Chapter 1

Introduction

Rheology is an interdisciplinary subject that involves the study of the deformation of materials under the influence of external stresses [Bar89, Fer91a, Bla69, Fre64]. Knowledge of the rheological properties and behaviour of matter is essential in many practical fields. These fields include chemical processing industries, plastic industries, synthetic fibre industries, pharmaceutical industries, food industries, lubricants, and so on.

In rheology, there are two basic concepts: stress and strain. Simplistically, stress may be thought of as the force per unit area exerted on a body by an external force. It describes the external action on matter. Strain refers to the relative change in shape of the affected material. Deformation is described quantitatively by strain. Thus in its most basic form, rheology is the study of the stress-strain relationship of matter.

Solid materials respond to an external stress by deforming their shape. If the stress is not too strong, then when it ceases the material will return to its original shape. This kind of response is called elastic. In the simplest situation of elastic response, the strain is proportional to the stress, and this is known as Hooke's Law. But there are still many elastic substances which do not obey this law [Bla69].

For fluids, if external stress is exerted on them, they will respond with continuous deformation. Because of the mobility of fluids, they will continue to change shape as long as the stress exists. Removal of these stresses will not result in the fluid returning to its original state. This kind of response is called viscous. The simplest example of viscous matter is the Newtonian fluid which obeys Newton's Law: the stress is proportional to the strain rate, but not the strain itself [Bla69]. There are many viscous materials which do not obey this law and they are called non-Newtonian fluids [Bla69].

Elastic matter which obeys Hooke's Law and viscous matter which obeys Newton's Law are two special cases. Both Hooke's Law and Newton's Law are linear relationships. The coefficients in their functional forms are constants and are thus proportionality factors. But in the general case, the linear relation between stress and strain or strain rate is not satisfied. And the coefficients which represent the material properties, like the rigidity modulus and viscosity, are not constants but can change with stress [Fer91a].

Elastic response and viscous response are two extreme situations. Some materials can exhibit elastic and viscous behaviours simultaneously [Bar89]. These materials are called viscoelastic materials.

Molecular simulation is a powerful tool in the study of rheology [All87, Sad99, Hey98, Fre02]. Given the microscopic properties such as structure and interactions of molecules in a many-body system, molecular simulation enables the computation of the macroscopic properties of the system. Molecular simulation can be divided into two classes. One is the Monte Carlo (MC) method [Sad99]. In the Monte Carlo method, the average of phase variables can be calculated by computing the probability of allowable configurations of the microscopic system. The other type of simulation methodology is molecular dynamics (MD) [Sad99]. In molecular dynamics, equations of motions are solved dynamically, and the evolution in time of a phase point is computed. The phase variables can be obtained from time averaging as long as the system is ergodic.

Rheological phenomena, such as shear flow, are in non-equilibrium states. Green-Kubo relations [Kub57, Ald57] can be used to calculate some nonequilibrium properties by observing fluctuations in equilibrium. One of its drawbacks is that the decay of the associated Green-Kubo integrands with time is very slow. Therefore accurate results need long simulation times. Moreover, the Green-Kubo method cannot be used when the system is far from equilibrium. Later, nonequilibrium molecular dynamics (NEMD) methods [Hey98] were developed. Nonequilibrium molecular dynamics uses strong fields to perturb a system towards a nonequilibrium steady state, so the signal-to-noise ratio is more favorable than that of the Green-Kubo method. NEMD is thus more efficient and more suitable for simulating rheological phenomena.

In the early days of NEMD, researchers used inhomogeneous techniques to calculate transport coefficients. In inhomogeneous NEMD, the boundary conditions of real experiments, such as walls, reservoirs, together with the studied system, are simulated [All87]. For the ordinary size of simulation systems, the inhomogeneous conditions will induce serious surface effects. In order to overcome this disadvantage, synthetic (homogeneous) nonequilibrium molecular dynamics methods were proposed [Eva90]. Synthetic methods use an external field. In synthetic NEMD, an external field maintains the thermodynamic gradients to prevent the system relaxing to equilibrium. Because this external field will do work on the system, hence heating it, a thermostat is needed to remove the heat and keep the system at a fixed temperature.

In this study, we will use homogeneous nonequilibrium molecular dynamics methods to investigate the state point dependence of the rheological properties of simple fluids. We will study how the stress, pressure, energy and other physical quantities vary with strain rate, whether the relationship between them is analytic or nonanalytic, and how the state point of the fluid affects these properties. We also use the combination of equilibrium MD and NEMD to determine the fluid-solid phase boundary for an equilibrium fluid. Finally, we use an algorithm called the transient time correlation function (TTCF) method to calculate the viscosity at very small fields.

In Chapter 2 we give a brief literature review of relevant work. In Chapter 3 we introduce some basic knowledge of shear flow. In Chapter 4 we give the details of our molecular simulations. In Chapter 5 we report the results of our simulations concerning the state point dependence of rhological properties. In Chapter 6 we show how to use the combination of equilibrium MD and NEMD to determine the fluid-solid phase boundary and apply this method to the Lennard-Jones fluid. In Chapter 7 the results of simulations for the Barker-Fisher-Watts fluid are reported, to determine the fluid-solid phase boundary. In Chapter 8 we report NEMD simulations at weak fields calculated by the TTCF method. Finally, in Chapter 9 we conclude this thesis and offer suggestions for future work.