The State Point Dependence of Classical Fluids under Shear

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Abstract

In this work, we use nonequilibrium molecular dynamics methods to investigate the relationship between the viscosity, pressure, energy and the strain rate for a Lennard-Jones fluid. Our aim is to investigate the predictions of mode coupling theory, namely that the pressure, energy and viscosity are half integer powers of strain rate. We particularly studied the state point effect on this relationship. Our simulation results showed that in the strain rate region we studied, the viscosity, pressure and energy can be expressed as power law functions of strain rate. The power exponent was found not to have a fixed value, but rather was state point dependent. We found that for the pressure and energy the exponent can be expressed as a linear function of both temperature and density. We convincingly demonstrate that the relationship is nonanalytic, but the predictions of mode coupling theory which state that the exponents have fixed values of 3/2, 3/2 and 1/2 for energy, pressure and viscosity respectively, are also not correct.

We observed that the exponent of the pressure (or energy) decreased with increasing density at constant temperature, and when the density is the value of the melting density, the exponent is approximately 1. This observation was used to determine the fluid-solid phase transition. We also found a method which uses the combination of equilibrium and nonequilibrium molecular dynamics 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 attempted to use our methods to compute the fluid-solid phase boundary for the Barker-Fisher-Watts fluid and studied its power exponent. We found that it displays similar behaviour to the Lennard-Jones fluid.
In our final series of simulations, we used the transient time correlation function (TTCF) 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 (reduced units). 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 fits the data better than a power law form.
This manuscript would have not been completed without the help of many people. I would like to take this opportunity to express my sincere gratitude to the following persons and organizations for their contributions toward this project.

Firstly, I would like to thank my supervisors, Billy Todd and Richard Sadus, for giving me the opportunity to undertake this mighty task, for their constant encouragement, patient guidance, tolerance and insightful advice through the entire candidature, and for their assistance in the preparation of this manuscript.

Many thanks go to Guanwen Wu and all researchers and Ph. D. students at our Centre for their help and valuable discussions. They have been such good friends during the whole period I stayed at the Centre.

I thank the Australian Government for an International Postgraduate Research Scholarship (IPRS). I also thank the Australian Partnership for Advanced Computing National Facility (APAC), Victorian Partnership for Advanced Computing (VPAC), CSIRO Joint High Performance Computing and Communications Centre (HPCCC) and the Swinburne Supercomputer Centre for providing me with generous allocations of computer time.

Finally, I reserve my deepest gratitude to my wife Xiangyun and my mum Wei. They have been a constant source of love and support. Their substantial help and care in the family allow me so luxurious a time to complete my project.
Declaration

I hereby declare that the thesis entitled “The State Point Dependence of Classical Fluids under Shear”, and submitted in fulfilment of the requirements for the Degree of Doctor of Philosophy in the School of Information Technology of Swinburne University of Technology, is my own work and that it contains no material which has been accepted for the award to the candidate of any other degree or diploma, except where due reference is made in the text of the thesis. To the best of my knowledge and belief, it contains no material previously published or written by another person except where due reference is made in the text of the thesis.

Jialin Ge

February 2004
Publication from this thesis

The following papers have been based on part of this work:


Table of contents

Abstract ii

Acknowledgement iv

Declaration v

Publication from This Thesis vi

Table of Contents vii

List of Figures x

List of Tables xv

Glossary of Important Symbols xvi

Chapter 1 Introduction 1

Chapter 2 Literature review 5

Chapter 3 Shear Flow 14
  3.1: Transport processes and transport coefficients 14
  3.2: Navier-Stockes equations 16
### Chapter 4 Molecular Simulation

4.1: Introduction 29
4.2: Molecular dynamics 31
4.3: Intermolecular potential 35
4.4: Neighbour list 37
4.5: Green-Kubo relations 40
4.6: Non-equilibrium molecular dynamics 41
4.7: SLLOD algorithm and Lees-Edwards periodic boundary conditions 42
4.8: Transient time correlation function and mapping 45

### Chapter 5 State point dependence of power exponents

5.1: Analytic expansion of pressure tensor and energy 49
5.2: Simulation at three state points 55
5.3: Relationship between exponent and state point 70

### Chapter 6 Use of equilibrium and nonequilibrium molecular dynamics to determine solid-liquid phase coexistence at equilibrium

6.1: Introduction 85
6.2: Simulation method 86
6.3: Determination of the equilibrium solid-liquid phase boundary 87
   6.3.1. Melting transition 87
   6.3.2. Freezing transition 98
   6.3.3 Melting transition revisited 102
   6.3.4. Comparison with other algorithms 103
6.4: Conclusions 104
Chapter 7  Barker-Fisher-Watts fluid: its power exponents and liquid-solid boundary

7.1 The exponent  
7.2 Fluid-solid boundary  

Chapter 8  Use of TTCF to calculate the viscosity in a weak field

8.1 Introduction  
8.2 Methodology  
8.3 Comparison between direct NEMD and TTCF  
8.4 Viscosity at small shear rate  
8.5 The long-time tail  
8.6 Conclusions  

Chapter 9  Conclusions  

References
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>An elementary tetrahedron with three of its faces parallel to the coordinate planes through point P and the fourth with normal ( n ).</td>
</tr>
<tr>
<td>3.2</td>
<td>Planar Couette flow of a viscous fluid between a moving upper plate and a stationary lower plate.</td>
</tr>
<tr>
<td>4.1</td>
<td>Diagram demonstrating periodic boundary condition, minimum image convention and cutoff.</td>
</tr>
<tr>
<td>4.2</td>
<td>Diagram showing the construction of neighbour list.</td>
</tr>
<tr>
<td>4.3</td>
<td>Representation of a shearing cell under the Lees-Edwards periodic boundary conditions.</td>
</tr>
<tr>
<td>5.1</td>
<td>Potential energy per atom as a function of ( \dot{\gamma}^{3/2} ) at triple point. The solid line shows a linear fit with an AAD of 0.11%.</td>
</tr>
<tr>
<td>5.2</td>
<td>Potential energy per atom as a function of ( \dot{\gamma}^2 ) at triple point. The solid line shows a linear fit with an AAD of 0.30%.</td>
</tr>
<tr>
<td>5.3</td>
<td>Pressure as a function of ( \dot{\gamma}^{3/2} ) at triple point. The solid line shows a linear fit with an AAD of 1.55%.</td>
</tr>
<tr>
<td>5.4</td>
<td>Pressure as a function of ( \dot{\gamma}^2 ) at triple point. The solid line shows a linear fit with an AAD of 3.78%.</td>
</tr>
<tr>
<td>5.5</td>
<td>Potential energy per atom as a function of ( \dot{\gamma}^{3/2} ) at middle point. The solid line shows a linear fit with an AAD of 0.05%.</td>
</tr>
<tr>
<td>5.6</td>
<td>Potential energy per atom as a function of ( \dot{\gamma}^2 ) at middle point. The solid line shows a linear fit with an AAD of 0.02%.</td>
</tr>
<tr>
<td>5.7</td>
<td>Pressure as a function of ( \dot{\gamma}^{3/2} ) at middle point. The solid line</td>
</tr>
</tbody>
</table>
Figure 5.8  Shows a linear fit with an AAD of 2.81%.

Figure 5.9  Pressure as a function of $\dot{\gamma}^2$ at middle point. The solid line shows a linear fit with an AAD of 0.76%.

Figure 5.10  Potential energy per atom as a function of $\dot{\gamma}^{3/2}$ at high point. The solid line shows a linear fit with an AAD of 0.05%.

Figure 5.11  Potential energy per atom as a function of $\dot{\gamma}^2$ at high point. The solid line shows a linear fit with an AAD of 0.01%.

Figure 5.12  Pressure as a function of $\dot{\gamma}^{3/2}$ at high point. The solid line shows a linear fit with an AAD of 0.84%.

Figure 5.13  Pressure as a function of $\dot{\gamma}^2$ at high point. The solid line shows a linear fit with an AAD of 0.19%.

Figure 5.14  Phase diagram for the 6-12 Lennard-Jones fluid with a cut-off radius of $r_c = 3.5\sigma$. The triple point is located at $(\rho, T) = (0.85, 0.687)$, in agreement with ref [Kof93, Agr95], and the critical point is estimated as $(\rho, T) = (0.31, 1.26)$. The solid-liquid line is also obtained from [Agr95]. The vapour, liquid, fluid and solid phase regions are indicated by the symbols V, L, F and S, respectively.

Figure 5.15  $\alpha$ as a function of density for different temperatures. All open symbols represent fits determined from the potential energy profile, whereas solid symbols refer to fits determined from the pressure profile.

Figure 5.16  Coefficient $a$ for energy at different temperatures.

Figure 5.17  Coefficient $b$ for pressure at different temperatures.

Figure 5.18  $\alpha$ as a function of density at $T = 1.0$ for cut-off $r_c = 3.5\sigma$ and $r_c = L/2$, where $L$ is the simulation box length.

Figure 5.19  $\alpha$ as a function of temperature at $\rho = 0.8442$. Circles represent fits obtained from the potential energy profile, and triangles
represent fits obtained from pressure profile.

Figure 5.20a Viscosity vs. strain rate at the Lennard-Jones triple point.

Figure 5.20b Same plot as Fig. 5.20, but on a logarithmic scale.

Figure 5.21 Exponent for the viscosity at two temperatures.

Figure 6.1 Phase diagram of the Lennard-Jones liquid determined by Gibbs ensemble (crosses) and NEMD (open and filled squares and open circles) simulations. Solid lines are data from Kofke [Kof93, Agr95], and dotted lines are data from Hansen and Verlet [Han69].

Figure 6.2 α as a function of system density at three temperatures in the liquid region. The symbols represent simulation data (open triangles, $T = 0.722$; open squares, $T = 1.00$; filled circles, $T = 1.25$). The straight lines are linear fits to the data based upon the coefficients of Eqn (6.2), and the arrows represent extrapolation to $\alpha = 1.0$.

Figure 6.3 The effect of shear rate on equilibration of the dense system at $T = 1.00$.

Figure 6.4 Pressure as a function of time step at a density of 0.96 and temperature 1.0. Simulations start from an fcc lattice configuration.

Figure 6.5 Pressure vs. time step for an initial fcc lattice perturbed by a constant strain rate for several different strain rates. The field is then switched off after a time of $t = 250000\tau$ and the liquid allowed to relax to equilibrium.

Figure 6.6 Pressure as a function of strain rate at different densities and constant temperature $T = 1.00$. Entry into the two-phase liquid-solid region is clearly seen at higher densities (open symbols) by the sudden drop in pressure at zero strain rate. Filled symbols represent liquid phase densities. The densities from bottom to top curves are, 0.74, 0.76, 0.78, 0.80, 0.82, 0.8442, 0.88, 0.92, 0.94, 0.96, 0.98 and 1.0 respectively.
Figure 6.7 Pressure as a function of density at $T = 1.00$. Two phase transition regions are clearly visible. The vapour-liquid equilibria is computed by Gibbs ensemble (GEMC) simulation and the solid-liquid transition is determined by our NEMD method (open and filled triangles). Crosses at low density represent equilibrium ($NVT$) MD simulation data. Open diamonds represent the liquid phase obtained by equilibrium ($NVT$) MD simulation, while crossed open diamonds represent the two-phase region obtained by NEMD simulation. Open circles represent the solid branch, again obtained by equilibrium ($NVT$) MD. Beyond the solid-liquid phase transition point, extension of the solid branch indicates the superheated solid. The symbols G, L and S refer to gas, liquid and solid, respectively.

Figure 7.1 Pressure vs. strain rate for the BFW fluid at $(T, \rho) = (0.85, 0.84)$.

Figure 7.2 Exponents as a function of density at three temperatures. The solid symbols are exponents obtained from the pressure and the hollow symbols are obtained from the energy.

Figure 7.3 Exponents as a function of temperature at a density $\rho = 0.85$.

Figure 7.4 BFW phase diagram. Fluid-solid boundary denoted by solid symbols is obtained from our work. Gas-liquid boundary denoted by hollow symbols is from reference [Mar99].

Figure 8.1 (a) $P_yy$ as a function of time at shear rate $\dot{\gamma} = 1$. Circle symbols are direct NEMD data, while triangle symbols are TTCF data.

Figure 8.1 (b) $P_{xx}$ as a function of time at shear rate $\dot{\gamma} = 1$.

Figure 8.1 (c) $P_{yy}$ as a function of time at shear rate $\dot{\gamma} = 1$.

Figure 8.1 (d) $P_{zz}$ as a function of time at shear rate $\dot{\gamma} = 1$.

Figure 8.1 (e) $E$ as a function of time at shear rate $\dot{\gamma} = 1$.

Figure 8.1 (f) $p$ as a function of time at shear rate $\dot{\gamma} = 1$. 
Figure 8.1 (g) $\eta$ as a function of time at shear rate $\dot{\gamma} = 1$.  

Figure 8.2 (a) $P_{xy}$ as a function of time at shear rate $\dot{\gamma} = 0.002$. Circle symbols are direct NEMD data, while triangle symbols are TTCF data. 

Figure 8.2 (b) $P_{xx}$ as a function of time at shear rate $\dot{\gamma} = 0.002$. 

Figure 8.2 (c) $P_{yy}$ as a function of time at shear rate $\dot{\gamma} = 0.002$. 

Figure 8.2 (d) $P_{zz}$ as a function of time at shear rate $\dot{\gamma} = 0.002$. 

Figure 8.2 (e) $E$ as a function of time at shear rate $\dot{\gamma} = 0.002$. 

Figure 8.2 (f) $p$ as a function of time at shear rate $\dot{\gamma} = 0.002$. 

Figure 8.2 (g) $\eta$ as a function of time at shear rate $\dot{\gamma} = 0.002$. 

Figure 8.3 Shear stress vs. time. 

Figure 8.4 Shear stress vs. shear rate. 

Figure 8.5 Time correlation function $<P_{xy}(0)P(t)>$ at the Lennard-Jones triple point with a shear rate of $\dot{\gamma} = 0.01$. 

Figure 8.6 Time correlation function $<P_{xy}(0)P(t)>$ at the state point $(T, \rho) = (0.722, 0.72)$ with a shear rate of $\dot{\gamma} = 0.01$. 

List of Tables

Table 6.1  Comparison of melting densities, obtained by Hansen and Verlet [Han69], Kofke [Kof93, Agr95], and the present work. 94
Table 7.1  Parameters for the BFW potential for argon [Bar71]. 106
Table 7.2  Comparison between the coefficients of the linear function for the LJ and BFW potentials. 111
Table 7.3  Fluid-solid boundary density at four temperatures. 112
Glossary of important symbols

**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAD</td>
<td>Absolute average deviation</td>
</tr>
<tr>
<td>AT</td>
<td>Axilrod-Teler Potential</td>
</tr>
<tr>
<td>BFW</td>
<td>Barker-Fisher-Watts intermolecular potential</td>
</tr>
<tr>
<td>fcc</td>
<td>Face-centred cubic</td>
</tr>
<tr>
<td>GEMC</td>
<td>Gibbs ensemble Monte Carlo</td>
</tr>
<tr>
<td>LJ</td>
<td>Lennard-Jones</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular dynamics</td>
</tr>
<tr>
<td>MC</td>
<td>Monte Carlo</td>
</tr>
<tr>
<td>NEMD</td>
<td>Nonequilibrium molecular dynamics</td>
</tr>
<tr>
<td>NVT</td>
<td>Ensemble where number of particles, volume and temperature are kept constant</td>
</tr>
<tr>
<td>TTCF</td>
<td>Transient time correlation function formalism</td>
</tr>
<tr>
<td>WCA</td>
<td>Weeks-Chandler-Andersen intermolecular potential</td>
</tr>
</tbody>
</table>

**Subscripts and superscripts**

* Reduced units

**Latin alphabet**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>Self-diffusion coefficient</td>
</tr>
<tr>
<td>E</td>
<td>Internal energy or potential energy per particle</td>
</tr>
<tr>
<td>F&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Force acting on particle &lt;i&gt;i&lt;/i&gt;</td>
</tr>
<tr>
<td>H</td>
<td>Hamiltonian</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>L</td>
<td>Length of the simulation box</td>
</tr>
<tr>
<td>m</td>
<td>Mass</td>
</tr>
</tbody>
</table>
\( N \)  
Number of particles

\( p \)  
Isotropic pressure

\( \mathbf{P} \)  
Pressure tensor

\( \mathbf{p}_i \)  
Momentum of particle \( i \)

\( R \)  
Molar gas constant

\( \mathbf{r}_i \)  
Laboratory position of particle \( i \)

\( r_c \)  
Cutoff distance

\( \mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i \)  
Relative position of particles \( i \) and \( j \)

\( r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \)  
Distance between particles \( i \) and \( j \)

\( \dot{\mathbf{r}}_i, \ddot{\mathbf{r}}_i \)  
First and second time derivative of the position of particle \( i \)

\( T \)  
Temperature

\( t \)  
Time

\( \Delta t \)  
Time step

\( u \)  
Intermolecular potential function

\( \mathbf{u} \)  
Streaming velocity

\( U \)  
Potential energy per particle

\( V \)  
Volume

\( \nabla \mathbf{u} \)  
Strain rate tensor

\( x, y, z \)  
Cartesian coordinates

\( \mathbf{i}, \mathbf{j}, \mathbf{k} \)  
Cartesian unit vectors

**Greek alphabet**

\( \alpha \)  
Power exponent and thermostat multiplier

\( \sigma \)  
Effective atomic diameter

\( \varepsilon \)  
Energy per particle and depth of potential well

\( \lambda \)  
Thermal conductivity

\( \dot{\gamma} \)  
Shear rate

\( \eta \)  
Shear viscosity

\( \eta_v \)  
Bulk viscosity

\( \pi \)  
P\(i\)
\( \rho \quad \text{density} \)

\( \Pi \quad \text{Viscous pressure tensor} \)