CHAOTIC AND RHEOLOGICAL PROPERTIES OF LIQUIDS UNDER PLANAR SHEAR AND ELONGATIONAL FLOWS

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Dissertation submitted
in fulfilment of requirements for the degree of
Doctor of Philosophy

Centre for Molecular Simulation
Swinburne University of Technology
2007

Abstract

The aim of this work is to present relevant rheological and chaotic properties of atomic liquid systems under steady planar shear (PSF) and elongational (PEF) flows, with the use of Nonequilibrium Molecular Dynamics (NEMD) techniques. These flows are widely employed in industrial applications, and, at a fundamental level, represent interesting models for the discussion of theoretical assumptions of statistical mechanics and dynamical systems theory. Whereas the use of the SLLOD algorithm of NEMD for PSF has been established for more than twenty years, the simulation of PEF for arbitrarily long times has recently been made possible through the combination of the SLLOD formulation with the so-called Kraynik-Reinelt (KR) periodic boundary conditions (pbcs) for the unit cell.

Firstly, aspects regarding the chaotic behaviour of these types of flow are discussed, with an analysis of the spectra of Lyapunov exponents for systems of different sizes and at a number of different state points, under Gaussian isoenergetic and isokinetic constrained dynamics. The so-called conjugate-pairing rule (CPR), which, loosely speaking, pertains to systems with a homogeneous distribution of chaoticity among internal degrees of freedom, is established for PEF, whereas robust evidence for its violation under PSF is provided. Considerations about the link between Lyapunov exponents and viscosity, structural ordering at high values of external fields and phase space contractions are also put forward.

Secondly, a novel algorithm for the implementation of the Nosé-Hoover mechanism for pressure conservation for PEF systems is illustrated and used in conjunction with a Gaussian isokinetic thermostat to achieve a so-called isokinetic-isobaric (or *NpT*) ensemble. Accurate results for the viscosity of a simple liquid in this ensemble are obtained, and a comparison with analogous findings for the isokinetic-isochoric (*NVT*) regime is provided.

Furthermore, the analysis of the chaotic properties for PSF and PEF systems is extended to the case of *NpT* constrained dynamics with the use of the above method, showing that the degrees of freedom associated with the Nosé-Hoover (NH) barostat have no influence on chaoticity, regardless of whether the underlying algorithm describing the flow is symplectic.

Then, a study that shows the independence of physical properties of homogeneous systems under steady PEF from KR pbcs is carried out. Using CPR and inspecting the Lyapunov exponents associated with the conserved degrees of freedom, the dynamics of phase-space trajectories and the values of transport coefficients are proven to be insensitive to any choice of initial parameters of periodic mappings on the unit cell.

Finally, some concluding remarks and suggestions for future work complete the Thesis.

Acknowledgements

Firstly, let me thank my two excellent supervisors, Prof. B. D. Todd and Prof. D. J. Searles for their ideas, vision, help, support and humanity. They are indeed extraordinary persons whom I really enjoyed working with. By means of their advice and suggestions, I feel I truly grew up as a physicist and as a human being.

My praise also goes to Prof. R. J. Sadus, who proved to be a great Centre Director and a person endowed with unparallel gentleness.

Deciding to live fifteen thousand kilometres away from Modena, a city of rare beauty and extremely frank and good-humoured dwellers, is painful. Thanks for all the emotions you still hide around every single corner of your streets each time I visit you.

I am indebted to my 'extended' family for their support and constant care, which were never missing.

Huge thanks also go to my friends in Melbourne, who have looked after me and eased my unpredictable Italian temper. I would like especially to remember Tom, Jesper, Signe, Dave and Samil. I am lucky enough to have good friends in Italy that have contributed to preserve my equilibrium and to keep my spirit high: Roberto, Sederani, Marietto, Matteo and dr. Vellani.

Sara stands in a completely different class of her own and this work is dedicated to her. It would have never been written had she not been in my life.

Declaration

I hereby declare that the Thesis entitled "Chaotic and rheological properties of liquids under planar shear and elongational flows", and submitted in fulfilment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Information and Communication Technologies 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.

Federico Frascoli

December 2007.

Publications from this Thesis

Frascoli, F., Searles, D.J. and Todd, B.D. (2006), "*A comparison of the chaotic properties of planar elongational flow and planar shear flow for systems in a steady state: Lyapunov exponents, conjugate-pairing rule and phase-space contraction*", Phys. Rev. E **73**, 046206.

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Notation

Abbreviations

CPR	Conjugate pairing rule
dev	Deviation
Eq	Equilibrium
fcc	Face-centred cubic
IE	Isoenergetic-isochoric
IK	Isokinetic-isochoric
KR	Kraynik-Reinelt
LR	Lagrangian-Rhomboid
NEMD	Nonequilibrium molecular dynamics
NEq	Nonequilibrium
NH	Nosé-Hoover
NpT	Isokinetic-isobaric ensemble
NVE	Isoenergetic-isochoric ensemble
NVT	Isokinetic-isochoric ensemble
pbcs	Periodic boundary conditions
PBT	Profile biased thermostat
PEF	Planar elongational flow
PSF	Planar shear flow
PUT	Profile unbiased thermostat
WCA	Weeks-Chandler-Andersen interatomic potential

Latin alphabet

II	Second scalar invariant
$\mathbf{C}_i$, $\mathbf{D}_i$	Coupling constants
$\mathbf{D}$	Diagonal strain rate tensor for extensional flows
D_{KY}	Kaplan-Yorke dimension
D_{MZ}	Machta-Zwanzig diffusion coefficient for the Lorentz gas
D	Diffusion coefficient in the Lorentz gas
D_{11}, D_{22}, D_{33}	Components of the diagonal strain rate tensor for extensional flows
d	Dimensionality of the system or distance between scatterers in the Lorentz gas
$\mathbf{E}$	Constant external field in the driven Lorentz gas
$E(\mathbf{\Gamma})$, $E(\mathbf{r}_{ij},\mathbf{p})$, E	Total energy of the system
$\mathbf{e}_{\max}$	Eigenvector of the Cat map matrix associated with the maximum eigenvalue
$F_{ext}(t)$	Generic external force
$\mathbf{F}_i$	Total force acting on particle i
$\mathbf{F}_{ij}$	Force acting on particle i due to particle j

$\mathbf{F}_x$, $\mathbf{F}_y$	Forces acting on plates or box dimensions under shear or elongation
F_e	Constant colour field
$f(\mathbf{\Gamma},t)$	Phase space density function
$f_T(\mathbf{\Gamma})$	Isokinetic distribution function
$f_c(\mathbf{\Gamma},\zeta)$	Nosé-Hoover canonical distribution function
$f_{PSF}^{eq}(\mathbf{\Gamma})$	Equilibrium phase space distribution for planar shear flow
$\mathbf{G}(\mathbf{\Gamma},t)$	Matrix of the equations of motions
H	Hamiltonian of the system
$\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$	Cartesian unit vectors
$\mathbf{J}$	Symplectic matrix
$\mathbf{J}(\mathbf{r}_i,t)$	Local momentum current
$\mathbf{J}(\mathbf{F_e})$	Thermodynamic flux as a function of the thermodynamic force
$\mathbf{J}_Q$	Heat flux vector
J_i, X_i	Zeroth (scalar) order component of the thermodynamic flux (or force)
J_i, X_i	First (vector) order component of the thermodynamic flux (or force)
J_i, X_i	Second (tensor) order component of the thermodynamic flux or force
$\mathbf{K}$	Time-independent matrix for conjugate pairing
$K(t)$, $K(\mathbf{\Gamma})$	Kinetic energy
$\mathbf{k}$	Wavevector in k-space
k_B	Boltzmann's constant
$\mathbf{L}_i$	Lattice vector of the simulation box
$\mathbf{L}(t)$	System propagator
$L(\mathbf{F_e})$	Transport coefficient as a function of the thermodynamic force
L_i	Length of dimension *i* of the simulation box
L_{ij}	Fourth-rank transport tensor
${}^{new}L_{T,ix}(t')$	Elongated and rescaled *x* component of boxlength *i* at time t' in the new-cell method
${}^{new}L_{T,ix}^{0}$	Rescaled *x* component of boxlength *i* in the new-cell method
$\mathbf{M}$	Cat map matrix
M	Sum of all the masses of the particles
δM	Number of ensemble points
m_i	Mass of particle *i*
m_1, m_2, m_3	Elements of the cat map matrix
N	Number of atoms/particles
N_c	Constrained degrees of freedom
N_f	Actual degrees of freedom
n_x, n_y	Number of nodes associated with Lyapunov modes
$\mathbf{P}(\mathbf{r},t)$	Pressure tensor
$\tilde{\mathbf{P}}(\mathbf{k},t)$	Fourier transform of the Pressure tensor

P_{xx}, P_{yy}	Diagonal components of the Pressure tensor
P_{xy}	Shear stress
$P_{\delta}(t)$	Sum of peculiar momenta of the particles
P, p	Instantaneous pressure of the system or probability in the fluctuation theorems
P	Probability in the fluctuation theorems
$\mathbf{p}_i$	Peculiar momentum of particle *i*
p_0	Isotropic pressure or target pressure
Q	Heat exchanged or damping factor in the constant pressure algorithm
$\mathbf{q}_i$	Laboratory position of particle *i*
$\mathbf{R}_{\delta}$	Centre of mass vector
$\mathbf{R}_{\theta(t)}$	Antisymmetric rotation matrix
$\mathbf{r}_i$	Laboratory or reduced position of particle *i*
$\mathbf{r}_{ij}$	Laboratory or reduced distance between particles *i* and *j*
r_c	Cutoff distance for the interatomic potential
S	Entropy or entropy rate
s	Degree of freedom coupled to thermal bath in the configurational thermostat
$\mathbf{T}$	Stability (or Jacobian) matrix
T, $T(t)$	Temperature
$T(\mathbf{r},t)$	Local temperature
T_C	Configurational temperature
T_0	Target temperature
t	Time or total length of a simulation
Δt	Timestep
$U(\mathbf{r}_{ij})$, U	Potential or internal Energy of the system
V	Volume
$V_T(t')$	Target volume at time t'
$\hat{V}(t)$	Phase space volume
$\mathbf{u}_i$	Peculiar velocity of particle *i*
u_i	Local internal energy of particle *i*
$\mathbf{v}_i$	Velocity of particle *i*
$\mathbf{v}(\mathbf{r}_i)$	Streaming velocity of the fluid
$\mathbf{v}(\mathbf{r},t)$	Local velocity
$\mathbf{v}_{PEF}(\mathbf{r},t)$	Linear streaming velocity for planar elongational flow
$\mathbf{v}_{PSF}(\mathbf{r},t)$	Linear streaming velocity for planar shear flow
$\nabla\mathbf{v}$	Strain rate or velocity gradient tensor
x, y, z	Cartesian coordinates
$X(t)$, $Y(t)$, $Z(t)$	Components of the centre of mass vector

Greek alphabet

α, $\alpha(\mathbf{\Gamma})$	Gaussian thermostat multiplier, Cartesian index or multiplicative constant
β	Boltzmann factor, Cartesian index or power constant
$\mathbf{\Gamma}(t)$	Phase space vector
$\mathbf{\Gamma}_0$	Initial state of the system
$\mathbf{\Gamma}_0$, $\mathbf{\Gamma}_i$	"Mother" system and "daughter" system i in the Hoover-Posch algorithm for Lyapunov exponents
$\delta\mathbf{\Gamma}_i$	Infinitesimal displacement vector i
$\delta\mathbf{\Gamma}_i^c$	Constrained infinitesimal displacement vector i
$\dot{\gamma}$	Shear rate
δ	Cartesian index
ε	Lennard-Jones energy parameter
$\dot{\varepsilon}$	Elongational rate
ε_P	Hencky strain
ζ	Nosé-Hoover multiplier for isokinetic and configurational thermostats
η	Newtonian viscosity
η_{PEF}, $\eta_T(\dot{\varepsilon})$, $\eta(\dot{\varepsilon})$	Nonequilibrium elongational viscosity
η_{PSF}	Nonequilibrium shear viscosity
η_V	Bulk viscosity
$\Theta(t)$	Heaviside step function
θ_0	Initial angle of rotation of the unit cell with respect to the x axis in planar elongation
$\theta(t)$	Angle between one elongated boxlength and the x axis
${}^{new}\theta(t')$	Angle between one elongated boxlength and the x axis at time t' after rescaling through the-new cell method
κ	Conductivity of the Lorentz gas
$\Lambda(\mathbf{\Gamma})$	Phase space compression factor
λ	Thermal conductivity
$\lambda(t')$	Rescaling factor at time t' for constant pressure simulations
λ_i, $\lambda_{i'}$	Conjugate Lyapunov exponents
$\lambda_{\max}$, $\lambda_{\min}$	Eigenvalues of Arnold cat map matrix or maximum and minimum Lyapunov exponents
λ_{up}	Unpaired Lyapunov exponent
$\Delta\lambda$	Difference between Lyapunov exponents
μ	Power constant
$\mu_i(\tau)$	Invariant measure in the phase space
ξ_{ij}	Lagrangian constraints in the Hoover-Posch algorithm for Lyapunov exponents
$\dot{\xi}$	Piston-like term in the Nosé-Hoover barostatting mechanism
$\rho(\mathbf{r},t)$	Local density
ρ	Homogeneous density of the sample
$\boldsymbol{\sigma}$	Stress tensor

σ	Density of rate of entropy production, effective atomic diameter in Lennard-Jones units or standard error
τ_i	Time length of trajectory i in the fluctuation theorems
τ_P	Period of the unit cell under elongation
ϕ, $\phi(\mathbf{r}_{ij})$	Interatomic effective pairwise potentia
$\Phi(\mathbf{r})$, $\Phi(\mathbf{\Gamma})$	Potential energy of the system
ϕ_c	Shift constant in the Weeks-Chandler-Andersen potential
$\varphi(t)$	Angle between sheared boxlengths or between elongated boxlength and the x axis
${}^{new}\varphi(t')$	Angle between one elongated boxlength and the x axis at time t' after rescaling through the-new cell method
χ	Conjugate pairing constant
Ω	Dissipation function in fluctuation theorems