

## Chapter 9

### Conclusion and Recommendations

The central theme of this thesis has been to quantify exactly the dependence of the energy and pressure of shearing simple fluids as a function of strain rate by the use of nonequilibrium molecular dynamics. Our aim has been to determine whether this dependence obeys the mode coupling theory of Kawasaki and Gunton, or whether the dependence is analytic.

In our work, we first derived the functional forms for the pressure tensor and energy. This was done by assuming analyticity and taking a Taylor series expansion. We found that if the pressure tensor or energy are analytic functions of strain rate, then the leading terms of the isotropic pressure and energy are quadratic in the strain rate.

The power law dependence was observed by force-fitting the quantities over a range of strain rates up to 0.6. Our simulation results for energy, pressure and viscosity indicated that the value of the exponent depended on the state point of the fluid. In particular, we found that for the strain rates studied in this thesis the dependence was neither analytic or in conformity with the mode coupling exponent values of  $3/2$ ,  $3/2$  and  $1/2$  respectively. Instead, our simulations demonstrated a simple power law dependence. The value of the exponent and the coefficients of the power law are functions of state point.

For the pressure and energy, we find a surprisingly simple relationship clearly demonstrating that the exponent is a continuous linear function of the temperature and density and that the coefficients of these linear terms must be either potential-independent

or universal. Increasing the density or decreasing the temperature results in a decrease of the value of the exponent. The exponent varies continuously between  $\sim 1.2$  and 2. There is therefore nothing special about the  $3/2$  exponent predicted by the mode-coupling theory of Kawasaki and Gunton [Kaw73]. While it does occur near the triple point, it also occurs at higher density and temperature state points. That previous NEMD simulations have agreed with the mode-coupling theory prediction of a  $3/2$  exponent is a fortuitous consequence of performing simulations at the triple point. Agreement with the mode-coupling theory prediction breaks down at most other state-points. Prior to our work it was generally assumed that the exponent was fixed. Our conclusion proved that the dependence is, in general, nonanalytic, but also negated the prediction of mode coupling theory, at least in the range of strain rates typically used in such simulations.

In the process of the above study, we observed that at a fixed temperature, the exponent of the pressure (or energy) will decrease while increasing density. We found that the exponent is approximately 1 when the density corresponds to the solid phase density. We showed how we can use this to determine the fluid-solid phase boundary. We also found a method which uses the combination of MD and NEMD techniques to determine the fluid-solid boundary. Our methods were tested on the Lennard-Jones fluid and the results were consistent with those of previous published data.

We next used our methods to compute the fluid-solid phase boundary for the Barker-Fisher-Watts fluid and found that it displays similar behaviour to the Lennard-Jones fluid. The exponents are also linear functions of temperature and density. As far as we are aware, this is the first time that the BFW fluid-solid phase boundary has been computed.

In our final series of simulations, we used the transient time correlation function algorithm to calculate the viscosity of the WCA fluid at very small shear rates. We found that the viscosity is constant in the shear rate regime less than 0.01. We also found that at large shear rates, direct NEMD is a better method to calculate rheological properties, and our results are in accordance with those of others. We estimated a critical shear rate for the WCA fluid of about 0.05. If the shear rate is smaller than this, TTCF is the better

method. If the shear rate is larger than 0.05, then direct NEMD is more efficient. We also considered the long time tail of the stress autocorrelation function and found that an exponential function fit the data better than a power law form.

An atomic fluid is a simple system. Despite the theoretical and practical interests of its own, its study is instructive for other complex systems. Our studies of the state point dependence of the rheological behaviour of simple fluids suggest it may be worthwhile to investigate if generalizations to molecular systems (e.g. polymers, suspensions, etc.) can be made. This would make an interesting and potentially useful study.

Because only the BFW potential cannot accurately describe the behaviour of real materials, the three-body potential, such as the Axilrod-Teller potential, should be included. By re-doing the BFW simulations with the three-body force, greater agreement with experiment could be expected.

The observed phenomenon that  $\alpha = 1$  close to the solid boundary can be further studied. Can this assumption predict the fluid-solid boundary accurately? If the fluid-solid boundary decided by this method has some deviation from the real value, then what is the reason? Is the calculation of  $\alpha$  not accurate enough, or is the  $\alpha = 1$  assumption not exact? It would also be of interest to further explore if this exponent and boundary relation can be performed in other systems. Our combined MD/NEMD method of computing the fluid-solid phase boundary could be trialed for molecular systems, and may prove a viable route of determining phase equilibrium for practical systems.

Finally, we stress the importance of performing definitive TTCF studies at weak shear rates. In this regime we have yet to prove whether the fluid is analytic, whether it conforms to mode-coupling predictions, or whether a power-law behaviour is still valid.