

Chapter 2

Literature Review

In this chapter, a literature review on the relationship between phase variables and strain rate will be presented. In classical hydrodynamics, if one knows the transport coefficients: thermal conductivity, shear viscosity and bulk viscosity, then the Navier-Stokes equations can describe the behaviour of the fluid completely. Here, the transport coefficients are considered as constant, no matter how big the gradients of the thermodynamic quantities. But this is not the case far from equilibrium. When the system is far from equilibrium, the coefficients will change with the gradients. For example, the viscosity can not remain constant, but changes with the shear rate. In rheology, the stress-stain (or stress-strain rate) relationship is one of the most important relationships. To obtain the correct relationship, various theories have been proposed. For the work presented in this thesis, the most relevant of these theories is the mode coupling theory, which predicts that in the weak field limit, the viscosity, pressure and energy vary with strain rate as $\dot{\gamma}^{1/2}$, $\dot{\gamma}^{3/2}$ and $\dot{\gamma}^{3/2}$ respectively.

Nonequilibrium molecular dynamics (NEMD) [Eva90], is a very powerful tool to study transport processes. However, at the time when we began our work, computer simulation results were not able to conclusively determine whether or not the shear viscosity, pressure and energy are analytical functions of strain rate in the zero field limit. For both two dimensional and three dimensional fluids, there existed contradictory conclusions from simulation results.

In nonequilibrium systems, flow of mass, momentum and energy, are involved. Transport coefficients are used to describe these flows. Green and Kubo showed that these transport coefficients can be calculated by monitoring fluctuations of proper thermodynamic fluxes in the equilibrium state [Kub57, Ald57]. These fluxes are velocity, heat flux vector, pressure tensor, etc. In general, molecular simulations require long times to obtain accurate values for the transport coefficients because the decay of equilibrium fluctuations is very slow. To overcome this drawback, and to obtain an independent method for comparison purposes, nonequilibrium molecular dynamics was developed. Nonequilibrium molecular dynamics (NEMD) has some benefits. It can be used to calculate transport coefficients directly and this calculation is more efficient than that of the Green-Kubo relations. It is also helpful in generating nonequilibrium distribution functions and studying nonlinear effects. But its shortcoming is that the results of calculations need to be extrapolated to zero field to get the Navier-Stokes transport coefficients.

In the early days of NEMD, workers used inhomogenous nonequilibrium molecular dynamics to calculate transport coefficients. These kinds of techniques closely simulate the conditions of real experimental processes. Shear flow and heat flow were both simulated by carrying out such simulations with “reservoirs” [Ash75, Hoo75]. These reservoirs help to maintain constant velocities and temperatures at the boundaries.

The bulk viscosity is another transport coefficient that describes the extra stress due to dilation or compression. Because this effect depends upon volume change, a change of thermodynamic state, bulk viscosity cannot be measured in a steady state reservoir experiment. Hoover *et al.* [Hoo80] developed a nonequilibrium molecular dynamics method which allowed the system volume to cycle over a small range with a fixed frequency. With a proposed perturbed-Hamiltonian, they were able to obtain the bulk viscosity either by determining the strain rate component of stress, or by averaging the work done by the forces cycling the volume, over a complete cycle of dilation and compression.

In a subsequent paper, Evans [Eva81] presented his results of nonequilibrium molecular dynamics simulations of a Lennard-Jones fluid undergoing shear flow at the triple point. He computed the shear viscosity, stress and hydrostatic pressure both as a function of frequency (after extrapolating to zero shear rate) and as a function of strain rate (at zero frequency). His results demonstrated agreement between the prediction of long time tail theories [Pom75, Kaw73, Yam75, Ern78] and the observed functional forms. But the coefficients in the functions obtained from simulation are much larger than the prediction of the theories. He conjectured that the simulation results might be calculated at too high strain rates or frequencies for the asymptotic theories to be appropriate.

Evans [Eva80a] also studied shear flow in two dimensional systems. He performed nonequilibrium molecular dynamics for soft disks, and found that the strain rate dependence of shear viscosity η and hydrostatic pressure p could be expressed as logarithmic functional forms. These functional forms agreed with those predicted by using asymptotic “long-time-tail” theories [Pom75, Kaw73, Yam75, Ern78]. But for the coefficients in the functions, the numerical values obtained from the simulations were several orders of magnitude greater than what theory predicted. These coefficients, as we shall see later in this thesis, are state point dependent constants. In his calculation results, the magnitude of the coefficients was observed to increase rapidly as the triple point was approached, whereas theory predicts the opposite behavior.

Lee and Cummings [Lee94] carried out nonequilibrium molecular dynamics simulations of pure argon at a temperature of 135 K and density of 1.034 g/cm^3 . The highly accurate Barker-Fisher-Watts (BFW) model was used for the intermolecular potential. They considered the BFW potential both with and without the Axilrod-Teller three-body interaction. They found that the three-body potential had a very small effect on the shear viscosity. The resulting pressure and viscosity were consistent with the prediction of kinetic and mode coupling theory, that is $\eta \sim \dot{\gamma}^{1/2}$, $p \sim \dot{\gamma}^{3/2}$.

Travis et al. [Tra99] performed nonequilibrium molecular dynamics (NEMD) simulations for a Weeks-Chandler-Andersen (WCA) fluid at the Lennard-Jones triple point. They

calculated the wavevector and strain rate dependent shear viscosity by employing the sinusoidal transverse force (STF) method. And they also calculated a strain rate dependent zero wavevector shear viscosity by using the spatially homogeneous SLLOD algorithm. It was found that the shear viscosity could not be described by a single square-root function over the whole range of shear rates, irrespective of the wavevector value q . Instead, the shear viscosity could be fitted by two functions of $\dot{\gamma}^{1/2}$ over two different ranges of strain rate. The strain rate dependence of the shear viscosity obeyed an empirical formula called the Cross equation [Cro65] which is often used by rheologists to characterize the flow curves of real materials, and the prediction of Quentrec's local order theory [Que82]. The extrapolated zero strain rate viscosities obtained from the STF simulations could be fitted well with all three functional forms: $q^{3/2}$ prediction of mode coupling theory, Lorentzian function form and a Taylor series expansion in q^2 .

Travis et al. [Tra98] reported a study of the shear flow of the Weeks-Chandler-Andersen fluid at the Lennard-Jones triple point. They investigated the strain rate dependence of a range of rheological properties by nonequilibrium molecular dynamics simulations. To get high statistical precision at low strain rate, they used a rather large system and long simulation times (their smallest shear rate is the order of 10^{-2}). They found that the internal energy per particle and the hydrostatic pressure vary with shear rate as $\dot{\gamma}^{3/2}$, consistent with the prediction of mode coupling theory. However, for the shear viscosity, they found that the simulation data could not be fit by a single square root function as theory predicts. Nevertheless, the data could be characterized by fitting two square root functions in two different strain rate regimes. The viscosity data could also be fit to the Cross equation and Quentrec local-order theory. They suggested that the result of Ryckaert et al [Ryc88], that showed that $\eta \sim \dot{\gamma}^2$, was not reliable because the shear rates they studied were relatively large and their statistical uncertainties were also quite large.

Evans et al. [Eva89] studied the effects of both the number of particles in a simulation system and the cutoff radius of the potential in three dimensional Lennard-Jones fluids. They computed the shear viscosity by homogeneous nonequilibrium molecular dynamics

using 108, 256 and 2048 particles. The three different potential truncation radii they used were: $r_c = 2^{1/6} \sigma$ (WCA), 2.5σ and 3.5σ . In all cases the potential was shifted so that beyond the truncation distance, the potential was zero. They found that for systems of 256 particles or more, the shear viscosity was, within 0.5 per cent, independent of the number of particles used in the simulation. They estimated that the zero shear rate viscosity of the Lennard-Jones fluid at the triple point was ≈ 3.41 . They noticed a small but statistically significant deviation from the square root dependence of viscosity with respect to strain rate. They concluded that truncating the Lennard-Jones potential at 2.5σ , would only change the viscosity by less than 0.5 per cent compared to the untruncated fluid.

Ryckaert et al. [Ryc88] used NEMD to study the relationship of shear viscosity with shear rate using a Lennard-Jones fluid. The state point was chosen to be $\rho = 0.7$, $T = 2.75$ (reduced unit). $\eta(\dot{\gamma})$ was deduced from the transient behavior of the system suddenly subjected to a planar Couette flow, without the application of a thermostat. They found that the viscosity η was insensitive to the shear rate $\dot{\gamma}$ for $\dot{\gamma} < 1$. At higher $\dot{\gamma}$, the expression $\eta(\dot{\gamma}) \approx 1.29 - 0.013 \dot{\gamma}^2$ reproduced the data better than Holian and Evans' [Hol83] result: $\eta(\dot{\gamma}) \approx 1.37 - 0.097 \dot{\gamma}^{1/2}$. They found that the best linear fit of $\eta(\dot{\gamma})$ vs $\dot{\gamma}^v$ occurred for $v \approx 3$, not $3/2$ or 2 .

Ferrario et al. [Fer91b] studied the shear rate dependence of the viscosity of the Lennard-Jones fluid at the triple point. In their paper, high-precision molecular-dynamics data were reported for the shear viscosity η as a function of the shear rate $\dot{\gamma}$ for a large system. They had three main conclusions: first, all numerical data did not suggest any significant difference between the results at the Lennard-Jones triple point and those obtained for other fluid-state points. Second, they found no numerical evidence for a hypothetical long-time tail in the stress-stress time correlation function, as predicted by mode-coupling theory. Exponential decay seemed to be preferable to algebraic decay, namely $t^{-3/2}$. Third, the data supported an analytical (quadratic at low shear rate) dependence of the viscosity on $\dot{\gamma}$. Nonanalyticity, such as the square-root dependence suggested by mode-coupling theory, was not supported by their data.

The simulation data of Evans and Morriss [Eva88, Mor87] showed that at very small external fields, the TTCF formalism provided the most efficient method of calculating transport properties. Evans and Morriss also remarked on the results of Ryckaert *et al.* [Ryc88]. Ryckaert *et al.* studied the Lennard-Jones fluid at a dense liquid-state point and found no evidence for a nonanalytic variation of the viscosity with strain rate. Evans and Morriss commented that this result was not surprising as it had long been realized that the coefficient of the $\dot{\gamma}^{1/2}$ dependence increased dramatically as the glass transition was approached, and for the state point Ryckaert *et al.* considered the coefficient was very small. Evans and Morriss [Eva88] noticed that the strongest evidence for the square-root dependence was from the Lennard-Jones triple-point data.

Marcelli et al. [Mar00, Mar01a] reported NEMD simulations of the shear viscosity, pressure and energy of argon and xenon interacting via accurate two-body and three-body potentials at the state points $(\rho, T) = (0.592, 0.95)$ and $(\rho, T) = (0.6, 0.9)$ respectively. The two-body potential was the Barker-Fisher-Watts potential [Bar71] and the three-body potential was the Axilrod-Teller potential [Axi43]. They showed that the pressure and energy were clearly not linear functions of $\dot{\gamma}^{3/2}$, but could be well described by an analytic $\dot{\gamma}^2$ dependence. This was in contrast to the results reported by Lee and Cummings [Lee94] which showed results consist with mode-coupling theory. This relationship was independent of the three-body potential interaction and was only a consequence of two-body interactions. The three-body term only served to raise the magnitude of the total pressure and energy.

In practical use and in the laboratory, the rheological properties of fluids under small shear rates are important as these correspond to typical processing rates in industry. But with direct NEMD simulations, one cannot get accurate results in the small field, because in the small field limit the signal-to-noise ratio goes to zero. In contrast to direct NEMD, the transient time correlation function (TTCF) approach [Eva88, Mor87] can yield much more accurate results in very weak fields.

The Green-Kubo relations are an example of linear response theory. Some non-linear response theories have also been proposed. Among these non-linear response theories, only two are useful in practice. They are the Kawasaki representation [Yam67] and the transient time correlation function method [Eva88]. Both of these theories give exact descriptions of the nonlinear response of classical many-body systems to the dissipative perturbation induced by an external field. The Kawasaki representation is very valuable in its use as a nonequilibrium partition function. It leads to steady-state fluctuation expressions for the derived properties such as the specific heats, the thermal expansion coefficients, and the compressibilities. The TTCF representation is less useful in this aspect. However, the TTCF method is much easier to compute numerically than Kawasaki, and hence it can be directly applied in computer simulations.

In the zero field limit the TTCF formalism reduces to the Green-Kubo relations. The agreement of the TTCF and the Green-Kubo methods at small fields means that unlike direct NEMD, the TTCF method can be used at very small fields. Direct NEMD is very efficient at strong fields, but very poor at small fields due to the unfavorable signal-to-noise ratio. The Green-Kubo method can only be used at equilibrium, or in the weak linear regime. Thus the transient-time correlation-function method is a link between the Green-Kubo method and direct NEMD.

Evans and Morriss [Eva88, Mor87] derived the transient time correlation function expressions for planar Couette flow and tested its validity by using NEMD simulations. They used TTCF to study the transient rheology of classical fluids at the Lennard-Jones triple point and compared the predictions of the TTCF formalism with three other ways of calculating the nonlinear nonequilibrium response. The three ways are the Green-Kubo method, direct NEMD and NEMD subtraction technique respectively. Todd [Tod97b, Tod98] later extended the TTCF formalism to elongation flows.

In their work, the Green-Kubo method calculates the average of a phase variable by the time integration of an equilibrium time correlation function. Direct NEMD involves simulating a classical fluid undergoing thermostatted flow, such as planar Couette flow. At

very small external field direct NEMD becomes very inefficient because the signal-to-noise ratio is poor. The genuine nonequilibrium response becomes comparable or even smaller than the equilibrium fluctuations in the phase variables of interest. In order to use NEMD at small fields, Ciccotti et al. [Cic75, Cic76, Cic79] developed the NEMD subtraction technique. This technique can improve the signal-to-noise ratio by reducing noise in NEMD simulations so that it enables the measurement of the systematic nonequilibrium response at small fields. This subtraction method involves averaging the difference of phase variables computed with and without the perturbing external field. The two trajectories begin from exactly the same point in phase space. For short times the two phase-space trajectories are highly correlated and the noise in the nonequilibrium trajectory is very similar to that in the equilibrium trajectory. Consequently, one can reduce the noise by subtracting the value of the corresponding equilibrium phase variables. At larger times the two trajectories become uncorrelated, and the noise cannot be subtracted in this way. In contrast, the TTCF formalism, in conjunction with appropriate phase space mapping schemes, can reduce background noise at long times and does not suffer from this limitation [Eva90].

Borzsak et al. [Bor02], calculated the shear viscosity of the Weeks-Chandler-Andersen (WCA) fluid at the Lennard-Jones triple point in a wide range of strain rates using the transient time correlation function (TTCF) formalism. They found that below $\dot{\gamma} = 10^{-2}$ the viscosity was constant as a function of $\dot{\gamma}$, so this was the crossover strain rate below which the fluid becomes Newtonian. In this area, the viscosity value obtained from the TTCF calculation was essentially the Green-Kubo value, since there was no dependence on strain rate in the Newtonian regime. The transition from non-Newtonian to Newtonian was not sharp, so the crossover strain rate could not be decided precisely. To calculate the viscosity of the WCA fluid, TTCF was the good choice for $\dot{\gamma} \leq 0.01$ and NEMD for $\dot{\gamma} \geq 0.1$. There seemed to be separate regions in strain rate where the viscosity varies linearly with $\dot{\gamma}^{1/2}$ but with different slopes.

From the above simulation results, we can see that the stress-strain rate relationship problem has not yet been solved. Some results support the nonanalytical mode coupling

theory predictions, that is, $\eta \sim \dot{\gamma}^{1/2}$, and $p, \varepsilon \sim \dot{\gamma}^{3/2}$ (ε is energy per particle). But other results suggest that the stress varies with strain rate in a quadratic dependence on $\dot{\gamma}$. One reason these contradictions have arisen is because it was assumed the power exponents for $\dot{\gamma}$ were just a few fixed values, namely, 1/2, 3/2, and 2 (only Ryckaert *et al.* [Ryc88] suggested a power exponent $\nu \approx 3$ was a better fit than 2 in their simulations). No one had considered if there are other possible exponents. The other reason is that most simulations were performed at the Lennard-Jones triple point, and only a few at other state points. Researchers generally have not considered whether the exponent changed with state point or not. Only Ferrario *et al.* [Fer91b] considered this. Their conclusion was that all numerical data did not suggest any qualitative difference between the Lennard-Jones triple-point results and those obtained for other fluid-state points. However their conclusion was premature, because they didn't actually perform simulations at other state points themselves. It appears that they just compared their results with those of other authors without clearly stating whose work they had compared to. Since there were not many results at hand, and other works might be calculated for different potentials, different number of particles, different cutoff distances, and different statistical errors, their conclusions are not fully justified. They assumed the power exponent is independent of state point, and only the coefficients depend upon state point. We believe this assumption is not complete. In this thesis one of our main tasks is to study how the power exponent of the viscosity, pressure and energy varies with state point.