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SUMMARY AND CONCLUSIONS

In this thesis, the method of Non-Equilibrium Molecular Dynamics (NEMD) computer simulations was employed to investigate the structural and dynamic properties of atomic and polymeric fluids undergoing planar Poiseuille flow. The fluids are confined between channels of several atomic diameters width and subjected to a uniform external force field. For the atomic fluids, the dependences of the number density, streaming velocity, shear stress, strain rate, and viscosity kernel as functions of channel width, average fluid density and field strength were investigated. As to the polymeric fluids, in addition to all the quantities studied for atomic fluids, the extension and rotation of the confined polymers were explored.

In Chapter 1 the background of the theoretical and experimental studies of atomic and molecular fluids was sketched, including the computational study of nano-scale flows. In Chapter 2 the basic theoretical framework of this thesis was introduced, in particular the microscopic expressions for the continuity equations in hydrodynamics. We then proceeded to derive the method of planes (MOP) expressions for the pressure tensor and heat flux vector for an atomic fluid under the influence of three-body forces.

In Chapter 3 the basic simulation methodologies used in this work were described. We gave a brief introduction to the equations of motion, force calculations, periodic boundary conditions, time integration algorithms, Gaussian constraints and the SLLOD algorithm. In Chapter 4, a concise description of parallel programming with a message

passing interface (MPI) was provided. The emphasis was placed on the demonstration of the frequently used MPI subroutines by analysing the sample of parallelized program for Poiseuille flow which we have developed and implemented in this work.

In Chapter 5 the validity of the theoretical derivations obtained in Chapter 2 was checked by performing non-equilibrium molecular dynamics computer simulations of a confined field driven fluid acted upon by a two-body Barker-Fisher-Watts (BFW) force coupled with the Axilrod-Teller (AT) three-body force. The MOP calculations were found to be in excellent agreement with independent calculations based upon direct integration of the hydrodynamic momentum and energy continuity equations. Our simulation results showed that the isotropic pressure is sensitive to the presence of three-body forces, whereas the shear stress and heat flux vector seem to be largely independent of them. Further work is required to study the potential, temperature and density dependence on the relative magnitudes of the two to three-body force contributions. While such effects are clearly small for noble gas fluids such as argon, they will most likely play a significant and important role for heavier atomic and molecular fluids and liquid metals. It is hoped that our MOP expressions will be useful for the study of such liquids in the future.

In Chapter 6 we used the non-local linear hydrodynamic constitutive model for computing a viscosity kernel, a function of compact support, for inhomogeneous nonequilibrium fluids. We applied the model to a simple atomic fluid undergoing planar Poiseuille flow in a channel of several atomic diameters width. We validate our Discrete Fourier Transforms applied in this work and analyse the behaviour of our system by using suitable test functions to study the effects of truncations in our system. Our results show that the viscosity kernel, $\eta(y)$, has a peak at $y = 0$, and decays to zero as y increases, where y represents the separation between where we want to know the stress and where the strain rate is. Physically, it means that the strain rate at the location where we want

to know the stress contributes most to the stress, and the contribution of the strain rate becomes less significant as the relative distance y increases. The integral over the viscosity kernel, which is the value of $\tilde{\eta}(k_y)$ when $k_y = 0$, compares reasonably well with the Navier-Stokes viscosity. We demonstrate that there are limitations in the model when it is applied to our confined fluids due to the effect of domain restriction on inverse convolution.

Finally, in Chapter 7 we studied the rheology of highly confined polymeric fluids undergoing Poiseuille flow. The structural and dynamic properties as simulated via NEMD were discussed in terms of the density profiles, the squared average radius of gyration, the squared average end-to-end distance, streaming velocity, strain rate, shear stress, and streaming angular velocity. Our simulation results show that sufficiently far from the walls, the radius of gyration for molecules under shear in the middle of the channel follows the power law $R_g \propto N^\nu$, where N is the number of bonds and the exponent has a value $\nu = 0.60 \pm 0.04$, which is larger than the melt value of 0.5 for a homogeneous equilibrium fluid. Under the conditions simulated, we find that viscous forces dominate the flow, resulting in the onset of plug-like flow velocity profiles with some wall slippage. An examination of the streaming angular velocity displays a strong correlation with the radius of gyration, being maximum in those regions where R_g is minimum and vice-versa. The angular velocity is shown to be proportional to half the strain rate sufficiently far from the walls, consistent with the behaviour for homogeneous fluids in the linear regime.

Further work in this field should focus on the influence of wall affinities on the spatially dependent structural and dynamic properties and boundary conditions for inhomogeneous nonequilibrium fluids using nonequilibrium molecular dynamics simulations. Slip boundary conditions were suggested in several molecular dynamics simulations [78, 79, 97, 98]. Recently rate-dependent slip [99] and shear-dependent slip [100] of

Newtonian fluids were detected. We demonstrated in this work, through direct measurement of the streaming velocity, that slip is also detectable in a highly confined atomic fluid bounded by solid surfaces. Further investigation on the slip length and dynamic friction is needed as nano-scale flow is dominated by surface properties [101, 102, 103].

It is clear that the simple homogeneous linear constitutive equation used to model confined fluids is limited to low densities and relatively large pore widths. Progress in this work will require theoretical methodologies to compute the inhomogeneous kernel, $\eta(\mathbf{r}, \mathbf{r}')$. This is a significant theoretical challenge, but an important one in the science of nanofluidics.

Finally, it might also be desirable to simulate rheological properties for much longer chains and polymer solutions to provide a better understanding of the behaviour of highly confined polymeric fluids at the molecular level. To be able to apply the simulation results to industrially relevant polymeric systems, techniques to enable accurate mapping between simulated and real molecules need to be established.