

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.

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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

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Publication from this thesis

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

- [1] Ge J., Marcelli G., Todd B. D. and Sadus R. J. (2001), *Energy and pressure of shearing fluids at different state points*, Phys. Rev. E 64, 021201; Erratum, (2002), *ibid*, Phys. Rev. E 65, 069901(E).
- [2] Ge J., Todd B. D., Wu G. and Sadus R. J. (2003), *Scaling behavior for the pressure and energy of shearing fluids*, Phys. Rev. E 67, 061201.
- [3] Ge J., Wu G., Todd B. D. and Sadus R. J. (2003), *Equilibrium and nonequilibrium molecular dynamics methods for determining solid-liquid phase coexistence at equilibrium*, *J. Chem. Phys.* 119, 11017.

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Glossary of important symbols

Abbreviations

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

Subscripts and superscripts

*	Reduced units
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Latin alphabet

D	Self-diffusion coefficient
E	Internal energy or potential energy per particle
\mathbf{F}_i	Force acting on particle i
H	Hamiltonian
k	Boltzmann's constant
L	Length of the simulation box
m	Mass

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
Δt	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	
α	Power exponent and thermostat multiplier
σ	Effective atomic diameter
ε	Energy per particle and depth of potential well
λ	Thermal conductivity
$\dot{\gamma}$	Shear rate
η	Shear viscosity
η_v	Bulk viscosity
π	Pi

ρ	density
Π	Viscous pressure tensor