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GENERAL INTRODUCTION

In this introduction we start with our research motivation and then give a brief overview of the history of the rheological study of flows, and more specifically nano-scale flows.

1.1 Motivation

The study of the rheology of fluids in nanoporous materials is very important because of the technological applications as well as the fundamental scientific interest. For example, a lubricant is applied to the disk surface to protect the disk from being damaged during operation [2]. Many applications exist where the situation of boundary lubrication is encountered, in which the spacing between the confining solid surfaces reaches nanometer length scales. When fluid is narrowly confined within spacing comparable to the molecular dimension, its structural and dynamic properties deviate strongly from the bulk behaviour in various respects. It was shown that a deviation from typical quadratic velocity profiles predicted by classical Navier-Stokes dynamic theory can be observed for planar Poiseuille flow [3]. The shear stress exhibits oscillations about the classical linear profile and highly layer-structured density profiles are present. Strong density variations across the fluid channel result in spatial inhomogeneities in all transport properties [4, 5, 6, 7] that deviate substantially from their bulk properties.

An understanding of these properties can be very important in adhesion, lubrication, colloidal stability, separations, and materials synthesis. In fact, these properties

of confined fluids, such as viscosity, heat flux, and boundary conditions are far from fully understood, primarily due to the failure of continuum theories at such small length scales, and the apparent difficulty of current real experimental techniques to probe the transport properties at the atomic and molecular level, since most experiments only provide macroscopic manifestations of the actual microscopic phenomena. This leads to a loss of crucial microscopic information. Even the most advanced experimental technique such as the surface force apparatus (SFA) provides only very limited information. Therefore, molecular simulation [8, 9, 10], the most powerful tool, has mostly been used to investigate the behaviour of such a confined system, as it has the advantage of providing more detailed information on the microscopic level.

The goal of this study is to fundamentally understand the spatially dependent structural and dynamic properties for inhomogeneous nonequilibrium fluids using nonequilibrium molecular dynamics. Molecular simulations not only provide the capability to probe the behaviour of confined fluids at a microscopic level, thus providing the most fundamental understanding of the rheological properties which cannot be captured from existing theories, but also enable us to probe nonlinear phenomena at extreme nanoscale conditions which is impossible to achieve using existing experimental equipment.

1.2 Review of previous work

Rheological behaviours are a subject of practical and long-lasting interest. At a fundamental level, they are usually studied in the framework of the Boltzmann equation and related kinetic equations. To first order in Knudsen number (mean free path divided by hydrodynamic length scale), the Chapman-Enskog expansion leads to the Navier-Stokes equations [11]. Higher order expansions (i.e., Burnett and super Burnett) however, have had limited success, particularly with regard to convergence and boundary conditions [12].

The moment method, introduced by Maxwell, proves to be more successful in theoretical work but is not yet widely used as the basis for numerical calculations. While theoretical advances continue to be made [13, 14, 15], a general approach to solving the Boltzmann equation has not been established.

In this regard, numerical experiments have played an important role in modern kinetic theory. Historically, computational simulations of dilute systems have been done by two groups. The first is the statistical physics community [16], which has focused primarily on molecular dynamics simulations of gases and lattice-based schemes with simplified collision dynamics. The second branch is in the engineering community. Stochastic particle methods such as direct simulation Monte Carlo (DSMC) [17] and its variants were introduced by aerospace engineers during the 1960's and 70's, when space exploration was the primary application for rarefied flows. The two branches developed separate numerical approaches since they focused on different problems. In statistical physics the work was primarily in equilibrium and simple non-equilibrium states, such as Couette and Poiseuille flow. The engineering community was interested in complex systems such as hypersonic flight and extreme non-equilibrium flows. In recent years, the two communities have discovered the utility of the algorithms developed by each, especially as their interests turn to meso- or nano- scale applications. Some of the new directions in computational study of flows include [18]:

Particle/Continuum hybrids:

Many interesting flows that require the use of microscopic simulation have not been studied due to their computational expense, which is several orders of magnitude greater than that of continuum hydrodynamic methods. However, one needs to simulate fluids at the atomic level to understand their chemical and physical behaviour. Hybrid schemes, which combine a microscopic algorithm with a continuum hydrodynamic calculation have proved useful. The need for such hybrid methods arises from the fact that hydrodynamics

modelled by continuum representations are often inaccurate while solutions generated using molecular resolution globally are not feasible. For example, the Adaptive Mesh and Algorithm Refinement (AMAR) scheme uses direct simulation Monte Carlo at the finest grid scale in an adaptive mesh refinement hierarchy and a Navier-Stokes solver at other scales [19]. The atomistic model is applied locally in regions where the continuum description is invalid or inaccurate. The continuum and atomistic representations are coupled by proper averaging and interpolation of data between scales, adjusting grids as the flow solution evolves, adaptively deciding where and when the calculation should switch from a continuum algorithm to a microscopic algorithm.

Plasma flows:

The properties of plasma flow has been a very interesting topic to study due to the many important applications for plasmas such as semiconductor processing, surface treatments and pollution control. Molecular dynamic simulations of charged fluids are extremely time consuming, mainly because of the long-ranged Coulomb interactions. The question then arises as to the possibility of setting up alternative mesoscopic methods. Today, there are some plasma problems that have been analysed by direct simulation Monte Carlo (DSMC) and Particle-In-Cell techniques [20], where charged plasma species are modelled as individual macro-particles (each macro-particle represents a large number of real particles). Particles move in the plasma using Newton's laws and self-consistently calculated electric fields resulting from applied voltages and inter-particle Coulomb forces.

Nano-scale flows:

Nano-scale flows play an increasingly important role in fluid dynamics, thanks to advances in computer technology. When the characteristic length scale of a flow is comparable to the mean free path of the constituent molecules, the traditional macroscopic description breaks down. Molecular simulations, primarily molecular dynamics [10, 21]

and direct simulation Monte Carlo [16], are at present the main computational tools in the study of these transitional flows. An example is the simple Poiseuille flow confined to a channel only several molecular diameters wide. Perhaps the first molecular dynamics simulation of Poiseuille flow is the one reported in [22]. Possibly the first study of Poiseuille flow driven by an external force was carried out by Bitsanis *et al.* [3] and Kadanoff *et al.* [23], who simulated laminar pipe flow with lattice-gas automata to verify the parabolic profile of momentum density for this system and observe the well-known logarithmic divergence in the viscosity. Esposito *et al.* [24] studied the Boltzmann equation and found that if the force is sufficiently weak there is a solution which converges, in the hydrodynamic limit, to the local equilibrium distribution with parameters given by the stationary solution of the Navier-Stokes (NS) equations. Alaoui and Santos [25] carried out kinetic theory analysis of Poiseuille flow clearly exhibiting non-Newtonian behaviour. They found an exact solution of the Bhatnagar-Gross-Krook (BGK) kinetic equation for a gas of Maxwell molecules. An exact solution was found for a particular value of the force parameter. At a hydrodynamic level, the solution is characterized by a parabolic profile of the flow velocity with respect to a space variable scaled with the local collision frequency. The general solution of the BGK model under the form of an expansion in powers of acceleration through fifth order was obtained by Tij and Santos [26].

Contrary to bulk fluids, interfacial or confined fluids exhibit strong density variations on a microscopic, molecular scale, which has been observed in many molecular simulations [27, 28, 29] and has been deduced experimentally [30]. This fact introduces serious conceptual and operational difficulties in the description of their transport behaviour. Recently, Sokhan and Quirke studied the influence of the boundary conditions at the solid-fluid interface on tracer diffusivity and collective diffusivity. They obtained a relationship between the collective diffusivity and the Maxwell coefficient describing wall

collisions [31]. Supple and Quirke carried out molecular dynamics simulations of carbon nanotubes imbibing oil at an oil/vapour interface [32]. They derived expressions for the penetration length and the velocity of the imbibing oil and related both to the solid-fluid surface tensions and interfacial friction via the Maxwell coefficient.

For interfacial or confined fluid systems, due to the lack of uniformity on a molecular scale, the traditional microscopic identification of the mass flux, stress tensor, streaming velocity and energy flux is inappropriate for fluids in nano dimension space. Due to the difficulties in obtaining information from real experiments, the molecular dynamics (MD) method has been used for the calculation of transport properties of fluids. Equilibrium MD calculations employ the well-known formula of linear response theory, the so-called Green-Kubo relations [33, 34], which are not expected to be applicable for systems far from equilibrium. Despite the success of this approach in diffusivity calculations [35, 36], it runs into difficulties when applied for the calculation of viscosity [37, 38]. In order to overcome these difficulties a number of nonequilibrium simulation techniques were developed which calculate the shear viscosity directly from a constitutive relation [39]. According to usual hydrodynamics, local transport coefficients can be assigned at each point inside an inhomogeneous fluid. These are the same as the transport coefficients of a homogeneous fluid at the local density, i.e., they are point functions of the density. Usual hydrodynamics is of course applicable only if the fluid density, despite its macroscopic variation, hardly changes over molecular distances. Bitsanis *et al.* [29] have noticed that the effects of strong density inhomogeneities on the flow and transport behaviour are much weaker than what they would have been, had the local transport coefficients been literally point functions of the density. Therefore they presented a model, the local average density model (LADM), which allows for viscosity variations over the pore cross section by evaluating the local viscosity at a coarse-grained density obtained upon local averaging of the density over a sphere of radius half the molecular diameter.

However, their analysis assumes a uniform pressure over the cross section, while using the equilibrium density profiles in violation of the Gibbs-Duhem relation.

The most successful approach to the confined system was first attempted by Davis and co-workers [4] who have generalized Enskog's kinetic theory to fluids with strong density inhomogeneities over molecular distances. The constitutive equations resulting from such a generalization are different and more complicated than those of bulk fluids due to the inherent anisotropy of the strongly inhomogeneous medium. The corresponding hydrodynamic equations, therefore, are much more complex than the usual Navier-Stokes equations, which makes their application tedious to all but the simplest flows.

The generalized Enskog's kinetic theory was applied to self-diffusion in fluids confined between flat, solid surfaces, i.e., fluids in a slit pore [6]. Such an approach follows the idea that local transport coefficients in an inhomogeneous fluid can be set equal to those for a homogeneous fluid whose density is set equal to some density obtained by averaging over densities in the immediate region of the point of interest in the inhomogeneous system. Although the use of such averaged density rests on rigorous foundations for the equilibrium case, no analogous foundations exists for their use for nonequilibrium fluids and the expressions for the transport coefficients were found only for the cases of a local equilibrium velocity distribution for weakly inhomogeneous fluids, with inhomogeneity in one direction. Pozhar and Gubbins [40] have developed a microscopic theory, a functional perturbation theory, describing nonequilibrium behaviour of dense, strongly inhomogeneous fluids and have shown that generalized Langevin equations should be regarded as the first order form of the functional perturbation theory. Subsequently, the generalized Langevin equations were used to obtain linearized kinetic equations which were solved [41] to obtain linearized Navier-Stokes equations and the associated transport coefficients. The major limitation to this theory is that it relates local values of

transport coefficients to integrals over equilibrium inhomogeneous singlet and pair correlation functions. It is unlikely that the theory will hold when systems are far from equilibrium. A comparison of the Pozhar-Gubbins (PG) theory was made with the local viscosity from NEMD simulations of a fluid undergoing planar Poiseuille flow [42]. However, larger numerical uncertainty is observed in the computation of local NEMD viscosities. Strong density variations across the fluid channel results in spatial inhomogeneities in all transport properties, which were also observed by many experimental investigations using the surface force apparatus [30, 43].

In this work, we apply NEMD techniques to study the rheological behaviour of fluids undergoing Poiseuille flow in a highly confined slit pore. Structural and dynamic properties in terms of the density profile, streaming velocity, shear stress, strain rate and shear viscosity are investigated.

This thesis is structured as follows. Chapter 1 gives a general introduction to the history of the rheological study of flows, and more specifically nano-scale flows. Chapter 2 describes the theoretical background and derives the pressure tensor and heat flux vector for fluids under the influence of three-body force. Our derivation is validated against nonequilibrium molecular dynamics simulations of a confined fluid acted upon by a two-body Barker-Fisher-Watts force coupled with the Axilrod-Teller three-body force in Chapter 5. In Chapter 3, an introduction to the basic simulation methodologies used in this work is given. In Chapter 4 we describe the parallel programming scheme used to implement our code with message passing interface (MPI). In Chapter 6 we use the non-local linear hydrodynamic constitutive model proposed by Evans and Morris [1] for computing the viscosity kernel for inhomogeneous nonequilibrium fluids. In Chapter 7 we study the rheology of highly confined polymeric fluids undergoing Poiseuille flow.