The Role of Three-Body Interactions on the Equilibrium and Non-Equilibrium Properties of Fluids from Molecular Simulation

Gianluca Marcelli

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Alla mia famiglia e
agli amici piu’ cari
che non si sono fatti
distrarre dalla lontananza.

Declaration

I hereby declare that the thesis entitled "The Role of Three-Body Interactions on the Equilibrium and Non-Equilibrium Properties of Fluids from Molecular Simulation", and submitted in fulfilment of the requirements for the Degree of Doctor of Philosophy in 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.

Gianluca MARCELLI

February 2001

Abstract

The aim of this work is to use molecular simulation to investigate the role of three-body interatomic potentials in noble gas systems for two distinct phenomena: phase equilibria and shear flow. In particular we studied the vapour-liquid coexisting phase for pure systems (argon, krypton and xenon) and for an argon-krypton mixture, utilizing the technique called Monte Carlo Gibbs ensemble. We also studied the dependence of the shear viscosity, pressure and energy with the strain rate in planar Couette flow, using a non-equilibrium molecular simulation (NEMD) technique.

The results we present in this work demonstrate that three-body interactions play an important role in the overall interatomic interactions of noble gases. This is demonstrated by the good agreement between our simulation results and the experimental data for both equilibrium and non-equilibrium systems.

The good results for vapour-liquid coexisting phases encourage performing further computer simulations with realistic potentials. This may improve the prediction of quantities like critical temperature and density, in particular of substances for which these properties are difficult to obtain from experiment.

We have demonstrated that use of accurate two- and three-body potentials for shearing liquid argon and xenon displays significant departure from the expected strain rate dependencies of the pressure, energy and shear viscosity. For the first time, the pressure is convincingly observed to vary linearly with an apparent analytic $\dot{\gamma}^{2}$ dependence, in contrast to the predicted $\dot{\gamma}^{3/2}$ dependence of mode-coupling theory. Our best extrapolation of the zero-shear viscosity for argon gives excellent agreement (within 1%) with the known experimental data. To the best of our knowledge, this the first time that such accuracy has been

achieved with NEMD simulations. This encourages performing simulations with accurate potentials for transport properties.

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Publications from this thesis

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

[1] **Marcelli G. and Sadus R. J. (1999),** ***Molecular simulation of the phase behavior of noble gases using accurate two-body and three-body intermolecular potentials,*** **J. Chem. Phys.** 111**, 1533-1540.**

[2] Marcelli G. and Sadus R. J. (2000), *A link between the two-body and three-body interaction energies of fluids from molecular simulation*, J. Chem. Phys. **112**, 6382-6385.

[3] Marcelli G. and Sadus R. J. (2001), *Three-body interactions and the phase equilibria of mixtures*, High Temp. -High Pressures **33**, 111-118.

[4] Marcelli G., Todd B. D. and Sadus R. J. (2001), *Analytic dependence of the pressure and energy of an atomic fluid under shear*, Phys. Rev. E **63**, in press.

[5] **Marcelli G., Todd B. D. and Sadus R. J. (2001),** ***The strain rate dependence of shear viscosity, pressure and energy from two-body and three-body interactions*****, Fluid Phase Equilib., in press.**

[6] **Marcelli G., Todd B. D. and Sadus R. J. (2001),** ***On the relationship between two-body and three-body interactions from non-equilibrium molecular dynamics simulation*****, J. Chem. Phys., submitted.**

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Table of Symbols

Abbreviations

AAD	**Absolute average deviations**
AT	**Axilrod -Teller Potential**
BFW	**Barker-Fisher-Watts intermolecular potential**
fcc	**Face-centred cubic**
LHS	**Left-hand-side**
LJ	**Lennard-Jones potential**
hcp	**Hexagonal close-packed**
MD	**Molecular dynamics**
MC	**Monte Carlo**
MPPT	**Møller-Plesset perturbation theory**
NEMD	**Non-equilibrium molecular dynamics**
NPT	**Ensemble where number of particles, pressure and temperature are kept constant**
NVT	**Ensemble where number of particles, volume and temperature are kept constant**
RHS	**Right-hand-side**
WCA	**Weeks-Chandler-Andersen intermolecular potential**

Subscripts and superscripts

*****	**Reduce units**
I	**Phase *I***
2b, 2body	**Two body potential contribution**

3b, 3body	**Three body potential contribution**
$\boldsymbol{acc}(old \rightarrow new)$	**Acceptance probability of a move from *old* to *new***
conf.	**Configurational**
crit.	**Critical property**
D	**Dipole**
Disp	**Dispersion**
L, liq.	**Liquid phase**
O	**Octupole**
Q	**Quadrupole or partition function**
tot	**Total**
V, vap.	**Vapour phase**

Latin alphabet

B	**Second virial coefficient**
C	**Third virial coefficient**
E	**Potential energy**
e	**Euler number**
$\boldsymbol{F}_i$	**Force acting on particle** i
G(r)	**Radial distribution function**
H	**Hamiltonian or enthalpy**
k	**Boltzmann’s constant**
L	**Length of the simulation box**
m	**Mass**
N	**Number of particles**

$\boldsymbol{P}$	**Hydrostatic pressure**
P	**Pressure tensor**
$\boldsymbol{p}_i$	**Momentum of particle** i
$\boldsymbol{Q}$	**Partition function**
$\boldsymbol{R}$	**Molar gas constant**
$\boldsymbol{r}_i$	**Position of particle** i
$r_{ij}= r_{\boldsymbol{i}} - r_{\boldsymbol{j}}$	**Relative position of particle** i ***and j***
$\boldsymbol{r}_{ij}= \lvert r_{\boldsymbol{i}} - r_j \rvert$	
$\dot{\boldsymbol{r}}_i , \ddot{\boldsymbol{r}}_i$	**First and second time derivative of the position of particle** i
r ,q, f	**Polar coordinates**
$\boldsymbol{T}$	**Temperature**
t	**Time**
Δt	**Time step**
u	**Intermolecular potential function**
$\boldsymbol{V}$	**Volume**
$\nabla \boldsymbol{v}$	**Strain rate tensor**
$\boldsymbol{x, y, z}$	**Cartesian coordinates**
$\hat{x}, \hat{y}, \hat{z}$	**Cartesian unit vectors**
x_I^a	**Composition of species** $\boldsymbol{a}$ **in phase** $\boldsymbol{I}$**.**

Greek alphabet

$a\ (old \rightarrow new)$	**Probability of generating configuration *new* starting from *old***
$\dot{g}$	**Shear rate**

h	**Shear viscosity**
Λ	**Thermal de Broglie wavelength**
m	**Chemical potential**
$\boldsymbol{v}$	**Non-additive coefficient**
p	**Pi**
$p\ (old \to new)$	**Transition probability from *old* to *new***
r	**Numeric density**
y, c, f	**Wave functions as defined in Eqs. (2.1) and (2.3)**