

Computer Simulation of Nanorheology for Inhomogeneous Fluids

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DECLARATION

I hereby declare that all work described in this thesis was done by the author, except where due reference is made in the text. The work contained in this thesis was carried out since the initial commencement date, and has not been submitted previously, in part or whole, for the award of any other degree or qualification at any university.

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This thesis is partly based on the following papers:

Chapter 2 and 5:

Junfang Zhang and B. D. Todd, *Pressure tensor and heat flux vector for inhomogeneous nonequilibrium fluids under the influence of three-body forces*, Phys. Rev. E **69**, 031111 (2004).

Chapter 6:

Junfang Zhang, B. D. Todd, and Karl P. Travis, *Viscosity of confined inhomogeneous nonequilibrium fluids*, J. Chem. Phys. **121**, 10778 (2004); Erratum, J. Chem. Phys. **122**, 219901 (2005)

Chapter 6:

Nonlocal hydrodynamic model for the shear viscosity of confined fluids: analysis of homogeneous kernel, P. J. Cadusch, B. D. Todd, Junfang Zhang and Peter J. Daivis, in preparation (2005).

Chapter 7:

Structural and dynamical properties for confined polymers undergoing planar Poiseuille flow, Junfang Zhang, B. D. Todd, and Peter J. Daivis, in preparation (2005).

ABSTRACT

In this thesis, we use nonequilibrium molecular dynamics (NEMD) methods to investigate the structural and dynamic properties of highly confined atomic and polymeric fluids undergoing planar Poiseuille flow.

We derive “method of planes” expressions for pressure tensor and heat flux vector for confined inhomogeneous atomic fluids under the influence of three-body forces. Our derivation is validated against NEMD simulations of a confined atomic fluid acted upon by a two-body Barker-Fisher-Watts force coupled with the Axilrod-Teller three-body force. Our method of planes calculations are in excellent agreement with the equivalent mesoscopic route of integrating the momentum and energy continuity equations directly from the simulation data. Our calculations reveal that three-body forces have an important consequence for the isotropic pressure, but have negligible influence on the shear stress and heat flux vector for a confined simple fluid.

We use the non-local linear hydrodynamic constitutive model, proposed by Evans and Morriss [1] for computing a viscosity kernel, a function of compact support, for inhomogeneous nonequilibrium fluids. Our results show that the viscosity kernel, $\eta(y)$, has a peak at $y = 0$, and gets smaller and decays to zero as y increases. 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. We demonstrate that there is a limitation in the model when it is applied to our confined fluids due to the effect of domain restriction on inverse convolution.

We study the nanorheology of simple polymeric fluids. Our NEMD 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.

Finally, we make some concluding remarks and suggestions for future work in the final chapter.

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