sum_{m=0}^{n_l} \frac{\partial V_{ijlm}}{\partial R_{ijk}}(\vec{R}_{ij}, \vec{R}_{lm})
 \end{aligned} \tag{5.3}$$

$$\begin{aligned}
 & \sum_{ij} m \left\langle \left( \frac{p_{ij+\xi k}}{m} - u_{\xi+1k} \right) \left( \frac{p_{ij+\zeta\psi}}{m} - u_{\zeta+1\psi} \right) \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\
 &= \sum_{ij} \frac{1}{m} \left\langle p_{ij+\xi k} p_{ij+\zeta\psi} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle - u_{\xi+1k} u_{\zeta+1\psi} \rho
 \end{aligned} \tag{5.4}$$

By considering the operator  $\sum_i \sum_{j=0}^{n_i-1} p_{ij+\xi k} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2) = \alpha$  and applying equation (5.2)

$$\begin{aligned}
 & \frac{\partial}{\partial t} \sum_i \sum_{j=0}^{n_i-1} \left\langle p_{ij+\xi k} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\
 = & -\frac{\partial}{\partial r_{1\psi}} \sum_i \sum_{j=0}^{n_i-1} \frac{1}{m} \left\langle p_{ij+\xi k} p_{ij\psi} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\
 & -\frac{\partial}{\partial r_{2\psi}} \sum_i \sum_{j=0}^{n_i-1} \frac{1}{m} \left\langle p_{ij+\xi k} p_{ij+1\psi} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\
 & - \sum_i \sum_{j=0}^{n_i-1} \left\langle \frac{\partial U}{\partial R_{ij+\xi k}} \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle
 \end{aligned}$$

A combination of algebraic manipulation and the application of equations (5.3) and (5.4) allows the right-hand side to be expressed as

$$\begin{aligned}
 & -\frac{\partial}{\partial r_{1\psi}} \sum_i \sum_{j=0}^{n_i-1} m \left\langle \left( \frac{p_{ij+\xi k}}{m} - u_{\xi+1k} \right) \left( \frac{p_{ij\psi}}{m} - u_{1\psi} \right) \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\
 & -\frac{\partial}{\partial r_{2\psi}} \sum_i \sum_{j=0}^{n_i-1} m \left\langle \left( \frac{p_{ij+\xi k}}{m} - u_{\xi+1k} \right) \left( \frac{p_{ij+1\psi}}{m} - u_{2\psi} \right) \delta(\vec{R}_{ij} - \vec{r}_1) \delta(\vec{R}_{ij+1} - \vec{r}_2); f \right\rangle \\
 & \quad -\frac{\partial}{\partial r_{1\psi}} u_{\xi+1k} u_{1\psi} \rho - \frac{\partial}{\partial r_{2\psi}} u_{\xi+1k} u_{2\psi} \rho \\
 & -\frac{1}{2} \sum_{i,l} \sum_{m=1}^{n_i-1} \sum_{j=1}^{n_i-1} \left\langle \frac{\partial V_{ijlm}}{\partial R_{ijk}}(\vec{R}_{ij}, \vec{R}_{lm}) \left( \delta(\vec{R}_{ij-\xi} - \vec{r}_1) \delta(\vec{R}_{ij+1-\xi} - \vec{r}_2) \right. \right. \\
 & \quad \left. \left. - \delta(\vec{R}_{lm-\xi} - \vec{r}_1) \delta(\vec{R}_{lm+1-\xi} - \vec{r}_2) \right); f \right\rangle \\
 & - \sum_{i,l} \sum_{j=1}^{n_i-1} \left\langle \left( \frac{\partial V_{ijl0}}{\partial R_{ijk}}(\vec{R}_{ij}, \vec{R}_{l0}) + \frac{\partial V_{ijln_i}}{\partial R_{ijk}}(\vec{R}_{ij}, \vec{R}_{ln_i}) \right) \times \right. \\
 & \quad \left. \delta(\vec{R}_{ij-\xi} - \vec{r}_1) \delta(\vec{R}_{ij+1-\xi} - \vec{r}_2); f \right\rangle \\
 & -(1-\xi) \sum_{i,l} \sum_{j=0}^{n_i} \left\langle \frac{\partial V_{i0lj}}{\partial R_{i0k}}(\vec{R}_{i0}, \vec{R}_{lj}) \delta(\vec{R}_{i0} - \vec{r}_1) \delta(\vec{R}_{i1} - \vec{r}_2); f \right\rangle \\
 & -\xi \sum_{i,l} \sum_{j=0}^{n_i} \left\langle \frac{\partial V_{inilj}}{\partial R_{in_i k}}(\vec{R}_{in_i}, \vec{R}_{lj}) \delta(\vec{R}_{in_i-1} - \vec{r}_1) \delta(\vec{R}_{in_i} - \vec{r}_2); f \right\rangle
 \end{aligned}$$

It is expedient to define some new variables

$$\bar{R}_{ijlm\xi} = (\bar{R}_{lm-\xi} - \bar{R}_{ij-\xi}, \bar{R}_{lm+1-\xi} - \bar{R}_{ij+1-\xi}), \quad \bar{r} = (\bar{r}_1, \bar{r}_2)$$

Using these we can take the Taylor series of  $\delta(\bar{R}_{lm-\xi} - \bar{r}_1)\delta(\bar{R}_{lm+1-\xi} - \bar{r}_2)$  for variable  $(\bar{R}_{lm-\xi}, \bar{R}_{lm+1-\xi})$  around the point  $(\bar{R}_{ij-\xi}, \bar{R}_{ij+1-\xi})$  and so redefine the expression

$$\begin{aligned} & \delta(\bar{R}_{ij-\xi} - \bar{r}_1)\delta(\bar{R}_{ij+1-\xi} - \bar{r}_2) - \delta(\bar{R}_{lm-\xi} - \bar{r}_1)\delta(\bar{R}_{lm+1-\xi} - \bar{r}_2) \\ &= - \sum_{\bar{a}>\bar{0}} \prod_k \frac{R_{ijlm\xi k}^{a_k}}{a_k!} \frac{\partial^{\sum_k a_k}}{\prod_k \partial^{a_k}(\bar{R}_{ij-\xi}, \bar{R}_{ij+1-\xi})_k} \delta(\bar{R}_{ij-\xi} - \bar{r}_1)\delta(\bar{R}_{ij+1-\xi} - \bar{r}_2) \\ &\cong - \sum_{|\bar{a}|>0} \frac{\bar{R}_{ijlm\xi}^{\bar{a}}}{\bar{a}!} \partial_{\bar{r}}^{\bar{a}} \delta(\bar{R}_{ij-\xi} - \bar{r}_1)\delta(\bar{R}_{ij+1-\xi} - \bar{r}_2) \end{aligned}$$

where  $\cong$  signifies that the expressions are equivalent when placed inside the inner-product and  $\bar{a}$  is a multi index. We also assume  $V_{ijlm}(\bar{R}_{ij}, \bar{R}_{lm_i}) = V_{ijlm}(\bar{R}_{ijlm_0})$ .

Considering this we may rewrite the equation we have defined so far for momentum-like conservation in the form

$$\begin{aligned} & \frac{\partial}{\partial t} u_{\xi k \rho} + \frac{\partial}{\partial r_{1\psi}} u_{\xi+1k} u_{1\psi \rho} + \frac{\partial}{\partial r_{2\psi}} u_{\xi+1k} u_{2\psi \rho} \\ &= - \frac{\partial}{\partial r_{1\psi}} \sigma_{\xi k 1\psi} - \frac{\partial}{\partial r_{2\psi}} \sigma_{\xi k 2\psi} \\ &+ \frac{1}{2} \sum_{i,l} \sum_{m=1}^{n_i-1} \sum_{j=1}^{n_i-1} \left\langle \frac{\partial V_{ijlm}}{\partial R_{ijk}}(\bar{R}_{ij}, \bar{R}_{lm}) \sum_{|\bar{a}|>0} \frac{\bar{R}_{ijlm\xi}^{\bar{a}}}{\bar{a}!} \partial_{\bar{r}}^{\bar{a}} \delta(\bar{R}_{ij-\xi} - \bar{r}_1)\delta(\bar{R}_{ij+1-\xi} - \bar{r}_2); f \right\rangle \\ &- \sum_{i,l} \sum_{j=1}^{n_i-1} \left\langle \left( \frac{\partial V_{ijl_0}}{\partial R_{ijk}}(\bar{R}_{ij}, \bar{R}_{l_0}) + \frac{\partial V_{ijlm_i}}{\partial R_{ijk}}(\bar{R}_{ij}, \bar{R}_{m_i}) \right) \right. \\ &\quad \left. \times \delta(\bar{R}_{ij-\xi} - \bar{r}_1)\delta(\bar{R}_{ij+1-\xi} - \bar{r}_2); f \right\rangle \\ &- (1-\xi) \sum_{i,l} \sum_{j=0}^{n_i} \left\langle \frac{\partial V_{i_0lj}}{\partial R_{i_0k}}(\bar{R}_{i_0}, \bar{R}_{lj}) \delta(\bar{R}_{i_0} - \bar{r}_1)\delta(\bar{R}_{i_1} - \bar{r}_2); f \right\rangle \\ &- \xi \sum_{i,l} \sum_{j=0}^{n_i} \left\langle \frac{\partial V_{in_i lj}}{\partial R_{in_i k}}(\bar{R}_{in_i}, \bar{R}_{lj}) \delta(\bar{R}_{in_i-1} - \bar{r}_1)\delta(\bar{R}_{in_i} - \bar{r}_2); f \right\rangle \end{aligned}$$

$\sigma$  represents that expression in the equation that bears resemblance to the stress

strain tensor in gas kinetics. This leaves the remaining terms on the right hand side that would normally be associated with the effect of inter molecular forces and in our case inner molecular forces on the stress strain tensor. Normally, following Kirkwood's strategy, we would introduce an integral and Dirac delta function that would allow us to move unwieldy elements out of the inner product, eventually allowing us to make the approximation

$$g(\vec{r}_1, \vec{r}_2, \vec{r}'_1, \vec{r}'_2, t)\rho(\vec{r}_1, \vec{r}_2, t)\rho(\vec{r}'_1, \vec{r}'_2, t) \\ \approx m^2 \sum_{i \neq l, j \neq m} \left\langle \delta(\vec{R}_{ij} - \vec{r}_1)\delta(\vec{R}_{ij+1} - \vec{r}_2)\delta(\vec{R}_{lm} - \vec{r}'_1)\delta(\vec{R}_{lm+1} - \vec{r}'_2); f \right\rangle$$

for some  $g$  yet to be defined, allowing us to remove all explicit reference to the co-ordinates of individual monomers. However, in this case it is not clear how to perform manipulations to perform this approximation and due to the difficulty of the manipulations and the limitations of time and the promises displayed by other methods this was not pursued further. Possible future approaches to producing a Kirkwood style model for polymer dynamics is discussed in the recommendations for further work.

## 5.2 Analysis of the Form of W

In the analysis of gas kinetics the form of the kernel function representing the collision of molecules can be further restricted by considering what must be conserved in such collisions and then simplified still further by making assumptions about properties such as the elasticity or inelasticity of collisions. We sought some helpful set of restrictions on the kernel function with limited success. These are after all assumptions and their validity is not without ambiguity. The first assumption is that the collisions are more or less instantaneous; an assumption we have used in

earlier chapters and that is explicitly stated in Grmela's paper [2]. This is to say

$$\vec{r}_i = \vec{r}'_i, \sigma_i = \sigma'_i$$

where we use the prime superscript to denote states after collision as opposed to states before. This implies

$$W \propto \delta(\vec{r}_1 - \vec{r}'_1) \cdots \delta(\vec{r}_4 - \vec{r}'_4) \delta(\sigma_1 - \sigma'_1) \delta(\sigma_2 - \sigma'_2).$$

The second potential assumption considered was the need for physical intersection of the 'dumbbells' modelling sections of polymer chain. If we consider them as straight lines between two points, this requirement would be to say the lines meet between these two points. Thus we can write the point of intersection as

$$\vec{P}_i = \vec{r}_1 + s_1(\vec{r}_2 - \vec{r}_1), 0 \leq s_1 \leq 1$$

If we assume the second polymer chain segment intersects with orientation  $\hat{k}$  we can write  $\vec{r}_3$  and  $\vec{r}_4$  as

$$\vec{r}_3 = \hat{k}s_2s_3 + \vec{P}_i, \vec{r}_4 = -\hat{k}(1-s_2)s_3 + \vec{P}_i, s_3, s_4 \geq 0$$

Suppose we wanted to rewrite this expression so  $\vec{r}_3$  and  $\vec{r}_4$  could have any value, we could do so by allowing  $s_i$  to vary freely and introducing a new term in expressions like so:

$$\vec{r}_3 = \hat{k}s_2s_3 + \vec{P}_i + \widehat{\vec{r}_2 - \vec{r}_1} \times \vec{k}s_4, \vec{r}_4 = -\hat{k}(1-s_2)s_3 + \vec{P}_i + \widehat{\vec{r}_2 - \vec{r}_1} \times \vec{k}s_4$$

In effect we could rewrite  $\vec{r}_3$  and  $\vec{r}_4$  in terms of new variables, introduce a change of

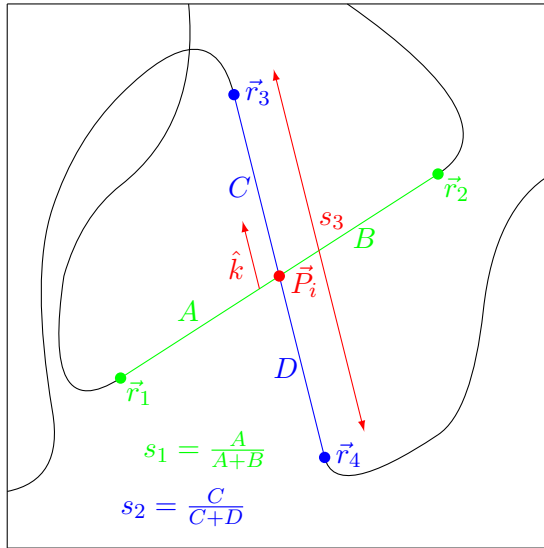


Figure 5.1: Here we see diagrammatically some of the key variables introduced in our intersection assumption.  $\hat{k}$  a unit vector pointing to  $\vec{r}_3$  from the point of intersection  $\vec{P}_i$ .  $s_1$  the fraction of the length of the part the section from  $\vec{r}_1$  to  $\vec{P}_i$  composes of the whole ‘dumbbell’ and  $s_2$  the fraction of length that the section between  $\vec{r}_3$  and  $\vec{P}_i$  composes of its ‘dumbbell’.  $s_3$  is merely the length of the indicated ‘dumbbell’.

variables into the integral and then require that

$$W \propto \delta(s_4)H(s_1)H(s_2)H(s_3)H(1-s_1)H(1-s_2)$$

where  $H$  is the Heaviside function.

The third approximation is to assume conservation of momentum. We call it an approximation because it requires some assumptions about how the total momentum of a chain segment is defined. The problem that is the variable  $\nu$ , which is interpreted as the chain segments motion through the dumbbells two end points. We have chosen to think of this as being like a thread drawn through the eye of two needles. While the eye of each needle may have its own momentum there is also momentum from the thread being pulled through them. This suggests the momentum for each chain segment is

$$m_i \vec{U}_i = m_i \vec{v}_{2i-1} + m_i \vec{v}_{2i} + 2m_i \widehat{\vec{r}_{2i} - \vec{r}_{2i-1}} \nu_i$$

$m_i$  is a mass-like variable. However, we have no guarantee that  $m_i$  is a constant. It might rely on the length of the chain segment ( $|\vec{r}_{2i} - \vec{r}_{2i-1}|$ ) for instance. Conserva-



tion of momentum would then be written as

$$m_1\vec{U}_1 + m_2\vec{U}_2 = m_1\vec{U}'_1 + m_2\vec{U}'_2$$

The fourth assumption is that the chain segment is like a rubber band and that there is the same amount of material, and hence mass stretched between two given end points. This is consistent with the term  $\phi^{int}$ , a potential energy contribution, being dependent only on  $|\vec{r}_2 - \vec{r}_1|$ . Under this assumption,  $m_i = m$  and

$$\vec{U}_1 + \vec{U}_2 = \vec{U}'_1 + \vec{U}'_2$$

$$\begin{aligned} \Rightarrow \vec{v}_1 + \cdots + \vec{v}_4 + 2\widehat{\vec{r}_2 - \vec{r}_1}\nu_1 + 2\widehat{\vec{r}_4 - \vec{r}_3}\nu_2 &= \vec{v}'_1 + \cdots + \vec{v}'_4 + 2\widehat{\vec{r}_2 - \vec{r}_1}\nu'_1 + 2\widehat{\vec{r}_4 - \vec{r}_3}\nu'_2 \\ \Rightarrow 0 &= (\vec{v}'_1 - \vec{v}_1) + \cdots + (\vec{v}'_4 - \vec{v}_4) + 2\widehat{\vec{r}_2 - \vec{r}_1}(\nu'_1 - \nu_1) + 2\widehat{\vec{r}_4 - \vec{r}_3}(\nu'_2 - \nu_2) \end{aligned}$$

The fifth assumption is that the momentum is exchanged in the collision only at the point of intersection, this value being defined as.

$$\begin{aligned} \vec{U}_t &= -(\vec{v}'_1 - \vec{v}_1) - (\vec{v}'_2 - \vec{v}_2) - 2\widehat{\vec{r}_2 - \vec{r}_1}(\nu'_1 - \nu_1) \\ &= (\vec{v}'_3 - \vec{v}_3) + (\vec{v}'_4 - \vec{v}_4) + 2\widehat{\vec{r}_4 - \vec{r}_3}(\nu'_2 - \nu_2) \end{aligned}$$

The sixth assumption is that the effect of this momentum exchange is distributed between the momentum of the two end points according to the ratio of the distance of the end points from the intersection, giving equations for the differences of

momentum for the collision as

$$\begin{aligned}
 -s_1 \vec{U}_t + s_1 s_5 \widehat{\vec{r}_2 - \vec{r}_1} \cdot \vec{U}_t &= \vec{v}'_1 - \vec{v}_1 \\
 -(1-s_1) \vec{U}_t + (1-s_1) s_5 \widehat{\vec{r}_2 - \vec{r}_1} \cdot \vec{U}_t &= \vec{v}'_2 - \vec{v}_2 \\
 -\frac{s_5 \widehat{\vec{r}_2 - \vec{r}_1} \cdot \vec{U}_t}{2} &= \nu'_1 - \nu_1 \\
 s_2 \vec{U}_t - s_2 s_6 \widehat{\vec{r}_4 - \vec{r}_3} \cdot \vec{U}_t &= \vec{v}'_3 - \vec{v}_3 \\
 (1-s_2) \vec{U}_t - (1-s_2) s_6 \widehat{\vec{r}_4 - \vec{r}_3} \cdot \vec{U}_t &= \vec{v}'_4 - \vec{v}_4 \\
 \frac{s_6 \widehat{\vec{r}_4 - \vec{r}_3} \cdot \vec{U}_t}{2} &= \nu'_2 - \nu_2
 \end{aligned} \tag{5.5}$$

$s_5$  and  $s_6$  quantify the amount of momentum absorbed into the  $\nu$  components, which is unknown at this moment. Our next step involves no assumptions. We have already referred to Grmela's definition of energy, and the fact that that it is conserved in collisions has been an important point in his proofs [2]. Energy conservation in collisions may be expressed as

$$\vec{v}_1^2 + \dots + \vec{v}_4^2 + 2\nu_1^2 + 2\nu_2^2 = \vec{v}'_1{}^2 + \dots + \vec{v}'_4{}^2 + 2\nu_1'^2 + 2\nu_2'^2$$

Inserting our previous equations (5.5) for the change in velocities we obtain the equation

$$\begin{aligned}
 -\vec{U}_t \cdot \left( \vec{U}_t (s_1^2 + s_1'^2 + s_2^2 + s_2'^2) + 2(s_2 \vec{v}_3 - s_1 \vec{v}_1 - s_1' \vec{v}_2 + s_2' \vec{v}_4) \right) \\
 + \hat{r}_{21} \cdot \vec{U}_t \left( 2\hat{r}_{21} \cdot \left( \vec{U}_t (s_1^2 + s_1'^2) - s_1 v_1 - s_1' v_2 \right) + \nu_1 \right) s_5 \\
 + \hat{r}_{43} \cdot \vec{U}_t \left( 2\hat{r}_{43} \cdot \left( \vec{U}_t (s_2^2 + s_2'^2) + s_2 v_3 + s_2' v_4 \right) - \nu_2 \right) s_6 \\
 - \frac{1}{4} \left( \hat{r}_{21} \cdot \vec{U}_t \right)^2 (1 + 4s_1^2 + 4s_1'^2) s_5^2 - \frac{1}{4} \left( \hat{r}_{43} \cdot \vec{U}_t \right)^2 (1 + 4s_2^2 + 4s_2'^2) s_6^2 = 0
 \end{aligned}$$

$\vec{r}'_{ij} = \vec{r}'_i - \vec{r}'_j$  and  $s'_i = 1 - s_i$  are convenient short hands. Assuming this equation admits solutions, it's general case can be categorised as elliptical in  $s_5$  and  $s_6$  and

mapped to a circle using the substitutions

$$\begin{aligned}
 s_5 &= 2 \frac{\left(2\hat{r}_{21} \cdot \left(\vec{U}_t (s_1^2 + s_1'^2) - s_1\vec{v}_1 - s_1'\vec{v}_2\right) + \nu_1\right)}{\hat{r}_{21} \cdot \vec{U}_t (1 + 4s_1^2 + 4s_1'^2)} \\
 &+ \frac{2s_7}{\sqrt{\left(\hat{r}_{21} \cdot \vec{U}_t\right)^2 (1 + 4s_1^2 + 4s_1'^2)^2 (1 + 4s_2^2 + 4s_2'^2)}} \\
 &\times \sqrt{-\vec{U}_t \cdot \left(\vec{U}_t (s_1^2 + s_2^2 + s_1'^2 + s_2'^2) - 2s_1\vec{v}_1 - 2s_1'\vec{v}_2 + 2s_2\vec{v}_3 + 2s_2'\vec{v}_4\right)} \\
 &\quad \times \sqrt{(1 + 4s_1^2 + 4s_1'^2) (1 + 4s_2^2 + 4s_2'^2)} \\
 &\quad \times \frac{\left(1 + 4s_2^2 + 4s_2'^2\right) \left(2\hat{r}_{21} \cdot \left(\vec{U}_t (s_1^2 + s_1'^2) - s_1\vec{v}_1 - s_1'\vec{v}_2\right) + \nu_1\right)^2}{\left(1 + 4s_1^2 + 4s_1'^2\right) \left(2\hat{r}_{43} \cdot \left(\vec{U}_t (s_2^2 + s_2'^2) + s_2\vec{v}_3 + s_2'\vec{v}_4\right) - \nu_2\right)^2} \\
 s_6 &= 2 \frac{2\hat{r}_{43} \cdot \left(\vec{U}_t (s_2^2 + s_2'^2) + s_2\vec{v}_3 + s_2'\vec{v}_4\right) - \nu_2}{\hat{r}_{43} \cdot \vec{U}_t (1 + 4s_2^2 + 4s_2'^2)} \\
 &+ \frac{2s_8}{\sqrt{\left(\hat{r}_{43} \cdot \vec{U}_t\right)^2 (1 + 4s_1^2 + 4s_1'^2) (1 + 4s_2^2 + 4s_2'^2)^2}} \\
 &\times \sqrt{-\vec{U}_t \cdot \left(\vec{U}_t (s_1^2 + s_2^2 + s_1'^2 + s_2'^2) - 2s_1\vec{v}_1 - 2s_1'\vec{v}_2 + 2s_2\vec{v}_3 + 2s_2'\vec{v}_4\right)} \\
 &\quad \times \sqrt{(1 + 4s_1^2 + 4s_1'^2) (1 + 4s_2^2 + 4s_2'^2)} \\
 &\quad \times \frac{\left(1 + 4s_2^2 + 4s_2'^2\right) \left(2\hat{r}_{21} \cdot \left(\vec{U}_t (s_1^2 + s_1'^2) - s_1\vec{v}_1 - s_1'\vec{v}_2\right) + \nu_1\right)^2}{\left(1 + 4s_1^2 + 4s_1'^2\right) \left(2\hat{r}_{43} \cdot \left(\vec{U}_t (s_2^2 + s_2'^2) + s_2\vec{v}_3 + s_2'\vec{v}_4\right) - \nu_2\right)^2}
 \end{aligned}$$

Giving  $s_7^2 + s_8^2 = 1$ , we could then define  $s_7 = \cos(\theta)$ ,  $s_8 = \sin(\theta)$ . However, the substitution contains square roots so as a condition we would require that their arguments were non negative. Also, we may wish to adopt a seventh assumption,  $0 \leq s_5 \leq 1$ ,  $0 \leq s_6 \leq 1$ . Values outside this range imply that momentum is being transferred around within the chain segment in the collision as opposed to only between chain segments. It is difficult to then impose these values on  $\theta$ . As an alternative we considered the substitution  $\vec{U}_t = a\hat{U}_t$  which gives the equation for

energy conservation

$$\begin{aligned} & \frac{1}{4}a^2 \left( -4(s_1^2 + s_2^2 + s_1'^2 + s_2'^2) - (\hat{r}_{21} \cdot \hat{U}_t)^2 s_5 (4s_1^2(s_5 - 2) + 4s_1'^2(s_5 - 2) + s_5) - \right. \\ & \quad \left. (\hat{r}_{43} \cdot \hat{U}_t)^2 s_6 (4s_2^2(s_6 - 2) + 4s_2'^2(s_6 - 2) + s_6) \right) + \\ & a \left( -2\hat{U}_t \cdot (-s_1\vec{v}_1 - s_1'\vec{v}_2 + s_2\vec{v}_3 + s_2'\vec{v}_4) + \hat{r}_{21} \cdot \hat{U}_t s_5 (-2\hat{r}_{21} \cdot (s_1\vec{v}_1 + s_1'\vec{v}_2) + \nu_1) + \right. \\ & \quad \left. \hat{r}_{43} \cdot \hat{U}_t s_6 (2\hat{r}_{43} \cdot (s_2\vec{v}_3 + s_2'\vec{v}_4) - \nu_2) \right) = 0 \end{aligned}$$

Only the non-zero solution is meaningful as we are considering collisions, and a zero result represents a non collision. Thus energy conservation sets  $a$  at

$$\begin{aligned} & -\frac{8\hat{U}_t \cdot (\hat{r}_{21} \cdot (s_1\vec{v}_1 + s_1'\vec{v}_2) \hat{r}_{21} s_5 - \hat{r}_{43} \cdot (s_2\vec{v}_3 + s_2'\vec{v}_4) \hat{r}_{43} s_6 - \frac{1}{2}\hat{r}_{21} s_5 \nu_1 + \frac{1}{2}\hat{r}_{43} s_6 \nu_2}{\hat{U}_t \cdot \left( 4\hat{U}_t (s_1^2 + s_2^2 + s_1'^2 + s_2'^2) + \hat{r}_{21} \cdot \hat{U}_t \hat{r}_{21} s_5 (4s_1^2(-2 + s_5) + 4s_1'^2(-2 + s_5) + s_5) \right.} \\ & \quad \left. \dots \frac{-s_1\vec{v}_1 - s_1'\vec{v}_2 + s_2\vec{v}_3 + s_2'\vec{v}_4}{+\hat{r}_{43} \cdot \hat{U}_t \hat{r}_{43} s_6 (4s_2^2(-2 + s_6) + 4s_2'^2(-2 + s_6) + s_6)} \right) = a \end{aligned}$$

Note the special case where transferred momentum is perpendicular to both dumbbells  $\hat{U}_t \cdot \hat{r}_{21} = \hat{U}_t \cdot \hat{r}_{43} = 0$

$$\frac{2\hat{U}_t \cdot (s_1\vec{v}_1 + s_1'\vec{v}_2 - s_2\vec{v}_3 - s_2'\vec{v}_4)}{s_1^2 + s_2^2 + s_1'^2 + s_2'^2} = a$$

Deriving these conditions is not too difficult but carrying them through into the analysis of solutions did not seem helpful<sup>1</sup> and is left for others to consider (see the section on recommendations for further work).

### 5.3 Quasi Equilibrium Manifolds

In deriving equation (3.20) we had to make some non-trivial assumptions about what quantities should be conserved in collisions. We now show that the same expression can be derived from independent means by physical argument. Because Grmela

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<sup>1</sup>Inserting these conditions into the collision integral would give a less symmetrical form of the integral all be it with fewer variables

has demonstrated [1, 2] that entropy tends to a maximum as in the second law of thermodynamics, it is not unreasonable to suppose the Chapman-Enskog expansion might be an expansion around maximum entropy subject to certain constraints. We can use the Volterra functional derivative [30] to find the extrema of a functional such as entropy, and which can also be modified to find the extrema subject to constraints. Our entropy-like functional as defined in equation (3.2), and simplified by taking  $\omega^{rept} = \omega = \mathcal{L} = 0$ , takes the form

$$\mathcal{S}(f(x, v, t)) = \int f(x, v, t) \ln f(x, v, t) d^6 \bar{r} d\sigma d^6 \bar{v} d\nu \quad (5.6)$$

The Volterra functional derivative is given by considering an arbitrary small change in the function  $\delta f$  multiplied by a scalar. It's explicit form for a functional over  $d^6 \bar{r} d\sigma d^6 \bar{v} d\nu$  is given by

$$\left. \frac{d}{d\lambda} \mathcal{S}(f + \lambda \delta f) \right|_{\lambda=0} = \int \delta f \frac{\delta \mathcal{S}}{\delta f} d^6 \bar{r} d\sigma d^6 \bar{v} d\nu \quad (5.7)$$

To add constraints we first consider restrictions to  $\delta f$  to force the mass momentum and energy fields to stay constant as we vary  $\lambda$ . These conditions are

$$\begin{aligned} \int f + \lambda \delta f d^6 \bar{v} d\nu - \int f d^6 \bar{v} d\nu &= 0 = \lambda \int \delta f d^6 \bar{v} d\nu \\ \int \bar{v} f + \lambda \bar{v} \delta f d^6 \bar{v} d\nu - \int \bar{v} f d^6 \bar{v} d\nu &= 0 = \lambda \int \bar{v} \delta f d^6 \bar{v} d\nu \\ \int \left( \frac{1}{2} \bar{v}^2 + \nu^2 \right) (f + \lambda \delta f) d^6 \bar{v} d\nu - \int \left( \frac{1}{2} \bar{v}^2 + \nu^2 \right) f d^6 \bar{v} d\nu \\ &= 0 = \lambda \int \left( \frac{1}{2} \bar{v}^2 + \nu^2 \right) \delta f d^6 \bar{v} d\nu \end{aligned} \quad (5.8)$$

So, it is possible to add expressions to the inside of the integral of equation (5.7) that will evaluate to zero because of the restrictions given in equation (5.8). Therefore it is possible to insert these into equation (5.7) and then insert our definition of  $\mathcal{S}$

(equation (5.6)) to give

$$\begin{aligned}
 \left. \frac{d}{d\lambda} \mathcal{S}(f + \lambda \delta f) \right|_{\lambda=0} &= \int \delta f \left( \frac{\delta \mathcal{S}}{\delta f} + A(\bar{r}, \sigma, t) \right. \\
 &\quad \left. + \bar{B}(\bar{r}, \sigma, t) \cdot \bar{v} + C(\bar{r}, \sigma, t) \left( \frac{1}{2} \bar{v}^2 + \nu^2 \right) \right) d^6 \bar{r} d\sigma d^6 \bar{v} d\nu \\
 &= \int \frac{d}{d\lambda} ((f + \lambda \delta f) \ln(f + \lambda \delta f)) \Big|_{\lambda=0} d^6 \bar{r} d\sigma d^6 \bar{v} d\nu = \int \delta f (1 + \ln f) d^6 \bar{r} d\sigma d^6 \bar{v} d\nu
 \end{aligned} \tag{5.9}$$

Due to the arbitrary nature of  $\delta f$ , subject to constraints, this implies

$$1 + \ln f = \frac{\delta \mathcal{S}}{\delta f} + A(\bar{r}, \sigma, t) + \bar{B}(\bar{r}, \sigma, t) \cdot \bar{v} + C(\bar{r}, \sigma, t) \left( \frac{1}{2} \bar{v}^2 + \nu^2 \right)$$

To find the extrema we set  $\frac{\delta \mathcal{S}}{\delta f} = 0$  giving

$$\ln f = A(\bar{r}, \sigma, t) - 1 + \bar{B}(\bar{r}, \sigma, t) \cdot \bar{v} + C(\bar{r}, \sigma, t) \left( \frac{1}{2} \bar{v}^2 + \nu^2 \right)$$

Consequently this expression has the same form as equation (3.20) except that we must first absorb  $-1$  into the field  $A$ . This therefore tends to validate our original choice of  $f_0$ .

## 5.4 Summary

Several notable endeavours have taken place in this chapter including

- An attempt to formulate a variation on Kirkwood's method for deriving the hydrodynamic equations, a variation that attempts to include the orientation dynamics of polymer chains by defining it's macroscopic variables using pairs of bonded monomers.
- This variation is not successfully concluded in momentum or energy conservation equations although a mass conservation equation is obtained.
- An investigation into the allowable and likely forms of the function  $W$  which

## CHAPTER 5. MISCELLANEOUS INVESTIGATIONS

describe probabilistically the outcome of collision events yielded several insights. This included an ansatz reducing  $W$ 's degrees of freedom by 25 from 56 to 31.

- An analysis determining, subject to the constraint of having given macroscopic variables, what distribution function has maximum entropy for the simplified Gmela equation. The answer obtained is the same as the result for the zeroth order Chapman-Enskog expansion which tends to validate that result.

# Chapter 6

## Summary, Conclusions, and Recommendations

### 6.1 Summary of Major Results

In summarising the work we have had to consider how best to categorise it's parts, no easy task when so many aspects of this work touch upon others. We have decided to present the work in two sections: one based upon the attempts to treat things analytically, looking for general results derived from the models considered, and the other section composed of our attempts to hammer the models in hand into something tractable for computer implementation.

#### 6.1.1 Analytical Results

An architecture for deriving a seven dimensional continuum model of polymer flow, where the four extra dimensions relate to internal aspects of the polymeric fluid, from both conventional continuous and linearized discretized Boltzmann like models, has been described. The major aspects and important ancillary results of this process are laid out below.

First it is important to consider the steps taken which, while not novel, are



fundamental to the rest of our results. These preliminary steps were as follows:

- Simplifications were applied to the modelling equations in the paper by Grmela and Carreau [2] leading to the simplified equation (3.7) which we found more amenable to treatment.
- In line with standard methods in the theory of Boltzmann equations we derive a linearized equation (4.1) based upon the solution to the zeroth order Chapman-Enskog expansion (4.2), subject to the application of a useful variable substitution (4.3).
- In line with He and Lou's paper [6] a discrete time equation (4.4) is derived with the equilibrium function  $f_0$  approximated by function (4.5) and the equation further approximated based upon quadrature methods to give a discrete time and velocity equation (4.26).

This sets the stage for the following results relating our attempts to apply a Chapman-Enskog method to the continuous equation (3.7).

1. The zeroth order in the Chapman-Enskog expansion is calculated giving the equation (3.19) the solution for which is found to be the function (3.21). This result is further validated as physically sensible by the techniques explored in Section 5.3.
2. The solution to the zeroth order expansion is used to calculate equations for mass (3.23), generalised velocity (3.26), and temperature (3.27) that are comparable to the Euler equations that can be derived by similar methods.
3. The first order of the Chapman-Enskog expansion is calculated using the previous results giving (3.32). This is further simplified through a suitable substitution giving the equation (3.34), which we are able to rearrange to demonstrate that it is a Fredholm integral equation (3.36).

## CHAPTER 6. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

In the process of attempting to solve the Fredholm equations we were presented with, we developed several techniques for solving Fredholm equations that we have not been able to find reference to in literature and so suspect to be original.

1. A rather obvious generalisation of the contraction mapping theorem to equations composed of multiple linear operators as proved by equation (3.38), which slightly expands the number and type of equations upon which Neumann series can be used.
2. A method of solving Fredholm equations with multiple solutions subject to constraints using the expression (3.48) based upon the skew projection operator (3.42) constructed from our constraints, validity of the solution being ensured by certain variable functions being subject to the constraint derived in equation (3.47). A worked example is constructed in Section 3.4.
3. We derived the correct form for the skew projection operator (3.45) that could be used in an attempt to solve the equation produced in the continuous case of the first order part of the Chapman-Enskog expansion. This is subject to the constraints (3.46).

We also attempted a Chapman-Enskog expansion on the linearized, discrete (in both time and velocity) equation.

1. We introduced a generalisation of the equilibrium function (4.10) that we hope will encompass a greater range of useful material behaviours having demonstrated it's physical consistency.
2. From the Chapman-Enskog expansion we derived a 'ladder' of equations up to the third order given in equations (4.30), (4.31), and (4.32) used to construct the idealised solutions.
3. Using the 'ladder' equations we constructed equations for mass (4.41), momentum (4.42), and energy (4.43) from who's terms are derived the idealised

solutions as described by equations (4.40).

### 6.1.2 Algorithmic Results

We developed the linearized discrete time equation into a model with discrete but temperature dependant velocity and then showed how it can be mapped into a set of stationary lattice points with more or less arbitrary boundaries by applying various approximations. We further expand it to include force derived from an approximation of a potential field over the lattice.

- We followed He and Lou’s method [6] using a simple quadrature formula (4.14) with abscissae and weights (4.15) to prescribe a way to convert the linearized equation to one with discrete velocities having the necessary isotropy conditions.
  - We develop a new quadrature rule (4.17) for the the radial part of spherical co-ordinates and in particular use its first order form (4.18) to effect.

We derive a quadrature rule (4.24) based on spherical co-ordinates with abscissae and weights given in expressions (4.23) and (4.25) which is quite suited to our preferred lattice but lacks the level of isotropy desired.

- In efforts to match discrete velocity schemes to disparate lattices we developed a number of interpolation techniques.
  1. We derived two methods of interpolating physical variables at arbitrary points in our space to nearby FCC lattice points in a way that ensures consistency over the whole lattice. The first involves distributing values at points within the cells of the dual of the Voronoi diagram to the vertices of these cells which are lattice points (see figure 4.2). This is given by equation (4.49) for octahedral cells and equation (4.48) for tetrahedral cells. The second is a smoother mapping to the related lattice points of

## CHAPTER 6. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

the cubic lattice given by equation (4.50) where the values assigned to the extraneous lattice points are then redistributed to the nearest neighbours.

2. We developed a method of merging the contributions from the different lattice points in the previous time step into a single population for a given discrete velocity with the proviso that that velocities' magnitude must change. The new population is given by equation (4.54) and the new velocity by equation (4.53). A small addition to the discrete velocity with zero magnitude must also be made, given by equation (4.55). In this way mass, momentum, and energy are conserved.
  3. Having altered the magnitude of various discrete velocities it is necessary to bring them back in line with the proper magnitude as prescribed by the lattice point temperature. The method of Lagrange multipliers is used to ensure that the minimum amount of change is made while conserving mass, momentum, and energy. This is achieved by solving the linear system of equations (4.68) where functions  $A$  and  $B$  are given by expressions (4.67), and  $K$  and  $J$  by expressions (4.62). The solution is then given by inserting this result into equation (4.63).
- Based on the work of Shan and Chen [17, 18] we incorporate a force term into our equilibrium function by substituting velocity with a pseudo velocity given by equation (4.69) and defining a discrete gradient-like operator on a discrete potential given a force contribution defined by equation (4.70), subject to conditions (4.71). We also generalise Shan and Chen's work [17] on interacting fluid components to the action of a continuum fluid over three dimensions upon our seven dimensional 'fluid' in equation (4.73) and vice versa in equation (4.74).
  - We also generalise existing bounce back conditions to work on arbitrary curved boundaries, the method given in equation (4.77).

## 6.2 Work in Progress

### 6.2.1 Analysis of the Continuous Case

In the initial work in analysing the collision operators we sought to follow the methods used in gas dynamics where the restrictions on the values allowed by  $W$  can be well understood as restrictions on the geometry of the quadrilateral composed of  $\vec{v}_1$ ,  $\vec{v}_2$ ,  $\vec{v}'_1$  and  $\vec{v}'_2$ . However, in the case of Grmela's model we must consider all eight velocity-like vectors and four speed-like scalars; in addition we must consider the position-like vectors and scalars before the collision as we can no longer model the dynamics as point-like. In spite of numerous sketches of outlandish geometry we were not able to follow through with this approach. At last we fixed upon the idea of a point of transfer where the two polymer chains could interact and a transfer of momentum and energy could take place. However, the result was not satisfactorily simplified and concerns remain that approximations made may prove invalid. No analysis of the transfer of angular momentum was made for example. In any event, after such considerations as were made, we had one unit vector and four scalars so essentially six degrees of freedom over which a function varies to determine the characteristic properties of  $W$ . This is a lot compared to the two scalars in the gas dynamic case. It would be desirable to find a formulation that took arbitrary scalars rather than a unit vectors as an argument at least. Possibly  $\hat{U}_t \cdot \hat{r}_{21}$  and  $\hat{U}_t \cdot \hat{r}_{43}$  in this approximation would give the collision process invariance under reflection perpendicular to the plane of the colliding polymer chains.

Even when the exact relationships have been determined it is another matter to frame them in a form that facilitates and simplifies the Chapman-Enskog process. Ideally we would like something that allows the mostly symmetrical form of the first order expansion to remain quite symmetrical after the necessary substitutions and simplifications via Dirac delta functions are made. Hopefully that would facilitate an attempt to finish the Chapman-Enskog procedure for the most general form of

$W$  allowable, or possibly some large (probably dense) subset conducive to the skew projection method.

It may also be necessary to perform a more detailed analysis of  $\phi^{(int)}$  and  $\phi^{(ext)}$  to ensure that the inhomogeneous part of the first order expansion is of a form that is solvable and that is also physically meaningful.

### 6.2.2 Analysis of the Discrete Case

The work on the discrete case and the lattice Boltzmann like models was able to proceed much further than the continuous case. However, there are still some important unresolved issues. It would be very desirable to complete the Chapman-Enskog procedure for some very general form of  $f^{(eq)}$ . The particular issue was the unwieldiness of the procedure (in attempting to do it by hand many mistakes would invariably occur). Computer algebra systems, on the other hand, could not properly handle the tensors. Given that there is one redundant equation in our version of the procedure we would expect to simplify to  $0 = 0$  with reference to the other equations. If not it may impose an additional condition on  $f^{(eq)}$ .

On the other hand we never fully investigated what forms  $\phi^{(int)}$  and  $\phi^{(ext)}$ , as defined over the lattice points, might take. That is what might be physically allowable and tractable. Since the effect of these potential energy fields is to cause a pseudo-velocity to replace the standard velocity in our time evolution equation, the new equation might still be possible to be analysed with the Chapman-Enskog procedure. This is an interesting possibility for future research.

Further research on heat exchange through boundaries would also be useful. Ideally we would like a system whereby a boundary can allow a certain amount of heat to escape or indeed enter the fluid but also conserve mass and the no slip condition consistently with the curved boundary.

### 6.2.3 Construction of Kirkwood Models

The nature of our adaptation of Kirkwood's work to this new problem is so experimental and novel that it is really not clear how to proceed in attempting to derive useful results from the model. It requires an inspired leap, not merely hard work. However, one way to proceed might be to change the definition of the operators to make them only dependent upon  $\vec{R}_{ij}$  rather than  $\vec{R}_{ij}$  and  $\vec{R}_{ij+1}$ , and add internal variables for orientation, extension, and so on. In short we could think of the monomers in a polymer chain as stretchy rods and give them potential energy functions dependent on internal variables that compel monomers to line up end to end.

If some insight could be gained, and a suitable approximation found, it might be possible to take the model to its next logical step and link the ends of the 'chains' to each other by modifying potentials at the end points giving them attractive potentials to two or more other end points thus creating a branched polymer. If whatever inspired approximation we might find for the first model also applied to this one, we would have a very general model of branched polymers, a model that included polymer chain orientation and extension as a factor on the most fundamental level.

### 6.2.4 Comparison to Existing Models

If we had progressed further in the work we might have had opportunity to improve the conceptual understanding of aspects of the discrete and continuous models, namely  $f^{(eq)}$ ,  $\phi^{(int)}$ ,  $\phi^{(ext)}$ ,  $W$  and the functions derived from them, that typify the behaviour of the material modelled. Ideally we would like to link their functions to the functions appearing in fluid dynamics. That was very much the direction of Grmela's work [2] and we would attempt to refine it further. Likewise in the case of the discrete, lattice Boltzmann like model we could attempt to construct a Chapman-Enskog expansion relating models (possibly using an equilibrium function

$f^{(eq)}$  augmented by a potential function  $\phi$  as shown in equations (4.69) and (4.70)) to models of the conventional four dimensions of space and time so recovering equations like those of standard fluid dynamics. This would give us a set of expressions relating normal fluid dynamics to our models and hopefully allow us to make deductions about the physical significance of functions that concern us as well as offering us existing forms of functions in fluid dynamics, functions like the stress strain tensor for instance, as guidelines and sanity tests for constructing equivalent functions for the same materials in our models.

Of course, if all such analytical methods proved ineffectual it would still be possible to make comparisons by building up a large body of simulations in both our models and standard fluid dynamics for a standard set of boundary and initial conditions, but varying the values of the key functions we seek to examine. By looking for similar ‘points’ in our two ‘spaces’ of data results an empirical mapping from one to the other might be obtained.

### 6.2.5 Coding, Simulation, Experimental Validation

Initially attempts were made to implement some of the ideas used in the lattice Boltzmann like model in a traditional 3 dimensional fluid simulation. Some effort was put into programming os x based cocoa applications to define initial conditions and mould geometry’s and also to actually perform the simulation. It was our hope that development in cocoa would make it easy to subsequently parallelise the simulation by distributing objects over different processors. Indeed since then several extra tools have been added to cocoa to make this easier. We were inspired to use cocoa by the creation of the macintosh G5 based “system x” computer in Virginia and our familiarity with the cocoa language. However, while the application for defining the mould geometry was completed, the simulating code required extensive debugging and further developments made much of this code obsolete long before debugging could be finished.



## CHAPTER 6. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

The lattice Boltzmann like simulation lends it self quite neatly to easy parallelization and it would seem quite natural to code a simulator with parallel architecture in mind. The obvious and versatile choice would be a linux based system running c++ code with open MPI. However, specialist architectures were considered quite seriously as candidates. As previously mentioned cocoa now supports a more robust parallel processing framework called “Grand Central Dispatch” for parallel processing on multi core machines and “Xgrid” for cluster computing. This would substantially accelerate the development phase. This would have been our first choice. We also considered a Cell Broadband Engine based simulation possibly based on an cluster of repurposed PS3s or a system built from components cannibalised from them but comparatively little work was done on this as implementation would be work intensive and dependent upon the willingness to devote resources and manpower to building a CBE based super computer for the general use of the department.

Adapting the algorithm to run efficiently on a parallel processing system will be an interesting challenge that should ideally be closely wedded to the hardware used. Presumably the full spectrum of fluid dynamic simulation methods will be applicable to the continuous case the vast majority of these amenable to parallelization. However, this remains a totally unexplored problem since we made less progress in the analysis of the continuous case.

Assuming that a body of simulation software for the continuous, discreet and possibly Kirkwood models was created, or even if some very simple analytical solutions were found, one has to give thought to exactly what body of simulation data should accumulated to test the validity of the model. This remains very much an open question but one possibility that comes to mind is a phenomenon where a polymer melt disk spun at high speed will solidify with two phases, one mostly randomly oriented and another on the other side of a certain radius where the polymer chains are mostly oriented. It is worth considering further experimental set

ups and corresponding simulations that will hopefully facilitate the calibration and validation of the models through experimental testing, although realistically it may be more effective to cannibalise previous experimental data to make the necessary comparisons.

### 6.2.6 Optimisation

We were and are strongly aware that this project was (tasked) with the hope of progressing towards better optimisation methods for micro-injection moulding. To that end it was of concern to us how improved modelling might be used to optimise the process. Our reasoning was that it is typically far easier to move forwards from initial conditions to result rather than backwards from results to initial conditions. So, although the possibility of using the models to make some sort of backwards analysis was not ruled out, the most logical way to proceed seemed to be the use of heuristic techniques such as genetic algorithms and neural nets. In these schemes a number of parameters relating to the moulding process are allowed to vary and the simulation repeated over and over, a number of criteria are set to judge the level of effectiveness of a set of parameters. Thus the heuristic technique ‘homes in’ on a good set of parameters. These parameters might be non essential (for the intended function) mould features, the speed, temperature, density, and polymer orientation of injected material, the rate at which the polymer melt is allowed to lose heat through the mould surface (probably by active heating or cooling of sections of the mould).

This step would represent the final development of the research to the stage of application.

## 6.3 Critical Assessment

Nobody is perfect is a long repeated maxim and we must not be blind to the shortcomings of our own work any more so than to its merits. Here we explore the strengths and weaknesses of the work presented beginning with the negative aspects.

### 6.3.1 Weaknesses and Limitations

The principal weakness of the research is most likely the lack of physical validation. No calculation has been carried through to the point where it could be compared to existing models either through direct mathematical analysis or by running parallel simulations.

This is in part why we do not have any definitive data on the functions ( $W$ ,  $\phi^{(ext)}$ ,  $\phi^{(int)}$  and  $f^{(eq)}$ ) that determine the modelled behaviour of different polymers, thus characterising the materials. As the Chapman-Enskog calculation was never fully completed in either the continuous or lattice model there is at present no mechanism to compare these functions to the stress strain tensor and heat flux tensor of fluid dynamics, which could act as a guide for their determination. Likewise, because a full analysis of the characterising functions based on the microscopic interactions of the polymer was incomplete, it is not possible to relate the characterising functions to the known microscopic dynamics of a given polymer material. A completed simulation code would allow us to run an extensive series of simulations against known experimental data using a heuristic algorithm to ‘home in’ on the correct functions.

The last major issue is inherent to the model from which our work was taken. Grmelas model had to be substantially simplified for our purposes yet in its initial form it seemed to be conceptually based on interactions of unbranched polymers. That does not necessarily mean it is incapable of modelling branched polymers.

## CHAPTER 6. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Some times in mathematical modelling you ‘get lucky’ and models with a few functions tweaked here and there provide good approximations for systems they were not conceived for. Had we been able to complete the work on an unbranched model inspired by the work of Kirkwood it would have been easy to formulate a branched version.

After all of these weaknesses of the model are considered it must still be admitted that the model is not easy to implement. In the continuous case we have a seven (or perhaps six if we can somehow dispense with  $\sigma$ ) dimensional fluid flow simulation. In the discreet case we have a situation where each cell has 506 adjacent neighbours and 2187 important values plus ancillary values used in the calculation. Granted, if you take more than a few steps in most of those 506 directions you will hit a boundary but the load on a computer must be significant.

Even when implementation is perfect there may be an issue with usability. There is an old joke about physicists and engineers: that the physicist’s approximation is that all infinite series converge and the engineer’s that they all converge to the first term. Levity aside, engineers are not traditionally comfortable with research level mathematics and while academic research engineers might cope, there are concerns about how easily industrial engineers will ‘wrap their heads around’ the model.

In summary we have a model that is not yet linked to known materials or models, and for which no simulation data exists, that is in addition computationally demanding and hard to understand and that has only our intuition to vouch for its validity<sup>1</sup>.

### 6.3.2 Strengths, Assets, and Advantages

In spite of the conclusion in the previous section, this work has a great deal to recommend it. Fundamentally, by construction it incorporates very fully the notion of the range of polymer orientations being a factor in the dynamics. That includes the

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<sup>1</sup>Clearly we are putting a lot of weight on our intuition.

## CHAPTER 6. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

effect of a potentially quite anisotropic distribution on viscosity and heat transport as well as the potential for polymer chains with different orientations to be effected differently by those properties. We are not aware of any other fluid-like model, as opposed to Boltzmann-like or microscopic models, of polymer dynamics that can boast that.

On the other hand the discrete, lattice based, model has the virtue of being highly parallelizable. By simply dividing nodes of a simulation of this model between different processors of a parallel computer, lattices of arbitrary size are easily handled, provided that a sufficiently large parallel system is available.

Also many lattice Boltzmann-like simulations are unable to implement curved boundaries but our model has incorporated some of the latest theories on boundary methods in lattice Boltzmann methods therefore making the implementation of curved boundaries fairly simple.

In both the continuous and discrete case our models can be linked fairly directly to the behaviour of the components of a fluid on the microscopic level. In this sense the model could be seen as a useful bridge between microscopic and macroscopic fluid dynamic. It may allow us to build up models from their most basic elements or possibly to infer things about the dynamic of those elements from the behaviour of larger systems.

I believe that the biggest possible asset, and our biggest hope, is that this research will find application beyond polymer physics. In so much as this thesis may make a contribution to the theory of integral equations it could potentially have application to the range of mathematical physics. More specifically, the theory of Boltzmann-like equations has a huge application, to plasma physics, biology, and potentially to material science. We would like to think that the work might be used as a guide by others, further publicising the techniques we have acquired from the work of others as well as those we've developed. If nothing else we feel that the techniques for interpolating in lattice Boltzmann methods may lead to better thermal lattice

Boltzmann simulations and the techniques for introducing potentials might open up new possibilities.

## 6.4 Recommendations

As the final duty, it falls to us to recommend how this work might best be continued in future research. As well as recommendations on how the theoretical work could be further developed, we've also seen fit to include some ideas regarding engineering developments that might facilitate the exploitation of the theory.

### 6.4.1 Theoretical Work

The first and most important line of inquiry in both the discreet and continuous case must be to finish the Chapman-Enskog expansion. Interestingly the obstacles are quite different in each case so we will treat them separately.

- There is a certain sequence to the problems that must be solved to achieve a Chapman-Enskog expansion of the continuous equation (3.7), namely:
  1. A suitable anzats for  $W$  must be found. As mentioned, the analysis never included the possibility that angular momentum might be transferred between elements during collisions. More importantly it is not at all clear what anzats for  $W$  will give a tractable kernel in the Neumann series. Ideally we want the kernel  $\frac{C(n;\mathbf{1},\mathbf{1}')}{B(n;\mathbf{1})}$  (see equation (3.36)) when applied as an integral operator on the left of our projection operator  $\mathcal{P}$  (see equation (3.47)) to give an operator with a kernel expressed as a finite sum of orthonormal basis functions multiplied by scalars. This makes a solution of the Neumann series tractable via matrix diagonalisation. At present it is unclear just how this would be achieved. This is particularly difficult when you consider the scalars by which these orthonormal functions will

be multiplied are themselves functionals of the macroscopic variables. Whether or not it is possible to approximate the kernel and retain this dependency upon the macroscopic variables in a meaningful way should also be investigated.

2. It is necessary to find a good ansatz for  $\varphi^{(int)}$  and  $\varphi^{(ext)}$ . In particular  $\varphi^{(ext)}$  must be consistent with equation (3.4). However, this is not expected to be very difficult.
  3. Most importantly the Neumann series must be constructed for a sufficiently general projection operator and solved. The variable parameters of the solution set must then be constrained to satisfy equation (3.47) which will hopefully give us a unique solution.
  4. This solution must be reinserted into previous equation of constraint (3.40), as previously described, to derive a first order result of the Chapman-Enskog expansion, namely those equations that are analogues of the NavierStokes equation and its mass and energy counterparts.
- The Chapman-Enskog procedure can be carried out on the discrete time equation (4.4) using integration over velocity or the discrete time and velocity equation (4.26) using a summation over the discrete velocities. Performing so many integrations or summations over complicated tensor expressions is too difficult to do by hand. A computer algebra application is needed. Unfortunately, the existing products were not suitable or capable of handling simplifications of complex tensor expressions. There are two likely options. One would be to take the existing computer algebra manipulation C++ library GiNaC and improve its tensor simplification subroutines. The other would be writing a tensor manipulation package for the computer algebra system mathematica. Either way we suggest that a good place to start might be Portugal's paper [34]. Once the Chapman-Enskog procedure has been completed it may

be worth trying to substitute the pseudo velocity given by equation (4.69) into the equilibrium function and using a continuous potential function re-perform the Chapman-Enskog procedure.

Once the Chapman-Enskog procedure is completed it will be possible to write a simulation for that model, like those used in fluid dynamics with additional dimensions. Irrespective of that it should be possible to write code for a lattice Boltzmann like simulation based on the work in this report. Right now it is impossible for us to quantify the level of computing resources this would need to run feasibly, although we expect it to be significant. However, the code should definitely be written with parallelization in mind and with careful thought with regard to the hardware it will run on<sup>2</sup>.

Having devised a simulation package we suggest further work into optimisation code based upon heuristic methods, as previous described, by varying a number of parameters including but not limited to mould geometry, rates of cooling on the mould surface, and the initial orientation of injected polymer material.

### 6.4.2 Engineering Investigations

Traditionally a number of factors have been investigated when trying to optimise injection moulding including the heat, density, and choice of the injected material, the circumstances of its injection, and not least the mould geometry. Here we suggest that the greater complexity of injection moulding on a micro scale warrants investigation into methods of controlling conditions of the process even more tightly, that is, in attempting to control aspects of the process that have not typically been addressed. We present two ideas regarding how this might be achieved:

- By studying the dynamics of polymers in the injection mechanism it may be possible to construct an injection mechanism which can control, as a parame-

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<sup>2</sup>The School of Engineering, Design and Technology may wish to carefully consider what provisions if any for high performance computing it would like to make in the next few years.



## CHAPTER 6. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

ter, the degree of orientation (orientation as opposed to a random distribution) in the polymer. We would expect polymers that are different in this respect to behave differently in the way they fill the mould.

- One of the major characteristics that we expect polymer orientation to affect is heat transport through the polymer. Consequently we can expect localised differences in cooling, combined with the fact that it may sometimes be desirable to effect mould filling by modifying viscosity with local temperature differences. It is worth investigating how the temperature of the mould surface could be controlled both locally and varied over time. One solution might be to incorporate a separate system of channels into the mould in close proximity to the mould surface. The distinct channel systems could then be pumped with heated or cooled fluids as needed.
- Obviously the order in which different parts of the mould are filled, and the direction of flow that fills them, is going to have an effect upon the final quality of the part. We suggest incorporating a mechanism into the mould allowing retractable pins or blocks to be moved in and out of the mould void in a fast controlled manner acting as valves. In this way the flow of polymer in a given section of mould could be blocked, begun, redirected, or reversed in the middle of the filling process thereby hopefully improving part quality.

# Appendix A

## Thermal Polymer LBM

### Pseudocode

What follows in this chapter is pseudocode outlining how the techniques, particularly those in chapter 4 could be implemented. It represents implementation on a non parallel single core system beginning with this main function loop.

**repeat**

    PostCollisionFrame:=DoForce:PreCollisionFrame

ForCoFluid:FluidCollisionFrame;

    FluidCollisionFrame:=DoFluidLBM:FluidCollisionFrame;

    PostCollisionFrame:=DoCollision:PostCollisionFrame;

    PostCollisionFrame:=DoTransport:PostCollisionFrame;

    PostCollisionFrame:=DoScaling:PostCollisionFrame;

    Push:PostCollisionFrame onto:TimeStack;

    PreCollisionFrame:=PostCollisionFrame;

**until** we are done

**function** SPREADBETWEENCELLSFORPOINT( $\bar{P}$ )

    ( $\bar{P}_+$ ,  $\bar{P}_-$ ,  $P_\sigma$ ):= $\bar{P}$ ;

## APPENDIX A. THERMAL POLYMER LBM PSEUDOCODE

```

PlusInterpolatingCellsAndWeights:=SpreadBetweenCellsForPoint3: $\vec{P}_+$ ;
MinusInterpolatingCellsAndWeights:=SpreadBetweenCellsForPoint3: $\vec{P}_-$ ;
 $C_{l\sigma}$ :=SigmaLowerInterpolatingCell: $P_\sigma$  mod SigmaWidth;
 $C_{u\sigma}$ :=SigmaUpperInterpolatingCell: $P_\sigma$  mod SigmaWidth;
 $W_{l\sigma}$ :=SigmaLowerInterpolatingWeight: $P_\sigma$ ;
 $W_{u\sigma}$ :=SigmaUpperInterpolatingWeight: $P_\sigma$ ;
repeat
  repeat
     $W_+$ :=GetWeightInList:PlusInterpolatingCellsAndWeights;
     $W_-$ :=GetWeightInList:MinusInterpolatingCellsAndWeights;
     $C_+$ :=GetCellInList:PlusInterpolatingCellsAndWeights;
     $C_-$ :=GetCellInList:MinusInterpolatingCellsAndWeights;
     $I_+$ :=GetInversionInList:PlusInterpolatingCellsAndWeights;
     $I_-$ :=GetInversionInList:MinusInterpolatingCellsAndWeights;
    CurentTarget:InterpolatingCellsAndWeights:=
ConvertTo7CellFromPlus: $C_+$  Minus: $C_-$  AndSigma: $C_{l\sigma}$ ;
    CurentWeigh:InterpolatingCellsAndWeights:= $W_+ W_- W_{l\sigma}$ ;
    CurentInversion:InterpolatingCellsAndWeights:= $I_+$ ;
    CurentPsudoInversion:InterpolatingCellsAndWeights:= $I_-$ ;
    AppendList:InterpolatingCellsAndWeights;
    CurentTarget:InterpolatingCellsAndWeights:=
ConvertTo7CellFromPlus: $C_+$  Minus: $C_-$  AndSigma: $C_{u\sigma}$ ;
    CurentWeigh:InterpolatingCellsAndWeights:= $W_+ W_- W_{u\sigma}$ ;
    CurentInversion:InterpolatingCellsAndWeights:= $I_+$ ;
    CurentPsudoInversion:InterpolatingCellsAndWeights:= $I_-$ ;
    AppendList:InterpolatingCellsAndWeights;
    ProgressList:MinusInterpolatingCellsAndWeights;
  until Minus List End

```

## APPENDIX A. THERMAL POLYMER LBM PSEUDOCODE

```

ProgressList:PlusInterpolatingCellsAndWeights;
ToStartOfList:MinusInterpolatingCellsAndWeights;
until Plus List End return InterpolatingCellsAndWeights;
end function

function SPREADBETWEENCELLSFORPOINT3( $\vec{P}$ )
 $\vec{P}' := L(\vec{P} - \text{PolyhedronCentre}:\vec{P})$ ;
if IsInOctahedron: $\vec{P}$  then
    for i=1 to 6 do
        AppendList:InterpolatingCellsAndWeights;
        CurentWeight:InterpolatingCellsAndWeights:=
 $\frac{1-|P'_x|-|P'_y|-|P'_z|}{6} + \frac{|\vec{P}' \cdot \vec{p}_i^{oct}| + |\vec{P}' \cdot \vec{p}_i^{oct}|}{2}$ ;
        CurentTarget:InterpolatingCellsAndWeights:=OctCellFor: $\vec{P}$ 
Offset:i;
        CurentInversion:InterpolatingCellsAndWeights:=false;
    end for
else if IsInLeftTetrahedron: $P$  then
    for i=1 to 4 do
        AppendList:InterpolatingCellsAndWeights;
        CurentWeight:InterpolatingCellsAndWeights:= $\vec{P}' \cdot \vec{p}_i^{ltet} + \frac{1}{4}$ ;
        CurentTarget:InterpolatingCellsAndWeights:=LTetCellFor: $\vec{P}$ 
Offset:i;
        CurentInversion:InterpolatingCellsAndWeights:=false;
    end for
else if IsInRightTetrahedron: $P$  then
    for i=1 to 4 do
        AppendList:InterpolatingCellsAndWeights;
        CurentWeight:InterpolatingCellsAndWeights:= $\vec{P}' \cdot \vec{p}_i^{rtet} + \frac{1}{4}$ ;

```

## APPENDIX A. THERMAL POLYMER LBM PSEUDOCODE

```

CurentTarget:InterpolatingCellsAndWeights:=RTetCellFor: $\vec{P}$ 
Offset:i;
    CurentInversion:InterpolatingCellsAndWeights:=false;
end for
else
    you're using non Euclidian geometry, ... don't;
end if
RunningWeightTotal:=0;
ToStartOfList:InterpolatingCellsAndWeights;
repeat
    if NOT IsFluid:GetCellInList:InterpolatingCellsAndWeights then
        RunningWeightTotal:+=
GetWeightInList:InterpolatingCellsAndWeights;
        RemoveThisListEntry:InterpolatingCellsAndWeights;
    else
        ProgressList:InterpolatingCellsAndWeights;
    end if
until end of list
ToStartOfList:InterpolatingCellsAndWeights;
if RunningWeightTotal<0 then
    Adjustment:=RunningWeightTotal/(RunningWeightTotal-1);
    repeat
        CurentTarget:TempInterpolatingCellsAndWeights:=
GetCellInList:InterpolatingCellsAndWeights;
        CurentWeight:TempInterpolatingCellsAndWeights:=
Adjustment*GetWeightInList:InterpolatingCellsAndWeights;
        CurentInversion:TempInterpolatingCellsAndWeights:=true;
        AppendList:TempInterpolatingCellsAndWeights;

```

## APPENDIX A. THERMAL POLYMER LBM PSEUDOCODE

```

ProgressList:InterpolatingCellsAndWeights;
until end of list
Append:TempInterpolatingCellsAndWeights
ToList:InterpolatingCellsAndWeights;
end if return InterpolatingCellsAndWeights;
end function

function DoFORCE(CollisionFrame, FluidCollisionFrame)
Potential:=CalculatePotential:CollisionFrame;
for all Cell do
for i=1 to 168 do
 $\phi(\vec{r} + \vec{e}_i) := \text{Potential}[\text{CellToPlusAndMinus:Cell} + \text{offset6}[i]];$ 
end for
for i=1 to 12 do
 $\tilde{\rho}(\vec{r}_+ + \vec{e}_{+i}) :=$ 
FluidCollisionFrame[CellToPlus:Cell+offset3[i]].density;
end for
 $\frac{d\bar{p}_p}{dt} := -\frac{1}{28} \sum_{i=1}^{168} \frac{\phi(\vec{r} + \vec{e}_i) \vec{e}_i}{e_i^2};$ 
 $\rho(\vec{r}, \sigma) := \text{CollisionFrame}[\text{Cell}].\text{density};$ 
 $\frac{d\bar{p}_p}{dt} := + -\psi_p(\rho(\vec{r}, \sigma)) G_{pf} \sum_{i=1}^{12} \psi_f(\tilde{\rho}(\vec{r}_+ + \vec{e}_{+i})) (\vec{e}_{+i}, \vec{0});$ 
CollisionFrame[Cell].force :=  $\frac{d\bar{p}_p}{dt}$ ;
end for
for all FluidCell do
for all MinusCell & SigmaCell & i=1 to 12 do
 $\rho(\vec{r}_+ + \vec{e}_{+i}, \vec{r}_-, \sigma) :=$ 
CollisionFrame[ConvertTo7CellFromPlus:(FluidCell+offset3[i])
Minus:MinusCell AndSigma:SigmaCell].density;
end for

```

## APPENDIX A. THERMAL POLYMER LBM PSEUDOCODE

```

 $\tilde{\rho}(\vec{r}_+) := \text{FluidCollisionFrame}[\text{FluidCell}].\text{density};$ 
 $\frac{d\vec{p}_f}{dt} := -\psi_f(\tilde{\rho}(\vec{r}_+))G_{fp} \sum_{i=1}^{12} \psi_p \left( \sum_{\vec{r}_-, \sigma} \rho(\vec{r}_+ + \vec{e}_{+i}, \vec{r}_-, \sigma) \right) \vec{e}_{+i};$ 
 $\text{FluidCollisionFrame}[\text{FluidCell}].\text{force} := \frac{d\vec{p}_f}{dt};$ 
end for

return CollisionFrame;

end function

```

```

function DoCOLLISION(CollisionFrame)

```

```

for all Cell do

```

```

    if IsFluid:Cell then

```

```

        NewCell := DoCellCollision:CollisionFrame[Cell];

```

```

    else if IsInlet:Cell then

```

```

        NewCell := CollisionFrame[Cell];

```

```

    else

```

```

        NewCell := Zero;

```

```

    end if

```

```

        NewCollisionFrame[Cell] := NewCell;

```

```

end for

```

```

return NewCollisionFrame;

```

```

end function

```

```

function DoCELLCOLLISION(Cell)

```

```

    NewCell := zero;

```

```

for all  $-1 \leq i_x, \dots, j_z, k \leq 1$  do

```

```

     $T := \text{Cell}.\text{temperature};$ 

```

```

     $\vec{v}_+ = \sqrt{\frac{3T}{7}} \vec{i};$ 

```

```

     $\vec{v}_- = \sqrt{\frac{3T}{7}} \vec{j};$ 

```

```

     $\nu_k = \sqrt{\frac{3T}{7}} \vec{k};$ 

```

## APPENDIX A. THERMAL POLYMER LBM PSEUDOCODE

```

f:=Cell.populations[ $i_x, \dots, j_z, k$ ];
 $\bar{U}$ :=Cell.velocity;
 $\rho$ :=Cell.density;
 $\frac{d\bar{p}}{dt}$ :=Cell.force;
 $\bar{U} := \bar{U} + \frac{\tau}{\rho} \frac{d\bar{p}}{dt}$ ;
 $f^{(eq)} := \frac{16\rho 4^{-(|i|^2+|j|^2+k^2)}}{2187} \left( 1 + \frac{7}{T} \vec{U}_i \cdot \vec{v}_i + \frac{c_{ijkl}}{T^2} \vec{U}_i \cdot \vec{v}_j \vec{U}_k \cdot \vec{v}_l \right. \\ \left. - \frac{7}{2T} \vec{U}_i \cdot \vec{U}_i - \frac{3h_{klmjm}}{7T^2} \vec{U}_i \cdot \vec{U}_j \vec{U}_k \cdot \vec{v}_l + \frac{h_{ijklmnm}}{T^3} \vec{U}_i \cdot \vec{v}_j \vec{U}_k \cdot \vec{v}_l \vec{U}_m \cdot \vec{v}_n \right)$ ;
 $f' = f - \frac{1}{\tau} (f - f^{(eq)})$ ;
NewCell.populations[ $i_x, \dots, j_z, k$ ]:=f';
end for
return NewCell;
end function

```

```

function DoTRANSPORT(CollisionFrame)
NewCollisionFrame:=zero;
for all cell do
if IsFluid:Cell or IsInlet:Cell then
for all  $-1 \leq i_x, \dots, j_z, k \leq 1$  do
if  $(\vec{i}, \vec{j}, k) = (\vec{0}, \vec{0}, 0)$  then
NewCollisionFrame[Cell].population[ $(\vec{0}, \vec{0}, 0)$ ]:+=
CollisionFrame[Cell].population[ $(\vec{0}, \vec{0}, 0)$ ];
Skip rest of this time through the loop;
end if
 $\bar{P}$ :=PositionOfCell:Cell;
 $T$ :=CollisionFrame[Cell].temperature;
 $\vec{v}_+ = \sqrt{\frac{3T}{7}} \vec{i}$ ;
 $\vec{v}_- = \sqrt{\frac{3T}{7}} \vec{j}$ ;
 $\nu = \sqrt{\frac{3T}{7}} k$ ;

```



## APPENDIX A. THERMAL POLYMER LBM PSEUDOCODE

```

 $|\bar{v}_a| := \sqrt{\bar{v}_+^2 + \bar{v}_-^2 + \nu^2};$ 
 $f_a := \text{CollisionFrame}[\text{Cell}].\text{population}[(\vec{i}, \vec{j}, k)];$ 
 $\lambda := \text{BounceBackOf}:\bar{v}_+ \text{ From}:\bar{P};$ 
 $\mu := \text{PsudoBounceBackOf}:\bar{v}_- \text{ From}:\bar{P};$ 
 $\bar{P}' := \bar{P} + ((2\lambda - 1)\bar{v}_+, (2\mu - 1)\bar{v}_-) \delta_t;$ 
InterpolatingCellsAndWeights := SpreadBetweenCellsForPoint: $\bar{P}'$ ;
repeat
    TargetCell := GetCellInList:InterpolatingCellsAndWeights;
    TargetWeight :=
GetWeightInList:InterpolatingCellsAndWeights;
    TargetInversion :=
GetInversionInList:InterpolatingCellsAndWeights;
    PsudoTargetInversion :=
GetPsudoInversionInList:InterpolatingCellsAndWeights;
    if  $\lambda > 0$  XOR TargetInversion then
         $\vec{i}' := -\vec{i};$ 
    else
         $\vec{i}' := \vec{i};$ 
    end if
    if  $\mu > 0$  XOR PsudoTargetInversion then
         $\vec{j}' := -\vec{j};$ 
    else
         $\vec{j}' := \vec{j};$ 
    end if
     $|\bar{v}'_a| := \text{NewCollisionFrame}[\text{TargetCell}].\text{speed}[(\vec{i}', \vec{j}', k)];$ 
     $f'_a := \text{TargetWeight}$ 
*NewCollisionFrame[TargetCell].population[( $\vec{i}', \vec{j}', k$ )];
 $|\bar{v}''_a| := \frac{\bar{v}_a^2 f_a + \bar{v}'_a{}^2 f'_a}{|\bar{v}_a| f_a + |\bar{v}'_a| f'_a};$ 

```

## APPENDIX A. THERMAL POLYMER LBM PSEUDOCODE

$$f_a'' := \frac{(|\bar{v}_a|f_a + |\bar{v}_a'|f_a')^2}{\bar{v}_a^2 f_a + \bar{v}_a'^2 f_a'};$$

$$f_0 := \frac{(|\bar{v}_a| - |\bar{v}_a'|)^2 f_a f_a'}{\bar{v}_a^2 f_a + \bar{v}_a'^2 f_a'};$$

NewCollisionFrame[TargetCell].speed[( $\vec{i}'$ ,  $\vec{j}'$ ,  $k$ )] :=  $|\bar{v}_a''|$ ;

NewCollisionFrame[TargetCell].population[( $\vec{i}'$ ,  $\vec{j}'$ ,  $k$ )] :=  $f_a''$ ;

NewCollisionFrame[TargetCell].population[( $\vec{0}$ ,  $\vec{0}$ , 0)] +=  $f_0$ ;

ProgressList:InterpolatingCellsAndWeights;

**until** ListExhausted:InterpolatingCellsAndWeights

**end for**

**end if**

**end for**

**return** NewCollisionFrame;

**end function**

**function** DoSCALING(CollisionFrame)

**for all** Cell **do**

**if** IsFluid:Cell **then**

NewCell := DoCellScaling:CollisionFrame[Cell];

**else if** IsInlet:Cell **then**

NewCell := CollisionFrame[Cell];

**else**

NewCell := Zero;

**end if**

NewCollisionFrame[Cell] := NewCell;

**end for**

**return** NewCollisionFrame;

**end function**

**function** DoCELLSCALING(Cell)

APPENDIX A. THERMAL POLYMER LBM PSEUDOCODE

**for all**  $-1 \leq i_x, \dots, j_z, k \leq 1$  **do**

$$\bar{v}_{\vec{i}, \vec{j}, k} := \text{Cell.speed}[(\vec{i}, \vec{j}, k)] * \widehat{(\vec{i}, \vec{j}, k)};$$

$$f_{\vec{i}, \vec{j}, k} := \text{Cell.population}[(\vec{i}, \vec{j}, k)];$$

**end for**

$$\rho := \sum_{\vec{i}, \vec{j}, k} f_{\vec{i}, \vec{j}, k};$$

$$\rho \bar{U} := \sum_{\vec{i}, \vec{j}, k} \bar{v}_{\vec{i}, \vec{j}, k} f_{\vec{i}, \vec{j}, k};$$

$$\rho E := \sum_{\vec{i}, \vec{j}, k} \bar{v}_{\vec{i}, \vec{j}, k}^2 f_{\vec{i}, \vec{j}, k};$$

$$\bar{U} := \frac{\rho \bar{U}}{\rho};$$

$$E := \frac{\rho E}{\rho};$$

$$\bar{U}' := (U_1, \dots, U_6);$$

$$T := E - \bar{U}'^2;$$

NewCell=Zero;

NewCell.density:= $\rho$ ;

NewCell.velocity:= $\bar{U}'$ ;

NewCell.temperature:= $T$ ;

**for all**  $-1 \leq i_x, \dots, j_z, k \leq 1$  **do**

$$\bar{v}'_{\vec{i}, \vec{j}, k} := \sqrt{\frac{3T}{7}}(\vec{i}, \vec{j}, k);$$

$$K_{\vec{i}, \vec{j}, k} := \alpha \bar{v}'_{\vec{i}, \vec{j}, k} \cdot \bar{v}_{\vec{i}, \vec{j}, k} + \beta \bar{v}_{\vec{i}, \vec{j}, k}'^2 \bar{v}_{\vec{i}, \vec{j}, k}^2 + \gamma;$$

$$J_{\vec{i}, \vec{j}, k} := \alpha \bar{v}_{\vec{i}, \vec{j}, k}'^2 + \beta \bar{v}_{\vec{i}, \vec{j}, k}'^4 + \gamma;$$

**end for**

**for all**  $1 \leq \xi \dots \zeta \leq 7$  such as needed **do**

$$A_{\xi \dots \zeta} := \sum_{\vec{i}, \vec{j}, k} \frac{\bar{v}'_{\vec{i}, \vec{j}, k; \xi} \dots \bar{v}'_{\vec{i}, \vec{j}, k; \zeta}}{2J_{\vec{i}, \vec{j}, k}};$$

$$B_{\xi \dots \zeta} := \sum_{\vec{i}, \vec{j}, k} \frac{\bar{v}'_{\vec{i}, \vec{j}, k; \xi} \dots \bar{v}'_{\vec{i}, \vec{j}, k; \zeta} K_{\vec{i}, \vec{j}, k} f_{\vec{i}, \vec{j}, k}}{J_{\vec{i}, \vec{j}, k}};$$

**end for**

$$0 = B - \rho + A\lambda_0 + A_i\lambda_i + A_{ii}\lambda_8$$

SolveSystem:  $0 = B_i - \rho U'_i + A_i\lambda_0 + A_{ij}\lambda_j + A_{ijj}\lambda_8$  For:  $(\lambda_0, \vec{\lambda}, \lambda_8)$ ;

$$0 = B_{ii} - \rho E + A_{ii}\lambda_0 + A_{iij}\lambda_j + A_{iijj}\lambda_8$$

**for all**  $-1 \leq i_x, \dots, j_z, k \leq 1$  **do**

## APPENDIX A. THERMAL POLYMER LBM PSEUDOCODE

```

 $f'_{\vec{i}, \vec{j}, k} := \frac{2K_{\vec{i}, \vec{j}, k} f_{\vec{i}, \vec{j}, k} + \lambda_0 + \bar{\lambda} \cdot \bar{v}'_{\vec{i}, \vec{j}, k} + \lambda_8 \bar{v}'_{\vec{i}, \vec{j}, k}{}^2}{2J_{\vec{i}, \vec{j}, k}};$ 
NewCell.population[( $\vec{i}, \vec{j}, k$ )] :=  $f'_{\vec{i}, \vec{j}, k}$ ;
NewCell.speed[( $\vec{i}, \vec{j}, k$ )] :=  $|\bar{v}'_{\vec{i}, \vec{j}, k}|;$ 
end for
return NewCell;
end function

```

# Bibliography

- [1] M. Grmela and W. G. Laidlaw, “Mesoscopic kinetic theory,” *J. Chem. Phys.*, vol. 78, no. 8, pp. 5151–5163, 1983.
- [2] M. Grmela and P. J. Carreau, “Mesoscopic kinetic theory of polymer melts,” *J. Chem. Phys.*, vol. 78, no. 8, pp. 5164–5174, april 1983.
- [3] H. C. Öttinger, *Beyond Equilibrium Thermodynamics*. Hoboken, NJ: John Wiley and Sons, 2005.
- [4] R. A. Mashelkar, A. S. Mujumdar, and R. Kamal, *Transport Phenomena in Polymeric Systems*. Chichester: Ellis Horwood Limited, 1989.
- [5] J. Embery. (2009, july 6) *Microscale polymer processing 2*. [Online]. Available: <http://www.irc.leeds.ac.uk/mupp2/> [Accessed: 6 July 2012].
- [6] X. He and L.-S. Luo, “A priori derivation of the lattice boltzmann equation,” *Phys. Rev. E*, vol. 55, no. 6, pp. R6333–R6336, 1997.
- [7] S. G. Brush, *Kinetic Theory*, 1st ed. Oxford: Pergamon Press, 1972, vol. 3.
- [8] S. Harris, *An Introduction to the Theory of the Boltzmann Equation*. London: Holt, Rinehart and Winston, Inc., 1971.
- [9] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases*, 3rd ed. London: Cambridge University Press, 1970.

- [10] R. Mei, L.-S. Luo, and W. Shyy, “An accurate curved boundary treatment in the lattice boltzmann method,” *J. Comput. Phys.*, vol. 155, pp. 307–330, 1999.
- [11] R. Mei, W. Shyy, D. Yu, and L.-S. Luo, “Lattice boltzmann method for 3-d flows with curved boundary,” *J. Comput. Phys.*, vol. 161, pp. 680–699, 2000.
- [12] X. He and G. Doolen, “Thermodynamic foundations of kinetic theory and lattice boltzmann models for multiphase flows,” *J. Stat. Phys.*, vol. 107, pp. 309–328, 2002.
- [13] B. J. Palmer and D. R. Rector, “Lattice boltzmann algorithm for simulating thermal two-phase flow,” *Phys. Rev. E*, vol. 61, pp. 5295–5306, 2000.
- [14] P. Pavlo, G. Vahala, L. Vahala, and M. Soey, “Linear stability analysis of thermo-lattice boltzmann models,” *J. Comput. Phys.*, vol. 139, pp. 79–91, 1998.
- [15] L.-S. Luo, “lattice-gas automata and lattice boltzmann equations for two-dimensional hydrodynamics,” PhD thesis, Department of Physics, Georgia Institute of Technology, Atlanta, GA, 1993.
- [16] R. R. Nourgaliev, T. N. Dinh, and B. R. Sehgal, “On lattice boltzmann modeling of phase transitions in an isothermal non-ideal fluid,” *Nucl. Engng. Des.*, vol. 211, pp. 153–171, 2002.
- [17] X. Shan and H. Chen, “Lattice boltzmann model for simulating flows with multiple phases and components,” *Phys. Rev. E*, vol. 47, pp. 1815–1819, 1993.
- [18] X. Shan and H. Chen, “Simulation of nonideal gases and liquid-gas phase transitions by the lattice boltzmann equation,” *Phys. Rev. E*, vol. 49, pp. 2941–2948, 1994.
- [19] X. He, X. Shan, and G. D. Doolen, “Discrete boltzmann equation model for nonideal gases,” *Phys. Rev. E*, vol. 57, pp. R13–R16, 1998.

- [20] Q. Chang, J. Iwan, and D. Alexander, Application of Lattice Boltzmann Method. Saarbrücken: VDM Verlag Dr. Müller, 2008.
- [21] N. Bellomo, Modeling Complex Living Systems. Boston, Mass: Birkhauser, 2007.
- [22] N. Bellomo and M. Pulvirenti, Modeling in Applied Sciences. Boston, Mass: Birkhäuser, 2000.
- [23] N. Bellomo and M. L. Schiavo, Lecture Notes on the Mathematical Theory of Generalized Boltzmann Models, ser. Series on advances in mathematics for applied sciences. London: World Scientific Publishing Company, 2000.
- [24] A. Bellouquid and M. Delitala, Mathematical Modeling of Complex Biological Systems, 1st ed. Birkhäuser Boston, 2006.
- [25] M. Grmela, B. Z. Dlugogorski, and G. Lebon, “Extended kinetic theory of polymeric fluids,” *Macromol. Theory Simul.*, vol. 5, no. 6, pp. 1121–1142, June 1996.
- [26] W. V. Lovitt, Linear Integral Equations, 1st ed. New York: McGraw-Hill Book Company, 1924.
- [27] E. I. Fredholm, “Sur une classe d’équations fonctionnelles,” *Acta Math*, vol. 27, pp. 365–390, 1903.
- [28] A. F. Ruston, Fredholm Theory in Banach Spaces. Cambridge: Cambridge University Press, 1986.
- [29] L. Debnath and P. Mikusiński, Introduction to Hilbert Spaces with Applications, 2nd ed. San Diego: Academic Press, 1999.
- [30] V. Volterra, Theory of Functionals and of Integral and Integro-Differential Equations. Mineola, NY: Dover, 1959.

## BIBLIOGRAPHY

- [31] P. J. Davis and P. Rabinowitz, *Methods of numerical integration*, 2nd ed. London: Academic Press, 1984.
- [32] J. H. Irving and J. G. Kirkwood, “The statistical mechanical theory of transport processes. iv. the equations of hydrodynamics,” *J. Chem. Phys.*, vol. 18, no. 6, pp. 817–829, june 1950.
- [33] A. Ben-Israel and T. N. E. Greville, *Generalized Inverses: Theory and applications*, 2nd ed. London: Springer, 2003.
- [34] R. Portugal, “An algorithm to simplify tensor expressions,” *Comput. Phys. Commun.*, vol. 115, pp. 215–230, 1998.