Heat and Mass Transport in Nanoconfined Colloidal Fluids

A thesis submitted in fulfilment of the requirements for the degree Doctor of Philosophy.

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Declaration

I certify that;

• except where due acknowledgement has been made, the work is that of the candidate alone;

• the work has not been submitted previously, in whole or in part, to qualify for any other academic award;

• the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program;

• any editorial work, paid or unpaid, carried out by a third party is acknowledged;

• ethics procedures and guidelines have been followed.

Nicholas A.T. Miller
19th September 2013
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Summary

This study has been undertaken to help advance knowledge in the field of nanotechnology. Our motivation is to provide insights into the principles that govern physics on the nanoscale. To do this we must first consider how to approach nanoscale science. Experimentalists are often limited in their ability to perform research due to the inaccessibility of the subject to be studied, as is currently the case with a variety of fields of research on the nanoscale. Experiments performed through computational methods provide efficient, accessible and often more robust methods for exploring nanoscale phenomena. Such is the case with highly confined colloidal fluids.

Colloidal fluids are of significant interest due to their occurrence in both natural and synthetic systems. To understand how colloidal fluids behave on the nanoscale, we have investigated heat and mass transport of bulk homogeneous fluids, and the effects of heat and mass transport in highly confined systems. This has facilitated our understanding of the separation of colloidal fluids and their behaviour when subject to a temperature difference, or experiencing planar Poiseuille flow. Understanding and characterising the separation behaviour of colloidal fluids is important to a number of fields of science and engineering, including lab-on-a-chip technology.

As we wish to study systems that are still difficult to access experimentally, we have elected to use molecular dynamics to investigate the transport properties of colloidal fluids. The techniques used in molecular dynamics allow us to simulate systems comprised of tens of thousands of particles, investigate phenomena that are currently inaccessible with experiments, and access properties of a fluid that are often difficult to access, or even impossible to access in experiment. These include properties such as the temperature and concentration across the channel of confining the fluid. Using molecular dynamics also allows for a colloid to be studied in its natural state, without the addition of any other substances that may change the properties of the fluid, such as fluorescing dyes which may be required to observe velocity profiles in experiments.

This study begins with the continuum theory of transport in binary fluids. This theory accounts for the effects of diffusive and heat fluxes that are different from a one component fluid. We show how to appropriately calculate the various transport coefficients from homogeneous two component systems, then how these coefficients can be used to obtain a continuum description of the velocity, temperature and concentration profiles across a confining channel. This is done for two fluids, first for an equimolar argon-krypton mixture that is widely studied in literature. Second, for a fluid that is a slightly more realistic model of colloids, with the unique inclusion of a hard core. Transport coefficients are calculated over a range of temperatures and concentrations for the second type of fluid.
We then show how the values of the transport coefficients obtained from the bulk can be used to predict the separation of two component fluids. Two situations are presented, firstly a temperature gradient system with no flow. The temperature gradient is imparted on the fluid by maintaining different temperatures at the confining walls. The second system is planar Poiseuille flow, where the temperatures of the walls are equal, and a gravitational like field is applied equally to all species of the fluid. We successfully show that for both equimolar argon-krypton and the colloid, that the separation of species can be predicted. We then show the limitations of the theory presented in this work, when the colloidal fluid is subject to higher field strengths, and experiences subsequent increased flow rates.

By completing this work we have successfully contributed knowledge about the role diffusive and heat fluxes play in the field of colloidal science and nanotechnology. We provide a framework for the correct evaluation of transport coefficients of binary solutions, and show how to predict colloid separation for confined systems.
Chapter 1

Introduction

In this study we have used Molecular Dynamics (MD) to investigate the transport properties and separation characteristics of colloidal fluids. The investigation of colloidal dispersions has yielded valuable insights on statistical mechanics and condensed matter physics [1]. The suspension of solute particles in a solvent medium is representative of a variety of natural and synthetic colloidal systems. Colloidal transport mechanisms are widely utilised in the flocculation and flotation separation of minerals [2, 3], the engineering of coatings, electronics, catalysis, separations, diagnostics [4], and many other fields of research and manufacturing. Understanding heat and mass transport mechanisms in two component systems is important when trying to understand the physical characteristics of colloidal fluids.

Fluids confined by walls and undergoing flow are of particular interest to the field of separation science and engineering. Examples where confined geometries of colloidal fluids are of particular interest include lab-on-a-chip [5], optical modulation for the alignment of particles contained in liquid crystals [6] and the use of desalination mediums like hollow fibre membranes [7]. A planar confined geometry is chosen as a simple three dimensional system to understand the contribution that heat and mass transport have in the separation of two component colloidal fluids.

In Ch. 2 we present the continuum theory of transport in binary fluids. We consider the effects of diffusion and heat fluxes that are different from the one component fluid, and show how to obtain the relevant components used to calculate transport coefficients for binary fluids. In this study we will apply the transport coefficients of a colloidal fluid calculated from bulk fluids at equilibrium, to the continuum description of fluids experiencing a temperature gradient applied by maintaining a differing temperature of the walls, and to systems undergoing planar Poiseuille flow. The continuum theory to obtain velocity, temperature and concentration profiles for confined colloids experiencing planar, Poiseuille flow is also presented in Ch. 2.

MD is a useful method for investigating physical processes that may be beyond the scope of current experimental techniques. For example the local temperature and concentration can
be obtained as a function of position over the volume of the experiment, and not estimated or measured by the addition of fluorescing particles that may change the fluid properties. In Ch. 3 we present details about the techniques used to obtain transport coefficients of binary fluids from Equilibrium Molecular Dynamics (EMD) simulations, and details of the techniques used for confined systems, simulated using Non-Equilibrium Molecular Dynamics (NEMD). In this study we simulate two different types of fluid, the first an equimolar Argon-Krypton (Ar-Kr) fluid used to compare with results in literature and confirm the theory presented in Ch. 2. The second fluid is a more complex and slightly more realistic description of a colloidal solution. In Ch. 3 we present details of the Lennard-Jones (LJ) and Weeks-Chandler-Andersen (WCA) interaction potentials used to model the fluid particles, and the parameters chosen to define particles for the two types of fluid.

In Ch. 4 we report the transport coefficients for equimolar Ar-Kr, and for the colloidal fluid over a range of temperatures and concentrations. We show that the method for obtaining the transport coefficients presented in Ch. 2 improves upon previous methods by correctly accounting for the mass and diffusive flux effects bought about by the addition of a second species. The transport coefficients obtained for an equimolar Argon-Krypton fluid are used to verify the techniques presented in this study, with a successful comparison to results in literature [8]. The advantage of the method presented in this work is the ability to calculate the mutual diffusion and thermal diffusion transport coefficients separately.

Fluids that are subject to a temperature difference are of interest for their separation characteristics via thermal diffusion, or the ‘Soret effect’. The application of a temperature gradient across a fluid has been well established as an effective method for separation. Thermal diffusion exits from the consequence that a temperature gradient applied to a mixture of two components will give rise to a gradient in the concentration of these components [9]. Early techniques for isotope separation were achieved by Clausius and Dickel who built the first thermal diffusion column [10]. They obtained a separation factor, $q$, for $\text{HCl}^{35}$ and $\text{HCl}^{37}$ of 1.01, which compared favourably to the separation factors for distillation, chemical exchange and centrifugal techniques of the time. Uranium enrichment and deuterium recovery are notable fields of research [11, 12], and an extensive range of experimental techniques has been developed to explore and exploit the effect including Soret cells, thermodiffusion columns, and thermodiffusion cells [13]. The Soret effect is also abundant in natural processes involving convective phenomena, including lava flows and the movements of the earth’s mantle [1]. The transport coefficients presented in Ch. 4 are further confirmed in Ch. 5, with their incorporation into a continuum prediction of the separation of the respective two species when a fluid is subject to a temperature difference through thermostated walls. The continuum description that is presented in this work uses the ratio of the thermal diffusion to mass diffusion coefficients, termed the Soret coefficient [14]. For both the argon-krypton and colloidal fluids, the theory is shown
to be applicable when the temperature difference across the fluid is small enough such that the Soret coefficient can be assumed constant across the whole fluid.

In Ch. 6 we present the results for a system undergoing planar Poiseuille flow for both equimolar Ar-Kr and the colloidal fluid. Velocity profiles in Poiseuille flow have been successfully predicted in work by Kairn for the two component colloidal fluid [15, 16]. We confirm the results obtained by Kairn, and also show that at relatively low flow rates, a continuum description of the temperature profile can be obtained by incorporating the coupling to the gradient of the strain rate into the description of the heat flux vector. This description can subsequently be used in combination with the value of the Soret coefficient calculated using EMD, to predict the temperature dependent concentration profile. In Ch. 7 we show that at increase flow rates, the ability to describe the temperature profile with the incorporation of the coupling to the gradient of the strain rate becomes insufficient. We also show that incorporating the temperature dependence of the transport coefficients does not improve the description of the observed temperature profiles.

By obtaining the transport coefficients for a two component system, and applying these coefficients in the continuum description of confined systems, we have contributed to the understanding of heat and mass transport mechanisms in highly confined colloidal fluids. We provide a theoretical framework for the evaluation of transport coefficients of binary solutions, and prove the validity of the methodology with comparison to literature and through the continuum descriptions for confined systems obtained in this study.
Chapter 2

Continuum theory of transport in binary fluids

2.1 Introduction

In this chapter we introduce the theory of transport in binary fluids. We present the conservation equations for a fluid driven by a field, undergoing planar Poiseuille flow. For binary systems we consider the effects of diffusion and heat fluxes that differ from the one component fluid. The transport coefficients for the binary fluid are defined in terms of the ‘primed’ phenomenological coefficients. To obtain the transport coefficients we also require calculation of the thermodynamic factor, which is obtained from the radial distribution function by the method outlined in this chapter. The transport coefficients are calculated for bulk fluids using the theory presented in this chapter and values reported in Ch. 4. The transport coefficients are then used in the continuum descriptions derived in this section, for the velocity, concentration and temperature profiles of systems undergoing planar Poiseuille flow. They are also used in the prediction of temperature and concentration profiles for systems experiencing a temperature gradient by imposing different temperatures at the two walls, and no flow. The applications of the theory for confined systems presented in this chapter are seen in Chaps. 5, 6 and 7.

Temperature gradients and concentration gradients both contribute to the net transport of a species in a binary fluid. Depending on the sign and strength of the contributions of the temperature gradient and concentration gradient, species will migrate either towards a heated region of a fluid or away from it until the fluid reaches a steady state. If concentration gradients are not too large and it is valid to assume uniform density, then we can obtain the temperature dependent concentration from the energy equation, mass equation and phenomenological relations [14].

In experiment and certain simulation techniques a combination of the transport coefficients, \( D' \) the thermal diffusion coefficient, and \( D_m \) the mutual diffusion coefficient, are measured
and they can not be separated [8]. This combination is denoted in the literature as the Soret coefficient \( \frac{D'}{D_m} \), multiplied by the temperature, as the thermal diffusion factor \( \alpha = T \frac{D'}{D_m} \) or multiplied by the concentration of components 1 and 2 respectively, as the thermal diffusion ratio \( k_T = c_1 c_2 T \frac{D'}{D_m} \) [14]. The method outlined in this chapter is unique in the ability to calculate the components of the Soret coefficient independently. This requires an understanding of how the Green-Kubo (GK) functions can be used to calculate the transport coefficients of two component system, which is found to differ from the utilisation of GK functions in one component systems. We also require an accurate value of the thermodynamic factor \( \frac{\partial \mu_i}{\partial c_i} \), where \( \mu_i \) is the chemical potential of component \( i \), as the assumption of ideality which is often used to obtain the thermodynamic factor is proven to be incorrect for the binary systems studied here.

This follows from the work of Jolly and Bearman [17] who used the GK relations to obtain the mutual diffusion coefficient with the assumption of ideality, over a range of temperatures for an Ar-Kr fluid. The work by Jolly and Bearman followed the original work of Jaccuci and McDonald [18] who obtained the mutual diffusion coefficient at various mass fractions and temperatures. Further values of the mutual diffusion coefficient were obtained by Schoen and Hoheisel [19], however we believe our work correctly accounts for the non-ideality in calculating the mutual diffusion coefficient, and correctly applies the GK functions in the calculation of the thermal diffusion coefficient for binary systems. The values obtained for the integrals of the GK correlation functions are in good agreement with those reported by MacGowan [20], Sarman and Evans [21] as seen in Ch. 4.

### 2.2 Conservation equations

The continuity equation for component \( i \) can be written in the form presented by De Groot and Mazur [14]

\[
\frac{\partial \rho_i}{\partial t} = -\nabla \cdot (\rho_i \mathbf{v}_i),
\]

where \( \mathbf{v}_i \) is the velocity for component \( i \), \( \rho_i \) the density of component \( i \) and \( t \) time. If we denote the convective part of the velocity as \( \mathbf{v} \), the diffusive flux of component \( i \) can be written as [14]

\[
\mathbf{J}_i = \rho_i (\mathbf{v}_i - \mathbf{v})
\]

where the barycentric velocity \( \mathbf{v} \), multiplied by the total mass density \( \rho \), is defined by

\[
\rho \mathbf{v} = \sum_i \rho_i \mathbf{v}_i.
\]

With Eq. (2.2), Eq. (2.1) becomes

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\[
\frac{\partial \rho_i}{\partial t} = -\nabla \cdot (\rho_i \mathbf{v}_i) = -\nabla \cdot \mathbf{J}_i - \nabla \cdot (\rho \mathbf{v}). \tag{2.4}
\]

The second term on the right hand side of this equation is the convective part. If we apply Newton’s second law to the fluid, the momentum balance equation is obtained [14, 22]

\[
\frac{\partial \rho \mathbf{v}}{\partial t} = -\nabla \cdot \mathbf{P} - \nabla \cdot (\rho \mathbf{v} \mathbf{v}) + \sum_i \rho_i \mathbf{F}_i^e. \tag{2.5}
\]

In Eq. (2.5) the first term on the right hand side is the diffusive momentum flux term with \( \mathbf{P} \) the pressure tensor, the second term is the convective momentum flux, and the final term the effect of the body force \( \mathbf{F}_i^e \). This relationship leads to the familiar Navier-Stokes (NS) equations for incompressible, viscous fluid flow [23]. Finally when we consider the derivative of the internal energy density with respect to time, we obtain the internal energy balance equation

\[
\frac{\partial \rho u}{\partial t} = -\nabla \cdot \mathbf{J}_q - \nabla \cdot (\rho \mathbf{u} \mathbf{v}) - \mathbf{P}^T : \nabla \mathbf{v} + \sum_i \mathbf{J}_i \cdot \mathbf{F}_i^e, \tag{2.6}
\]

where \( u \) is the specific internal energy, \( \mathbf{J}_q \) is the heat flux, the second right hand term the convection of internal energy, \( \mathbf{P}^T : \nabla \mathbf{v} \) the thermodynamic part of work done by stresses, and the last term the change in the internal energy due to mass diffusion in the presence of an external field and \( \mathbf{J}_i \) the mass flux. We can evaluate the fluxes \( \mathbf{J}_i, \mathbf{J}_q, \) and \( \mathbf{P} \) occurring in the hydrodynamic equations (2.1), (2.5) and (2.6) and determine the macroscopic behaviour of the system.

We now consider the equation for temperature, by using the following hydrodynamic and thermodynamic definitions and relationships [25]

\[
\frac{\partial \rho u}{\partial t} = \rho \frac{du}{dt} - \nabla \cdot (\rho \mathbf{u} \mathbf{v}), \tag{2.7}
\]

\[
u = h - \frac{p}{\rho}. \quad \tag{2.8}
\]

where \( p \) is the hydrostatic part of the pressure and \( h \) the specific enthalpy. If \( c_k \) is the mass fraction of component \( k \) and we consider

\[
h = h(p, T, c_k), \tag{2.9}
\]

then the change in enthalpy is defined as

\[
dh = \left( \frac{\partial h}{\partial p} \right)_{T, \{c\}} dp + \left( \frac{\partial h}{\partial T} \right)_{p, \{c\}} dT + \sum_k \left( \frac{\partial h}{\partial c_k} \right)_{p, T, \{c\}} dc_k, \tag{2.10}
\]
and the pressure derivative of the enthalpy as
\[
\frac{\partial h}{\partial p} = \sum c_k \frac{\partial h_k}{\partial p} = \frac{1}{\rho} (\rho L_s + 1). \tag{2.11}
\]

Here \(L_s\) is the specific latent heat and 1 the ideal gas term. The heat capacity at constant pressure is defined by the equation
\[
\frac{\partial h}{\partial T} = c_p, \tag{2.12}
\]
and since \(h\) is a homogeneous function, Euler’s theorem gives
\[
h = \sum h_k c_k, \tag{2.13}
\]
where
\[
h_k = \frac{\partial h}{\partial c_k} \bigg|_{p,T}. \tag{2.14}
\]

At constant temperature and pressure
\[
dh = \sum \frac{\partial h}{\partial c_k} dc_k = \sum h_k dc_k \tag{2.15}
\]
then
\[
\rho \frac{dh}{dt} = (\rho L + 1) \frac{dp}{dt} + \rho c_p \frac{dT}{dt} - \sum h_k \nabla \cdot J_k. \tag{2.16}
\]

Expanding the final term in the above equation,
\[
\sum h_k \nabla \cdot J_k = \nabla \cdot \sum h_k J_k - \sum J_k \cdot \nabla h_k \tag{2.17}
\]
and substituting equations (2.7) to (2.17) into the internal energy equation, we find
\[
\rho c_p \frac{dT}{dt} = -\nabla \cdot \left( J_q - \sum h_k J_k \right) - \sum J_k \cdot \nabla h_k - \rho L \frac{dp}{dt} - \frac{p}{\rho} \frac{dp}{dt} - \mathbf{p} \cdot \mathbf{v} + \sum J_k \cdot \mathbf{F}^e_k. \tag{2.18}
\]

We can define the primed heat flux vector as [14]
\[
J'_q = J_q - \sum h_k J_k \tag{2.19}
\]
then our final equation converting the internal energy into an equation for the temperature is
\[ \rho c_p \frac{dT}{dt} = -\nabla \cdot \mathbf{J}'_q - \sum_k \mathbf{J}_k \cdot \nabla h_k - \rho L \frac{dp}{dt} - \frac{p}{\rho} \frac{dp}{dt} - \mathbf{P}^T : \nabla \mathbf{v} + \sum_k \mathbf{J}_k \cdot \mathbf{F}^e_k. \]  

(2.20)

We have now introduced the primed heat flux vector \( \mathbf{J}'_q \), the difference from \( \mathbf{J}_q \) being the transfer of heat due to diffusion. The different notion of heat flux leads to a special form of the entropy production, \( \sigma \) [14].

### 2.3 Entropy production

The Gibbs equation for a multi component fluid is [25]

\[ T \, ds = du - \frac{p_0}{\rho^2} d\rho - \sum_{i=1}^n \mu_i dN_i \]  

(2.21)

where \( p_0 \) is the equilibrium pressure, \( \mu_i \) the chemical potential and \( N \) the total number of particles. The local equilibrium hypothesis says that the local values of the thermodynamic variables are all that are required for entropy density, as expressed by the Gibbs equation i.e. \( s = s(u, \rho, c_k) \). The time derivative of Eq. (2.21) is therefore

\[ \rho \frac{ds}{dt} = \frac{\rho}{T} \frac{du}{dt} - \frac{p}{T \rho} \frac{dp}{dt} - \sum_{k=1}^n \mu_k \frac{dc_k}{dt}. \]  

(2.22)

Into this equation the balance equations for the internal energy, density and mass fraction are substituted and expressed in their most convenient Lagrangian form

\[ \frac{d\rho}{dt} = -\rho \nabla \cdot \mathbf{v} \]

\[ \rho \frac{du}{dt} = -\nabla \cdot \mathbf{J}_q - \mathbf{P}^T : \nabla \mathbf{v} + \sum_k \mathbf{J}_k \cdot \mathbf{F}^e_k \]  

(2.23)

\[ \rho \frac{dc_k}{dt} = -\nabla \cdot \mathbf{J}_k. \]

The rate of change of entropy is then

\[ \rho \frac{ds}{dt} = -\frac{1}{T} \left( \nabla \cdot \mathbf{J}_q + \mathbf{P}^T : \nabla \mathbf{v} - \sum_k \mathbf{J}_k \cdot \mathbf{F}^e_k \right) + \frac{p_0}{T} \nabla \cdot \mathbf{v} + \frac{1}{T} \sum_{k=1}^n \mu_k \nabla \cdot \mathbf{J}_k. \]  

(2.24)

The divergences can be written in the form
\[ \nabla \cdot \left( \frac{J_q}{T} \right) = \frac{1}{T} \nabla \cdot J_q + J_q \cdot \nabla \left( \frac{1}{T} \right) \]
\[ = \frac{1}{T} \nabla \cdot J_q - \frac{1}{T^2} J_q \cdot \nabla T \]  

(2.25)

and

\[ \nabla \cdot \left( \frac{\mu_k J_k}{T} \right) = \frac{\mu_k}{T} \nabla \cdot J_k + J_k \cdot \nabla \left( \frac{\mu_k}{T} \right). \]

(2.26)

Substituting Eqs. (2.25) and (2.26) into the rate of change of entropy in Eq. (2.24)

\[ \rho \frac{ds}{dt} = -\nabla \cdot \left[ \frac{1}{T} \left( J_q - \sum_{k=1}^{n} \mu_k J_k \right) \right] - \frac{1}{T^2} J_q \cdot \nabla T - \frac{1}{T} P^T : \nabla v - \frac{1}{T} \frac{p_0}{T} \nabla \cdot v - \frac{1}{T} \sum_{k=1}^{n} J_k \cdot \left[ T \nabla \left( \frac{\mu_k}{T} \right) - F_k \right]. \]

(2.27)

This can be compared to the balance equation for the rate of change of local entropy

\[ \rho \frac{ds}{dt} = -\nabla \cdot J_s + \sigma \]  

(2.28)

resulting in the entropy flux

\[ J_s = \frac{1}{T} \left( J_q - \sum_{k=1}^{n} \mu_k J_k \right) \]  

(2.29)

and the entropy production

\[ \sigma = -\frac{1}{T^2} J_q \cdot \nabla T - \frac{1}{T} P^T : \nabla v + \frac{p_0}{T} \nabla \cdot v - \frac{1}{T} \sum_{k=1}^{n} J_k \cdot \left[ T \nabla \left( \frac{\mu_k}{T} \right) - F_k \right]. \]

(2.30)

The viscous entropy production is simplified into a single term by decomposing the pressure tensor into its local equilibrium and non-equilibrium parts

\[ P = p_0 1 + \Pi \]  

(2.31)

and using the relation

\[ P^T : \nabla v = (p_0 1 + \Pi^T) : \nabla v \]
\[ = p_0 \nabla \cdot v + \Pi^T : \nabla v, \]

(2.32)

the final result for the entropy production is
\[ \sigma = -\frac{1}{T^2} \mathbf{J}_q \cdot \nabla T - \frac{1}{T^2} \mathbf{n} : \nabla \mathbf{v} - \frac{1}{T^2} \sum_{k=1}^{n} \mathbf{J}_k \cdot \left[ T \nabla \left( \frac{\mu_k}{T} \right) - F_k' \right]. \quad (2.33) \]

In Section 2.5 we show how this form of the entropy production with the introduction of the primed heat flux vector \( \mathbf{J}_q' \), can be used to account for the effects of diffusion and heat fluxes in two component fluids, and how including these effects differs from the one component situation.

### 2.4 Partial specific enthalpy and volume

#### 2.4.1 Enthalpy

An alternate form of the entropy production is obtained by writing the gradient of the chemical potential in a different form. Chemical potential is a function of temperature, so the gradient in chemical potential contains a contribution due to the gradient in temperature. This can be expressed as [25]

\[ \nabla \mu_k (T, p, \{c_i\}) = \left( \frac{\partial \mu_k}{\partial T} \right)_{p, \{c_i\}} \nabla T + (\nabla \mu_k)_T. \quad (2.34) \]

The specific Gibbs free energy is given by

\[ dg = -s dT + v dp + \sum_{k=1}^{n} \mu_k dc_k \]

where \( v \) is the specific volume. From this we obtain the Maxwell relation

\[ \left( \frac{\partial \mu_k}{\partial T} \right)_{T, p, \{c_i\}} = - \left( \frac{\partial s}{\partial c_k} \right)_{p, \{c_i \neq k\}} = - \left( \frac{\partial s}{\partial M_k} \right)_{T, p, \{M_i \neq k\}} = -s_k. \quad (2.36) \]

Euler’s theorem of homogeneous functions allows the expression of extensive properties such as entropy \( S \) in the form

\[ S = \sum_{k=1}^{n} \left( \frac{\partial S}{\partial M_k} \right)_{T, p, M_l} \]

where
\[ M_k = \sum_{k=1}^{n} s_k M_k. \] (2.38)

Using the definitions of the specific entropy as \( S = sM \) and the mass fraction as \( M_k = c_k M \) the differential of the entropy can be written

\[
dS = sdM + Mds = \sum_{k=1}^{n} c_k M ds_k + \sum_{k=1}^{n} s_k M d c_k + \sum_{k=1}^{n} s_k c_k dM
\] (2.39)

and knowing

\[ s = \sum_{k=1}^{n} s_k c_k \] (2.40)

we find

\[
ds = \sum_{k=1}^{n} c_k ds_k + \sum_{k=1}^{n} s_k d c_k.
\] (2.41)

Specific entropy is a function of \( T, p \) and \( c_i \) so we can write

\[
ds = \left( \frac{\partial s}{\partial T} \right)_{p,c_i} dT + \left( \frac{\partial s}{\partial p} \right)_{T,c_i} dp + \sum_{k=1}^{n} \left( \frac{\partial s}{\partial c_k} \right)_{T,p,c_i} dc_k
\] (2.42)

and comparing Eqs. (2.41) and (2.42)

\[ s_k = \left( \frac{\partial s}{\partial c_k} \right)_{T,p,c_i}. \] (2.43)

The partial specific entropy can be related to the partial specific enthalpy by the definition of Gibbs free energy [26]

\[ G = H - TS \] (2.44)

and taking the derivative with respect to the mass of component \( k \) to obtain

\[
\left( \frac{\partial G}{\partial M_k} \right)_{T,p,M_{i\neq k}} = \left( \frac{\partial H}{\partial M_k} \right)_{T,p,M_{i\neq k}} - T \left( \frac{\partial S}{\partial M_k} \right)_{T,p,M_{i\neq k}}.
\] (2.45)

These are all definitions of the corresponding partial specific quantities, so we can simplify to

\[ \mu_k = h_k - TS_k. \] (2.46)

To obtain the transport coefficients outlined in Section 2.5 the partial specific enthalpies are
required. As can be seen in Eq. (2.45)

\[ h_k = \left( \frac{\partial H}{\partial M_k} \right)_{T, p, \{M_{\neq k}\}} \]  

(2.47)

which are obtained for the colloid and solvent by holding the number of either solvent or colloid particles constant while varying the number of colloid or solvent particles respectively. As an extensive property the total enthalpy will change, and it is obtained by calculating [26]

\[ H = U + pV. \]  

(2.48)

### 2.4.2 Chemical potential and partial volume

The chemical potential \( \mu \), is the Gibbs energy per particle that represents the “free” energy that is available in a system for mechanical work

\[ \mu = \left( \frac{\partial G}{\partial N_i} \right)_{p, T}, \]  

(2.49)

where

\[ dG = -SdT + Vdp + \mu dN. \]  

(2.50)

In multicomponent systems the chemical potential expressed in molecular units can be described as a partial free energy for each component [27]

\[ \mu_i = \left( \frac{\partial G}{\partial N_i} \right)_{p, T, N_{j \neq i}}. \]  

(2.51)

These quantities can be measured computationally by a method devised by Kirkwood and Buff to relate partial values to the radial distribution functions for two component solutions [28]. The probability of finding particle \( b \) with respect to \( a \), at some distance \( r \) with \( a \) taken as the origin is denoted as \( g_{ab}(r) \), where

\[ g_{ab}(r) = \frac{1}{n_1 n_2 V 4\pi r^2} \left\langle \sum_i \sum_{j \neq i} \delta \left( r - r_{ij} \right) \right\rangle. \]  

(2.52)

Here \( n_i \) is the bulk molecular concentration of component \( i \). The relation between the radial distribution functions and the density fluctuations leads to an integral over the volume \( V \)

\[ \int \left( g_{ab}(r) - 1 \right) dV = V \frac{\langle N_a N_b \rangle - \langle N_a \rangle \langle N_b \rangle}{\langle N_a \rangle \langle N_b \rangle} - \frac{\delta_{ab}}{n_a}. \]  

(2.53)

where \( N_i \) is the number of molecules of component \( i \). This can be used to find \( G_{ab}(r) \) where
\[ G_{ab}(r) = \int (g_{ab}(r) - 1) dV = 4\pi \int r^2(g_{ab}(r) - 1) dr. \] (2.54)

Defining the solute as component 1 and solvent as component 2, the partial molecular volume for the colloid can be calculated using Kirwood-Buff theory as

\[ \bar{v}_1 = \frac{1 + (G_{22} - G_{12}) n_2}{n_1 + n_2 + n_1 n_2 (G_{11} + G_{22} - 2G_{12})} \] (2.55)

where \( n_1 \) and \( n_2 \) are the number densities of component 1 and 2 respectively, and

\[ n_1 \bar{v}_1 + n_2 \bar{v}_2 = 1. \] (2.56)

Kirkwood and Buff extend these relations to obtain the thermodynamic factor of Eq. (2.51) in molecular units for component 1

\[ \left( \frac{\partial \mu_1}{\partial n_1} \right)_{p,T} = k_B T \left( \frac{G_{12} - G_{11}}{1 + n_1 (G_{11} - G_{12})} \right), \] (2.57)

and component 2

\[ \left( \frac{\partial \mu_2}{\partial n_2} \right)_{p,T} = k_B T \left( \frac{G_{12} - G_{22}}{1 + n_1 (G_{22} - G_{12})} \right). \] (2.58)

These can be converted to the specific thermodynamic factors for component 1

\[ \left( \frac{\partial \mu_1}{\partial c_1} \right)_{p,T} = k_B T \rho \left( \frac{G_{12} - G_{11}}{1 + c_1 (G_{11} - G_{12})} \right), \] (2.59)

and component 2

\[ \left( \frac{\partial \mu_2}{\partial c_2} \right)_{p,T} = k_B T \rho \left( \frac{G_{12} - G_{22}}{1 + c_1 (G_{22} - G_{12})} \right). \] (2.60)

### 2.5 Modified transport coefficients in binary fluids

The transport coefficients in a binary fluid are different to those in a single component fluid. The inclusion of a second species requires an understanding of the effects of heat conduction and diffusion that is specific to binary mixtures. This section will detail how GK functions are used to calculate transport properties of binary fluids by expressing the ‘primed’ phenomenological coefficients in terms of the ‘unprimed’ coefficients. The GK integrals give the unprimed phe-
nomenological coefficients but the continuum theory for binary systems is most conveniently written in terms of the primed coefficients.

The entropy production for a binary fluid that has temperature and concentration gradients but no viscous flow or external fields, is derived from Eq. (2.33)

\[ \sigma = -\frac{1}{T^2} \mathbf{J}_q \cdot \nabla T - \sum_{k=1}^{2} \mathbf{J}_k \cdot \nabla \left( \frac{\mu_k}{T} \right). \]  

(2.61)

From this we can write [25]

\[ \nabla \left( \frac{\mu_k}{T} \right) = \frac{1}{T} \nabla \mu_k - \frac{\mu_k}{T^2} \nabla T. \]  

(2.62)

The chemical potential gradient can be further decomposed into concentration and temperature dependent parts at constant pressure as

\[ \nabla \mu_k = \frac{\mu_k - h_k}{T} \nabla T + \left( \nabla \mu_k \right)_{T,p}. \]  

(2.63)

Using Eqs. (2.62), (2.63) and the equation for entropy production Eq. (2.61) we obtain

\[ \sigma = -\frac{1}{T^2} \mathbf{J}_q \cdot \nabla T - \sum_{k=1}^{2} \mathbf{J}_k \cdot \left( \frac{1}{T} \left( \nabla \mu_k \right)_{T,p} - \frac{h_k}{T^2} \nabla T \right). \]  

(2.64)

The Gibbs-Duhem equation for the chemical potential gradients at constant temperature and pressure gives [14]

\[ \sum_{k=1}^{r} c_k \left( \nabla \mu_k \right)_{T,p} = 0 \]  

(2.65)

and the diffusive fluxes satisfy

\[ \sum_{k=1}^{2} \mathbf{J}_k \cdot \left( \nabla \mu_k \right)_{T,p} = \mathbf{J}_1 \cdot \left( \nabla \mu_1 \right)_{T,p} + \frac{c_1}{c_2} \mathbf{J}_1 \cdot \left( \nabla \mu_1 \right)_{T,p} \]

\[ = \left( 1 + \frac{c_1}{c_2} \right) \mathbf{J}_1 \cdot \left( \nabla \mu_1 \right)_{T,p}. \]  

(2.66)

The entropy production in Eq. (2.64) can now be written as [25]

\[ \sigma = -\frac{1}{T^2} \mathbf{J}_q \cdot \nabla T - \frac{1}{T} \mathbf{J}_1 \cdot \left[ \left( 1 + \frac{c_1}{c_2} \right) \left( \nabla \mu_k \right)_{T,p} - \frac{1}{T} (h_1 - h_2) \nabla T \right]. \]  

(2.67)

The entropy production can be written with the fluxes left in their original form and the thermodynamic forces written as [25]
\[
X_q = \left( \nabla T \frac{T}{T^2} \right) \quad (2.68)
\]

and
\[
X_1 = \frac{1}{T} \left[ \left( 1 + \frac{c_1}{c_2} \right) (\nabla \mu_k)_{T,p} - \frac{1}{T} (h_1 - h_2) \nabla T \right] \quad (2.69)
\]

resulting in the entropy production written in the form
\[
\sigma = -J_q \cdot X_q - J_1 \cdot X_1. \quad (2.70)
\]

Now we introduce the primed heat flux vector from Eq. (2.19) into the entropy production
\[
\sigma = -\frac{1}{T^2} \left( J_q - \sum_{k=1}^{r} h_k J_k \right) \cdot \nabla T - \frac{1}{T} J_1 \cdot \left( 1 + \frac{c_1}{c_2} \right) (\nabla \mu_1)_{T,p} \quad (2.71)
\]
or
\[
\sigma = -J'_q \cdot X_q - J'_1 \cdot X'_1. \quad (2.72)
\]

The linear phenomenological equations for the unprimed variables are defined for the heat flux and mass flux as
\[
J_q = -L_{qq} X_q - L_{q1} X_1, \quad (2.73)
\]
\[
J_1 = -L_{11} X_1 - L_{1q} X_q, \quad (2.74)
\]
and for the primed variables
\[
J'_q = -L'_{qq} X_q - L'_{q1} X'_1, \quad (2.75)
\]
\[
J'_1 = -L'_{11} X'_1 - L'_{1q} X_q. \quad (2.76)
\]

In this notation Eq. (2.69) becomes
\[
X_1 = X'_1 - (h_1 - h_2) X_q \quad (2.77)
\]
and now the entropy production can be written in terms of the primed flux phenomenological coefficients as
\[
\sigma = L'_{qq} X_q \cdot X_q + L'_{q1} X'_1 \cdot X_q + L'_{11} X'_1 \cdot X'_1 + L'_{1q} X_q \cdot X'_1 \quad (2.78)
\]
and for the unprimed variables the entropy production is
\[ \sigma = L_{qq} \mathbf{X}_q \cdot \mathbf{X}_q + L_{q1} \mathbf{X}_1 \cdot \mathbf{X}_q + L_{11} \mathbf{X}_1 \cdot \mathbf{X}_1 + L_{1q} \mathbf{X}_q \cdot \mathbf{X}_1. \] (2.79)

If we substitute the primed thermodynamic forces into Eq. (2.79) above we obtain

\[ \sigma = L_{qq} \mathbf{X}_q \cdot \mathbf{X}_q + L_{q1} \left( \mathbf{X}_1' - (h_1 - h_2) \mathbf{X}_q \right) \cdot \mathbf{X}_q + L_{11} \left( \mathbf{X}_1' - (h_1 - h_2) \mathbf{X}_q \right)^2 + L_{1q} \mathbf{X}_q \cdot \left( \mathbf{X}_1' - (h_1 - h_2) \mathbf{X}_q \right). \] (2.80)

Comparing this with the entropy production in Eq. (2.78) we find

\[ L_{qq}' = L_{qq} - L_{q1} (h_1 - h_2) + L_{11} (h_1 - h_2)^2 - L_{1q} (h_1 - h_2) \] (2.81)
\[ L_{q1}' = L_{q1} - L_{11} (h_1 - h_2) \] (2.82)
\[ L_{11}' = L_{11} \] (2.83)
\[ L_{1q}' = L_{q1} - L_{11} (h_1 - h_2). \] (2.84)

The Onsager reciprocal relations still hold in this case, therefore \( L_{1q}' = L_{q1}'. \)

By expressing the primed phenomenological coefficients in terms of the unprimed coefficients, the effects of heat conduction and diffusion with inclusion of a second species are appropriately accounted for. We can now use the GK functions in the calculation of transport properties for binary fluids. To use the unprimed coefficients we require the partial enthalpies, \( h_i \), and to calculate the mutual diffusion coefficient \( D_m \), the thermodynamic factor \( \frac{\partial \mu_i}{\partial c_i} \). We show how these are obtained in the following sections.

2.6 Diffusion and heat fluxes of fluids

When we consider a two component fluid the effects of diffusion and heat fluxes differ from the one component fluid. In the absence of flow, diffusion is driven by the combination of the concentration and temperature gradients. We note that the sum of the diffusive fluxes is zero, or

\[ \sum_k J_k = \sum_k \rho_k (v_k - v) = 0 \] (2.85)

where \( v \) is the streaming velocity and we consider 1 as the solute and 2 as the solvent. The equation for the mass flux of component 1 is \([25]\)
\[ J_1 = -\frac{L'_{11}}{T} \left[ \left( 1 + \frac{c_1}{c_2} \right) \frac{\partial \mu_1}{\partial c_1} \nabla c_1 \right]_{p,T} - \frac{L'_{1q}}{T^2} \nabla T \] (2.86)

and the heat flux is defined as

\[ J'_q = -\frac{L'_{qq}}{T^2} \nabla T - \frac{L'_{q1}}{T} \left[ \left( 1 + \frac{c_1}{c_2} \right) \frac{\partial \mu_1}{\partial c_1} \nabla c_1 \right]_{p,T}. \] (2.87)

The mass flux due to a temperature gradient is called the Soret effect, and the heat flux due to a concentration gradient is called the Dufour effect. The practical transport coefficients are defined by the constitutive relations [14]

\[ J_1 = -\rho D_m \nabla c_1 - \rho c_1 c_2 D' \nabla T \] (2.88)

and

\[ J'_q = -\lambda \nabla T - \rho_1 \frac{\partial \mu_1}{\partial c_1} T D'' \nabla c_1 \] (2.89)

where the transport coefficients are defined in terms of the phenomenological coefficients listed below [14]. These are the thermal conductivity

\[ \lambda = \frac{L'_{qq}}{T^2}, \] (2.90)

mutual diffusion coefficient

\[ D_m = \frac{L'_{11}}{\rho_2 c_2 T} \left( \frac{\partial \mu_1}{\partial c_1} \right)_{p,T} \] (2.91)

thermal diffusion coefficient

\[ D' = \frac{L'_{1q}}{\rho c_1 c_2 T^2} \] (2.92)

and Dufour coefficient

\[ D'' = \frac{L'_{q1}}{\rho c_1 c_2 T^2}. \] (2.93)

In order to obtain the phenomenological coefficients the integrals of the equilibrium Green-Kubo time correlation functions are used. These are the normal form of the Green-Kubo relations, described by [29]
\[ L_{ab} = \lim_{t \to \infty} L_{ab}(t) \quad (2.94) \]
\[ L_{ab}(t) = \int_0^t C_{ab}(t') dt' \quad (2.95) \]
\[ C_{ab}(t) = \frac{V}{3k_B} \langle J_a(t) \cdot J_b(0) \rangle. \quad (2.96) \]

These equations are used to calculate the mass-mass phenomenological coefficient \( L_{11} \), the heat-heat phenomenological coefficient \( L_{qq} \), and the mass-heat and heat-mass cross-correlated phenomenological coefficients, \( L_{1q} \) and \( L_{q1} \) respectively for the colloidal fluid. Due to the Onsager reciprocal relations the cross-correlated phenomenological coefficients are equal, \( L_{1q} = L_{q1} \).

The correlation functions in Eq. (2.96) are normalised to obtain the phenomenological coefficients for the colloidal species as per Eqs. (2.97) to (2.100) from time 0 to time \( t \). The correlation functions are the mass-mass autocorrelation function
\[ C_{11}(t) = \frac{V}{3k_B} \langle J_1(0) \cdot J_1(t) \rangle, \quad (2.97) \]
the heat autocorrelation function
\[ C_{qq}(t) = \frac{V}{3k_B} \langle J_q(0) \cdot J_q(t) \rangle, \quad (2.98) \]
and the cross correlation functions
\[ C_{1q}(t) = \frac{V}{3k_B} \langle J_1(0) \cdot J_q(t) \rangle \quad (2.99) \]
and
\[ C_{q1}(t) = \frac{V}{3k_B} \langle J_q(0) \cdot J_1(t) \rangle. \quad (2.100) \]

The values of these correlation functions are used in Eqs. (2.81) to (2.84) to obtain the primed phenomenological coefficients, which are subsequently used in Eqs. (2.90) to (2.93) to calculate the transport coefficients. The ratio of the thermal diffusion to mutual diffusion coefficients is called the the Soret coefficient and is denoted [14]
\[ S_T = \frac{D'}{D_m} \quad (2.101) \]
multiplying this by temperature we obtain the thermal diffusion factor
\[ \alpha = \frac{D'}{D_m} T. \quad (2.102) \]
2.7 Pressure tensor

The viscous pressure tensor can be broken down into an isotropic local equilibrium part and a non-equilibrium part [14]

\[ \mathbf{P} = p \mathbf{1} + \mathbf{\Pi}. \]  (2.103)

The non-equilibrium part can be further decomposed into the isotropic, traceless symmetric and antisymmetric parts

\[ \mathbf{\Pi} = \mathbf{\Pi}^I + \mathbf{\Pi}^{ts} + \mathbf{\Pi}^a. \]  (2.104)

The velocity gradient tensor can also be broken down into the isotropic, traceless symmetric and antisymmetric parts

\[ \nabla \mathbf{v} = \frac{1}{3} \nabla \cdot \mathbf{v} \mathbf{1} + (\nabla \mathbf{v})^{ts} + (\nabla \mathbf{v})^a, \]  (2.105)

in this work the antisymmetric part of the pressure tensor is zero. Our expression for entropy production that includes the viscous pressure and the velocity gradient splits into two linear equations corresponding to the two parts of the viscous pressure and velocity gradient tensors, and we need only consider the traceless symmetric part

\[ \mathbf{\Pi}^{ts} = -2\eta (\nabla \mathbf{v})^{ts}. \]  (2.106)

In this study we ignore the effects of molecular spin to simplify the treatment of shear, concentration and temperature effects.

2.8 Viscometric properties

The viscosity of a binary system is calculated from the stress autocorrelation function, and methods for calculating viscosity are well established [29, 30]. For a homogeneous and isotropic fluid at equilibrium, the symmetry of the material can be used, and the zero strain rate (Newtonian) viscosity calculated by averaging over the elements of the symmetric traceless pressure tensor [31]. The shear viscosity is generally defined as a fourth rank tensor using the GK relation [32]

\[ \eta = \frac{V}{k_B T} \int_0^\infty \langle \mathbf{P}^{ts}(t) \mathbf{P}^{ts}(0) \rangle \, dt \]  (2.107)
where $\eta$ is the fourth rank shear viscosity and $P^{\prime}$ is the traceless symmetric part of the pressure tensor. The shear viscosity can be written as a linear combination of the three isotropic fourth rank polar tensors. If deltas are second rank unit tensors

$$
\eta_{\alpha\beta\gamma\delta} = c_1 \delta_{\alpha\beta} \delta_{\gamma\delta} + c_2 \delta_{\alpha\gamma} \delta_{\beta\delta} + c_3 \delta_{\alpha\delta} \delta_{\beta\gamma}.
$$

(2.108)

where $c_1$, $c_2$ and $c_3$ are the three scalar invariants of the isotropic viscosity tensor. These coefficients are not independent due to the symmetrical properties of the GK integral. The GK relation is an outer product of the two symmetric traceless pressure tensors [32]. As such, the fourth rank viscosity tensor must be symmetric with respect to the first two indices, and again with respect to the second two indices. This implies that

$$
\eta_{\alpha\beta\gamma\delta} = \eta_{\beta\alpha\gamma\delta} = \eta_{\alpha\delta\beta\gamma}
$$

(2.109)

from which we obtain

$$
\eta_{\alpha\beta\gamma\delta} = c_1 \delta_{\alpha\beta} \delta_{\gamma\delta} + c_2 \delta_{\alpha\gamma} \delta_{\beta\delta} + c_3 \delta_{\alpha\delta} \delta_{\beta\gamma}
= c_1 \delta_{\alpha\beta} \delta_{\gamma\delta} + c_2 \delta_{\beta\gamma} \delta_{\alpha\delta} + c_3 \delta_{\beta\delta} \delta_{\alpha\gamma}
= c_1 \delta_{\alpha\beta} \delta_{\gamma\delta} + c_2 \delta_{\alpha\delta} \delta_{\beta\gamma} + c_3 \delta_{\alpha\gamma} \delta_{\beta\delta}.
$$

(2.110)

We can obtain from this equation $c_2 = c_3$, and as the fourth rank viscosity tensor must be traceless with respect to the first two and second two indices,

$$
\sum_{\alpha} \eta_{\alpha\alpha\gamma\delta} = \sum_{\alpha} (c_1 \delta_{\alpha\alpha} \delta_{\gamma\delta} + 2c_2 \delta_{\alpha\gamma} \delta_{\alpha\delta})
= 3c_1 \delta_{\gamma\delta} + 2c_2 \delta_{\gamma\delta}
= 0
$$

(2.111)

or

$$
c_2 = -\frac{3}{2} c_1.
$$

(2.112)

With one independent constant $c_1$, the shear viscosity can be written as

$$
\eta_{\alpha\beta\gamma\delta} = c_1 \delta_{\alpha\beta} \delta_{\gamma\delta} - \frac{3}{2} c_1 \left( \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma} \right).
$$

(2.113)

A fourth rank isotropic polar tensor can generally be expressed as a function of three scalar invariants. These are found by representing the tensor as an outer product of four vectors [32],

23
\[ \eta = abcd \] (2.114)

and forming scalar combinations of the constituent vectors. This gives the invariants as

\[ I_1 = (a \cdot b)(c \cdot d) \] (2.115a)
\[ I_2 = (a \cdot c)(b \cdot d) \] (2.115b)
\[ I_3 = (a \cdot d)(b \cdot c). \] (2.115c)

For the shear viscosity tensor, the invariant \( I_1 \) is zero because the trace with respect to the first and last two indices is zero. The second and third invariants are equal due to the additional symmetry. Using the GK formula, the scalar invariant \( I_3 \) can be written as \[ I_3 = \frac{V}{k_B T} \int_0^\infty \langle \mathbf{P}^{ts}(t) : \mathbf{P}^{ts}(0) \rangle dt. \] (2.116)

We can use the general form of the viscosity tensor in terms of the scalar viscosity coefficient and obtain

\[ I_3 = \frac{4}{3} \eta + \eta + \eta + \eta + \eta + \eta + \frac{4}{3} \eta + \eta + \frac{4}{3} \eta \] (2.117)

therefore

\[ \eta = \frac{V}{10k_B T} \int_0^\infty \langle \mathbf{P}^{ts}(t) : \mathbf{P}^{ts}(0) \rangle dt. \] (2.118)

From the symmetry of the traceless symmetric pressure tensor, there are only five independent components, \( P_{xx}^{ts}, P_{yy}^{ts}, P_{xy}^{ts}, P_{xz}^{ts} \) and \( P_{yz}^{ts} \). We can also express \( \eta_{3333} \) in terms of these components, such that

\[ P_{zz}^{ts} = -(P_{xx}^{ts} + P_{yy}^{ts}) \] (2.119)

or

\[ \eta_{3333} = \eta_{1111} + \eta_{1122} + \eta_{2211} + \eta_{2222}. \] (2.120)
Therefore we arrive at the most efficient method for the computation of the viscosity from

\[
\eta = \frac{1}{10} (\eta_{1111} + \eta_{1221} + \eta_{1331} + \eta_{2112} + \eta_{2222} + \eta_{2332} + \eta_{3113} + \eta_{3223} + \eta_{3333})
\]

\[
= \frac{1}{5} \left( \eta_{1111} + \frac{1}{2} \eta_{1122} + \frac{1}{2} \eta_{2211} + \eta_{1221} + \eta_{1331} + \eta_{2332} + \eta_{3113} + \eta_{2222} + \eta_{3333} \right).
\]

(2.121)

Using the sum of five different correlation functions makes use of the available information to increases the statistical reliability of the viscosity computation [31], yet maintains computational efficiency.

We have shown how to calculate various transport coefficients from a bulk, homogeneous binary fluid. We will now show how the transport coefficients are used to make continuum predictions of the observed velocity, temperature and concentration profiles for systems experiencing planar field driven Poiseuille flow.

2.9 Planar field driven Poiseuille flow

In steady planar Poiseuille flow density does not fluctuate with time and the velocity \( \mathbf{v} \) is in one direction, or

\[
\frac{\partial \rho}{\partial t} = 0
\]

(2.122)

and

\[
\mathbf{v} = v_x(y) \mathbf{i}.
\]

(2.123)

2.9.1 Velocity profile

Using the constitutive relations for the pressure tensor in the momentum equation (2.5), the resulting components of the equation are [25]

\[
\frac{\partial \rho \mathbf{v}}{\partial t} = 0,
\]

(2.124)

\[
\nabla p = 0,
\]

(2.125)

\[
\nabla (\rho \mathbf{v}) = \rho \nabla \mathbf{v} + \mathbf{v} \nabla \rho = 0,
\]

(2.126)

and
\[ \sum_k \rho_k F_k^e = (\rho_1 + \rho_2) F^e = \rho F^e. \quad (2.127) \]

The previous equation is due to the fact that the field is the same for all species. The gradient in the velocity is related to the strain rate by

\[ \nabla v = j i \dot{\gamma}(y) \quad (2.128) \]

where

\[ \dot{\gamma} = \frac{\partial v_x}{\partial y}. \quad (2.129) \]

From the \( x \)-component of the momentum equation we obtain

\[ -\frac{\partial (\eta \dot{\gamma})}{\partial y} = \rho F^e. \quad (2.130) \]

Assuming constant viscosity and integrating twice with stick boundary conditions, we obtain

\[ v_x(y) = -\frac{\rho F^e}{2\eta} \left( y^2 - \frac{L^2}{4} \right) \quad (2.131) \]

where \( L \) is the channel width. This is the same result obtained by Todd and Evans for the one component fluid, and is the classical Navier-Stokes solution to the velocity profile [33].

Applying the momentum equation in the \( y \)-direction we find

\[ \frac{\partial p(y)}{\partial y} = 0. \quad (2.132) \]

The hydrostatic pressure \( p \), which is a function of temperature, number density and concentration must satisfy this equation [33]. As the field is only applied in the \( x \)-direction, in the momentum conservation equation, Eq. (2.5), \( (\nabla \cdot P)_x \) is the only non-zero component of \( \nabla \cdot P \).

### 2.9.2 Temperature Profile

The linear constitutive relations in planar Poiseuille flow can be used to make a prediction of the temperature profile. Knowing that the velocity gradient can be defined as [25]

\[ \nabla v = j i \frac{\partial v_x(y)}{\partial y} = -j i \frac{\rho F^e y}{\eta} \quad (2.133) \]

in the steady state, there are zero gradients in the flow direction

\[ \nabla \cdot v = 0. \quad (2.134) \]
This results in zero time dependent changes in temperature, density and pressure

\[ \frac{dT}{dt} = 0, \quad (2.135) \]

\[ \frac{d\rho}{dt} = 0, \quad (2.136) \]

and

\[ \frac{dp}{dt} = 0. \quad (2.137) \]

In the steady state there is zero mass flux at the walls, giving the relation for the mass fluxes

\[ J_1 = -J_2 = 0. \quad (2.138) \]

In the heat equation (2.18) only the heat flux and viscous dissipation terms are non-zero, and we find

\[ -\nabla \cdot J'_q - P^T : \nabla \mathbf{v} = 0. \quad (2.139) \]

In this case the primed heat flux vector is given by [14]

\[ J'_q = -\lambda \frac{\partial T}{\partial y} - \rho \frac{\partial \mu_1}{\partial c_1} T D'' \frac{\partial c_1}{\partial y} \quad (2.140) \]

and the dissipation term is given by

\[ P^T : \nabla \mathbf{v} = P_{yx} \frac{\partial v_x}{\partial y} = -\eta \left[ \frac{\partial v_x(y)}{\partial y} \right]^2 = -\eta \left( \frac{\rho F_e y}{\eta} \right)^2 = -\frac{\rho^2 (F_e)^2 y^2}{\eta}. \quad (2.141) \]

The differential equation for the temperature profile is now

\[ -\lambda \frac{\partial^2 T}{\partial y^2} - \rho \frac{\partial \mu_1}{\partial c_1} T D'' \frac{\partial^2 c_1}{\partial y^2} = \frac{\rho^2 (F_e)^2 y^2}{\eta} \quad (2.142) \]

We first try a simple approximation to obtain the temperature profile by assuming the thermal diffusion term is negligible, giving

\[ -\lambda \frac{\partial^2 T}{\partial y^2} = \frac{\rho^2 (F_e)^2 y^2}{\eta} \quad (2.143) \]

which has a very simple solution when we use the boundary conditions

\[ T \left( \frac{L}{2} \right) = T \left( -\frac{L}{2} \right) = T_w. \quad (2.144) \]
This solution is

\[ T(y) = -\frac{\rho (F^e)^2}{12\eta\lambda} \left( y^4 - \frac{L^4}{16} \right) + T_w. \]  

(2.145)

In this equation we have assumed that the transport coefficients are constant over the channel width of the fluid, and applied Fourier’s law \( \mathbf{J}_q = -\lambda \nabla T \). This is the classical weak-field NS solution for the temperature profile [33]. The quartic profile predicted with the NS solution has been observed for planar confined Poiseuille flow of dilute gases. Mansour, Baras and Garcia observe the quartic temperature profile at sufficiently wide channels, and the deviation from the NS description for more highly confined gases [34]. The formation of a bimodal ‘dimple’ in the centre of the temperature profile as it deviates from the NS description is also observed for 2-D simulation of laminar flow, and described by Boltzmann-Grad gas-dynamics [35]. In 3-D simulations the observed dimple has been described by extensions of Fourier’s law, where higher order spatial derivatives are taken into account [36], or with derivations of the Burnett description of planar Poiseuille flow [37].

Less work has been done to understand the deviation from the NS description for liquids or dense fluids undergoing planar Poiseuille flow. Baranyai, Evans and Daivis postulated that the heat flux should account for the coupling of vectorial fluxes to the gradient of the strain rate [38]

\[ \mathbf{J}_q = -\lambda \nabla T - \xi \left[ \nabla \mathbf{v} : \left( \nabla \mathbf{v} \right)^T \right]. \]  

(2.146)

For shear flow Daivis and Coelho showed that this is equivalent to the relation [39]

\[ \mathbf{J}_q = -\lambda \frac{\partial T}{\partial y} - \xi \dot{\gamma} \frac{\partial \dot{\gamma}}{\partial y}, \]  

(2.147)

which can be derived from a Taylor series expansion. This is for a single component fluid where there are no concentration gradients, and has been used to predict temperature profiles that deviate from the NS description by Todd and Evans [33]. In this work a quadratic component is added to the quartic NS description of the temperature profile to successfully describe the observed temperature profile. For the two component fluid, Eq. (2.140) becomes

\[ \mathbf{J}'_q = -\lambda \frac{\partial T}{\partial y} - \rho_1 \frac{\partial \mu_1}{\partial c_1} T D' \frac{\partial c_1}{\partial y} - \xi \dot{\gamma} \frac{\partial \dot{\gamma}}{\partial y}, \]  

(2.148)

and for the diffusive mass flux

\[ \mathbf{J}_1 = -\rho D_m \frac{\partial c_1}{\partial y} - \rho c_1 c_2 D' \frac{\partial T}{\partial y} - \chi \dot{\gamma} \frac{\partial \dot{\gamma}}{\partial y}. \]  

(2.149)
2.9.3 Concentration profile

To derive our predictions of the concentration profile for a confined fluid, the quantities we know are

$$\frac{\partial \rho_k}{\partial t} = 0 \quad (2.150)$$

and

$$\nabla \cdot (\rho_k \mathbf{v}) = \rho_k \nabla \cdot \mathbf{v} + \mathbf{v} \cdot \nabla \rho_k = 0. \quad (2.151)$$

The implications of these give

$$\nabla \cdot \mathbf{J}_1 = 0 \quad (2.152)$$

or

$$\nabla \cdot (\rho D \nabla c_1 + \rho c_1 c_2 D' \nabla T) = \rho D \frac{\partial^2 c_1}{\partial y^2} + \rho D' \frac{\partial}{\partial y} \left( c_1 c_2 \frac{\partial T}{\partial y} \right) = 0. \quad (2.153)$$

This is also the consequence of a much simpler condition, that in the steady state the diffusive fluxes are zero

$$\mathbf{J}_1 = -\rho D \nabla c_1 - \rho c_1 c_2 D' \nabla T = 0 \quad (2.154)$$

or

$$D \frac{\partial c_1}{\partial y} + c_1 c_2 D' \frac{\partial T}{\partial y} = 0. \quad (2.155)$$

We can use this to give the relationship between the concentration and temperature profiles. Knowing the partial derivatives are ordinary derivatives in this geometry, we can write

$$\frac{dc}{dy} = -c(1-c) \frac{D' dT}{D dy} \quad (2.156)$$

rearranging

$$\frac{dc}{c(1-c)} = \frac{D'}{D} dT. \quad (2.157)$$

Taking the integral of this equation we find

$$\int \frac{dc}{c(1-c)} = \ln \left( \frac{ck}{1-c} \right) \quad (2.158)$$

where $k$ is the constant of integration. The result for the temperature dependent concentration
profile is then

\[ c(y) = \frac{1}{k \exp \left[ \frac{D'}{D} T'(y) \right] + 1}. \] (2.159)

The integration constant can be evaluated by using the fact that the concentration is equal to \( c_0 \) at the \( y \)-position where the temperature is \( T_0 \), i.e.

\[ c_0 = \frac{1}{k \exp \left[ \frac{D'}{D} T_0 \right] + 1} \] (2.160)

which leads to the final result

\[ c(y) = \frac{1}{\frac{1-c_0}{c_0} \exp \left[ \frac{D'}{D} (T(y) - T_0) \right] + 1}. \] (2.161)

where \( c_0 \) and \( T_0 \) are the concentration and temperature at some reference point in the system. This point is taken to be the average concentration and respective temperature from the observed results for the confined system for which the prediction is being made.

In Ch. 5 we simulate a confined fluid with now flow, and two different temperatures at each wall. For the continuum prediction of the temperature dependent concentration profile, Eq. (2.161) is also valid.
Chapter 3

Techniques

3.1 Introduction

Molecular dynamics (MD) is a computational method for simulating systems by solving Newton’s equations of motion for all particles in the system. The quantities that can be calculated from equilibrium (EMD) or non-equilibrium (NEMD) molecular dynamics are often beyond the reach of experimental techniques. For instance the concentration profile across a confined channel can not be viewed in experiment without addition components such as florescent dyes [1]. These particles can change the properties of the fluid studied. MD techniques can be utilised to overcome the need for additional components. However MD operates at very fine spatial and temporal resolution, typically in nanometer sized regions and in time regions of nanoseconds [40], and in larger spatial or time domains experimental methods or other computational methods may be more suitable. Larger spatial and time domains are becoming more accessible to MD, with the advent of more powerful computing facilities and novel programming methods [40]. In this chapter we will present details of the programming methods and computer infrastructure used in this study. The past limitations of computer infrastructure meant that short time frames of tens or hundreds of picoseconds, and small systems of only hundreds to one-thousand particles could be simulated using MD, for instance 864 particles in an argon-krypton (Ar-Kr) fluid [18], and in similar experiments 1024 particles more recently [21].

The simulations in this study focus on two fluids. The first is a comparison of Ar-Kr to that in literature, to validate our method of characterising the temperature dependent concentration profiles of highly confined fluids. The second is a more complex and slightly more realistic colloidal fluid, which incorporates a modified potential for the larger species. This is achieved by the use of a core region in one of the particles where interactions are excluded, and the particle has a significantly greater mass than the solvent species. The extension to larger system sizes of thousands and tens of thousands of particles, simulated up to nanoseconds, is aided by the choice of an appropriate model of the particle interactions, called the Weeks-Chandler-
Andersen (WCA) potential [41]. This purely repulsive potential limits the spatial range over which particles can interact by truncating and shifting the Lennard-Jones (LJ) potential, and is an established and tested method for simplifying the representation of fluid interactions as it maintains many of the physical attributes of the LJ system, and is a more realistic model for a colloidal particle than the crude hard-sphere potential [42].

Periodic boundary conditions (PBCs) allow the bulk fluid system sizes to be effectively extended to infinity [43], by periodically replicating the original system in all directions. This creates a significantly larger bulk fluid from which transport properties are calculated. For the confined systems the inclusion of walls permits the replicating nature of PBCs in only two of the three Cartesian coordinates.

3.2 Molecular Dynamics and the equations of motion

Molecular dynamics is a technique that utilises computer processing and storage capabilities to solve the classical equations of motion, known as Newton’s Laws. Newton’s second law [29]

\[ F(r, \dot{r}, t) = m \ddot{r} \]  

(3.1)

can be written for a system of \( N \) particles as

\[ F_i(r_i, \ldots, r_N) = m_i \ddot{r}_i. \]  

(3.2)

This second order differential equation is easily separated into two first order differential equations

\[ \dot{r}_i = \frac{p_i}{m_i}, \]  

(3.3)

and

\[ \dot{p}_i = F_i. \]  

(3.4)

Here \( m_i, r_i \) and \( p_i \) are the mass, position and thermal momentum of site \( i \) respectively, \( F_i \) is the sum of the forces on atom \( i \). By solving these equations we are explicitly accounting for the dynamic evolution of the coordinates and momenta of a classical system of \( N \) particles. From the time averages of phase variables, the expectation value of macroscopic properties can be obtained [44].

These equations of motion are solved using a fifth order Gear [45] predictor-corrector finite difference algorithm with a time step of either 0.001 or 0.003. This allows us to calculate the positions, velocities and other dynamic data to a significant level of accuracy at time \( t + \delta t \).
The Taylor series expansion for the particle coordinates is

\[
r_i(t + \delta t) = r(t) + \dot{r}(t) \delta t + \frac{1}{2!} \ddot{r}(t) + \ldots 
\]  

(3.5)

The Taylor series expansion can also be done for the higher order derivative \(\dot{r}_i(t + \delta t)\), and other higher order derivatives. This series is truncated at order \(n\), and the truncation introduces significant error in the predicted particle trajectories. To correct this, we consider the equation of motion Eq. (3.3) which may be written as

\[
\frac{d^m r_i}{dt^m} = f \left( \frac{d^{m-1} r_i}{dt^{m-1}}, \frac{d^{m-2} r_i}{dt^{m-2}}, \ldots, \frac{d r_i}{dt}, r_i \right).
\]

(3.6)

For the correction, the predicted positions in Eq. (3.5) and the predictions for the higher order derivatives are used to calculate the exact \(n^{th}\) derivative at time \((t + \delta t)\). The difference between the exact and predicted derivatives can be used to calculate all the other derivatives using a forward differencing scheme [44]. At time \((t + \delta t)\) Where the superscript 'p' is predicted and 'c' is corrected, \(f_k^m\) is a coefficient summarised in Table 3.1, \(m\) is the order of the differential equation and \(k\) is the term number of the Taylor series expansion, Gear showed that [45]

\[
\frac{d^k r_i^c}{dt^k} = \frac{d^k r_i^p}{dt^k} - \left( \frac{d^{m-1} r_i^p}{dt^{m-1}}, \frac{d^{m-2} r_i^p}{dt^{m-2}}, \ldots, \frac{d r_i^p}{dt}, r_i^p \right) f_k^m \frac{k!}{m!} \delta^{m-k}.
\]

(3.7)

Using this algorithm we obtain an accurate and efficient solution of the equations of motion for many body systems.

Table 3.1: Gear coefficients for a 1st order equation and 5th order Taylor series expansion [44].

<table>
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<th>(m)</th>
<th>(k)</th>
<th>(f_0^m)</th>
<th>(f_1^m)</th>
<th>(f_2^m)</th>
<th>(f_3^m)</th>
<th>(f_4^m)</th>
<th>(f_5^m)</th>
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<td>251/270</td>
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<td>25/24</td>
<td>35/72</td>
<td>5/48</td>
<td>1/120</td>
<td></td>
</tr>
</tbody>
</table>

3.2.1 Molecular dynamics for unconfined systems

With the application of a thermostat, the interaction sites progress in time using the equations of motion [29]
\[ \dot{r}_i = \frac{p_i}{m_i} \quad (3.8) \]

and

\[ \dot{p}_i = F_i - \xi^A p_i \quad (3.9) \]

where \( m_i, r_i \) and \( p_i \) are the mass, position and thermal momentum of site \( i \) respectively, \( F_i \) is the sum of the forces on site \( i \), and \( \xi^A \) is an atomic thermostat multiplier. If we wish to fix the kinetic temperature defined as

\[ T^A = \frac{1}{k_B f} \sum_{i=1}^{N} \frac{p_i^2}{m_i} \quad (3.10) \]

where \( N \) is the total number of particles in the system, and \( f \) is the number of translational centre of mass degrees of freedom, which is dependent on the total number of sites and constrains on the system, this study implements either a Gaussian or Nosé-Hoover type thermostat. The thermostats use a differential or integral temperature feedback multiplier respectively [38]. When applying a thermostat, Gauss' principle of least constraint can be employed to define our thermostat multiplier as [43]

\[ \xi^A = \frac{\sum_{i=1}^{N} F_i \cdot p_i}{\sum_{i=1}^{N} p_i^2} \quad (3.11) \]

This form of thermostat creates a rigid constraint and is extremely effective in ensuring \( \frac{dT}{dt} = 0 \). If we wish to change the temperature of a system, the Nosé-Hoover thermostat is more convenient. The Nosé-Hoover method of imposing a constraint on the temperature uses a thermodynamic friction coefficient \( \dot{\xi}^A \), which is defined by [46, 47, 48]

\[ \dot{\xi}^A = \frac{T - T_0}{Q_T} \quad (3.12) \]

Here \( T \) is the instantaneous temperature, \( T_0 \) the target temperature, and \( Q_T \) is a scaling factor controlling the rate of approach to the target temperature. If the value of \( Q_T \) chosen is small the low inertia of the heat bath and leads to rapid variations in temperature.

To maintain a specific pressure, we utilise a Nosé-Hoover type barostat. The time evolution of volume is determined by the equation

\[ \dot{V} = 3\dot{\varepsilon}V, \quad (3.13) \]

where \( \dot{\varepsilon} \) is the multiplier found by solving the differential equation
\[ \dot{\varepsilon} = \frac{(p - p_0)V}{Q_p N k_B T}. \]  

(3.14)

Here \( Q_p \) is a strength parameter, \( p \) is equated to \( (1/3)Tr(P) \) and \( p_0 \) is the target pressure. \( Q_p \) is again chosen by trial and error to give a good damping of the pressure fluctuations [31]. The full equations of motion including the thermostat and barostat are now

\[ \dot{r}_i = \frac{p_i}{m_i} + \dot{\varepsilon} r_i \]  

(3.15) and

\[ \dot{p}_i = F_i - \zeta A p_i - \dot{\varepsilon} p_i \]  

(3.16)

Using these methods we maintain the desired temperature and pressure for bulk simulations at the chosen state point. To obtain the transport coefficients of binary solutions in Ch. 4 systems are maintained at a constant temperature, and either constant density or pressure.

The pair distribution functions and GK integrals obtained from bulk fluids are calculated in the canonical \((NVT)\) ensemble. Systems containing \( N \) particles, are equilibrated at the desired volume, \( V \) and temperature, \( T \) through the equations of motion in Eq. (3.15) and (3.16). The target volumes and densities are achieved by the time evolution of volume. Once the target densities and temperatures are met, the \( NVT \) systems are simulated with the equations of motion in Eq. (3.8) and (3.9).

The partial specific enthalpies and volumes are calculated in the isothermal-isobaric \((NPT)\) ensemble. The systems containing \( N \) particles are maintained at the desired pressures and temperatures with the equations of motion Eq. (3.15) and (3.16). Once in the equilibrium state, the partial specific values are calculated with the same equations of motion.

Considering the convective term in the momentum conservation equation, we introduce the peculiar velocity

\[ c_i = v_i - v \]  

(3.17)

where \( v_i \) is the velocity of particle \( i \) relative to the laboratory frame, \( v \) is the streaming velocity and the equations of motion ensure that the sum of the peculiar momenta remains equal to zero for all time [22]. The microscopic expression for the molecular pressure tensor is

\[ VP(t) = \sum_i^N m_i c_i c_i - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N r_{ij} F_{ij}. \]  

(3.18)
The microscopic equations for the mass flux and heat flux vector are \cite{22, 24}

\[
J_1 = \sum_{i=1}^{N} m_i v_i
\]  

(3.19)

and

\[
VJ_q(t) = \sum_{i=1}^{N} u_i c_i - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} r_{ij} F_{ij} c_i.
\]  

(3.20)

where \(u_i\) is the internal energy of particle \(i\), \(r_{ij} = r_j - r_i\) is the vector separation between particles \(j\) and \(i\), and \(F_{ij}\) is the force on particle \(i\) due to particle \(j\). These are what we use in the calculation of the GK time correlation functions that are used to calculate the transport coefficients.

### 3.2.2 Molecular dynamics for confined systems

#### 3.2.2.1 Wall geometry and characteristics

Parallel walls confining the fluid provide a mechanism by which heat and momentum can be transferred. The set of uniformly distributed solvent like WCA particles are constrained to their equilibrium lattice positions \(r_{eq}^i\) by a harmonic tethering force

\[
F_w^i = -k_w (r_i - r_{eq}^i).
\]  

(3.21)

To calculate the spring constant \(k_w\) we use equation (3.22) which is obtained by substituting \(r = r_c\) into the second derivative of the interaction potential \cite{49, 50, 51}

\[
k_w = \frac{72 \epsilon}{21^{1/3} \sigma^2}
\]  

(3.22)

and the resulting value is 57.15 using the interaction parameters \(\epsilon = \sigma = 1\). This is utilised in the harmonic potential Eq. (3.23), to maintain lattice parameters of the boundary and simultaneously provide freedom for the boundary particles to act as momentum sink for the fluid.

\[
\phi \left( |r(t) - r_{eq}| \right) = \frac{1}{2} k_w \left( |r(t) - r_{eq}| \right)^2
\]  

(3.23)

Heat is removed by the application of a Gaussian isokinetic or Nosè-Hoover type thermostat which maintains the kinetic temperature of each wall, \(T_w\). Unless some form of constraint is applied, the presence of the fluid between the walls causes the walls to be pushed back \cite{50}. The resulting inaccuracy in the volume can be rectified by applying a constraint to the centre of mass of each particulate layer normal to the force of the fluid, in these simulations being the y-direction. This was detailed by Todd, Evans and Daivis \cite{51}, however the layer constraint
was not introduced concurrently with a thermostat constraint, causing minor errors in the later applied constraint. To overcome this the kinetic and centre of mass constraints need to be solved simultaneously. Eq. (3.9) which includes the thermostat term now includes a layer constraint term [29]

\[ \dot{p}_i = F_i - \alpha_w p_i + \lambda_\beta j \] (3.24)

The constraint multipliers \( \alpha_w \) and \( \lambda_\beta \) can be found from the thermostat force employed to keep the kinetic energy of each wall constant, \(-\alpha_w p_i\), chosen such that [57]

\[ K_w = \frac{1}{2m_w} \sum_{i \in w} p_i^2 = \text{constant} \] (3.25)

and the constraint on the centre of mass of the wall layers

\[ \sum_{i \in \beta} y_i = \text{constant}. \] (3.26)

Here \( K_w \) is the kinetic energy of the wall, \( m_w \) is the mass of a wall particle, \( p_i \) is the momentum of wall particle \( i \), \( y_i \) is the centre of mass position of species \( i \) in the \( y \)-direction, and \( \beta \) indicates the set of wall particles belonging to layer \( \beta \) and also the index of the layer. There are three layers per wall and hence \( \beta \) ranges from 1-6. Differentiating these equations we obtain the two constraint equations

\[ \sum_{i \in w} \dot{p}_i \cdot p_i = 0 \] (3.27)

and

\[ \sum_{i \in \beta} \dot{p}_{yi} = 0 \] (3.28)

Substituting the constrained momentum equation of motion Eq. (3.24) into these two equations, the thermostat multiplier is found to be

\[ \alpha_w = \frac{\sum_{i \in w} F_i \cdot p_i}{\sum_{i \in w} (p_i')^2} \] (3.29)

and the layer constraint multiplier is defined as

\[ \lambda_\beta = -\frac{1}{N_\beta} \sum_{i \in \beta} (F_{yi} - \alpha_w p_{si}). \] (3.30)

Here \( N_\beta \) is the number of wall particles in layer \( \beta \).
\[ F'_i = F_i - \frac{1}{N\beta} \sum_{j \in \beta} F_{ji} j \] (3.31)

and

\[ p'_i = p_i - \frac{1}{N\beta} \sum_{j \in \beta} p_{ji} j. \] (3.32)

The thermostat multiplier in this work is either Gaussian or the Nosé-Hoover method in Eqs. (3.11) and (3.12) respectively, applied to the wall particles.

The three layered wall is designed to act less like a thin layered material, and more like the surface of a much larger solid. The hexagonal close packed (HCP) structure is one of the two most dense crystalline sphere packing arrangements with a packing fraction of 0.74 \cite{52}.

### 3.2.2.2 Volume and density

To calculate the fluid volume we measure the positions of the first and last non-zero densities in the \( y \)-direction of the confined fluid. The difference between these two values is the channel width accessible by the fluid, \( D \). This differs from the total length of the simulation box \( L_y \) which includes the wall particles. Using the distance \( D \) we can calculate the fluid volume

\[ V = L_x L_z D. \] (3.33)

where \( L_x \) and \( L_z \) are the simulation box lengths in the \( x \) and \( z \) directions.

From this the average fluid density is simply calculated from Eq. (3.43). However when a fluid is subject to a large temperature difference imparted by the walls, the effects of particle packing create density variations in the region close to the walls. It is necessary to observe the spatial density fluctuations and recalculate the average fluid density where these fluctuations have decayed. Our theory is unable to include these effects in our predictions, and inclusion of these effects would be a subject of interest for more highly confined fluids where the wall effects dominate the density profiles across the entire channel.

### 3.2.2.3 Equation of motion for confined systems with no flow

In Ch. 5 we present results of a confined system that does not experience any flow, and the equations of motion in Eqs. (3.3) and (3.4) are used. Different temperatures are applied at each wall using Eq. 3.24, producing variations of the observable profiles in the \( y \)-direction. The fluid particles are not constrained by a thermostat or barostat, as this would create undesirable effects on the profiles we wish to observe.
3.2.2.4 Equation of motion for Poiseuille flow

In Chaps. 6 and 7 the confined fluid is subject to an external field which adds to the equations of motion

\[ p_i = F_i + F_{e,m} i. \]  (3.34)

\( F_e \) is applied in the \( x \)-direction producing variations of the observable profiles in the \( y \)-direction. Again the particles are not subject to any form of constraint as this would create undesirable effects on the profiles we wish to observe.

3.3 Interaction potentials and molecule parameters

Unconfined bulk fluids are simulated at a range of concentrations, temperatures and densities for the colloidal fluid, which represent the range seen in confined systems undergoing Poiseuille flow. The choice of state point for the Ar-Kr fluid was chosen to compare results of the Soret coefficient with that of Hafskjold, Ikeshoji and Ratkje [8]. Calculation of the transport coefficients allows for a model of continuum profiles of the confined fluid for both the colloid and Ar-Kr fluids.

Particles that comprise the unconfined bulk fluid and the confined systems are both modelled using the same potential energy functions. For equimolar Ar-Kr the LJ potential is used with a cutoff of the potential at \( 2.5 \sigma_{ij} \). This is the same potential used by MacGowan [20] and Sarman and Evans [21] to obtain phenomenological coefficients, and by Hafskjold, Ikeshoji and Ratkje [8] to calculate the Soret coefficient.

In the colloidal fluid each atom is modelled with a WCA interaction potential. For the colloidal particle, a core creates an excluded volume for the solvent-colloid and colloid-colloid interactions. The introduction of the core was previously used in MD simulations to study the size and mass ratio dependence of the self-diffusion coefficient of the solute by Nuevo, Morales and Hayes [53]. Snook, O’Malley, McPhie and Daivis have used this method to report the dynamical properties of particulate solutions approaching the Brownian limit [54]. McPhie, Daivis, and Snook also report the results from equilibrium and nonequilibrium MD simulations of the self diffusion coefficient, and shear rate dependence of viscosity, in colloidal fluids over a range of mass ratios modelled with this method [55]. The concept is further used in the calculation of the velocity autocorrelation function and diffusion constant for a fluid which the size and mass of the solute particle are related to approach the Brownian limit, in the publication by Schmidt and Skinner [56]. The method for modelling the colloidal fluid was also used by Kairn for the prediction of velocity profiles undergoing confined Poiseuille flow [15, 16]. We further extend this method for predicting the continuum mechanics description of the relationship be-
tween the temperature and concentration profiles of a colloidal fluid. The atoms have a colloid to solvent mass ratio of 10:1 and a diameter ratio of 2.2254:1, and no charge. The mass ratio and diameter ratio allows for the colloidal particle to be bigger than the solvent in both mass and size, yet still remain neutrally buoyant [54].

3.3.1 Interaction potentials

The colloidal fluid molecules are modelled using a Weeks-Chandler-Andersen (WCA) potential that is a shifted and truncated Lennard-Jones (LJ) potential [41]. The potentials are shown in Figures 3.1 (a) and (b).

The LJ potential has the functional form

$$\phi^\text{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right].$$  \hspace{1cm} (3.35)

For equimolar Ar-Kr this is shifted and truncated

$$\phi(r) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] - \phi^\text{LJ}_c & \text{if } r \leq r_c \\ 0 & \text{otherwise} \end{cases}$$  \hspace{1cm} (3.36)

where $r$ is the distance between the particles, $\epsilon$ is the depth of the potential well and $\sigma$ is the distance at which the potential is zero and $r_c$ is the cutoff distance of the LJ potential. This form of the interaction potential is short-ranged and computationally undemanding while retaining the physical reality of a fluid. This model may not give a precise agreement with experiment, however it will allow for this study to obtain reasonable results as it is well known that the repulsive part of the potential is dominant in determining liquid state transport properties [41].

McPhie [57] studied a 4% number fraction colloid system, sheared between solid moving walls, known as Couette flow. Kairn extended this work to Poiseuille flow, a situation where both walls are stationary and the fluid is driven by an applied field [15]. We elected to study two systems, Poiseuille flow and a steady state with no flow, where walls are held at different temperatures. The neutrally buoyant particles contain a repulsive hard core in the case of the colloid particle interaction. The modified WCA potential from Eq. (3.36) becomes

$$\phi(r) = \begin{cases} \text{undefined} & \text{if } r_{ij} < c_{ab} \\ 4\epsilon_{ab} \left[ \left( \frac{\sigma_{ab}}{r_{ij} - c_{ab}} \right)^{12} - \left( \frac{\sigma_{ab}}{r_{ij} - c_{ab}} \right)^{6} \right] + \epsilon_{ab} & \text{if } c_{ab} < r_{ij} < c_{ab} + 2^{1/6} \sigma_{ab} \\ 0 & \text{otherwise} \end{cases}$$  \hspace{1cm} (3.37)

where $\epsilon_{ab}$ and $\sigma_{ab}$ are the interaction parameters between species $a$ and $b$. The parameter $c_{ab}$
introduces a hard core to the colloid which is set to give a diameter \( d \) ratio of 2.2254:1, and mass ratio of approximately 10:1 for neutral buoyancy. These ratios satisfy a Brownian approach to describing colloidal dynamics [54]. The Brownian approach has been proven useful to describe experimental results [58, 59], and as the Brownian approach is satisfied with our choice of mass ratio, comparisons to real experimental systems can be made. In experimental systems the solvent to colloid mass ratio is generally very large and approaching infinity, these fluids are regarded as Brownian fluids [15]. Deutch and Oppenheim [60, 61], and Murphy and Aguirre [62] gave general assumptions needed to consider a Brownian approach from a molecular standing point. These are that all dynamic variables dependent on the suspension medium co-ordinates and/or momenta are uncorrelated for times greater than the relaxation time of the background in the presence of a fixed Brownian particle. The ratio of the mass of the solute particles to the solvent particles must tend to infinity. Also the momentum of the suspended particle should be much greater than the suspension medium particles. Finally the velocity of a suspended particle should be much less than that of a suspension particle. Snook, O’Malley, McPhie and Daivis [54] conclude that the solute self diffusion coefficients are approaching the limiting mass-independent behaviour at a mass ratio of 10:1, and agreement with the Brownian description is found. The Brownian approach has also been applied to suspensions in non-equilibrium states for both the macroscopic [59] and microscopic treatments [63].

To calculate the mass at which neutral buoyancy is reached, we consider the mass of the shell and core independently in the equations below.

\[
m_{\text{core}} = \frac{\pi}{6} c_{11} n_2
\]

\[
m_{\text{shell}} = (c_{11} + 1)^3 + c_{11}
\]

In both Kairn and McPhie’s studies the solvent number density is 0.85 and \( \sigma = 1.0 \) [57, 15]. Solving equations (3.38) and (3.39) numerically we obtain a value for \( c_{11} \) of 1.2254. The ratio of \( \frac{m_2}{m_1} \) is 9.999954 \( \approx \) 10, and the total diameter of the colloid particle is defined as

\[
d = c_{11} + \sigma.
\]

The LJ, WCA and hard core WCA potentials are seen in Figures 3.1 (a), 3.1 (b) and 3.2 below.

### 3.3.2 Simulation pair force parameters

To confirm the method detailed in Ch. 2 for obtaining transport coefficients, we applied the theory to equimolar Ar-Kr. All values are reduced with the argon Lennard-Jones molecular
(a) Lennard-Jones

(b) Weeks-Chandler-Andersen

Figure 3.1: Lennard-Jones and Weeks-Chandler-Andersen potentials.

Figure 3.2: Colloid WCA potential including a hard core.

fluid parameters used in the simulation presented in Table 3.2.

Table 3.2: Argon-krypton Lennard-Jones parameters.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Index</th>
<th>$\epsilon/J$</th>
<th>$\sigma/m$</th>
<th>$m/kg$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-Ar</td>
<td>2-2</td>
<td>$1.654 \times 10^{-21}$</td>
<td>$3.405 \times 10^{-10}$</td>
<td>$6.63385 \times 10^{-26}$</td>
</tr>
<tr>
<td>Kr-Kr</td>
<td>1-1</td>
<td>$2.305 \times 10^{-21}$</td>
<td>$3.663 \times 10^{-10}$</td>
<td>$13.9153 \times 10^{-26}$</td>
</tr>
<tr>
<td>Ar-Kr</td>
<td>2-1</td>
<td>$1.952 \times 10^{-21}$</td>
<td>$3.519 \times 10^{-10}$</td>
<td></td>
</tr>
</tbody>
</table>

Reducing with respect to the Ar-Ar parameters, and using $r_c = 2.5\sigma_{ij}$ for the cut-off of the L-J potential, the simulation parameters in reduced units are presented in Table 3.3 below.
Table 3.3: Reduced argon-krypton Lennard-Jones parameters.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Index</th>
<th>ε</th>
<th>σ</th>
<th>$r_c$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-Ar</td>
<td>2-2</td>
<td>1</td>
<td>1</td>
<td>2.5</td>
<td>1</td>
</tr>
<tr>
<td>Kr-Kr</td>
<td>1-1</td>
<td>1.39384</td>
<td>1.06696</td>
<td>2.6674</td>
<td>2.0976</td>
</tr>
<tr>
<td>Ar-Kr</td>
<td>2-1</td>
<td>1.180612</td>
<td>1.03348</td>
<td>2.5837</td>
<td></td>
</tr>
</tbody>
</table>

These values are used to obtain transport coefficients for equimolar Ar-Kr and in the continuum mechanics description of temperature and concentration for confined systems. The choice of simulation parameters is not necessarily the best representation of a real Ar-Kr mixture, however they were chosen for comparison with previous studies in literature [8, 21]. The values of the transport coefficient are compared primarily with the work of Hafskjold, and Ikeshoji and Ratkje [8] as detailed in Ch. 4.

This study is then extended to obtain transport coefficients and continuum predictions for a colloidal fluid. The interaction parameters are summarised in Table 3.4 below, where the cutoff distance is taken to be $2^{1/6} \sigma$ to maintain only the positive potential energies.

Table 3.4: Simulation pair force parameters.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$\varepsilon$</th>
<th>$\sigma$</th>
<th>$c$</th>
<th>$r_c$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1.12246</td>
<td>1</td>
</tr>
<tr>
<td>1-1</td>
<td>1</td>
<td>1</td>
<td>2.2254</td>
<td>2.34786</td>
<td>10</td>
</tr>
<tr>
<td>1-2</td>
<td>1</td>
<td>1</td>
<td>1.6127</td>
<td>1.73516</td>
<td></td>
</tr>
</tbody>
</table>

These pair force parameters were used by Kairn in the computation of velocity profiles of colloidal fluids undergoing Poiseuille flow [16].

### 3.4 Conventions and symbols

Bulk systems of various sizes and concentrations were utilised in this study. For a system of $N_1$ colloid particles and $N_2$ solvent particles, the mole fraction $x_i$ takes the form

$$x_i = \frac{N_i}{N}, \quad (N_1 + N_2 = N). \quad (3.41)$$
The mass of the component present in the fluid, \( m_i \), is the product of the number of particles of species \( i \) and molecular mass of each species \( M_i \),

\[
m_i = N_i M_i.
\]  
(3.42)

For a fluid volume \( V \), the individual mass densities \( \rho_i \) are

\[
\rho_i = \frac{m_i}{V}, \quad (\rho_1 + \rho_2 = \rho)
\]  
(3.43)

and \( \rho \) is the total mass density. The mass fraction is defined as the ratio of the mass of component \( i \) to the total mass of the solution

\[
c_i = \frac{m_i}{m}, \quad (c_1 + c_2 = 1)
\]  
(3.44)

where

\[
m = m_1 + m_2.
\]  
(3.45)

The number density is the number of particles of species \( i \) in volume \( V \)

\[
n_i = \frac{N_i}{V}.
\]  
(3.46)

It is important to highlight these quantities early as this study reports values in specific (per unit mass) form. This is contrary to quantities reported in molecular units as with Kirkwood and Buff [28], in which \( c_i \) is the bulk molecular concentration of component \( i \), or in studies that utilise different notation such as Hafskjold, and Ikeshoji and Ratkje [8] where \( w_i \) is ‘weight fraction’ of component \( i \), equivalent to our mass fraction \( c_i \).

### 3.5 Knudsen, Reynolds, Péclet, and Weissenberg

These numbers provide information about the fluids studied in this work, and validity of assumptions made with the systems studied here. The Knudsen number must remain small to avoid compromising the local equilibrium assumption, and a low Reynolds number of the order of 1 indicates a lack of turbulence and a considerable tendency towards viscous heating in the fluid. The Péclet number can be used to report the shear rate for the colloidal fluid, and the Weissenberg number gives an indication of any non-Newtonian effects.
3.5.1 Knudsen number

The Knudsen number, $Kn$, is calculated from Eq. (3.47) below, and must remain small to ensure there are enough collisions to restore the local Maxwellian distribution and avoid compromising the local equilibrium assumption [34]. Classical predictions are expected to be valid when $Kn$ is small and the flow rate is also small enough to avoid strong temperature and density variations in the fluid. This is seen in the work by Ansumali [64] who observed that Poiseuille flow could be described for a rarefied gas with $Kn < 0.2$, as long as the flow rate measured by the Mach number, $Ma$ is below 0.05.

The Knudsen number is a dimensionless number given by [34]

$$Kn = \frac{L}{D}$$

(3.47)

where the mean free path $L$, is calculated as the statistical average over all molecules, estimated by

$$L = \frac{1}{\sqrt{2\pi d^2 n_i}}$$

(3.48)

and $d$ the molecular diameter. The Knudsen number is a dimensionless parameter that when small means that intermolecular collisions are dominant, if the number is large, then molecules move almost freely in a confined space and the effects of the confining boundaries dominate. For the continuum hypothesis to be valid, and accurately assume that properties such as the density, pressure, temperature, and velocity vary continuously from one point to another, the Knudsen number should be much less than 1.

Wall-slip has been observed by Zheng et al [65], Xu [66] and Uribe and Garcia [37] in simulations of rarefied gases for planar Poiseuille flow with $Kn = 0.1$. Using kinetic theory to model confined gas flow, Uribe and Garcia also observed wall slip in wider channels down to $Kn = 0.025$. In the colloidal fluids studied by Kairn using MD techniques, wall-slip was observed for systems simulated with $Kn = 0.12$ [16]. This study uses a regime very similar to Kairn and $Kn = 0.0008$. Velocity slip is observed at this Knudsen value, where the flow of the colloid is driven by $F_e = 0.0001$. This shows that even at low $Kn$ velocity slip can be observed for the colloidal fluid.

3.5.2 Reynolds number

The Reynolds number $Re$ is calculated from

$$Re = \frac{D \bar{v}_x}{2\eta}.$$  

(3.49)
We have taken the characteristic length to be half the width of the channel \( L = D/2 \), and \( \bar{v}_x \) the average of the velocity in the \( x \)-direction. Taking the shear viscosity and mass density \( \rho \) as the averages across the profile, the Reynolds number is calculated from Eq. (3.49) and reported in Chaps. 6 and 7 for the various fluid velocities observed in this study.

Low Reynolds numbers of the order of 1 indicate laminar flow and a considerable tendency towards viscous heating in the fluid [64]. Reynolds numbers greater than 2000 are indicative of turbulent flow. In Ch. 6 the \( Re = 0.1206(6) \) for a system with a channel width of 80\( \sigma \) at a field strength of \( F_e = 0.0001 \), a value that is far from turbulence and indicative of laminar flow. For the strongest field of \( F_e = 0.01 \), \( Re = 11.35(3) \) and the flow still remains laminar.

### 3.5.3 Péclet number

The measurement of shear for the colloidal fluid can be reported as the Péclet number, \( Pe \). This is a dimensionless number defined as [67]

\[
Pe = \frac{\eta_0 \dot{\gamma} \frac{d}{\tau}}{k_B T}.
\]  

(3.50)

where \( \eta_0 \) is the viscosity of pure solvent. The Péclet numbers at the various field strengths are reported in Chaps. 6 and 7 for the maximum strain rates observed in the systems undergoing Poiseuille flow. The Péclet number can be used to evaluate the relative importance of transport by advection and transport by diffusion [68]. With the definition of Eq. (3.50) a value of \( Pe << 1 \) then transport by diffusion dominates.

### 3.5.4 Weissenberg number

The Weissenberg number \( Wi \) for steady shearing flow is defined as

\[
Wi = \dot{\gamma} \tau
\]  

(3.51)

where \( \tau \) is the viscoelastic relaxation time. To calculate the relaxation time we consider the first normal stress coefficient calculated by evaluating an expression derived by Coleman and Markovitz [69]

\[
\Psi_{1.0} = 2 \int_0^\infty tG(t)dt,
\]  

(3.52)

where \( G(t) \) is the stress relaxation modulus defined as

\[
G(t) = \frac{V}{10k_BT} \int_0^\infty \langle P^{ts}(t) : P^{ts}(0) \rangle dt.
\]  

(3.53)
Hartkamp, Daivis and Todd have shown that the relaxation time can be calculated as the ratio of the first normal stress coefficient to the viscosity \[ \tau = \frac{\psi_1}{2\eta} = \frac{\int_0^\infty tG(t)dt}{\int_0^\infty G(t)dt}. \] (3.54)

Both the first normal stress coefficient and the viscosity are calculated from the stress autocorrelation function. The Weissenberg number gives an indication of any unusual effects that may be produced by normal stress differences in fluids. Unless a deformation is very small or slow, at sufficiently high shear rates the fluid may show viscoelasticity, shear thinning, and other non-Newtonian phenomena. The Weissenberg number was first introduced by White [71], and named after Weissenberg who was the first to recognise the significance of normal stress differences in the behaviour of non-Newtonian fluids [72, 73].

The values of \( Wi \) are reported in Ch. 6 for a field of 0.0001. At this field strength the maximum strain rate is \( \dot{\gamma} = 0.0091 \), \( Wi = 0.0364 \) and we can make the assumption of linear viscous transport over the whole profile and the absence of any non-Newtonian behaviour. However in Ch. 7 the maximum strain is \( \dot{\gamma} = 0.91 \), and \( Wi = 0.3940 \). At relatively high strain rates we can no longer assume that linear viscous transport applies, and must consider if non-Newtonian behaviour is present. Non-Newtonian behaviour was observed by McPhie [57] for the colloidal fluid used in this study, at the higher values of the strain rates observed here.

### 3.6 Periodic Boundary Conditions

Using molecular dynamics we would like to simulate a bulk material with a finite number of particles, significantly fewer in number than a counterpart example of a real fluid. As we are interested in bulk characteristics, the use of periodic boundary conditions (PBCs) [43] allows for a fluid to be replicated in each Cartesian direction, creating a more accurate representation of a bulk fluid than infinite potential reflections at the boundary. With the primary cell surrounded by its image cells, Fig. 3.3 shows the central 9 of 27 boxes of a three-dimensional fluid that would be sandwiched together to form one example of PBCs. The 26 image cells have the same shape, size and number of particles contained in their volume as the primary cell, and particles that leave a cell are replaced by their images entering the cell from the opposite side.

Theoretically each particle can now interact with a significantly greater (potentially infinite) number of particles, creating a more accurate description of a bulk fluid. The potential cost of increasing the number of particle interactions is negated through the use of a cut-off length parameter \( r_c \leq L/2 \) which insures minimal interactions. Using this scheme the number of computed interactions is reduced by solving the pair interaction for the image of the particle that is closest [74]. To further reduce the number of computations we have also applied the WCA
potential which has a spherical short-ranged cut-off as described in Section 3.3.1. In the case of the unconfined colloidal fluid, the PBCs and the minimum image convention are applied in all three Cartesian directions. With the confined system we are interested in the surface effects of the confining walls, therefore we can only apply the PBCs in two of the three Cartesian directions (in our case, the $x$ and $z$ directions). Combining these techniques we can study the characteristics of bulk fluid with greater accuracy but without significant computational costs.

### 3.7 Hardware

Simulations were run on three high performance computer (HPC) clusters. RMIT’s HPC consists of 35 Sun X2200 M2 machines, each node having two AMD quad core Opteron™ (2356 2.3GHz) central processing units (CPUs), and 32GB of random access memory (RAM). The Sun Studio Fortran compiler was used on RMIT’s cluster. Tango is a Victorian Partnership for Advanced Computing (VPAC) AMD Opteron™ system. The facility boasts 111 compute nodes each with two AMD Quad Core Opteron™ (2376 2.3GHz or 2379 2.46GHz) each with 32GB of RAM. Programs were compiled on Tango using the Intel ifort compiler. Trifid is also a VPAC hosted machine with 2,880 cores of Intel E5-2670, 4 GB PC1600 memory per core (64 GB per node), with 6 nodes having 16 GB per core (256 GB per node). The Intel ifort compiler was
also used on this machine.

### 3.8 Software

The MD program is used for both bulk and confined systems. It is designed to obtain distributions of properties across the fluid including temperature, concentration, density, and velocity, and includes cell code for neighbour lists [75]. It also incorporates the ability to simulate Poiseuille flow using an external field applied to the fluid. McPhie improves the calculation of shear viscosity, $\eta_s$, from the $x - y$ components of the pressure tensor $P_{xy}$ [55], which has been included in this program. These program developments have been under the supervision of Peter Daivis, who has continually developed and maintained the MD program for a wide range of simulation capabilities. The program is employed in our work to simulate Poiseuille flow of colloids, temperature difference systems for confined Argon-Krypton and colloids, and the necessary transport coefficients for the continuum predictions.
Chapter 4

Transport properties of homogeneous colloidal fluids

4.1 Introduction

In this chapter we report the transport properties of two homogeneous fluids. The first is an equimolar Argon-Krypton (Ar-Kr) mixture and the second a slightly more realistic colloidal fluid. The Ar-Kr fluid is studied at a state point that is widely reported in literature to confirm the method of obtaining transport coefficients in Ch. 2. We then present the transport coefficients for the colloidal fluid over a range of concentrations and temperatures. The transport coefficients are used in the continuum mechanics predictions of the temperature and concentration profiles in Chaps. 5, 6 and 7.

In order to confirm the method used to obtain transport coefficients of the colloidal fluid, the combined use of Green-Kubo integrals, the pair distribution functions, and the partial specific enthalpies are tested on a simple and widely studied Ar-Kr fluid. The unconfined bulk fluid was previously studied by Jolly and Bearman [17], Jacucci and McDonald [18], Schoen and Hoheisel [19], MacGowan [76, 20], Sarman and Evans [21], Gardner [77] and Hafskjold, and Ikeshoji and Ratkje [8] all concerned with obtaining transport coefficients of the Ar-Kr fluid. It is noted that the thermal diffusion factor from Hafskjold, Ikeshoji and Ratkje [8] is most suitable for comparison with our results, as the particle-exchange technique overcomes the problems with the assumption of ideality, and appropriate consideration of the heat-mass cross correlation functions for fluids of two components. The difficulty of obtaining the thermodynamic factor from the radial distribution functions often leads to a comparison of $L_{11}$, instead of the diffusion coefficient as observed by MacGowan and Evans [78]. In Section 4.2.1 we detail a method to obtain the thermodynamic factor, overcoming the past difficulty encountered due to the extended length over which the radial distribution function decays.
4.2 Argon-krypton, the verifying case

In this section the calculation of equimolar Ar-Kr pair correlation functions, the Green-Kubo integrals, and the resultant transport coefficients are compared to values reported in various studies of similar systems. The state point studied has a number density of \( n = 0.7137 \) and temperature of \( T = 0.9650 \) chosen for comparison with the results in literature of the integrals of correlation functions with MacGowan and Evans [76], MacGowan [20] and [21], and the thermal diffusion factor obtained by Hafskjold, Ikeshoji and Ratkje [8]. Previous studies were often limited to a few hundred particles. We have taken advantage of modern computation capabilities to extended systems into one to two thousands of atoms.

4.2.1 Pair distribution function

The pair distribution function is the probability of finding a pair of atoms within the distance \( r \), relative to the probability expected for a completely random distribution at the same density [43]. It is calculated in radial distance bins over half the minimum box length vector for each of the three possible species pairs in equimolar Ar-Kr and the colloidal fluid. Equation (2.52) is calculated for a single system and its form can be seen for equimolar Ar-Kr in Fig. 4.1 below where component 1 is krypton and 2 argon.

![Figure 4.1: Pair distribution functions for equimolar argon-krypton, \( n = 0.7137 \) and \( T = 0.9650 \).](image)

To fit the remainder of this function that can not simulated due to the limited size of the simulation box, a modified decaying oscillator function used by Gaylor, Snook and van Megen [79] to fit structure factors, is employed in our work where
\[ g_{ab}(r) = 1 + A \cdot e^{-Br} \cdot \cos(Cr + D), \quad (4.1) \]

and the fitting parameters \(A, B, C\) and \(D\) are obtained using the method of least squares to minimise the residual difference in the fit of the tail of the pair distribution function. This allows extraction to a distance \(r\) where \(g_{ab}(r)\) is forced to converge to 1. The importance of this additional fit is made clear when calculating \(G_{ab}(r)\), the volume integral of the pair distribution function. A significant contribution to \(G_{ab}(r)\) remains in the region of \(g_{ab}(r)\) not simulated. Figures 4.2, 4.3 and 4.4 show the fitted \(g_{ab}(r)\), the resulting \(G_{ab}(r)\) and the residual of the fitted region for an equimolar Ar-Kr fluid of \(N = 864\) particles. The fit is made to approximately 10% of the tail of the accumulated distribution data. The ability of Eq. (4.1) to fit the tail is sensitive to the starting location of the fit, and the residual of the fit and the pair distribution can become large if the starting point involves too many data points, and may not describe the decay of the pair distributions appropriately if too few are chosen. The error associated with the starting location of the fit has been included in the error reported for the integrals of the pair distributions \(G_{ab}(r)\), by fitting Eq. (4.1) at a number of different points of the accumulated data, where the residual is still minimal, and calculating the deviation in the values obtained.

We note that in the canonical ensemble that the convergence does not necessarily converge to 1, but rather \(1 - 1/N\) [30]. However the system sizes allow for \(1/N\) to be smaller than the error in the fit used to force the convergence to 1. Figures 4.2 to 4.4 show the pair distribution and its integral, and the residual of the fit of the pair distribution and Eq. (4.1) for the relevant pair distributions. Nichols, Moore and Wheeler [80] present a method by which to calculate the exact expressions for finite volume KB integrals, also utilised by Krüger et al [81]. This would be particularly advantageous in situations where open systems are prohibited, and has the potential in future studies to improve the accuracy of the thermodynamic factor presented in this work. This method may also prove useful in overcoming the discrepancy of the partial volumes seen in Section 4.2.3.4. We note however, for the purposes of this study, the accuracy of the thermodynamic factor obtained from the Kirkwood-Buff integrals is adequate.
Figure 4.2: Equimolar argon-krypton fluid (a) pair distribution function, (b) its integral and (c) residual of the fit to the pair distribution for Kr-Kr, \( n = 0.7137 \) and \( T = 0.9650 \).

Figure 4.3: Equimolar argon-krypton fluid (a) pair distribution function, (b) its integral and (c) residual of the fit to the pair distribution for Ar-Kr, \( n = 0.7137 \) and \( T = 0.9650 \).
Figure 4.4: Equimolar argon-krypton fluid (a) pair distribution function, (b) its integral and (c) residual of the fit to the pair distribution for Ar-Ar, $n = 0.7137$ and $T = 0.9650$.

It can be seen from these graphs that the residual is small and non-systematic, which suggests systematic errors have been removed and the random error is small. As described in Ch. 2 the pair distribution function can be used to calculate the thermodynamic factor, partial volumes and a test of the ideality of a fluid for two component systems. The values of $G_{ab}(r)$ are summarised in Table 4.1. The errors are a combination of the residual, and changes in the value of the fit by shifting the start point of the fit of $g_{ab}(r)$.

Table 4.1: Integral of pair distribution functions for equimolar argon-krypton, $n = 0.7137$ and $T = 0.9650$

<table>
<thead>
<tr>
<th>$G_{11}(r)$</th>
<th>$G_{12}(r)$</th>
<th>$G_{22}(r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.903(1)</td>
<td>6.891(1)</td>
<td>7.273(1)</td>
</tr>
</tbody>
</table>
4.2.2 Green-Kubo integrals

The correlation functions detailed in Eq. (2.96) for the equimolar Ar-Kr liquid are seen below. These simulations were ensemble averaged over 32 systems at the same state point. These systems were replicated from one initial equilibrated system, varied by applying different temperature thermostats for a short number of steps, then re-equilibrating at the desired state point. Systems diverge at an exponential rate due to Lyapunov instability [29], and can then be used to obtain a more accurate averaged value of the relevant GK integral. The systems used here comprise 864 particles, and the zoomed boxes highlight the short time taken for the correlation values to converge to zero.

The stress auto-correlation function is calculated per Eq. (2.118). We have chosen component 2 for the Ar-Kr case to compare with the work of MacGowan [20], MacGowan and Evans [20], and Sarman and Evans [21] in Table 4.16.

Figure 4.5: Mass flux auto-correlation function and its integral for equimolar argon-krypton, component 2 (Ar), $T = 0.965$, $\rho = 1.105$. 
Figure 4.7: Stress auto-correlation function and its integral for equimolar argon-krypton, component 2 (Ar), $T = 0.965$, $\rho = 1.105$.

Figure 4.6: Heat flux auto-correlation function and its integral for equimolar argon-krypton, component 2 (Ar), $T = 0.965$, $\rho = 1.105$.  

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Figure 4.8: Mass-heat flux cross-correlation function and its integral for equimolar argon-krypton, component 2 (Ar), $T = 0.965$, $\rho = 1.105$. 
Figure 4.9: Heat-mass flux cross-correlation function and its integral for equimolar argon-krypton, component 2 (Ar), $T = 0.965$, $\rho = 1.105$. 
Figure 4.10: Average of heat-mass flux and mass-heat flux cross-correlation function and its integral for equimolar argon-krypton, component 2 (Ar), \( T = 0.965, \rho = 1.105 \).

The values of the integrals can be taken from any point after the correlation value has decayed to zero, any fluctuations due to noise are accounted for in the error of the values summarised in the table below. Comparison is made to publications that employ either EMD or NEMD techniques.

Table 4.2: Integrals of correlation functions for equimolar argon-krypton in bold font, with a comparison to various authors, component 2 (Ar), \( T = 0.965, \rho = 1.105 \)

<table>
<thead>
<tr>
<th>[Ref.] (Method)</th>
<th>( L_{22} )</th>
<th>( L_{qq} )</th>
<th>( L_{2q} )</th>
<th>( L_{q2} )</th>
<th>( \frac{L_{2q} + L_{q2}}{2} )</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[20] (EMD)</td>
<td>0.0155(4)</td>
<td>3.966(15)</td>
<td></td>
<td></td>
<td>-0.0154(14)</td>
<td></td>
</tr>
<tr>
<td>[21] (EMD)</td>
<td>0.0159(1)</td>
<td>4.11(2)</td>
<td></td>
<td></td>
<td>-0.0173(25)</td>
<td></td>
</tr>
<tr>
<td>[76] (NEMD)</td>
<td>0.0145(1)</td>
<td>3.95(5)</td>
<td>-0.0168(5)</td>
<td>-0.0164(13)</td>
<td>-0.0162(5)</td>
<td></td>
</tr>
<tr>
<td>[21] (NEMD)</td>
<td>0.0174(5)</td>
<td>4.24(1)</td>
<td>-0.0182(10)</td>
<td>-0.0167(20)</td>
<td>-0.0175(8)</td>
<td></td>
</tr>
<tr>
<td><strong>This work</strong></td>
<td><strong>0.01692(7)</strong></td>
<td><strong>4.14(2)</strong></td>
<td><strong>-0.0171(8)</strong></td>
<td><strong>-0.01736(2)</strong></td>
<td><strong>-0.0171(1)</strong></td>
<td><strong>2.581(9)</strong></td>
</tr>
</tbody>
</table>

The values reported in Table 4.16 are for argon or component 2. It is the convention of this work to consider the separation of the larger krypton or colloidal species, labelled component
1. This convention results in a change in sign of the cross correlation functions and the average of \((L_{1q} + L_{q1})\). The equivalence of the correlation values

\[
\langle J_1(t) \cdot J_1(0) \rangle = -\langle J_2(t) \cdot J_2(0) \rangle
\]  

(4.2)

can be derived from the fact that the sum of the diffusive fluxes must instantaneously by are zero, and

\[
J_1 = -J_2.
\]  

(4.3)

Care also needs to be taken to obtain the correct thermodynamic factor and partial specific enthalpies for the appropriate component as detailed in the following section.

## 4.2.3 Static and thermodynamic properties

### 4.2.3.1 Ideality

The degree of ideality of a two component fluid can be measured with the evaluation of the non-ideality factor, \(Q\), which is calculated from the pair distribution functions \(g_{ab}(r)\) [17]. The relation

\[
Q = 1 + \frac{1}{n_1 n_2 (G_{11} + G_{22} - 2G_{12})}
\]  

(4.4)

will indicate that a fluid is ideal when \(Q = 1.0\). For equimolar Ar-Kr we calculate the value of \(Q\) to be 0.626(3) which is far from ideal, and significantly different from the averaged thermodynamic quantity obtained by Jolly and Bearman [17] of 0.97(8). The issue in obtaining this value in the past can be directly attributed to the large spatial distance over which pair distribution functions decay, error associated with noisy tail data and erroneous truncation of the pair distributions. Without the assumption of ideality and using more reliable data for pair distribution functions, our value of \(Q\) is more accurate than previously calculated. This has been facilitated by increased accumulation times and through the use of an appropriate fit to the decay of the pair distribution functions.

### 4.2.3.2 Thermodynamic factor

If a fluid is assumed to be ideal, the thermodynamic factor can simply be calculated from a relation utilised by Perronance et al [82]
\[
\left( \frac{\partial \mu_a}{\partial c_a} \right) = \frac{RT}{c_a [M_a - c_a (M_a - M_b)]}
\] (4.5)

where \( M_a \) is the molar mass of component \( a \). This can be compared to the values obtained from \( g_{ab}(r) \) as detailed the relations of Eqs. (2.59) and (2.60) in Table 4.3. It is clear that the assumption of ideality will result in values of the thermodynamic factors that are significantly different to that calculated from \( g_{ab}(r) \), and considered in this work to be inappropriate for calculating the mutual diffusion coefficient \( D_m \).

Table 4.3: Thermodynamic factor for the assumed ideal, and non-ideal equimolar argon-krypton system

<table>
<thead>
<tr>
<th>Method</th>
<th>( \frac{\partial \mu_1}{\partial c_1} )</th>
<th>( \frac{\partial \mu_2}{\partial c_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eq. (4.5)</td>
<td>1.052</td>
<td>2.207</td>
</tr>
<tr>
<td>Eq.’s (2.59) and (2.60)</td>
<td>0.68 (2)</td>
<td>3.01(11)</td>
</tr>
</tbody>
</table>

Nichols, Moore and Wheeler present a method from which the thermodynamic factor can be calculated from the structure factor [80]. This method is less convenient because the radial distribution function is more readily available than the structure factors. However this method may be worth comparing to the outcomes of this study, as it may produce a more accurate result. Schnell et al present a fluctuation method that uses a Grand Canonical Monte Carlo particle insertion method that can be used to calculate thermodynamic factors. This method only utilises a small volume of the simulation box to make the calculation. Furthermore the issues of inserting particles into a higher density fluid, or more complex system of molecules or polymers may lead to a large number of rejected Monte Carlo moves before a molecule is inserted, if at all. The method presented here has the advantage of using radial distribution functions that are often already available, and does not require the insertion or deletion of particles.

### 4.2.3.3 Partial specific enthalpy

In order to obtain the Soret coefficient and the thermal diffusion coefficient \( D' \), we require the partial specific enthalpies of the fluid. These are obtained as discussed in Ch. 2 and shown in Figs. 4.11 and 4.12 below.
Figure 4.11: Enthalpy versus mass of krypton, \( T = 0.965, p = 8.967 \).

Figure 4.12: Enthalpy versus mass of argon, \( T = 0.965, p = 8.967 \).

The following table summarises the values obtained from a linear fit to the enthalpies for equimolar Ar-Kr.
Table 4.4: Partial specific enthalpies for argon-krypton, $T = 0.965$, $p = 8.967$.

<table>
<thead>
<tr>
<th>Component</th>
<th>$\tilde{h}_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr</td>
<td>-2.07(1)</td>
</tr>
<tr>
<td>Ar</td>
<td>-2.33(2)</td>
</tr>
</tbody>
</table>

4.2.3.4 Partial specific volume

The partial specific volumes $\bar{v}_k$ can be calculated by a similar method to the partial enthalpies. For component $k$

$$\bar{v}_k = \left( \frac{\partial V}{\partial M_k} \right)_{T,p,M_{\neq k}}.$$  \hspace{1cm} (4.6)

Using this method, the values presented in Table 4.5 below are extremely accurate as the fluctuations in volume are negligible. This can be seen in Fig. 4.13 and 4.14 below, where the error bars are smaller than the data points representing the volumes at varying masses.

![Graph](image)

Figure 4.13: Volume versus mass of krypton, $T = 0.965$, $p = 8.967$
Partial specific volumes are also calculated using Kirkwood-Buff theory [28] using Eq. (2.55).

Table 4.5: Partial specific volumes for equimolar argon-krypton, $T = 0.965, p = 8.967$.

<table>
<thead>
<tr>
<th>Method</th>
<th>Kr</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eq. (4.6)</td>
<td>1.352(2)</td>
<td>0.688(7)</td>
</tr>
<tr>
<td>Eq. (2.55)</td>
<td>1.3(1)</td>
<td>0.7(1)</td>
</tr>
</tbody>
</table>

The partial specific volumes for both Ar and Kr are in agreement, however using the distribution functions in Eq. (2.55) has a significantly larger error than using Eq. (4.6). This is a result of the propagation of the uncertainty in the integrals of the pair distribution functions when calculating the partial volumes using Eq. (2.55).

### 4.2.3.5 Transport coefficients

The results of our equimolar Ar-Kr simulations are presented in Table 4.7. Values of the mutual diffusion coefficient calculated using the assumption of ideality are also reported in Table 4.6.
Although this assumption is incorrect, the mutual diffusion coefficient has been calculated for the purpose of comparison with previous work which assumed ideality.

Table 4.6: Mutual diffusion coefficients of Kr assuming ideality with our results in bold, for equimolar argon-krypton, \( T = 0.965, \rho = 1.105 \).

<table>
<thead>
<tr>
<th>Reference</th>
<th>( D_m(\text{ideal}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jolly and Bearman [17]</td>
<td>0.0489(4)</td>
</tr>
<tr>
<td>Jaccuci and McDonald [18]</td>
<td>0.0521</td>
</tr>
<tr>
<td>Schoen and Hoheisel [19]</td>
<td>0.0532</td>
</tr>
<tr>
<td><strong>This work</strong></td>
<td><strong>0.0491(2)</strong></td>
</tr>
</tbody>
</table>

Table 4.7 below shows the transport coefficients calculated using Eqs. (2.90) to (2.93), and Eq. (2.118) with two significant inclusions for the equimolar Ar-Kr fluid. The first is the mutual diffusion coefficient without the assumption of ideality, and the second being the thermal diffusion coefficient \( D' \), calculated with the primed heat flux vector. These values will be used to predict the concentration profile for the Kr species, that is generated with temperature gradient across the confined fluid in Ch. 5. They are also used in the prediction of the concentration profile for a fluid undergoing Poiseuille flow in Ch. 6.

Table 4.7: Transport coefficients for equimolar argon-krypton, for component 1 (Kr), \( T = 0.965, \rho = 1.105 \)

<table>
<thead>
<tr>
<th></th>
<th>( D_m )</th>
<th>( D_m(\text{ideal}) )</th>
<th>( D' )</th>
<th>( \lambda )</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.033(1)</td>
<td>0.0491(2)</td>
<td>0.054(4)</td>
<td>4.28(4)</td>
<td>2.581(9)</td>
</tr>
</tbody>
</table>

Comparing the thermal diffusion factor \( \alpha_{12} \) as defined in Eq. (2.102), our value is within the error reported by Hafskjold, Ikesholi and Ratkje [8]. This confirms the treatment of equimolar Ar-Kr as a non-ideal fluid, and the method used to calculate \( D' \). The advantage of the method utilised in this study is the separation of the transport coefficients which is not achievable in the method utilised by Hafskjold, Ikesholi and Ratkje.
Table 4.8: Thermal diffusion factor for equimolar argon-krypton, $T = 0.965$, $\rho = 1.105$.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\alpha_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hafskjold [8]</td>
<td>1.5(1)</td>
</tr>
<tr>
<td><strong>This work</strong></td>
<td><strong>1.6(1)</strong></td>
</tr>
</tbody>
</table>

### 4.3 The colloidal fluid

Evaluation of the heat and mass diffusion coefficients for a fluid is required to facilitate the prediction of the temperature and concentration profiles of a fluid undergoing Poiseuille flow, or in a system with a temperature gradient. This is achieved by evaluating the coefficients for unconfined, bulk fluid systems that span the range of concentrations and temperatures observed in confined flow. The method is identical to the method utilised for the equimolar Ar-Kr, and is assumed viable for a range of two component systems. Care needs to be taken to obtain the transport coefficients at the correct temperature, pressure and concentration to match the values at the centre of the confined fluid channel, as the average concentration will be affected by density variations at the wall. The density near the walls will fluctuate from the average as a result of fluid particles packing against the wall. This effect has been observed in MD simulations of narrowly confined systems [83], and is a factor in the choice of state points for the transport coefficients reported in this section.

The pair distribution functions, GK integrals, and partial quantities for the colloidal fluid have been calculated over a range of concentrations, temperatures and densities. These state points were chosen as the extreme values observed across the channel of a fluid undergoing Poiseuille flow with an applied field of 0.001. The plots of the pair distribution functions and the GK integrals have been presented for one state point. The plots for other state points are omitted, however the values of the properties obtained from these state points are presented in Table 4.19.

The fluid parameters of the unconfined colloidal fluids used to calculate the concentration dependence of the transport coefficients are shown in Table 4.9 below.

For calculations of the transport coefficients at different temperatures, all systems consist of 121 colloid particles and 2906 solvent particles. The total mass density is 0.969 and the concentration of colloid (component 1) is $\rho_1 = 0.2939$. The temperature is controlled using a Gaussian thermostat at 1.05, 1.00, 0.95, 0.90 and 0.85.
Table 4.9: Unconfined colloidal fluid parameters for varying concentrations, $T = 1.000(3)$ and $p = 8.82(1)$.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$N_1$</th>
<th>$N_2$</th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$V$</th>
<th>$\rho_1$</th>
<th>$\rho_2$</th>
<th>$\rho$</th>
<th>$c_1$</th>
<th>$c_2$</th>
<th>$n_1$</th>
<th>$n_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2304</td>
<td>144</td>
<td>2160</td>
<td>0.0625</td>
<td>0.9735</td>
<td>3750</td>
<td>0.3840</td>
<td>0.5760</td>
<td>0.960</td>
<td>0.4000</td>
<td>0.6000</td>
<td>0.0384</td>
<td>0.5760</td>
</tr>
<tr>
<td>2818</td>
<td>144</td>
<td>2674</td>
<td>0.0511</td>
<td>0.9489</td>
<td>4285</td>
<td>0.3361</td>
<td>0.6240</td>
<td>0.960</td>
<td>0.3500</td>
<td>0.6500</td>
<td>0.0336</td>
<td>0.6240</td>
</tr>
<tr>
<td>3603</td>
<td>144</td>
<td>3459</td>
<td>0.0400</td>
<td>0.9600</td>
<td>5103</td>
<td>0.2822</td>
<td>0.6778</td>
<td>0.960</td>
<td>0.2939</td>
<td>0.7061</td>
<td>0.0282</td>
<td>0.6778</td>
</tr>
<tr>
<td>4464</td>
<td>144</td>
<td>4320</td>
<td>0.0323</td>
<td>0.9677</td>
<td>6000</td>
<td>0.2400</td>
<td>0.7200</td>
<td>0.960</td>
<td>0.2500</td>
<td>0.7500</td>
<td>0.0240</td>
<td>0.7200</td>
</tr>
<tr>
<td>5904</td>
<td>144</td>
<td>5760</td>
<td>0.0244</td>
<td>0.9756</td>
<td>7500</td>
<td>0.1920</td>
<td>0.7680</td>
<td>0.960</td>
<td>0.2000</td>
<td>0.8000</td>
<td>0.0192</td>
<td>0.7680</td>
</tr>
</tbody>
</table>
4.3.1 Pair distribution function

To obtain the thermodynamic factor Eq. (2.52) is calculated at the various concentrations and temperatures listed above. With component 1 as the colloidal species and 2 the solvent, the graphical representation of the pair distribution functions are shown in 4.15.

![Graph showing pair distribution functions](image)

Figure 4.15: Pair distribution functions for the colloidal fluid, \( T = 1.00 \) and \( c_1 = 0.2939, \rho = 0.960 \).

To fit the remainder of this function we have again employed Eq. (4.1), where the choice of the fitting parameters \( A, B, C \) and \( D \) were chosen to minimise the residual difference between the fit and the tail of the pair distribution function. The extrapolation is to a distance \( r \) where \( g_{ab}(r) \) is forced to converge to 1. From the residuals plotted in Figs. 4.16 to 4.18 it can be seen that this equation is fitted to fewer data points than the fit to the Ar-Kr fluid. This allows the residual to be minimised, and ensures the quality of the fit is not compromised. The region of fitting is approximately 10% of the tail of the accumulated pair correlation function length. The results of these simulations are shown in Tables 4.10 and 4.11 and are subsequently used to calculated the thermodynamic factors presented in Section 4.3.3.1, at the concentrations and temperatures listed above for the colloidal fluid.
Figure 4.16: (a) Pair distribution function for the colloidal fluid \((g_{11}(r))\), (b) integral of pair distribution function \((G_{11}(r))\), and (c) residual of fit for pair distribution function and Eq. (4.1), 
\(T = 1.00\) and \(c_1 = 0.2939, \rho = 0.960\).

Figure 4.17: (a) Pair distribution function for the colloidal fluid \((g_{12}(r))\), (b) integral of pair distribution function \((G_{12}(r))\), and (c) residual of fit for pair distribution function and Eq. (4.1), 
\(T = 1.00\) and \(c_1 = 0.2939, \rho = 0.960\).

Using the values of the integrals of the pair distribution functions in Tables 4.10 and 4.11 the values of the non-ideality factor, \(Q\) are calculated from Eq. (4.4) and reported in Table 4.12. The values obtained for the colloidal fluid confirm that the assumption of ideality can not be made for this mixture.
Figure 4.18: (a) Pair distribution function for the colloidal fluid \( (g_{22}(r)) \), (b) integral of pair distribution function \( (G_{22}(r)) \), and (c) residual of fit for pair distribution function and Eq. (4.1), \( T = 1.00 \) and \( c_1 = 0.2939, \rho = 0.960 \).

Table 4.10: Integral of pair distribution functions for the colloidal fluid as a function of concentration, \( T = 1.00 \) and \( c_1 = 0.2939, \rho = 0.960 \).

<table>
<thead>
<tr>
<th>( c_1 )</th>
<th>( G_{11}(r) )</th>
<th>( G_{12}(r) )</th>
<th>( G_{22}(r) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4000</td>
<td>88.119(1)</td>
<td>28.278(1)</td>
<td>5.3318(4)</td>
</tr>
<tr>
<td>0.3500</td>
<td>90.7764(10)</td>
<td>26.4968(10)</td>
<td>5.6626(4)</td>
</tr>
<tr>
<td>0.2939</td>
<td>96.7694(6)</td>
<td>26.9444(8)</td>
<td>5.7292(1)</td>
</tr>
<tr>
<td>0.2500</td>
<td>94.285(1)</td>
<td>28.3730(9)</td>
<td>5.6216(2)</td>
</tr>
<tr>
<td>0.2000</td>
<td>95.764(3)</td>
<td>27.531(1)</td>
<td>5.9503(8)</td>
</tr>
</tbody>
</table>

Table 4.11: Integral of pair distribution functions for the colloidal fluid, \( c_1 = 0.2939, \rho = 0.969 \)

<table>
<thead>
<tr>
<th>( T )</th>
<th>( G_{11}(r) )</th>
<th>( G_{12}(r) )</th>
<th>( G_{22}(r) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05</td>
<td>97.598(4)</td>
<td>26.983(1)</td>
<td>5.6751(4)</td>
</tr>
<tr>
<td>1.00</td>
<td>97.277(2)</td>
<td>26.927(1)</td>
<td>6.1363(6)</td>
</tr>
<tr>
<td>0.95</td>
<td>93.997(3)</td>
<td>27.668(1)</td>
<td>5.5494(5)</td>
</tr>
<tr>
<td>0.90</td>
<td>84.360(3)</td>
<td>30.8268(9)</td>
<td>4.9497(8)</td>
</tr>
<tr>
<td>0.85</td>
<td>93.202(4)</td>
<td>28.991(1)</td>
<td>5.7819(8)</td>
</tr>
</tbody>
</table>
Table 4.12: Non-ideality factors for the colloidal fluid at various concentrations and temperatures.

<table>
<thead>
<tr>
<th>Mass fraction</th>
<th>Temperature</th>
<th>Density</th>
<th>$Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4000</td>
<td>1.00</td>
<td>0.960</td>
<td>0.430(2)</td>
</tr>
<tr>
<td>0.3500</td>
<td>1.00</td>
<td>0.960</td>
<td>0.419(2)</td>
</tr>
<tr>
<td>0.2939</td>
<td>1.00</td>
<td>0.960</td>
<td>0.432(1)</td>
</tr>
<tr>
<td>0.2500</td>
<td>1.00</td>
<td>0.960</td>
<td>0.499(2)</td>
</tr>
<tr>
<td>0.2000</td>
<td>1.00</td>
<td>0.960</td>
<td>0.534(3)</td>
</tr>
<tr>
<td>0.2939</td>
<td>1.05</td>
<td>0.969</td>
<td>0.428(4)</td>
</tr>
<tr>
<td>0.2939</td>
<td>1.00</td>
<td>0.969</td>
<td>0.426(3)</td>
</tr>
<tr>
<td>0.2939</td>
<td>0.95</td>
<td>0.969</td>
<td>0.455(3)</td>
</tr>
<tr>
<td>0.2939</td>
<td>0.90</td>
<td>0.969</td>
<td>0.572(3)</td>
</tr>
<tr>
<td>0.2939</td>
<td>0.85</td>
<td>0.969</td>
<td>0.474(4)</td>
</tr>
</tbody>
</table>

4.3.2 Green-Kubo relations

The correlation functions defined by Eq. (2.96), for one state point of the colloidal fluid are shown below. All GK calculations were obtained by ensemble averaging over 64 microscopically different systems at the same macroscopic state. These are all time averaged over 20 reduced time steps, however only data up to 4 reduced time units are shown in Figs. 4.19 to 4.24, as the integrals have converged by this time.
Figure 4.19: Mass flux auto-correlation function and its integral for the colloidal fluid, $T = 1.00$ and $c_1 = 0.2939$, $\rho = 0.960$.

Figure 4.20: Heat flux auto-correlation function and its integral for the colloidal fluid, $T = 1.00$ and $c_1 = 0.2939$, $\rho = 0.960$. 

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Figure 4.21: Stress auto-correlation function and its integral for the colloidal fluid, $T = 1.00$ and $c_1 = 0.2939$, $\rho = 0.960$.

Figure 4.22: Mass-heat flux cross-correlation function and its integral the colloidal fluid, $T = 1.00$ and $c_1 = 0.2939$, $\rho = 0.960$. 
Figure 4.23: Heat-mass flux cross-correlation function and its integral for the colloidal fluid, $T = 1.00$ and $c_1 = 0.2939$, $\rho = 0.960$.

Figure 4.24: Average of heat-mass flux and mass-heat flux cross-correlation function and its integral for the colloidal fluid, $T = 1.00$ and $c_1 = 0.2939$, $\rho = 0.960$. 
Table 4.13: Integrals of correlation functions for the colloidal fluid at various concentrations, $T = 1.00$ and $\rho = 0.960$.

<table>
<thead>
<tr>
<th>$c_1$</th>
<th>$L_{11}$</th>
<th>$\lambda$</th>
<th>$L_{1q}$</th>
<th>$L_{q1}$</th>
<th>$\frac{L_{1q} + L_{q1}}{2}$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4000</td>
<td>0.0280(2)</td>
<td>4.53(3)</td>
<td>-0.109(2)</td>
<td>-0.111(2)</td>
<td>-0.110(2)</td>
<td>4.06(2)</td>
</tr>
<tr>
<td>0.3500</td>
<td>0.0266(4)</td>
<td>5.13(6)</td>
<td>-0.102(4)</td>
<td>-0.111(5)</td>
<td>-0.107(4)</td>
<td>4.08(4)</td>
</tr>
<tr>
<td>0.2939</td>
<td>0.0230(3)</td>
<td>6.0(1)</td>
<td>-0.104(6)</td>
<td>-0.102(7)</td>
<td>-0.103(6)</td>
<td>4.22(3)</td>
</tr>
<tr>
<td>0.2500</td>
<td>0.0214(2)</td>
<td>6.53(7)</td>
<td>-0.099(2)</td>
<td>-0.101(4)</td>
<td>-0.100(3)</td>
<td>4.34(3)</td>
</tr>
<tr>
<td>0.2000</td>
<td>0.0177(3)</td>
<td>7.2(1)</td>
<td>-0.084(6)</td>
<td>-0.091(4)</td>
<td>-0.088(5)</td>
<td>4.45(6)</td>
</tr>
</tbody>
</table>
Table 4.14: Integrals of correlation functions for the colloidal fluid at various temperatures, $c_1 = 0.2939$, $\rho = 0.969$.

<table>
<thead>
<tr>
<th>$T$</th>
<th>$L_{11}$</th>
<th>$\lambda$</th>
<th>$L_{1q}$</th>
<th>$L_{q1}$</th>
<th>$L_{1q} + L_{q1}$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05</td>
<td>0.0223(2)</td>
<td>6.34(6)</td>
<td>-0.104(3)</td>
<td>-0.101(2)</td>
<td>-0.102(2)</td>
<td>4.31(2)</td>
</tr>
<tr>
<td>1.00</td>
<td>0.0221(1)</td>
<td>5.96(4)</td>
<td>-0.097(1)</td>
<td>-0.098(2)</td>
<td>-0.098(1)</td>
<td>4.38(2)</td>
</tr>
<tr>
<td>0.95</td>
<td>0.0214(3)</td>
<td>5.75(8)</td>
<td>-0.096(6)</td>
<td>-0.097(3)</td>
<td>-0.097(4)</td>
<td>4.57(5)</td>
</tr>
<tr>
<td>0.90</td>
<td>0.0209(2)</td>
<td>5.17(6)</td>
<td>-0.087(3)</td>
<td>-0.083(6)</td>
<td>-0.085(4)</td>
<td>4.62(5)</td>
</tr>
<tr>
<td>0.85</td>
<td>0.0204(3)</td>
<td>4.97(5)</td>
<td>-0.078(4)</td>
<td>-0.081(5)</td>
<td>-0.079(5)</td>
<td>4.80(6)</td>
</tr>
</tbody>
</table>

4.3.3 Concentration and temperature dependent static properties

4.3.3.1 Thermodynamic factor

The thermodynamic factor is calculated from the integral of pair distributions from Tables 4.10 and 4.11 using Eq. (2.59). It can be seen that the value of the mutual diffusion coefficient, $D_m$, will change as a result of the concentration and temperature dependence of the thermodynamic factor.

Table 4.15: Thermodynamic factors for the colloidal fluid at various concentrations, $T = 1.00$ and $\rho = 0.960$.

<table>
<thead>
<tr>
<th>$c_1$</th>
<th>$\frac{\partial \mu_1}{\partial c_1}$</th>
<th>$\frac{\partial \mu_2}{\partial c_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4000</td>
<td>0.0963(5)</td>
<td>-0.125(1)</td>
</tr>
<tr>
<td>0.3500</td>
<td>0.118(1)</td>
<td>-0.1177(1)</td>
</tr>
<tr>
<td>0.2939</td>
<td>0.147(5)</td>
<td>-0.0968(5)</td>
</tr>
<tr>
<td>0.2500</td>
<td>0.218(2)</td>
<td>-0.079(1)</td>
</tr>
<tr>
<td>0.2000</td>
<td>0.314(8)</td>
<td>-0.067(5)</td>
</tr>
</tbody>
</table>

The thermodynamic factor of component 1 remains positive over the range of systems studied. It is known that in highly immiscible mixtures, such as water-butane, the thermodynamic factor may be negative which corresponds to a thermodynamic instability [84]. These systems may split into two liquid phases and contain negative diffusion coefficients in the immiscible region. This system maintains a positive thermodynamic factor showing that the solution is thermally stable at all concentrations and temperatures studied.
Table 4.16: Thermodynamic factors for the colloidal fluid at various temperatures, \( c_1 = 0.2939, \rho = 0.969 \).

<table>
<thead>
<tr>
<th>( T )</th>
<th>( \frac{\partial \mu_1}{\partial c_1} )</th>
<th>( \frac{\partial \mu_2}{\partial c_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05</td>
<td>0.159(4)</td>
<td>-0.1027(1)</td>
</tr>
<tr>
<td>1.00</td>
<td>0.147(5)</td>
<td>-0.968(5)</td>
</tr>
<tr>
<td>0.95</td>
<td>0.14(1)</td>
<td>-0.0894(2)</td>
</tr>
<tr>
<td>0.90</td>
<td>0.177(3)</td>
<td>-0.0715(1)</td>
</tr>
<tr>
<td>0.85</td>
<td>0.141(1)</td>
<td>-0.07587(5)</td>
</tr>
</tbody>
</table>

In Fig. 4.25 the thermodynamic factor is shown at the concentrations studied here. Although we could not fit this data set, there is an observable decrease in the thermodynamic factor as the mass fraction of component 1 increases.

![Figure 4.25](image)

**Figure 4.25:** Thermodynamic factor for the colloidal fluid as a function of concentration, \( T = 1.00 \) and \( \rho = 0.960 \).

The thermodynamic factor can be seen to increase with temperature in Fig. 4.26 below.
4.3.3.2 Partial specific enthalpy

The partial enthalpies required for our calculation of the transport coefficients are shown in Table 4.17 for the concentration and temperature dependent systems. The concentration dependencies can be seen graphically in Figs. 4.27 and 4.28, and for the temperature dependent partial enthalpies Figs. 4.29 and 4.30, for component 1, the colloid and 2, the solvent particles respectively. These values are calculated at constant temperature and pressure as seen in Eq. (2.13).
Table 4.17: Partial specific enthalpies for the colloidal fluid at various concentrations and temperatures.

<table>
<thead>
<tr>
<th>Mass fraction</th>
<th>Temperature</th>
<th>Density</th>
<th>$\bar{h}_1$</th>
<th>$\bar{h}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4000</td>
<td>1.00</td>
<td>0.960</td>
<td>5.87(2)</td>
<td>11.45(4)</td>
</tr>
<tr>
<td>0.3500</td>
<td>1.00</td>
<td>0.960</td>
<td>6.33(2)</td>
<td>12.03(4)</td>
</tr>
<tr>
<td>0.2939</td>
<td>1.00</td>
<td>0.960</td>
<td>6.85(2)</td>
<td>12.74(3)</td>
</tr>
<tr>
<td>0.2500</td>
<td>1.00</td>
<td>0.960</td>
<td>7.26(2)</td>
<td>13.13(3)</td>
</tr>
<tr>
<td>0.2000</td>
<td>1.00</td>
<td>0.960</td>
<td>7.77(2)</td>
<td>13.85(5)</td>
</tr>
<tr>
<td>0.2939</td>
<td>1.05</td>
<td>0.969</td>
<td>7.40(2)</td>
<td>13.51(4)</td>
</tr>
<tr>
<td>0.2939</td>
<td>1.00</td>
<td>0.969</td>
<td>7.11(2)</td>
<td>12.94(4)</td>
</tr>
<tr>
<td>0.2939</td>
<td>0.95</td>
<td>0.969</td>
<td>6.83(2)</td>
<td>12.58(4)</td>
</tr>
<tr>
<td>0.2939</td>
<td>0.90</td>
<td>0.969</td>
<td>6.57(5)</td>
<td>12.07(4)</td>
</tr>
<tr>
<td>0.2939</td>
<td>0.85</td>
<td>0.969</td>
<td>6.27(1)</td>
<td>11.55(4)</td>
</tr>
</tbody>
</table>

Figure 4.27: Partial enthalpy of component 1 for the colloidal fluid as a function of concentration, $T = 1.00$ and $\rho = 0.960$. 

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Figure 4.28: Partial enthalpy of component 2 for the colloidal fluid as a function of concentration $T = 1.00$ and $\rho = 0.960$.

Figure 4.29: Partial enthalpy of component 1 for the colloidal fluid as a function of temperature, $c_1 = 0.2939$, $\rho = 0.969$. 
Figure 4.30: Partial enthalpy of component 2 for the colloidal fluid as a function of temperature, $c_1 = 0.2939$, $\rho = 0.969$.

Each of these dependencies shows a linear relationship. For the concentration dependence,

$$h_1(c) = -9.64c + 9.64 \quad (4.7)$$

and

$$h_2(c) = -11.81c + 16.17, \quad (4.8)$$

and for the temperature dependence,

$$h_1(T) = 5.60T + 1.52 \quad (4.9)$$

and

$$h_2(T) = 9.58T + 3.43. \quad (4.10)$$

These relations are expected to hold as either the concentration or temperature increase or decreases outside of the range simulated.

### 4.3.3.3 Partial specific volumes

The partial volumes are also calculated using Eq. (4.6) for the colloidal mixtures and results are shown in Table 4.18. The concentration dependencies can be seen graphically in Figs. 4.31 and 4.32. All values are calculated at constant temperature and pressure.
Table 4.18: Partial specific volumes for the colloidal fluid at various concentrations and temperatures.

<table>
<thead>
<tr>
<th>Mass fraction</th>
<th>Temperature</th>
<th>Density</th>
<th>$v_1$</th>
<th>$v_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4000</td>
<td>1.00</td>
<td>0.960</td>
<td>0.793(3)</td>
<td>1.209(4)</td>
</tr>
<tr>
<td>0.3500</td>
<td>1.00</td>
<td>0.960</td>
<td>0.785(2)</td>
<td>1.180(5)</td>
</tr>
<tr>
<td>0.2939</td>
<td>1.00</td>
<td>0.960</td>
<td>0.775(2)</td>
<td>1.157(4)</td>
</tr>
<tr>
<td>0.2500</td>
<td>1.00</td>
<td>0.960</td>
<td>0.767(2)</td>
<td>1.129(4)</td>
</tr>
<tr>
<td>0.2000</td>
<td>1.00</td>
<td>0.960</td>
<td>0.761(2)</td>
<td>1.107(4)</td>
</tr>
<tr>
<td>0.2939</td>
<td>1.05</td>
<td>0.960</td>
<td>0.771(3)</td>
<td>1.140(4)</td>
</tr>
<tr>
<td>0.2939</td>
<td>1.00</td>
<td>0.969</td>
<td>0.773(4)</td>
<td>1.135(6)</td>
</tr>
<tr>
<td>0.2939</td>
<td>0.95</td>
<td>0.969</td>
<td>0.771(3)</td>
<td>1.141(4)</td>
</tr>
<tr>
<td>0.2939</td>
<td>0.90</td>
<td>0.969</td>
<td>0.771(3)</td>
<td>1.139(4)</td>
</tr>
<tr>
<td>0.2939</td>
<td>0.85</td>
<td>0.969</td>
<td>0.772(2)</td>
<td>1.135(4)</td>
</tr>
</tbody>
</table>

Figure 4.31: Partial volume of component 1 for the colloidal fluid as a function of concentration, $T = 1.00$ and $\rho = 0.960$. 

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Figure 4.32: Partial volume of component 2 for the colloidal fluid as a function of concentration $T = 1.00$ and $\rho = 0.960$.

The concentration dependencies for the partial volumes show the linear relationships

$$v_1(c) = 0.164c + 0.7272 \quad (4.11)$$

and

$$v_2(c) = 0.509c + 1.004. \quad (4.12)$$

For the temperature dependent partial volumes the values do not change within the reported errors over the range of the temperatures studied here.

### 4.3.4 Concentration and temperature dependent transport properties

The values obtained for the thermodynamic factor, partial enthalpies and Green-Kubo correlation functions allow us to calculate the transport coefficients for the colloidal fluid as a function of concentration and temperature using the relations in Eqs. (2.90) to (2.93). Table 4.19 summarises all of the concentration and temperature dependent transport properties, at the end of this section. We highlight the trends of the coefficients in Sections 4.3.4.1 to 4.3.4.3.
4.3.4.1 Mutual diffusion, thermal diffusion and Soret coefficients, and the thermal diffusion factor

From Fig. 4.33 the value of the mutual diffusion coefficient, \( D_m \), is seen to decrease with concentration. However the mutual diffusion coefficient does not exhibit an obvious quantifiable relation to temperature, seen in Fig. 4.34.

![Graph showing mutual diffusion coefficient as a function of concentration](image)

Figure 4.33: Diffusion coefficient of the colloidal fluid as a function of concentration, \( T = 1.00 \) and \( \rho = 0.960 \).
The thermal diffusion coefficient $D'$ shows a distinct linear relationship with concentration, described by the equation

$$D'(c) = 0.42c + 0.04$$  \hspace{1cm} (4.13)

which is shown below in Fig. 4.35 as the fitted red line. This relation is used to obtain the Soret coefficient used in the continuum description of the temperature dependent concentration profile in Ch. 5, where the colloidal fluid is confined between two walls at different temperatures with no flow.
There also exists a decreasing linear relationship with increasing temperature for $D'$ of the form

$$D'(T) = -0.21T + 0.37.$$ \hspace{1cm} (4.14)

This can be seen below in Fig. 4.36.
Figure 4.36: Thermal diffusion coefficient for the colloidal fluid as a function of temperature, $c_1 = 0.2939$, $\rho = 0.969$.

By taking the ratio of the thermal and mutual diffusion coefficients we obtain the Soret coefficient, shown as a function of concentration and temperature. Multiplying the Soret coefficient by $T$ gives us the thermal diffusion factor $\alpha$ as defined by Eq. (2.102). For the concentration dependent systems the Soret coefficient and thermal diffusion factor are equal as $T = 1.00$. For the temperature dependent systems the thermal diffusion factor can be seen in Fig. 4.39.
Figure 4.37: Soret coefficient for the colloidal fluid as a function of concentration, $T = 1.00$ and $\rho = 0.960$.

The Soret coefficient shows a linear relation to concentration that is well described by the equation

$$S_T(c) = \frac{D'}{D_m}(c) = 141c - 11.$$  \hspace{1cm} (4.15)

As this relation is mapped out over a large range of concentrations, it is expected to hold as the colloid becomes more dilute or concentrated at a temperature of 1.00.

The Soret coefficient and thermal diffusion factor are shown as a function of temperature in Figs. 4.38 and 4.39.
Both of these again show a linear relation, decreasing as the temperature increases. For the Soret coefficient

\[ S_T(T) = \frac{D'}{D_m}(T) = -49.61T - 83.07 \]  

(4.16)

and for the thermal diffusion factor
The gradients of $S_T(T)$ and $S_T(c)$ are significant. When obtaining the temperature dependent concentration profile of Eq. (2.161), we assume a constant value of $S_T$ as the temperature difference is only 0.005 at each wall. It is clear that if the observed temperature profile changes by even as little as 1% then we can not assume that the Soret coefficient remains constant.

4.3.4.2 Thermal conductivity

As with the previous transport properties of the colloidal fluid, the thermal conductivity is calculated from the theory of Ch. 2. From the values obtained there is a clear decrease in thermal conductivity as a function of concentration and temperature.

![Graph showing thermal conductivity as a function of concentration](image)

Figure 4.40: Thermal conductivity for the colloidal fluid as a function of concentration, $T = 1.00$ and $\rho = 0.960$. 

\[
\alpha(T) = -11.5T + 44.83. \quad (4.17)
\]
The relationship of thermal conductivity to concentration and temperature can be well described by the respective equations

\[ \lambda(c) = -12.94c - 9.92, \quad (4.18) \]

and

\[ \lambda(T) = -5.50T + 11.08. \quad (4.19) \]

When utilised in either the simplified approximation to the temperature profile prediction in Eq. (2.145), or when incorporating the coupling to the gradient of the strain rate as in Eq. (6.5), the thermal conductivity term should only be assumed constant when the temperature or concentration variation observed across the confined system is relatively small.

4.3.4.3 Viscosity

From the stress auto-correlation function we can calculate the viscosity of the bulk fluid. The concentration and temperature dependence of the viscosity are shown in Figs. 4.42 and 4.43 respectively.
The relationship of viscosity to concentration is reasonably described by the quadratic function

\[ \eta(c) = 5.49c^2 - 5.40c + 5.33. \]  

(4.20)

The temperature dependent viscosity is very well described by the equation

\[ \eta(T) = (0.9228T + 0.6921) \cdot e^{\frac{1}{T}}. \]  

(4.21)

This relation is seen as the red fitted line in Fig. 4.43.
The values of the viscosity are in reasonable agreement with those obtained by Kairn, who obtained a value for the viscosity of 4.10(6) at $T = 1.0$, $\rho = 0.960$ and $c_1 = 0.2939$ [15]. The viscosity is seen to vary with both concentration and temperature, although not as significantly as does the thermal conductivity or the Soret coefficient. Again it seems prudent to ensure that for the continuum mechanics description of the temperature profile in Eqs. (2.145) and (6.5) to be correct with the assumption of constant viscosity, neither the temperature nor the concentration should vary significantly over the channel width. This is also true for the velocity profiles predicted by Eq. (2.131).

### 4.3.5 Summary of colloidal fluid transport properties

Table 4.19 below provides a summary of the transport properties for the colloidal fluid at the concentrations and temperatures in the preceding sections.
Table 4.19: Transport properties of the colloidal fluid at various concentrations and temperatures.

<table>
<thead>
<tr>
<th>$c_1$</th>
<th>$T$</th>
<th>$\rho$</th>
<th>$D_m$</th>
<th>$D'$</th>
<th>$S_T$</th>
<th>$\alpha$</th>
<th>$\lambda'$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4000</td>
<td>1.00</td>
<td>0.960</td>
<td>0.0046(2)</td>
<td>0.20(2)</td>
<td>43(4)</td>
<td>4.17(5)</td>
<td>4.06(2)</td>
<td></td>
</tr>
<tr>
<td>0.3500</td>
<td>1.00</td>
<td>0.960</td>
<td>0.0050(1)</td>
<td>0.21(3)</td>
<td>41(6)</td>
<td>4.8(1)</td>
<td>4.08(4)</td>
<td></td>
</tr>
<tr>
<td>0.2939</td>
<td>1.00</td>
<td>0.960</td>
<td>0.0051(4)</td>
<td>0.16(3)</td>
<td>32(5)</td>
<td>5.47(9)</td>
<td>4.22(2)</td>
<td></td>
</tr>
<tr>
<td>0.2500</td>
<td>1.00</td>
<td>0.960</td>
<td>0.0065(1)</td>
<td>0.14(2)</td>
<td>22(4)</td>
<td>6.09(10)</td>
<td>4.34(3)</td>
<td></td>
</tr>
<tr>
<td>0.2000</td>
<td>1.00</td>
<td>0.960</td>
<td>0.0072(2)</td>
<td>0.13(4)</td>
<td>18(6)</td>
<td>6.8(2)</td>
<td>4.45(6)</td>
<td></td>
</tr>
<tr>
<td>0.2939</td>
<td>1.05</td>
<td>0.969</td>
<td>0.0049(1)</td>
<td>0.154(6)</td>
<td>31(1)</td>
<td>5.37(8)</td>
<td>4.31(2)</td>
<td></td>
</tr>
<tr>
<td>0.2939</td>
<td>1.00</td>
<td>0.969</td>
<td>0.0048(4)</td>
<td>0.157(7)</td>
<td>33(1)</td>
<td>5.58(6)</td>
<td>4.38(2)</td>
<td></td>
</tr>
<tr>
<td>0.2939</td>
<td>0.95</td>
<td>0.969</td>
<td>0.0048(3)</td>
<td>0.172(7)</td>
<td>36(2)</td>
<td>5.77(6)</td>
<td>4.49(1)</td>
<td></td>
</tr>
<tr>
<td>0.2939</td>
<td>0.90</td>
<td>0.969</td>
<td>0.0045(4)</td>
<td>0.18(1)</td>
<td>40(3)</td>
<td>6.07(7)</td>
<td>4.62(3)</td>
<td></td>
</tr>
<tr>
<td>0.2939</td>
<td>0.85</td>
<td>0.969</td>
<td>0.0049(1)</td>
<td>0.195(7)</td>
<td>40(2)</td>
<td>6.5(1)</td>
<td>4.80(6)</td>
<td></td>
</tr>
</tbody>
</table>

The densities studied in Table 4.19 represent two densities for the colloidal fluid. The first is the average density of the total fluid confined between parallel plates, $\rho = 0.960$. The second is the average density calculated from the observed density profiles in the colloidal systems where the effects of particle layering have dissipated, $\rho = 0.969$. Interestingly from Table 4.19 it can be seen that the transport properties of the colloidal fluid calculated at the same concentration and temperature are within the error at these two densities, except for $\eta$, the value of the viscosity.

### 4.4 Conclusions

By examining the pair distribution function for the binary system it is possible to evaluate static properties such as the thermodynamic factor and partial specific enthalpy for binary systems, and also quantify the degree of ideality of the fluid. The equimolar Ar-Kr fluid is found to be non-ideal, and we have used the thermodynamic factor to calculate the mutual diffusion coefficient, as far as we are aware at the time of this publication, for the first time.

Accounting for the effects of heat conduction and diffusion as the result of the inclusion of a second species has also been achieved for the first time when evaluating fluid transport coefficients. In particular we have shown that the method presented in this work is required to successfully calculate the correct value of thermal diffusion coefficient for equimolar Ar-Kr. The ratio of mutual diffusion and thermal diffusion coefficients have been shown to be in agreement with results in literature, and we believe for the first time the correct values of the
coefficients have been reported individually.

By comparison with previous work available in the literature, we have validated our method of calculating transport coefficients for binary systems. Applying the method to a slightly more realistic colloidal fluid model, we have elucidated the concentration and temperature dependency of the transport coefficients. These results are significant in their own right, and they will also help us to understand the temperature and concentration gradient contributions to the migration of particles in confined systems, in the following chapters.
Chapter 5

Temperature gradient NEMD

5.1 Introduction

In this chapter we will use the transport coefficients obtained in Ch. 4 for equimolar Ar-Kr, to predict the concentration profile of a confined fluid in a temperature gradient. This fluid is subject to an imposed temperature difference, by maintaining planar solid walls at different temperatures, causing a migration of colloid and solvent particles until they reach a steady state. We will also confirm the transport coefficients and our prediction of the concentration profile for the colloidal fluid in an equivalent simulation.

5.2 Confinement and system sizes

5.2.1 Confinement

A simple geometry is used in our work to allow us to understand how the transfer of mass and energy behaves in a confined fluid. It contains an effectively infinite periodic bulk material confined between two planes of infinite area, at a finite separation. The principle of periodic boundary conditions is utilised in the $x$ and $z$ coordinates to replicate an infinite confined bulk.

In Figs. 5.1 and 5.2 a snapshot of a simulated fluid at equilibrium, with suspended colloidal particles confined between two walls is displayed. Fig. 5.1 has the background medium of solvent particles reduced to points for clarity, the wall particles maintaining the real diameter ratio. Fig. 5.2 has all particles drawn to scale.

These figures only display a single system. All profiles obtained for the confined equimolar Ar-Kr and colloidal fluids are obtained by ensemble averaging the observed profiles over
32 macroscopically identical, but microscopically different systems. The N-H thermostat discussed in Section 3.2.1 is used to change the microscopic state of each system by applying a slightly increasing thermostat to each system, and then re-equilibrating at the desired temperature. The Gaussian type thermostat is also used to maintain the wall temperature for the confined systems.
Figure 5.1: Confined colloidal fluid with fluid solvent particles depicted as points for clarity, $T = 1.0$, $\rho = 0.96$, $c_1 = 0.2939$ [85].
Figure 5.2: Confined colloidal fluid with all particles represented at their actual size. $T = 1.0$, $\rho = 0.96$, $c_1 = 0.2939$ [85].
5.2.2 System sizes

The sizes of the confined systems studied in this and the following chapters are summarised in the Table 5.1.
Table 5.1: Confined binary solution parameters and lengths, $T = 1.00$, $c_1 = 0.2939$.

<table>
<thead>
<tr>
<th>Type</th>
<th>$N$</th>
<th>$N_{12}$</th>
<th>$N_1$</th>
<th>$N_2$</th>
<th>$n_1$</th>
<th>$\rho$</th>
<th>$V$</th>
<th>$L_x$</th>
<th>$L_y$</th>
<th>$L_z$</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-Kr</td>
<td>16896</td>
<td>15360</td>
<td>7680</td>
<td>7680</td>
<td>0.3574</td>
<td>1.101</td>
<td>21490.58</td>
<td>17.6697</td>
<td>85.0000</td>
<td>15.3024</td>
<td>79.4803</td>
</tr>
<tr>
<td>Colloid</td>
<td>16896</td>
<td>15360</td>
<td>614</td>
<td>14746</td>
<td>0.03997</td>
<td>0.962</td>
<td>21710.04</td>
<td>17.6697</td>
<td>85.8737</td>
<td>15.3024</td>
<td>80.2921</td>
</tr>
</tbody>
</table>
5.3 Equimolar Argon-Krypton

5.3.1 Temperature profile of a temperature difference system

In Ch. 4 we have obtained a value for the Soret coefficient of 1.6(1) for a bulk equimolar Ar-Kr fluid at a temperature of 0.965. The Soret coefficient appears as the ratio of the thermal diffusion and mass diffusion coefficients in the continuum mechanics description of Eq. (2.161). The temperature dependent concentration profile is predicted by the continuum description for a fluid subject to walls thermostated via a Gaussian type thermostat at the temperatures of 0.915 and 1.015 utilising the Soret coefficient independently calculated from the bulk. This further confirms the method used to obtain the transport coefficients, $D'$ and $D_m$, and also the continuum relationship in Eq. (2.161).

However we were unable to make any reasonable prediction of the observed temperature profile, which can be seen to be non-linear in Fig. 5.3 and is plotted as blue data points. For the colloidal fluid we observe a linear profile, and we predict the temperature profile with Eq. (5.4) in Section 5.4.1. We are unable to use the assumption that the transport coefficients, namely the thermal conductivity and viscosity, do not vary across the channel. Instead we use a fit to the observed temperature profile in the confined system which is quadratic. The concentration profile of Fig. 5.4 has an increase of 3% in the concentration of the Kr component at the cooler wall. Decreasing the temperature difference of the walls may lead to a linear and predictable temperature profile, however we expect this will result in a concentration profile that is indiscernible from the noise.
The temperature profile is well described by the quadratic function

\[ T(y) = -0.000095y^2 + 0.00196y + 0.92. \]  

(5.1)

The difference between the last value of the quadratic and the set value of the lower wall temperature of 0.915 suggests that there is a temperature jump of 0.05 at the walls for the confined equimolar Ar-Kr system.

### 5.3.2 Concentration profile and the continuum description

The predicted concentration profile is shown (red line) with the observed concentration (blue symbols) for a confined equimolar Ar-Kr fluid in Fig. 5.4. The continuum description of Eq. (2.161) holds valid, despite the non-uniformity of the density profile in Fig. 5.5, and the significant magnitude of the temperature difference between the walls. This suggests the assumption of a uniform Soret coefficient is valid as used in the continuum description. We have used the observed temperature profile in Fig. 5.3 to make the prediction in Fig. 5.4.
Figure 5.4: Krypton concentration profile for confined temperature difference system with wall temperatures of $T=0.915$ and 1.015.

The effects of mass diffusion and heat diffusion have led to a concentration difference of approximately 3% at a distance of $7\sigma$ from the walls where the density fluctuations due to packing have subsided.

5.3.3 Density profile of a temperature difference system

The density profile for the equimolar Ar-Kr fluid is seen in Fig. 5.5, where packing can be seen at the region close to the walls.
Figure 5.5: Equimolar Argon-Krypton density profile for confined temperature difference system with wall temperatures of T=0.915 and 1.015.

The linear fit of the density profile takes the form

\[ \rho(y) = -0.00061y + 1.1256. \]  

(5.2)

There is an approximate density variation of 3.3% at a distance of 7σ in from the wall, where the density variation becomes uniform and wall packing effects have stopped.

5.4 The colloidal fluid

5.4.1 Temperature profile of a temperature difference system

The confining walls for the colloidal fluid are thermostatted at 0.995 on the left of Fig. 5.6 and 1.0 on the right side. This temperature difference is significantly smaller than the difference applied for the Ar-Kr fluid, yet still results in a discernible concentration profile observed in Fig. 5.7. The temperature profile is linear, and trends from 0.995 to 1.0 without any temperature jump at the walls.

As the temperature difference is small, we assume constant thermal conductivity and that the effects of thermal diffusion on the temperature profile are negligible. The temperature profile
can be predicted from Eq. (2.143), where in this simulation

$$\frac{\partial^2 T}{\partial y^2} = 0. \quad (5.3)$$

Integrating twice we obtain the simple linear relation

$$T(y) = ay + b \quad (5.4)$$

where $a$ and $b$ are the constants of integration. This can be determined by the values of the wall temperatures, $T_1 = 0.995$ and $T_2 = 1.000$ resulting in the prediction of the temperature profile

$$T(y) = 0.0000625y + 0.995. \quad (5.5)$$

This prediction is shown as the red line in Fig. 5.6.
5.4.2 Concentration profile and the continuum description

The average concentration in the region where density is no longer affected by the walls from approximately $7\sigma$ to $73\sigma$ is 0.2889. Using Eq. (4.15) which is the relation between the Soret coefficient and concentration, we obtain $S_T = 25$. Using this value we can obtain an excellent prediction with no free parameters, of the temperature dependent concentration profile seen in Fig. 5.7 as the red line. This further confirms the method we have employed to calculate

![Figure 5.7: Colloid concentration profile for a temperature difference with wall temperature of $T=0.995$ and 1.0.](image)

the transport coefficients, and the continuum description of the temperature dependent concentration profile from Eq. (2.161). The assumption of using a constant value for the Soret coefficient, $S_T$ is reasonable, as the concentration and temperature differences are small. The colloidal species has migrated to the cold wall and the concentration has increased by 6.5%.

5.4.3 Density profiles of a temperature difference system

There is no discernible density difference across the channel of fluid when we apply the temperature difference of 0.005, other than the effects of packing at the region close to the walls. This can be seen in Fig. 5.8 below.
Figure 5.8: Colloid density profile for a temperature difference system with wall temperatures of $T=0.995$ and 1.0.

5.5 Conclusions

We have successfully shown that the transport coefficients obtained from a bulk fluid can be used to make predictions about the concentration profile across the channel of a colloidal fluid when subject to two different temperatures at the walls. The appropriate treatment for binary systems of the coefficient $D'$ and the calculation of the thermodynamic factor $\frac{\partial \mu_1}{\partial c_1}$ to be included when determining $D_m$, has led to a value of the Soret coefficient, $S_T$, that is used in the continuum description of the temperature dependent concentration profile for two different fluids. For systems with a small temperature difference and in the absence of flow, the assumption that the coefficients remain constant over the width of the channel is reasonable.

The application of this simple arrangement is promising, as even a small temperature difference of 0.005 for the colloidal fluid, led to a separation of 6.5%. In the following chapter we will look at a situation where the same confined fluid is undergoing Poiseuille flow with the two walls thermostated at the same temperature, to appreciate how temperature differences that are caused by the viscous heating effect the concentration profile in the same confining geometry.


Chapter 6

Poiseuille flow in the low flow regime

6.1 Introduction

In this chapter we apply a gravity like field to both the confined equimolar Ar-Kr fluid, and the colloidal fluid with the walls equally thermostated. We use the transport coefficients obtained in Ch. 4 to test our prediction of the temperature profile presented in Ch. 2. We demonstrate here that in the low flow rate regime, including the gradient of the strain rate and a coupling term allows for a very good description of the temperature profile for binary systems. We show how the observed temperature profile is used to calculate the coupling coefficient $\xi$. We also find that the temperature dependent concentration profile can be predicted using the Soret coefficient obtained in Ch. 4, with the continuum description presented in Ch. 2.

6.2 Velocity profiles and continuum predictions

Evaluating the Navier-Stokes equations for planar Poiseuille flow, with the assumption of constant transport coefficients across the channel and zero wall-slip, results in a quadratic prediction for the velocity profile with zero velocity at the walls. In this chapter where we apply a field of $F_e = 0.0001$ to the confined Ar-Kr and colloidal fluids, we find that the quadratic prediction holds in a channel width of $80\sigma$, however we need to account for the effects of wall-slip. This is done by shifting the Navier-Stokes prediction from Eq. (2.131) for the velocity profile in the $y$-direction by a factor which is determined from the observed velocity profiles. The potential for wall-slip to occur in dense fluids was appreciated by Navier for liquid flowing past a solid surface [86].

Navier’s hypothesis of wall-slip can be written in a form that relates the fluid velocity at the solid surface to the shear experienced in that region [87].
\[ v_w = \beta \left( \frac{dv_x}{dy} \right) = \beta \gamma_w \]  

(6.1)

Here \( \beta \) is the slip length. Rather than trying to relate the slip length to the strain rate, we instead choose a constant value for the slip length term, and the velocity profiles are shifted up the vertical axis by the determined constant value. Equation (2.131) now becomes

\[ v_x(y) = -\frac{\rho F_e}{2\eta} \left( y^2 - \frac{L^2}{4} \right) + v_w \]

(6.2)

including the streaming velocity of the fluid at wall, \( v_w \). Slip depends on a range of characteristics including but not limited to the composition of the wall and fluid, the interaction strength between them, the structure of the wall, the density of the wall surface and fluid, temperature, and viscosity [88]. Recent work in literature has shown that an intrinsic wall-fluid friction coefficient can be obtained from a single macroscopic EMD state point, by ensemble averaging simulations of the specific wall-fluid interaction in question [89]. This method has been applied to the slip length of water on graphene [90]. In this study, we have simply taken the wall velocity \( v_w \) from the NEMD simulations as the difference between the predicted velocity profiles excluding slip, and the observed velocity profiles.

### 6.2.1 Velocity profile of equimolar argon-krypton

When we apply the field in the \( x \)-direction to the Ar-Kr fluid, a quadratic velocity profile is obtained across the channel. The quadratic description of the velocity profile in Eq. (6.2) has the value \( v_w = 0.0008(3) \). With the inclusion of the fluid velocity at the wall, the prediction is shown in red in Fig. 6.1, in excellent agreement with the observed profile. The viscosity used in the prediction is assumed to be constant across the channel, at a value of 2.581(9) obtained from Table 4.7. This value is calculated as per the theory presented in Section 2.8, and the density is taken to be the average density across the channel of 1.105.
6.2.2 Velocity profile of the colloidal fluid

With an applied field of 0.0001, a quadratic velocity profile is also obtained across the channel of the colloidal fluid. With the value of the wall velocity being $v_w = 0.0006(2)$, the quadratic description of the velocity profile of Eq. (6.2) is shown in red in Fig. 6.2. Again this is in excellent agreement with the observed profile. The viscosity used in the prediction is 4.22(2) obtained from Table 4.19, and assumed to be constant across the channel with an average density of 0.960.
The existence of slip for this system of a relatively wide channel, and low flow rate was observed as a result of ensemble averaging 32 systems over 8, $10^7$ step runs with a time step of 0.001. This significant set of time averaged data was necessary to obtain the temperature profiles in the following section, and has also allowed us to measure a very accurate value of $v_w = 0.0006(2)$, despite the small value of the slip. We believe this is the first case of slip being observed and quantified at such low fields for this fluid.

### 6.2.3 Reynolds, Péclet and Weissenberg numbers of the colloidal fluid

Table 6.1 below summarises the Reynolds, Péclet and Weissenberg numbers for the colloidal fluid subject to field of $F_e = 0.0001$. The Péclet number is calculated using the pure solvent viscosity $\eta_0$, calculated by Kairn [15]. The value of 2.252(2) is obtained in the work by Kairn for a solvent that is made up of the same solvent particles, and at the same temperature and density of the colloidal fluid used in this work.

The Weissenberg number requires the viscoelastic relaxation time $\tau = 4$, which is calculated from the stress autocorrelation function obtained for the bulk colloidal fluid in Ch. 4. Both the Weissenberg and Péclet numbers have been calculated as the maximum values at the region near the walls, where the strain rate is greatest.
Table 6.1: Reynolds, Péclet and Weissenberg numbers of the colloidal fluid with channel width 80σ, an applied field of F_e = 0.0001, and maximum strain rate ˙γ = 0.00091(1).

<table>
<thead>
<tr>
<th>Re</th>
<th>Pe</th>
<th>We</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1206(6)</td>
<td>0.00282(3)</td>
<td>0.0036</td>
</tr>
</tbody>
</table>

Because Re is sufficiently small, this indicates laminar flow. At the walls where the strain rate is largest, its value is ˙γ = 0.00091(1). For a similar colloidal fluid studied here, McPhie, Daivis and Snook showed non-Newtonian effects are absent that at this strain rate [55]. This is also confirmed with We being much smaller than 1. We also conclude that transport by diffusion dominates over advection, as Pe is also much less than 1.

6.3 Temperature profiles and the continuum predictions

The continuum treatment in the Navier-Stokes limit, which does not include the effects of thermal diffusion and the coupling to the gradient of the strain rate, predicts a quartic temperature profile [33]. This prediction relies on there being no temperature-jump at the walls, a uniform value of the thermal conductivity, λ, and viscosity, η, and finally the assumption of uniform density across the channel as per Eq. (2.145).

Even at the low field of 0.0001, temperature jump is observed for the Ar-Kr fluid. It is not observed in the colloidal fluid at this field. Mansour, Baras and Garcia [34], in a Monte Carlo simulation of a dilute gas undergoing planar Poiseuille flow observed a jump in temperature in relatively wide channels. Both McPhie [57] and Kairn [15] observed temperature jumps in shearing and Poiseuille type flows respectively. McPhie’s work used particles of different mass but equal size, and Kairn’s work utilised the same colloidal fluid studied here. McPhie hypothesised that the temperature jump may due to the increased presence of the heavier particles at the walls.

For the equimolar Ar-Kr fluid we have included the jump in temperature in a method similar to the inclusion of wall-slip for the velocity profiles. The equations for the continuum mechanics prediction of the temperature profiles include, where necessary, a shifted temperature profile. For both the quartic temperature profile of Eq. (2.145), and prediction including the gradient of the strain per Eq. (6.5), we add △T_w. The value of temperature jump is obtained from the observed temperature profiles.

We observe for both equimolar Ar-Kr and the colloidal fluid, that we can neglect the con-
tribution of the thermal diffusion term in the prediction of the temperature profiles. Using our definition of the primed heat flux in Eq. (2.148) and assuming negligible thermal diffusivity

\[- \nabla \cdot \mathbf{J}_q' = \frac{d^2 T}{dy^2} + \frac{\xi}{\lambda} \left( \frac{d \dot{\gamma}}{dy} \right)^2. \tag{6.3}\]

Using the definition of $\dot{\gamma}$ from Eq. (2.129) and the velocity profile in the $x$-direction for planar Poiseuille flow of Eq. (2.131), we obtain for the strain rate

\[\dot{\gamma} = \frac{\partial}{\partial y} \left( -\frac{\rho F_e^2}{2\eta} \left( \frac{y^2}{4} - \frac{L^2}{4} \right) \right) = -\frac{\rho F_e^2}{\eta}. \tag{6.4}\]

Using the knowledge that in the steady state only the heat flux and viscous dissipation terms of Eq. (2.139) are non-zero,

\[- \nabla \cdot \mathbf{J}_q' - \mathbf{P}^T : \nabla \mathbf{v} = 0,\]

and the evaluation of the dissipation term from Eq. (2.141)

\[\mathbf{P}^T : \nabla \mathbf{v} = -\frac{\rho^2 (F_e)^2 y^2}{\eta},\]

from Eq. (6.3), we obtain an equation for the temperature

\[\frac{d^2 T}{dy^2} = -\frac{\rho^2 (F_e)^2 y^2}{\eta \lambda} - \frac{\xi \rho^2 (F_e)^2}{\lambda \eta^2}. \tag{6.5}\]

Having evaluating the transport coefficients $\lambda$ and $\eta$ in Ch. 4, we have obtained values for the coupling coefficient $\xi$ numerically, from the observed temperature profiles of the Ar-Kr and colloidal fluids in the following sections.

### 6.3.1 Temperature profile of equimolar argon-krypton

Figure 6.3 below shows the observed temperature profile with the continuum prediction of Eq. (2.145) including the value of the temperature jump, $\Delta T_w = 0.0026(3)$. This profile in seen as the black line and is clearly unable to adequately predict the observed data. The quartic shape of this prediction is more clearly seen for the colloidal fluid in Fig. 6.3 below.

The prediction including the coupling to the gradient of the strain rate from Eq. (6.5) is seen
in red. A value for the temperature jump of $\Delta T_w = 0.0026(3)$ has shifted the predicted profile up. The value of the coupling coefficient used to obtain the fit is $\xi = 53,000$. The values of $\lambda = 4.59(3)$, and $\eta = 2.581(9)$ were obtained from Table 4.7, and assumed constant across the channel. Again here we have also assumed a uniform value of the density, $\rho = 1.105$.

![Figure 6.3: Temperature profile of the equimolar Ar-Kr fluid, $F_e = 0.0001$. The quartic continuum prediction is the black line, and the prediction including the coupling to the gradient of the strain rate is in red.](image)

We have neglected the effect of thermal diffusion because the coefficients in the thermal diffusion term in Eq. (2.148) are two orders of magnitude smaller than the thermal conductivity and the coupling coefficient. For equimolar Ar-Kr these values are $\lambda = 4.59(3)$, $\rho \frac{\partial \mu}{\partial c_1} T D' = 0.028(3)$ and $\xi \dot{\gamma} = 1.0(1)$. We believe that this is the first work to conclusively show that for binary fluids, the contribution to the temperature profile from the thermal diffusion term is negligible. The importance of including the strain rate term for narrow channels agrees with the results in literature of Todd and Evans for one-component fluids [91].

### 6.3.2 Temperature profile of the colloidal fluid

For the colloidal fluid experiencing a field of $F_e = 0.0001$ in the $x$-direction, Fig. 6.4 shows the observed temperature profile. Unlike the Ar-Kr fluid, the colloidal fluid does not exhibit any discernible temperature jump at the walls.
The assumption of constant viscosity and thermal conductivity has been proven valid when obtaining the fit to the velocity and temperature profiles for equimolar Ar-Kr. For the colloidal fluid we can see from Fig. 6.4 that the temperature across the profile varies between 1.0000 at the walls, to 1.0007 near the centre of the channel. Referring to the temperature dependent transport coefficients calculated in Section 4.3 we find that the assumption of these values as constant in this temperature range is quite valid. Any change in the value of the transport coefficients over this temperature range will be so small that they are less then the error of the coefficient used.

The profile depicted with a black line is again the continuum prediction of Eq. (2.145). The resulting quartic shape is clearly different from the observed temperature profile. The prediction including the coupling to the gradient of the strain rate from Eq. (6.5) in red, is generated with a value of \(\xi = 6,500\). The values of \(\lambda = 5.47(9)\), and \(\eta = 4.22(2)\) are obtained from Table 4.19 and again we have assumed uniform density, which for the colloid is \(\rho = 0.960\). As with the Ar-Kr fluid, we can neglect the thermal diffusion term as the coefficient \(\rho \frac{\partial \mu}{\partial c_1} T D' = 0.045(1)\), and both the thermal conductivity and the coupling coefficient, \(\xi \dot{\gamma} = 1.5(1)\), are two orders of magnitude greater.

![Temperatur profile](image)

Figure 6.4: Temperature profile of the colloidal fluid, \(F_e = 0.0001\). The quartic continuum prediction is the black line, and the prediction including the coupling to the gradient of the strain rate is in red.

We see that with the inclusion of the coupling term to the gradient of the strain rate, we can
obtain a good description of temperature profile for the colloidal fluid. To obtain this profile it was required to ensemble average a significant number of accumulations of the temperature profile, as mentioned in the previous section. The error bars shown for the temperature profile are still quite large and may improve with continued averaging, however the computation time required to achieve this is prohibitive.

It is expected that the observed temperature profile will be quartic for a wider channels, where the contribution due to the coupling to the gradient of the strain rate becomes negligible. Baranyai, Evans and Daivis suggested that the quadratic term with dominate over the quartic term when [38]

\[ y < \sqrt{\frac{12\xi}{\eta}}, \]  

(6.6)

and this limit was also observed by Todd and Evans [91]. For the two component colloidal fluid studied here the limit on the minimum channel width is expected hold. At the channel width of \(80\sigma\) the coupling term is approximately 24% of the dissipative term. From Eq. (6.6) the channel width would have to be above \(136\sigma\) to negate the contribution due to the coupling to the gradient of the strain rate. Simulations of channel widths above this limit would be of great interest for future study, and confirm the value of the thermal conductivity obtained from EMD simulations.

### 6.4 Concentration profile and continuum predictions

In Ch. 5 we have seen that due to the diffusive mass flux and heat flux, a temperature difference across a confined fluid will result in a concentration difference across the channel. This can be predicted in the absence of flow, with the continuum predictions presented in Ch. 2. For a confined binary fluid undergoing planar Poiseuille flow, the separation of the two species is much harder to resolve. This is due to the temperature variation across the fluid being one order of magnitude smaller than the temperature variations in the temperature gradient systems.

If we exclude the coupling to the gradient of the strain rate, as is done to derive Eq. (2.161), and use the temperature profile obtained above, the continuum mechanics prediction of the concentration is quartic. We find for both the Ar-Kr and colloidal fluids, including the coupling to the gradient of the strain rate allows for the continuum prediction of the temperature dependent concentration profile. This is achieved using the values of the Soret coefficients calculated in Ch. 4. In Ch. 7 at higher flow rates for the colloidal fluid, we observe a much more distinct concentration variation across the channel. This occurs when the field is increased to more than one order of magnitude greater than the field used here of \(F_e = 0.0001\). However at the greater flow rate we can no longer obtain a reasonable description of the temperature profile using the method presented in this section.
6.4.1 Concentration profile of equimolar argon-krypton

Figure 6.5 shows the concentration profile for equimolar Ar-Kr, with the red line showing the prediction including the coupling to the gradient of the strain rate.

\[ c(y) = \frac{1}{1/c_0 - \exp \left[ \frac{\partial T}{\partial y} (T(y) - T_0) \right] + 1} \]

The Soret coefficient \( \partial T/\partial y \) is calculated from the transport coefficients reported in Section 4.2, and the variable \( c_0 \) is a reference concentration, and \( T_0 \) the temperature at the \( y \)-position where the concentration of species 1 is equal to \( c_0 \). For equimolar Ar-Kr these values are \( c_0 = 0.7442 \) and \( T_0 = 0.985(2) \). The dashed red lines indicate the maximum and minimum predictions when taking into account the error in obtaining \( T_0 \). The error in the Soret coefficient is insignificant compared to the error in \( T_0 \).

Figure 6.5: Concentration profile of the equimolar Ar-Kr fluid, \( F_e = 0.0001 \).

Figure 6.6 is a zoomed in portion of the concentration profile for equimolar Ar-Kr. The characteristic shape of the the prediction in red includes the coupling to the gradient of the strain rate for the description of the temperature profile. The predicted temperature dependent concentration profile is made with Eq. (2.161), i.e.

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Figure 6.6: Concentration profile of the equimolar Ar-Kr fluid, $F_e = 0.0001$.

Excluding the coupling to the gradient of the strain rate, the quadratic shape of the predicted concentration profile is seen as the black line in Fig. 6.6. The quadratic shape can be seen more clearly in Fig. 6.7.
The concentration profile is reasonably well predicted for equimolar Ar-Kr in Figure 6.6, with the inclusion of the coupling to the gradient of the strain rate in the description of the temperature profile. We note that the prediction only includes the coupling to the gradient of the strain rate in our description of the temperature profile. The coupling term in the diffusive flux of Eq. (2.149) was not required to make the prediction shown in red in Fig. 6.6.

Although the observed concentration profile is still somewhat noisy, we observe a concentration variation of approximately 1.3% from the centre of the channel to the walls. The ability to utilise the description of the temperature profile which incorporates the coupling term in the continuum description of the concentration profile, is also achieved in the following section for the colloidal fluid.

### 6.4.2 Concentration profile of the colloidal fluid

In Fig. 6.8 the concentration profile for the colloidal fluid from NEMD simulations is shown in blue, with the red line showing the prediction including the coupling to the gradient of the strain rate. Again the variations in concentration at the walls are due to the density variations from fluid packing in this region.
Figure 6.8: Concentration profile of the colloidal fluid, $F_e = 0.0001$.

Figure 6.9 is zoomed in on the concentration profile to highlight the concentration variation across the profile. The predicted profile excluding the coupling term is in black, and the concentration prediction with the coupling term for the temperature profile is shown in red. We have highlighted the range of the prediction by plotting the upper and lower predictions as dashed red lines, using the reference concentration $c_0 = 0.2874$ and temperature $T_0 = 1.0005(1)$. 
These results have shown for the first time that a prediction of the temperature dependent concentration profile in binary solutions can be made. This requires the inclusion of the coupling to the gradient of the strain rate in our description of the temperature profile. This also requires accurate values of the transport coefficients calculated from the bulk. This work has successfully shown how to include the diffusive heat flux and mass flux contributions to the movement of species in a system undergoing planar Poiseuille-like flow.

6.5 Density profiles

For both equimolar Ar-Kr and the colloidal fluid experiencing a field of $F_e = 0.0001$, the density is constant across the channel. The only variations in density are in the regions close to the walls, where the packing of molecules creates an oscillating density variation. Observation of these density variations have been made before in the region of the walls, and there are implications implications for the transport of momentum and heat as well as for the local viscosity in this region. Travis, Todd and Evans suggest that the deviation from generalised Navier-Stokes theory for the velocity profile is likely a result of molecular packing at the walls [83]. It is beyond the scope of this work to account for this variation.
6.5.1 Density profile of equimolar argon-krypton

In Fig. 6.10 the density profile for equimolar Ar-Kr is constant across the channel, with the red line showing the average density.

Figure 6.10: Density profile of the equimolar Ar-Kr fluid, $F_e = 0.0001$. 

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6.5.2 Density profile of the colloidal fluid

Fig. 6.11 shows the density profile for the colloidal fluid, constant across the channel with the red line showing the average density.

![Graph of density profile](image)

Figure 6.11: Density profile of the colloidal fluid, $F_e = 0.0001$.

6.6 Conclusions

We have successfully applied the Navier-Stokes equations for planar Poiseuille flow, with the assumption of constant transport coefficients and uniform density, to a continuum description of the velocity profile observed for two binary fluids. For the Ar-Kr fluid even at the relatively low field strength, the inclusion of a value to account for wall-slip is required. For the colloidal fluid, the existence of slip for this system of a relatively wide channel and low flow rate, is measurable to a high degree of accuracy despite being quite small.

The gravity like field leads to observable temperature profiles, that can be described by a continuum description including a free fitting parameter for the coupling to the gradient of the strain rate. This is true for the two different types of fluids that have different characteristic temperature profiles, but are confined in similar geometries, and experiencing the same field strength. Evaluating the transport coefficients for binary systems through the methods presented in this study, and combining these with the observed temperature profiles allows us to evaluate
the coefficient coupling the heat flux to the gradient of the strain rate. This value $\xi$, when used to describe the observed temperature profiles, can subsequently be used in a continuum description of the concentration profile. The continuum description uses the Soret coefficient and the temperature profile to provide a good description of the observed concentration profiles.

Although we have been able to confirm the method for calculating $D'$ and $D_m$, we have no data available to independently confirm our treatment for calculating the thermal conductivity $\lambda$ in two component systems. We have no reason to doubt this value, however more work is needed to confirm our treatment of the thermal conductivity, and hence the coupling factor we obtain. The value of $\lambda$ would be confirmed with a Poiseuille flow simulation at a field strength of 0.0001, and a channel width of approximately $136\sigma$. In this regime Fourier’s law is expected to be capable of describing an observed temperature profile.

The results of this work could be extended to future research of particular interest. Investigating Poiseuille flow and the migration of species in highly confined cylindrical confinement would be of great benefit. This geometry is found in promising new substances like carbon nanotubes. Further modelling of the separation of fluids such as sodium chloride in water, or comparison with the results of highly confined experimental colloidal fluids such as with the fluids studied by Yordanov, Best, Butt and Koynov [92], are also promising fields for future research.
Chapter 7

Poiseuille flow of colloids at higher flow rates

7.1 Introduction

Here we present the results obtained for the simulation of colloidal fluids undergoing Poiseuille flow, which are driven by field strengths greater than in the previous chapter. The velocity profiles observed at these higher field strengths are well described by the continuum theory, with the inclusion of wall-slip. However we observe that the assumption of uniform transport coefficients, and theory including the coupling to gradient of the strain rate can not adequately describe the observed temperature profiles at these higher flow rates. Having obtained the temperature dependent transport coefficients for the colloidal fluid, we allow the coefficients to vary across the channel according to the relationships to temperature described in Ch. 4. The combination of including the coupling to the gradient of the strain rate, and the temperature dependence of the transport coefficients is found to be insufficient to predict the observed temperature profiles at higher flow rates. We observe that colloidal separation continues to increase with an increase in field strength.

7.2 Velocity profile results and comparison

Applying a field of 0.0005 results in a quadratic velocity profile for the colloidal fluid. With the value of the wall velocity being $v_x = 0.003(1)$, the quadratic description of the velocity profile of Eq. (6.2) is in excellent agreement with the observed profile, shown in red in Fig. 7.1. The viscosity used in the fit is 4.22(2), and it is assumed to be constant across the channel with an average density of 0.960.
For a field of 0.001, the wall velocity is $v_w = 0.006(2)$ however the continuum description still holds.
For fields greater than 0.001, we start to observe deviations from the continuum description of Eq. (6.2). With applied fields of 0.005 and 0.01 and wall slip velocities of 0.04(2) and 0.17(1) respectively, Figs. 7.3 and 7.4 show the observed velocity profiles and predictions in red.

Figure 7.3: Velocity profile of the colloidal fluid, $F_e = 0.005$. 

![](image.png)
As we increase the field strength the strain rate increases to a value where non-Newtonian effects are observed [55]. With the applied fields of 0.005 and 0.01 the ability to describe the observed velocity profile with the continuum prediction breaks down. This is attributed to the presence of non-Newtonian effects, and accounting for these effects would be extremely useful as we head to higher flow rates where the separation of species is greater than at low flow rates. However including the non-Newtonian effects is beyond the scope of this work.

7.2.1 Reynolds, Péclet and Weissenberg numbers

Table 7.1 below summarises the Reynolds, Péclet and Weissenberg numbers for the colloidal fluid at various flow rates. The Péclet number has again been calculated with recourse to the pure solvent viscosity, $\eta_0 = 2.252(2)$ as calculated by Kairn [15]. The viscoelastic relaxation time is taken to be $\tau = 4$ calculated from the stress autocorrelation function obtained in Ch. 4, and the Weissenberg and Péclet numbers have been calculated as the maximum values using the largest value of the strain rate across the profile which occurs at the walls.

The Reynolds number has been calculated with the average value of the density, however as the flow rate increases, we begin to observe a non-uniform density. The maximum value of the Reynolds number would be near the walls, where density is seen to be greater than the average density. However with $Re = 14.00(4)$ in this region, the flow is still considered to be laminar.
Table 7.1: Reynolds, Péclet and Weissenberg numbers of the colloidal fluid with channel width 80\(\sigma\), at various field strengths and strain rates.

<table>
<thead>
<tr>
<th>(F_e)</th>
<th>(\dot{\gamma})</th>
<th>(Re)</th>
<th>(Pe)</th>
<th>(We)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0005</td>
<td>0.00455(2)</td>
<td>0.601(3)</td>
<td>0.0151(1)</td>
<td>0.0182</td>
</tr>
<tr>
<td>0.001</td>
<td>0.0091(4)</td>
<td>1.201(6)</td>
<td>0.0282(3)</td>
<td>0.0364</td>
</tr>
<tr>
<td>0.005</td>
<td>0.0455(2)</td>
<td>5.63(3)</td>
<td>0.1412(1)</td>
<td>0.1820</td>
</tr>
<tr>
<td>0.01</td>
<td>0.091(1)</td>
<td>11.35(3)</td>
<td>0.2823(3)</td>
<td>0.3640</td>
</tr>
</tbody>
</table>

At the higher flow rates the Weissenberg number is approaching 1, which further confirms the onset of non-Newtonian effects. Also the Péclet number is no longer much less than one. This means we can no longer assume that transport by diffusion is dominant, and transport due to advection may also be present.
7.3 Temperature profile results and comparison

In Fig. 7.5 the temperature profile that is observed for a fluid driven by a field of $F_e = 0.0005$ is shown. The prediction in red includes the coupling term to the gradient of the strain rate, where the coupling factor is $\xi = 2550$, and we find that the continuum description no longer predicts the observed temperature profile. In Ch. 4 we obtained the temperature dependence of the viscosity and thermal conductivity. Allowing these coefficients to vary with temperature, we obtain the prediction shown in black. The combination of a quartic and quadratic equation as per the derivation of Eq. (6.5), and the temperature dependent transport coefficients, is still inadequate for predicting the observed temperature profile at this higher field strength.

![Figure 7.5: Temperature profile of the colloidal fluid, $F_e = 0.0005$.](image-url)
The temperature profile that is observed for a fluid driven by a field of $F_e = 0.001$ is shown in Fig. 7.6. The prediction in red has a coupling factor value of $\xi = 2350$. At a field strength of $F_e = 0.001$ the temperature ranges from 1.0 at the walls to 1.028 at the centre of the channel.

Figure 7.6: Temperature profile of the colloidal fluid, $F_e = 0.001$. 

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At a field of $F_e = 0.005$ the temperature profile in Fig. 7.7 is observed. The prediction in red has a coupling factor value of $\xi = 2350$. The temperature has increased in the centre of the channel to $T = 1.67$.

Figure 7.7: Temperature profile of the colloidal fluid, $F_e = 0.005$. 
At a field of $F_e = 0.01$ we observe the temperature profile in Fig. 7.8. The prediction in red has a coupling factor value of $\xi = 2620$. At the highest field strength studied here, the temperature at the centre of the channel is $T = 4.0$.

![Temperature profile of the colloidal fluid, $F_e = 0.01$.](image)

Figure 7.8: Temperature profile of the colloidal fluid, $F_e = 0.01$. 
7.4 Concentration profile results and comparison

In Ch. 5 we saw for the colloidal fluid a temperature difference of as little as 0.005 resulted in a 4.5% difference in concentration across the profile. Although a similar temperature difference is observed from the walls to the centre of the channel for a fluid with an applied field of $F_e = 0.0005$, the concentration profile is not apparent. This can be seen in Fig. 7.9 below, and is expected to be the result of an insufficient amount of time allowed for the diffusion of the colloid to have occurred at the respective flow rates.

![Concentration profile of the colloidal fluid, $F_e = 0.0005$.](image-url)

Figure 7.9: Concentration profile of the colloidal fluid, $F_e = 0.0005$. 
Again with a field of $F_e = 0.001$, the significant amount of simulation time required to observe a concentration profile for this field has prohibited a discernible concentration variation across the channel, despite the clarity of the temperature profile in Fig. 7.6.

Figure 7.10: Concentration profile of the colloidal fluid, $F_e = 0.001$. 
In Fig. 7.11 where the field is $F_e = 0.005$, there is a distinct build up of the colloidal species at the wall, and the migration of the colloid from the warmer region at the centre of the channel, to the cooler region of the walls is clearly distinguishable. In the region where the oscillations due to packing have subsided, there is a 60% increase in colloidal concentration at both walls. The direction of the migration towards the cooler region of the fluid is the same as for the confined temperature difference systems without flow discussed in Ch. 5.

Figure 7.11: Concentration profile of the colloidal, $F_e = 0.005$. 

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In Fig. 7.12 with an applied field of $F_e = 0.01$ we see an even greater separation of the colloidal species. Where the oscillations due to packing have subsided at each wall, the concentration is over 300% higher than in the centre of the channel.

![Figure 7.12: Concentration profile of the colloidal fluid, $F_e = 0.01$.](image)

### 7.5 Density profile results and comparison

The density profiles for the fields of 0.0005 and 0.001 are both constant across the channel, at the average density of the fluid seen in Figs. 7.13 and 7.14 respectively. As with the previous systems we observe density oscillations at the walls due to the packing of molecules at the walls.

When the field strength is above $F_e = 0.001$, we start to observe non-uniform density profiles. In Figs. 7.15 and 7.16 below, we see that the density has increased at the regions near the wall.

Non-Newtonian behaviour, and the density, temperature and concentration dependence of the transport coefficients would need to be accounted for in an attempt to describe the observed temperature and concentration profiles at these higher strain rates.
Figure 7.13: Density profile of the colloidal fluid, $F_e = 0.0005$.

Figure 7.14: Density profile of the colloidal fluid, $F_e = 0.001$. 
Figure 7.15: Density profile of the colloidal fluid, $F_e = 0.005$.

Figure 7.16: Density profile of the colloidal fluid, $F_e = 0.01$. 

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7.6 Conclusions

We have seen that when the colloidal fluid undergoes planar Poiseuille flow the velocity profiles can be well predicted to relatively high field strengths. However the temperature profiles quickly diverge from the continuum description successfully applied in the previous chapter. Attempting to obtain a reasonable prediction of the temperature profile by allowing the viscosity, thermal conductivity and coupling coefficient to vary with temperature is still insufficient for describing the observed temperature profiles at higher field strengths.

The ability for Poiseuille flow to result in the separation of two component fluids is displayed over a range of flow rates. At relatively high field strength the separation of the colloidal species is very significant. The density is seen to remain uniform across the profile, unless the field strength is relatively high.
Chapter 8

Conclusions

In this study, using Molecular Dynamics (MD) to investigate the transport properties of colloidal fluids, we have provided further understanding of heat and mass transport in binary systems. We have shown that by considering the effects of diffusion and heat fluxes, and how they differ from the one component fluid, the relevant constituents used to calculate transport coefficients for binary fluids can be obtained.

Using a simplified planar confined geometry we have successfully applied the transport coefficients of an equimolar Ar-Kr fluid, and a colloidal fluid calculated from bulk fluids at equilibrium, to the continuum description of fluids with a temperature gradient applied by maintaining different temperatures of the walls, and to systems undergoing planar Poiseuille flow. We have proven the continuum theory to obtain velocity, temperature and concentration profiles correct for confined fluids, and shown how the theory can be used to predict colloid separation.

Having shown how to correctly account for the mass and diffusive flux effects attributed to a second species being present, we have successfully compared the transport coefficients for equimolar Ar-Kr with values in literature. Using this method we have also computed transport coefficients for a colloidal fluid over a range of temperatures and concentrations. We have also shown that the advantage of the method presented in this work is in the ability to calculate the mutual diffusion and thermal diffusion transport coefficients separately.

We have successfully shown how the transport coefficients can be used in a continuum prediction of the separation of the respective two species when a fluid is subject to a temperature difference through thermostated walls. Using the Soret coefficient, for both the Ar-Kr and colloidal fluids the separation is shown to be predictable when the temperature difference across the fluid is small enough to assume a constant value of the Soret coefficient.

We have also successfully shown that at relatively low flow rates for narrow channels, a continuum description of the temperature profile can be obtained by incorporating the coupling
to the gradient of the strain rate, and where this description breaks down. We also show that incorporating the temperature dependence of the transport coefficients does not account for the observed temperature profiles.

Although there is a significant contribution to the understanding of heat and mass transport mechanisms in colloidal fluids in this work, further questions of interest have arisen. A comparison of the thermodynamic factor obtained in this study with values obtained by employing the new method of Krüger et al. [81] and Nichols, Moore and Wheeler [80] would be appealing for future work. This would verify that calculation of the thermodynamic factor in the canonical ensemble by forcing the fit of the KB integrals to converge to 1 is valid. Understanding the density fluctuation observed at the walls, particularly for more highly confined fluids where these fluctuations dominate the profile would also be of significant value.

We have also seen that the ability to describe the temperature profile at higher flow rates breaks down, however at these higher flow rates the separation of the colloidal species is quite significant. It would be of great interest to be able to describe the observed temperature and concentration profiles at these higher flow rates. We have also postulated the channel width at which the coupling term should diminish, and it would be of interest to confirm our predictions of this channel width.

Also of particular interest would be the application of the theory presented in this work for other confining geometries and model fluids. Of particular interest is Poiseuille flow in highly confined cylindrical confinement, such as carbon nanotubes. Further modelling of the separation of fluids such as sodium chloride in water, or comparison with the results of highly confined experimental colloidal fluids are also promising fields for future research.
A. Appendices

A.1 Reduced units

Molecular dynamics systems are commonly simulated using scaling factors that change small parameters which describe particles into numbers whose order of magnitude are generally 1. This has the advantage of allowing higher accuracy of floating point representation of numbers and allows for a universality of the results through the principle of corresponding states. In this study quantities are generally discussed in the reduced form, and the reduction parameters are the solvent-solvent Lennard-Jones interaction parameters of interaction energy ($\varepsilon_{22}$), interaction length ($\sigma_{22}$), and the mass of a solvent particle ($m_2$).

The definitions of reduced quantities in Lennard-Jones units are presented in Table A.1 below [8], the asterisk representing the reduced quantities.

Table A.1: Definitions of reduced quantities and the reduced colloid values. Real values are calculated using the Ar-Ar parameters listed in table 3.2 Sec. 3.3.2.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Reducing formula</th>
<th>Colloid reduced value</th>
<th>Real value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>$T^* = \frac{k_B T}{\varepsilon_{22}}$</td>
<td>1.0</td>
<td>120 K</td>
</tr>
<tr>
<td>Pressure</td>
<td>$P^* = \frac{P \sigma_{22}^3}{\varepsilon_{22}}$</td>
<td>9.04</td>
<td>380 MPA</td>
</tr>
<tr>
<td>Mass</td>
<td>$m_i^* = \frac{m_i}{m_2}$</td>
<td>1.0</td>
<td>39.5 Da</td>
</tr>
<tr>
<td>Mass density</td>
<td>$\rho_m^* = \frac{\rho_m \sigma_{22}^3}{m_2}$</td>
<td>0.96</td>
<td>1613 kg.m$^{-3}$</td>
</tr>
<tr>
<td>Time</td>
<td>$t^* = \frac{t}{\sigma_{22} \left( \frac{m_2}{\varepsilon_{22}} \right)^{1/2}}$</td>
<td>0.001</td>
<td>0.2 ns</td>
</tr>
<tr>
<td>Length</td>
<td>$r^* = \frac{r}{\sigma_{22}}$</td>
<td>2.2254</td>
<td>0.76 nm</td>
</tr>
</tbody>
</table>
This work has presented the values in their reduced form and the convention of using the asterisk (*) to denote reduced units is omitted. All non-reduced values are presented with units where appropriate.

### A.2 Constants

The following constant values have been used in this study.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar gas constant [93]</td>
<td>$R$</td>
<td>8.3144621 (75)</td>
<td>$Jmol^{-1}K^{-1}$</td>
</tr>
<tr>
<td>Boltzmann’s constant [93]</td>
<td>$k_B$</td>
<td>1.3806488 (13)$ \times 10^{-23}$</td>
<td>$JK^{-1}$</td>
</tr>
<tr>
<td>Avogadro’s constant [93]</td>
<td>$N_A$</td>
<td>6.02214129 (27)$ \times 10^{23}$</td>
<td>$mol^{-1}$</td>
</tr>
</tbody>
</table>

### A.3 List of symbols

The following is a list of symbols and their definitions.

- $A, B, C, D$: Fitting parameters for decay in pair distribution function
- $C_{ab}$: Green-Kubo time correlation function
- $c_{ab}$: Hard core parameter
- $c_k$: Mass fraction of component $k$
- $c_p$: Heat capacity at constant pressure
- $c_0$: Reference concentration
- $D_m$: Mutual diffusion coefficient
- $D'$: Thermal diffusion coefficient
- $D''$: Dufour coefficient
- $d$: Molecular diameter
- $F_i$: Sum of forces on site $i$
- $F_i^e$: Body force on site $i$
- $F_i^w$: Wall harmonic tethering force on site $i$
- $f$: Number of translational centre of mass degrees of freedom
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_i^m$</td>
<td>$i^{th}$ Gear coefficient</td>
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</tr>
<tr>
<td>$F'_i$</td>
<td>Wall layer force</td>
<td>37</td>
</tr>
<tr>
<td>$g$</td>
<td>Gibbs' free energy</td>
<td>13</td>
</tr>
<tr>
<td>$g_{ab}$</td>
<td>Pair distribution</td>
<td>15</td>
</tr>
<tr>
<td>$G_{ab}$</td>
<td>Volume integral of pair distribution</td>
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<td>$G(r)$</td>
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<td>$h_k$</td>
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<td>10</td>
</tr>
<tr>
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<td>Force on particle $i$ due to particle $j$</td>
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</tr>
<tr>
<td>$J_i$</td>
<td>Diffusive flux for component $i$</td>
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</tr>
<tr>
<td>$J_q$</td>
<td>Heat flux</td>
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<tr>
<td>$J'_q$</td>
<td>Primed heat flux</td>
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</tr>
<tr>
<td>$Kn$</td>
<td>Knudsen number</td>
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<td>$L_{qq}$</td>
<td>Heat-heat phenomenological coefficient</td>
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<td>$L_{1q}$</td>
<td>Mass-heat phenomenological coefficient</td>
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<td>$L_{q1}$</td>
<td>Heat-mass phenomenological coefficient</td>
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<tr>
<td>$m$</td>
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<tr>
<td>$m_i$</td>
<td>Total mass of species $i$</td>
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<td>$N_i$</td>
<td>Total number of particles of component $i$</td>
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<tr>
<td>$n_i$</td>
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<td>$P$</td>
<td>Pressure</td>
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<td>Traceless symmetric part of the pressure tensor</td>
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<td>Isotropic local equilibrium and non-equilibrium parts of pressure</td>
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<tr>
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<td>$p_i$</td>
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<td>$Q_T$</td>
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<td>$Q$</td>
<td>Degree of ideality of a two component fluid</td>
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<tr>
<td>$R$</td>
<td>Molar gas constant</td>
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<td>Cutoff position for Lennard-Jones potential</td>
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<td>Vector separation between particles $j$ and $i$</td>
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<td>Temperature</td>
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<td>Reduced temperature</td>
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</tr>
<tr>
<td>$T_0$</td>
<td>Reference temperature</td>
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<tr>
<td>$\Delta T_w$</td>
<td>Temperature jump at the walls</td>
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<tr>
<td>$t$</td>
<td>Time</td>
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<tr>
<td>$t^*$</td>
<td>Reduced time</td>
<td>147</td>
</tr>
<tr>
<td>$u$</td>
<td>Internal energy</td>
<td>9</td>
</tr>
<tr>
<td>$u_i$</td>
<td>Internal energy of particle $i$</td>
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</tr>
<tr>
<td>$v$</td>
<td>Specific volume</td>
<td>13</td>
</tr>
<tr>
<td>$V$</td>
<td>Fluid volume</td>
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<tr>
<td>$\bar{v}_i$</td>
<td>Average velocity in the x-direction</td>
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<tr>
<td>$v$</td>
<td>Convective part of the velocity</td>
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</tr>
<tr>
<td>$v_i$</td>
<td>Velocity for component $i$</td>
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</tr>
<tr>
<td>$W_e$</td>
<td>Weissenberg number</td>
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</tr>
<tr>
<td>$X_q$</td>
<td>Thermodynamic force for heat</td>
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</tr>
<tr>
<td>$X_1$</td>
<td>Thermodynamic force for mass</td>
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<tr>
<td>$x_i$</td>
<td>Mole fraction of component $i$</td>
<td>43</td>
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<tr>
<td>$y_i$</td>
<td>Centre of mass position of component $i$ in y-direction</td>
<td>37</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Thermal diffusion factor</td>
<td>21</td>
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<tr>
<td>$\alpha_w$</td>
<td>Thermostat constraint multiplier</td>
<td>37</td>
</tr>
</tbody>
</table>
$\beta$ Wall-slip coefficient .............................................. 112
$\dot{\gamma}$ Strain rate ......................................................... 26
$\varepsilon$ Lennard-Jones potential well depth ......................... 40
$\varepsilon_{ab}$ Potential well depth for interaction $a$ and $b$ .......... 40
$\dot{\varepsilon}$ Volume multiplier for barostat .......................... 34
$\eta$ Shear viscosity ......................................................... 24
$\eta$ Fourth rank shear viscosity ......................................... 23
$\eta_0$ Shear viscosity of solvent ......................................... 46
$\lambda$ Thermal conductivity ................................................ 20
$\lambda_\beta$ Layer constraint multiplier ..................................... 37
$\mu_i$ Chemical potential of component $i$ ............................. 11
$\partial \frac{\mu_i}{\partial c_i}$ Thermodynamic factor of component $i$ .... 20
$\xi$ Coupling factor to the gradient of the strain rate for the heat flux .... 28
$\xi^A$ Atomic thermostat multiplier ....................................... 34
$\dot{\xi}^A$ Thermodynamic friction coefficient ........................... 34
$\Pi$ Isotropic part of the non-equilibrium pressure ....................... 22
$\Pi^{ts}$ Traceless symmetric part of the local non-equilibrium pressure .... 22
$\Pi^a$ Anisotropic part of the local non-equilibrium pressure ........... 22
$\rho$ Total mass density ...................................................... 8
$\rho_i$ Mass density of component $i$ ....................................... 8
$\rho^*$ Reduced mass density ............................................. 147
$\sigma$ Entropy production .................................................. 12
$\sigma$ Lennard-Jones potential well position ............................. 40
$\sigma_{ab}$ Potential well depth between species $a$ and $b$ ............... 40
$\tau$ Viscoelastic relaxation time .......................................... 46
$\chi$ Coupling factor to the gradient of the strain rate for the mass flux .... 28
$\Psi_{1,0}$ First normal stress coefficient .................................... 46
B. Bibliography


[11] O. Takayasu, “Possible enrichment of the uranium hexafluoride isotope by thermal diffusion modified with the addition of both an inert gas and perfluoromethylcyclohexane,”


