Molecular Dynamics Simulations of Nanofluids and their Chaotic Properties

by

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Abstract

In this work we analyze several aspects of atomic fluids, in either homogeneous or inhomogeneous conditions, using non-equilibrium molecular dynamics simulation techniques (NEMD). The main aim is to characterize the chaotic properties of nanofluids under several types of constraints and forces. To achieve this, in conjunction with NEMD we use the Lyapunov spectral analysis. Lyapunov exponents allow us to quantify the degree of chaoticity of a dynamical system measuring the sensitivity to small changes in initial conditions. NEMD allows us to study mechanical properties of atomic fluids but also to view them as dynamical systems so that the tools of dynamical systems theory can be used.

Many studies have been successfully performed in the past to characterize the chaoticity of homogeneous fluids, less were performed on inhomogeneous fluids in highly confined geometries and we focus our work on this class. We analyze if and how the chaoticity changes with confinement including analysis of the atomistic walls’ phase space. In particular we look at two types of flow: Poiseuille and Couette. The former is typically described by a fluid in a channel driven by gravity-like forces or pressure gradients, while the latter describes a fluid trapped between two surfaces sliding in opposite directions. Both are important in many engineering applications.

In the framework of confined fluids we also analyze the issue of how to properly thermostat such systems. When performing simulations of systems driven away from equilibrium, it is necessary to extract the heat produced by viscous heating. Several types of thermostats have been derived, and essentially they all act by modifying
the velocity or acceleration of the particles to which they are applied, mimicking
the collisions with the surroundings that would otherwise absorb the excess kinetic
energy.

In homogeneous systems the thermostat is usually applied to all particles, but in
confined systems the situation is more complex because of spacial inhomogeneities
and the difficult evaluation of streaming velocities even at low fields. We analyze
these issues showing that thermostatting the confining walls, as representative of
nature where the heat is always dissipated through the container’s walls, is a prefer-
able procedure from either a mechanical or dynamical point of view, rather than
thermostatting the fluid itself.

For homogeneous flows, we present a new algorithm for infinite time simulations
of fluids under mixed flow: a linear combination of pure shear flow and pure elon-
gational flow. Both flows are found in many industrial and biological processes,
and their models, even if idealizations, have been successfully employed to compute
transport coefficients for complex fluids and other meaningful physical quantities.
However in real situations they are often combined together, sometimes in addition
to rotational and/or elliptical flow. It is therefore important to be able to charac-
terize combinations of arbitrary flows. We derive new periodic boundary conditions
(PBCs) able to simulate a bulk region of fluid under mixed flow for an indefinite
amount of time (for the first time to our knowledge), without introducing non-
physical effects in the mechanical properties.
Given that Lyapunov exponents are properly defined only in the infinite time limit, the development we have made to enable the simulation of mixed flow for an infinite period means, in theory, that for the first time it is possible to characterize its chaotic properties and to understand its phase space structure viewed as a whole and as a sum of pure flows. Lyapunov spectra for both planar shear flow and planar elongational flow have been studied at length before and a comparison with previous results is also reported.
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I can never thank enough my family for their unconditioned and, thanks to Skype, constant support (often in the form of emoticons!). Cindy is the last but not least, for supporting me in moments of doubts and for learning how to cook Perfecto Italiano food as good as my Mum’s (that is actually impossible!).

Many others deserve to be mentioned but the space is limited and I am due for submission..

..I really need to go now..
Declaration

I hereby declare that the thesis entitled “Molecular Dynamics Simulations of Nanofluids and their Chaotic Properties”, 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 of any other candidate of any other degree or diploma, except where due reference is made in the text of the thesis. To 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.

Stefano Bernardi
May 2011.
Publications from this Thesis


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Notation

Scalars are denoted in plain font, 
**Vectors** are denoted in bold font, 
**Tensors** are denoted in Sans serif font.

Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>CPR</td>
<td>Conjugate pairing rule</td>
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<tr>
<td>FCC</td>
<td>Face-centered cubic</td>
</tr>
<tr>
<td>K-R</td>
<td>Kraynik Reinelt</td>
</tr>
<tr>
<td>LR</td>
<td>Lagrangian-Rhomboid</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>NEMD</td>
<td>Nonequilibrium Molecular Dynamics</td>
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<tr>
<td>NVE</td>
<td>Isoenergetic-Isochoric ensemble</td>
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<tr>
<td>PBCs</td>
<td>Periodic boundary conditions</td>
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<td>PBT</td>
<td>Profile biased thermostat</td>
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<td>PCF</td>
<td>Planar Couette flow</td>
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<td>PEF</td>
<td>Planar elongational flow</td>
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<td>PMF</td>
<td>Planar mixed flow</td>
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<td>PSF</td>
<td>Planar shear flow</td>
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<tr>
<td>PUT</td>
<td>Profile unbiased thermostat</td>
</tr>
<tr>
<td>USF</td>
<td>Uniaxial stretching flow</td>
</tr>
<tr>
<td>WCA</td>
<td>Weeks-Chandler-Andersen</td>
</tr>
<tr>
<td>WT</td>
<td>Wall-thermostatted</td>
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Greek pronumerals

$I$  Second scalar invariant of the strain rate tensor

$(II = 2\dot{\gamma}_2^2$ for PCF and $II = 8\dot{\epsilon}_2^2$ for PEF)

$\beta$  $1/k_B T$

$\delta$  Dirac Delta function

$\Delta$  Slab size

$\dot{\varepsilon}, \varepsilon$  Extensional strain rate

$\epsilon$  L-J well-depth potential

$\eta_{\text{mixed}}$  Mixed flow viscosity

$\eta_{\text{PCF}}$  Shear viscosity

$\eta_{\text{PEF}}$  Elongational viscosity

$\eta$  Viscosity

$\dot{\gamma}, \dot{g}, \dot{\gamma}_1, \dot{\gamma}_2$  Shear rate

$\lambda$  Thermal conductivity

$\lambda_i$  Eigenvalues of Kraynik-Reinelt map

$\dot{\lambda}_i$  Lyapunov Exponents

$\lambda^{n}_F, \lambda^{n}_W$  Subsystem Lyapunov exponents

$\Lambda(\Gamma)$  Phase space compression factor

$\Lambda(t)$  Oseledec Matrix

$\Gamma$  Phase-space vector

$\mu(\varepsilon)$  Integral measure of the phase-space hypersurface

$\omega$  Field frequency

$\phi$  Angle between contracting axis and the velocity gradient in PMF

$\phi(\Gamma)$  Potential energy

$\Phi_{\text{LJ}}$  Lennard-Jones 12-6 potential

$\Phi_{\text{WCA}}$  WCA Potential

$\Pi$  $\mathbf{P} - p\mathbf{I}$

$\Upsilon$  Lyapunov localization
\( \psi_{\text{canonical}}, \psi_{\text{non-canonical}} \) Angle between mixed flow velocity gradient’s eigenvectors

\( \rho(\mathbf{r},t) \) Density at position \( \mathbf{r} \) and time \( t \)

\( \sigma_s \) Entropy source strength

\( \sigma \) Value of \( r_{ij} \) for which L-J potential is zero

\( \tau_p \) Lattice reproducibility time

\( \dot{\gamma} \) Strain-rate tensor

\( \sigma \) Stress tensor

\( A \) Lattice evolution tensor operator

\( \Theta \) Heaviside step function

\( \theta \) Simulation box orientation angle

\( \varepsilon \) Phase-space hypersurface

\( \varepsilon_p \) Total Henky strain

\( \Pi \) Lattice evolution tensor operator

\( \frac{1}{3} \text{tr}(\Pi) \)

\( \xi \) Thermostat’s friction coefficient

Latin pronumerals

\( A \) Slab area

\( a_i \) Acceleration of particle \( i \)

\( \delta A \) Phase space area

\( B(\Gamma) \) Variable, function of the phase-space

\( c_i \) Gear Predictor-Corrector coefficients

\( C \) Square of the Curvature

\( \mathbf{c}_i \) \( i \)th component of the lattice basis vectors \( \mathbf{l}_j \)

superscript \( c \) Gear Predictor-Corrector corrected values

\( d \) Cartesian dimension

\( D \) Material derivative

\( \overline{D}_t \) Kaplan-Yorke dimension

\( D_m \) Minimum distance between lattice points

\( D(t) \) Distance between lattice points
**D**  Diagonal PEF strain rate tensor

**E**  Total Energy

**exp**\(_L\)  Left-ordered exponential

\(f(\Gamma), f_G(\Gamma), f_H(\Gamma)\)  Phase-space distribution function

\(f(|v|)\)  speed distribution function

\(f(v)\)  velocity distribution function

**F**\(_e\)  External force

**F**\(_i\)  Total force on particle \(i\)

superscript \(f\)  Fluid particle identifier

g  Degrees of freedom

\(H_0(\Gamma)\)  Adiabatic Hamiltonian

\(H(\Gamma)\)  Hamiltonian

**I**  Unit tensor

\(J_i\)  Thermodynamic fluxes

\(J_Q\)  Heat flux

\(k_B\)  Boltzmann constant

**K**  Kinetic energy

\(k_{n_x,n_y}\)  Wave number

\(k_w\)  Harmonic potential constant

\(k\)  Wave vector

\(L_\alpha\)  Length of the simulation box, \(\alpha = x, y, z\)

\(L_{ij}\)  Transport coefficients

\(l_i,l'_i\)  Linearly independent lattice vectors

\(L(t)\)  Phase space propagator

superscript \(L\)  Lattice site identifier

\(m_i\)  Mass of particle \(i\)

**M**  Total mass of the system

**M**  Anosov map

\(n_\alpha\)  Integers, \(\alpha = x, y, z\)
\( N_{ij} \)  
Set of integers  

\( N \)  
Number of particles  

\( n_p \)  
Set of integers  

\( \mathbf{N} \)  
Integer tensor  

\( P_\alpha \)  
Component of centre of mass momentum, \( \alpha = x, y, z \)  

\( p \)  
Isotropic pressure  

\( \mathbf{p}_s \)  
Reservoir’s momentum  

\( \mathbf{P} \)  
Pressure tensor  

\( P_{\alpha\beta} \)  
Components of the Pressure tensor, \( \alpha, \beta = x, y, z \)  

\( \mathbf{P}^K, \mathbf{P}^U \)  
Pressure tensor, kinetic and potential components  

superscript \( p \)  
Gear Predictor-Corrector predicted values  

\( \mathbf{p}_i \)  
Peculiar momentum of particle \( i \)  

\( \mathbf{q}_i \)  
Coordinate of particle \( i \)  

\( Q \)  
Reservoir’s fictitious mass  

\( r_c \)  
Cut-off potential distance  

\( r_{ij} \)  
Distance between atom \( i \) and atom \( j \)  

\( \mathbf{r}(t) \)  
Position vector at time \( t \)  

\( \mathbf{R}_\delta \)  
Centre of mass vector  

\( S \)  
Entropy  

\( S^n \)  
Entropy like quantity  

\( s \)  
Nosé-Hoover reservoir’s degree of freedom  

\( s, t, t' \)  
Time  

\( \mathbf{S} \)  
Diagonalizing matrix  

subscript \( s \)  
Symmetric traceless part of a Tensor  

\( T^\alpha \)  
Topological Torus of dimension \( \alpha = 2, 3 \)  

\( t_\perp \)  
Time for which the basis vectors for mixed flow are orthogonal  

\( t_m \)  
Time at which the distance between lattice points is minimum  

\( T, T_{\text{conf}}, T_K, T_s, T_{SS} \)  
Temperature  

\( \mathbf{T} \)  
Jacobian or Stability matrix  

\( \Delta t \)  
Time step  

\( U_{ij} \)  
Potential energy felt by particle \( i \) from particle \( j \)  

\( U_i \)  
Potential energy felt by particle \( i \)
\( \mathbf{u}_i, \mathbf{w}_i \) Eigenvectors
\( \mathbf{u}(r,t) \) Streaming velocity at position \( r \) and time \( t \)
\( \nabla \mathbf{u}, \nabla \mathbf{u}^c, \nabla \mathbf{u}^{nc} \) Velocity gradient tensor
\( \mathbf{v}_i(t) \) Laboratory velocity of particle \( i \) at time \( t \)
\( V \) Simulation box volume
\( \delta V_{2dN} \) Phase space hypervolume of dimension \( 2dN \)
\( W^n \) Localization width
\( W \) Number of configurations compatible with an Ensemble
\( \text{superscript } W \) Wall particle identifier
\( X_i \) Thermodynamic forces
\( X(t), Y(t), Z(t) \) Centre of mass coordinates at time \( t \)
Chapter 1

Nonequilibrium Molecular Dynamics

1.1 Introduction

With the present work we aim at the characterization of the chaotic structure of highly confined inhomogeneous fluids far from equilibrium. Nonequilibrium Molecular Dynamics (NEMD) techniques [EM90] and dynamical systems theory (in particular Lyapunov spectra analysis [Ose68]) have been employed for this purpose.

Nonequilibrium molecular dynamics has seen a huge growth in the past years because of the possibility to study transport coefficients and rheological properties of fluids mimicking real experiments [Hoo83]. What differentiates it from Equilibrium Molecular Dynamics (EMD) is the presence of an external force field that drives the system arbitrarily away from equilibrium. The basic principles are common to both algorithms, namely to solve numerically Newton’s equations of motion (governing the systems of interest) and computing the physical properties of the system as a function of its phase-space variables. However, while the theoretical framework for equilibrium systems is well established (Equilibrium Statistical Mechanics), for nonequilibrium systems it is still developing [dGM84]. NEMD in this case becomes
Nonequilibrium Molecular Dynamics is a very useful tool to recreate and test real experiments or otherwise situations impossible or very difficult to obtain in a laboratory. Other approaches exist in the field of numerical simulation, such as Monte Carlo methods, first introduced by Metropolis et al. [MRR+53]. However they rely on the evaluation of equilibrium ensemble probabilities and are therefore not well suited for nonequilibrium processes. Furthermore the evolution of the systems is static, meaning that the focus is on the configurational state of the system and the lack of a dynamical description makes the application of dynamical system theory impossible.

The first to introduce molecular dynamics simulations were Alder and Wainwright in 1957 [AW57] for hard spheres. Since then the field has evolved significantly and now complex molecular systems, polymers, DNA filaments, etc. can be simulated with the use of appropriate models and rapidly growing computational algorithms and computer hardware.

1.2 Statistical Mechanics Overview

Statistical mechanics, of which Maxwell, Boltzmann and Gibbs [Max71, Bol74, Gib81] are the fathers, provides the framework to bridge the gap between the knowledge of the behaviour of the microscopic constituents of a system and its macroscopic state which is well described by thermodynamics. In principle one could follow the dynamical evolution of all the degrees of freedom of a system (solving the classical equations of motion) and fully characterize the phase-space (i.e. the collection of positions and momenta of every particle) gaining a complete microscopic description of the system at present and future times. From the knowledge of the microscopic states that the system can visit during its evolution we can extrapolate the thermodynamic macroscopic quantities that identify our system unequivocally (i.e. pressure, temperature, volume, energy, etc.). However to compute macroscopic mechanical properties (such as pressure), we need to know their value for every microscopic state of the system (and this value will generally not be the same), according to the constraints to which it is subjected (total energy, volume, etc.), and average them with the appropriate weight for each state [McQ00]. The weights
describe the likelihood of a system to be in a particular state, or region of the phase-space, and are given by the product of the density distribution function centered in that region and the region’s volume. Using the Liouville theorem, that describes the evolution of the phase-space distribution function, if we know an initial distribution we can then assign appropriate statistical weights to each state.

For Hamiltonian systems, where the phase-space distribution is conserved, each microscopic state is equally probable, and therefore it has equal weight \([\text{Hoo91}].\) Systems in which the number of particles, volume and energy \((N, V, E)\) are conserved constitute the Gibbs’ microcanonical ensemble. An ensemble is the collection of copies of the original system each one representing every state that the system can visit. Boltzmann derived the equation that links the entropy to the number of states consistent with the conserved set \((N, V, E)\):

\[
S(N, V, E) = k_B \ln W(N, V, E) = k_B \ln \int_{\Gamma(E)} d\Gamma,
\]

where \(k_B\) is the Boltzmann constant, \(W\) is the number of configurations compatible with a given state, \(\Gamma\) is the phase-space vector, \(\Gamma = [q_1, ..., q_N, p_1, ..., p_N]\) and \(\Gamma(E)\) is the set of phase-space points with energy \(E\). From differentiating the entropy, it is possible to derive all the state variables. However a more useful ensemble, common in experimental settings and therefore often used in simulations, is the canonical ensemble, where the set \((N, V, T)\) is constant, and the system can exchange energy with a heat reservoir whose dimensions are big enough for its temperature not to be affected by energy transfers. The distribution function then becomes

\[
f(\Gamma) = \frac{\exp(-\beta E(\Gamma))}{\int d\Gamma \exp(-\beta E(\Gamma))},
\]

where \(\beta = 1/k_BT\), \(f(\Gamma)\) is the phase-space distribution function. Using these results it is possible to derive an expression for any state variable starting from microscopic considerations. For equilibrium systems the theory is complete, however for nonequilibrium systems we do not have the proper phase-space distribution function. The
generalized Liouville equation in this case becomes

$$\frac{df}{dt} = \frac{∂f}{∂t} + \dot{Γ} \cdot \frac{∂f}{∂Γ} = -f \frac{∂}{∂Γ} \dot{Γ}. \quad (1.3)$$

We will come back to this in the following chapters when discussing the Lyapunov exponents, but for now we just observe that for thermostatted systems, the RHS of Eq. (1.3) is non-zero and for non-equilibrium systems the ensemble average of the RHS is also non-zero. In Gibbs’ ensemble view, the average of the properties is performed over the entire collection (method used for example in Monte Carlo techniques), while in Molecular Dynamics simulations the ensemble average is substituted by a time average. It is however practically not possible, either to sample the whole phase-space, or to follow the system for infinite times. The accuracy of the results therefore depend on the length of the simulation. For nonequilibrium systems it is necessary to use time averages because the distribution function is not known. For the equivalence between the two averaging methods to be possible one invokes the **Ergodic Hypothesis**. Under the Ergodic Hypothesis it is reasonable to assume that the phase space average weighted using an invariant measure in phase-space, which becomes a probability measure or probability distribution function if it can be normalized, will equal the time average

$$\int_{Γ} dΓ f(Γ) B(Γ) = \lim_{t→∞} \frac{1}{t} \int_{0}^{t} B(Γ(0)) dt'. \quad (1.4)$$

Here $B$ is a generic variable (function of the phase-space). This equivalence is true for almost any initial condition $Γ(0)$ except for conditions chosen on sets of zero measure in phase-space. These sets do not usually represent a problem because in actual simulations they are very hard to sample. This is why simulations have given a new impulse to the field. It is now possible to follow the evolution of our system along one trajectory and, given “enough time” obtain a time average equivalent to an ensemble average. Ergodicity ensures that the dynamical properties are independent of the initial conditions, and this will become important later when define chaos in dynamical systems through the Lyapunov exponent (quantifying the rate of separation of neighboring trajectories in phase-space), because it will ensure that chaoticity is an intrinsic property of the system. Ergodicity is however very
hard to prove except for a few simple cases. Dynamical instability (chaos), ensures that the information about the initial conditions will be quickly lost, and that a close bundle of trajectories will depart to visit regions of the available phase-space. This in turn gives us an indication (without any a priori knowledge about the ergodicity of the system) that these will exist a phase-space subdomain in which the dynamics is likely to be ergodic.

Equilibrium statistical mechanics lays the theoretical foundations for EMD. In the rest of this section, we give some details of the connection between equilibrium and nonequilibrium systems from a microscopic point of view, while in the following section from a macroscopic perspective. For linear processes a link has been established with equilibrium statistical mechanics by Green and Kubo’s linear transport theory, which can be expressed as $\langle J_i \rangle = L_{ij} X_j$ and shows that the average of the fluxes ($\langle J_i \rangle$) are proportional to the product of the forces ($X_j$) and the related transport coefficients given by the integral of the equilibrium time autocorrelation functions [Kub57]

$$L_{ij} = \int_0^\infty \langle J_i(0) J_j(t) \rangle dt$$

(1.5)

Eq. (1.5) is therefore valid at equilibrium, and its results are equivalent to that of a system away from equilibrium but in the linear regime, i.e. vanishing fields. Transport coefficients can involve statistical (thermal) or mechanical forces. In NEMD it is usually convenient to translate thermal driving forces into mechanical forces, modifying the equations of motion with a fictitious field (these algorithms are called synthetic). It has to be stressed, however, that the correct linear result is assured only in the limit of zero force field. From linear response theory we have in fact

$$L_{ij} = \lim_{F_e \to 0} \lim_{t \to \infty} \frac{\langle J_i(t) \rangle}{F_e}.$$ 

(1.6)

In our work we use a modified version of Eq. (1.6)

$$L_{ij}(F_e) = \lim_{t \to \infty} \frac{\langle J_i(t) \rangle}{F_e},$$

(1.7)

valid in the nonlinear regime, where the field has an arbitrary value greater than
zero. It is also possible to extend linear response theory in the nonlinear regime using nonlinear response theory \([YK67]\). The formalism of the Transient Time Correlation Function method (TTCF) (developed by Evans and Morriss \([EM90, ESW08]\) for homogeneously thermostatted systems but already formulated for adiabatic systems \([Vis74, DL79, Coh83]\)) turns out to be of more practical use for both time independent \([ME85]\) and time dependent driving fields \([PE97]\). Even though the formal Green-Kubo expression looks similar to that of TTCF, in TTCF the time autocorrelation functions are evaluated away from equilibrium after the field has been switched on. For time independent fields we have, for an arbitrary phase-space variable \(B(t)\) and arbitrary field \(F_e\),

\[
\langle B(t) \rangle = \langle B(0) \rangle - \beta F_e \int_0^t \langle B(t') J(0) \rangle dt'
\]

where \(\beta = 1/k_B T\) and \(J(0)\) is the dissipative flux at time \(t = 0\). This expression has been tested for several nonequilibrium systems \([EM84b, ME89, Tod97]\), however for this connection to be possible, we need a modified version of the equations of motion where the driving field and the heat dissipation are explicitly included. An example is given by the so-called SLLOD equations of motion \([EM90]\) for homogeneous flows, and we will present them in more detail in the third chapter.

### 1.3 Connection between Macroscopic and Microscopic

In the previous section we have briefly described the theoretical background of Molecular Dynamics simulation techniques and the possibility to use them to extract important information about the behaviour of multiparticle systems, e.g. the transport coefficients. We now explain why the knowledge of these coefficients is important and establish in this way a connection with continuum mechanics.

The NEMD approach is microscopic, that is, it calculates the trajectory of every particle that constitutes the system of interest. For systems of the order of Avogadro’s number, this approach is clearly unfeasible, due to the incredible computational time required. If our intention were to analyze the motion of water in a
river we should rely on fluid mechanics. The equations describing the macroscopic behaviour (Navier-Stokes equations) treat the matter as a continuum, thereby losing the granular description of matter, and dealing with mass densities, streaming velocities, pressure gradients, etc. One can obtain these continuum equations from the expressions for the conservation of extensive variables such as mass, momentum and energy. For the mass:

\[ \frac{D \rho(r, t)}{Dt} = -\rho(r, t) \nabla \cdot \mathbf{u}(r, t), \]  

\( (1.9) \)

for the momentum:

\[ \rho(r, t) \frac{D \mathbf{u}(r, t)}{Dt} = -\nabla \cdot \mathbf{P}(r, t) + \rho \mathbf{F}, \]  

\( (1.10) \)

and for internal energy:

\[ \rho(r, t) \frac{D U(r, t)}{Dt} = -\nabla \cdot \mathbf{J}_Q(r, t) - \mathbf{P}(r, t): \nabla \mathbf{u}(r, t), \]  

\( (1.11) \)

where \( \rho(r, t) \) is the density at position \( r \) and time \( t \), \( \mathbf{u}(r, t) \) is the streaming velocity, \( \mathbf{J}_Q \) the heat flux, \( \mathbf{P} \) the pressure tensor and \( \mathbf{F} \) any external force acting on the fluid element. \( \frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \) is called the material derivative and expresses the rate of change of a quantity following the streamlines of the flow, therefore including changes due to time and to convection. These sets of equations, however, are not closed, i.e. cannot be solved because the number of unknowns is higher than the number of equations. To solve this problem, we introduce a set of linear constitutive equations (that put in relation forces and fluxes by means of thermophysical coefficients) together with suitable and well defined boundary conditions. Transport coefficients can be determined either experimentally (as it has been done for hundreds of years in the past, and still is) or by simulations using statistical mechanics principles. For MD, the Green-Kubo relations provide the link between the linear transport coefficients and the natural fluctuations occurring in the associated flux, this is valid only for linear transport coefficients [AT89]. NEMD simulation allows computation in both linear and nonlinear regimes and with better accuracy (signal to noise ratio). The nonlinear regime is hard to avoid in complex systems (e.g. complex fluids such as colloidal suspensions [Coh95] or polymers [HT09b] where mutual interac-
tions between the basic constituents is non trivial). Of course the precision of the computation depends on the careful choice of boundary conditions, thermostatting mechanism and the formulation of the equation of motions.

For fluids not too far from equilibrium we can assume the following postulates to hold [dGM84]:

1. The **Local Thermodynamic Equilibrium Hypothesis**, which postulates that, for systems close enough to equilibrium, the entropy will locally be a function of the same set of parameters necessary to define the macroscopic state of the system at equilibrium, and

2. The entropy source strength $\sigma_s$ for systems close to equilibrium takes the canonical form:

$$\sigma_s = \sum_i J_i X_i$$

where $J_i$ are the fluxes and $X_i$ the conjugate thermodynamic forces.

Owing to these postulates it is possible to define phenomenological linear transport coefficients for nonequilibrium systems linking the fluxes and the forces:

$$J_i = \sum L_{ij} X_{ij}$$

and obtain the linear constitutive equations, some of which were already known:

$$J_Q = -\lambda \nabla T \quad \text{Fourier’s law of heat conduction}$$

$$\Pi^s = -2\eta(\nabla \mathbf{u})^s \quad \text{Newton’s law of viscosity}$$

$$\Pi = -\eta_s \nabla \cdot \mathbf{u} \quad \text{Bulk viscosity}$$

where in Eq. (1.14) $J_Q$ is the heat flux, $\lambda$ the thermal conductivity, $T$ the temperature, in Eq. (1.15) $\Pi$ is the non-equilibrium pressure tensor, $\Pi = \mathbf{P} - p\mathbf{I}$ where $p$ is the isotropic pressure and $\mathbf{I}$ the unit tensor, the superscript $s$ indicates the symmetric traceless part, $\eta$ the shear viscosity and $\mathbf{u}$ the streaming velocity of the fluid, and in Eq. (1.16) $\Pi = \frac{1}{3} tr(\Pi)$. Substitution of Eqs. (1.14,1.15,1.16) in Eqs. (1.9,1.10,1.11)
1 Nonequilibrium Molecular Dynamics

reduces the number of unknowns, making it possible to solve the Navier-Stokes equations by numerical methods (Green’s functions, Fourier series, Finite-difference approximations, etc.). We note that these constitutive relations are local. That is, the transport coefficients are assumed to be time and position independent. For homogeneous isotropic simple fluids this assumption is justified, but for highly confined, complex fluids this is in general not true. To overcome these issues several statistical mechanical theories have been proposed, mostly based on modified versions of the Enskog theory [Dav87b, Dav87a, Poz94, PG91, PG93], however due to approximations they were all suffering from some deficiencies. Even though we do not use the following expression in our work, we note that Evans and Morriss [EM90] proposed a non-local form for the transport coefficients. For example Newton’s law of viscosity, Eq. (1.15), can be rewritten in non-local form as

\[
P_{xy}(r, t) = - \int_0^t dt' \int_{-\infty}^{\infty} d\mathbf{r}' \eta(\mathbf{r} - \mathbf{r}', t - t') \dot{\gamma}(\mathbf{r}', t'),
\]

where \(\eta(\mathbf{r} - \mathbf{r}', t - t')\) is called the viscosity kernel. It accounts for non-local spatial effects, depending on the strain rate distribution in surrounding areas and nonlocal temporal effects (memory effect) due to the strain rate history, similar to what happens in solids. Many recent studies have been done to characterize the viscosity kernel and prove its validity for systems out of equilibrium [PTDH10a, THD08, CTZD08, TH08, PTDH10b, HDTT07]. The nonlocality of transport coefficients becomes important in highly confined fluids, with channel widths less than 10 atomic diameters (in which case the classical Navier-Stokes theory is known to break down [TTE97a, TTE97b, HTD09]).

What we have presented in this chapter is a justification for the use of NEMD as a tool to investigate the behaviour of physical systems looking at their microscopic constituents. Our main focus is chaos and how it affects the phase-space of multiparticle systems at nonequilibrium, we therefore make extensive use of statistical mechanics (section 1.2), to analyze our results, while material properties (e.g. transport coefficients) are mainly used to test the validity of our algorithms.
Chapter 2

Algorithms

2.1 Introduction

Use of nonequilibrium molecular dynamics has seen a huge growth in the last 30 years because of the development of new algorithms and computer power, which has led to the possibility to study transport coefficients and rheological properties of fluids out of equilibrium, therefore mimicking real experiments [Hoo83]. Two main classes of algorithms can be distinguished, homogeneous [TD07] and inhomogeneous [LBC92]. The former class makes use of appropriate periodic boundary conditions (PBCs) in all directions to simulate a bulk region of fluid, avoiding problematic surface effects close to the boundaries. The external forces are implemented directly into the equations of motion to generate the flux of interest and the corresponding transport coefficients can be directly determined [EM90]. This approach is essential if one wants to model the properties of bulk systems accurately. In inhomogeneous methods, wall boundaries constrain the fluid in a defined geometry and the system is driven away from equilibrium by the movement of the walls themselves, as in the case of Couette flow or by the use of an external force field, a pressure gradient or a gravity-like force, as in the case of Poiseuille flow. In both methods however, work is performed on the fluid, and viscous heat has to be extracted in order to reach a steady state. A steady state is generated when the viscous heat produced
by performing work on the system is compensated by a thermostat, so that the macroscopic properties (density, temperature, streaming velocity, etc.) will, after a transient period, not change in time. In homogeneous methods a thermostat is applied directly to the fluid particles whilst in inhomogeneous methods the thermostat is usually applied either on the wall particles exclusively or fluid and wall particles together or only fluid particles, depending how the wall is implemented in the simulations. A section of this work is devoted to the issue regarding the effect that an improper choice of thermostating mechanism can have on confined fluids. The use of homogeneous algorithms has been rapidly increasing, particularly for molecular fluids such as polymers, where the system’s dimension is critical, and due to the possibility of reproducing complex types of flow (e.g. elongation) indefinitely. Also, if the underlying equations of motion are SLLOD, a link with non-linear response theory is possible. However, recently due to an increasing interest in nano-confined systems, more effort has been invested in modeling of systems with walls. In this work both homogeneous and inhomogeneous fluids have been considered. For what concerns inhomogeneous systems, we focus the research on two types of flow, planar Couette flow and Poiseuille flow. These types of flows have been investigated extensively in nonequilibrium molecular dynamics, and in the case of Couette flow, either for homogeneous or inhomogeneous systems. They are in fact relatively simple to model and provide a detailed understanding of the rheological properties of fluids, e.g. transport properties in nanopores, where the channel diameter can be of the order of a few nanometers. Research on these types of flow is important in many areas (biological, biomedical, nano-fluid dynamics, turbulence, etc.), and in industrial applications, largely in materials science.

In the study of homogeneous flow, we develop and implement appropriate periodic boundary conditions to simulate planar mixed flow (i.e. shear and extensional flow) for indefinite times, solving previous issues related to irreversible simulation box deformation. Periodically, the simulation box is mapped back into itself and the simulation can continue. Mixed flow is of primary importance in the study of polymer melts under mixed shear and extensional flows and it is present in extrusion processes, in journal bearings where an eccentric cylinder geometry is present, or
simply in contracting slit pores. We also note that a clear separation between shear and extensional flows is often possible only in theory and difficult to achieve in real situations.

2.2 Molecular Dynamics

The basic structure of a MD algorithm consists in numerically solving Newton’s equations of motion for the particles composing the system

\[
\begin{align*}
\dot{r}_i &= \frac{p_i}{m_i}, \\
\dot{p}_i &= -\nabla U_i = F_i.
\end{align*}
\] (2.1)

Here \( \mathbf{r}_i \) is the position vector in the laboratory frame of particle \( i \), \( \mathbf{p}_i \) is the momentum vector, \( U_i \) and \( F_i \) are respectively the total potential energy and total force felt by particle \( i \). The potential (describing the mutual interactions between particles) can be of different form depending on the atomic and molecular species and property one is interested in. Many numerical methods can be used to solve the differential Eqs. (2.1) [AT89] and we will present in some detail only the two that have been used in this work at different stages, namely the Leapfrog [HE81, Pot72] and Gear Predictor-Corrector [Gea71] algorithms that pertain to the category of finite difference methods. The most important characteristics to look for in a numerical integrator are speed, simplicity in coding and precision. Ideally the higher the order of the integrator the more precise will be the approximation to the real trajectory (but the more complex and slower the algorithm). Speed could mean either how fast one iteration can be performed on a machine, but also the size of the time step that is possible to use without the integrator becoming unstable. A higher time step means that, simulation time being equal, we can follow and predict the evolution of our system for longer “real” time. The Leapfrog integrator is a second order method, very simple to code, fast, time reversible, and symplectic.

\[
\begin{align*}
\mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t + \frac{1}{2}\Delta t), \\
\mathbf{v}_i(t + \frac{1}{2}\Delta t) &= \mathbf{v}_i(t - \frac{1}{2}\Delta t) + \Delta t \mathbf{a}_i(t),
\end{align*}
\] (2.2)
Here $v_i$ is the velocity vector of particle $i$ in the laboratory frame and $a_i$ its acceleration. The velocity at the current step can be computed by

$$v_i(t) = \frac{1}{2} \left( v_i(t + \frac{1}{2} \Delta t) + v_i(t - \frac{1}{2} \Delta t) \right). \quad (2.3)$$

Symplectic refers to the ability to preserve the Jacobian of the dynamics, which for Hamiltonian systems means that the phase-space volume is conserved. Every method can be considered as a mapping from and into the phase space, and constant phase space volume means that the system is bound to the same energy surface at all time. When used in MD simulations, symplectic algorithms ensure a correct sampling of the $(N, V, E)$ ensemble. The time reversal property ensures that forward and reverse trajectories are both solutions of the equations of motion.

We implemented the leapfrog scheme for the study of confined systems, while for homogeneous nonequilibrium algorithms we used the Gear scheme because of easier implementation when additional constraints need to be included explicitly into the equations of motion. In the Gear scheme in fact, positions and velocities are updated at the same point in time, while in the leapfrog algorithm the update is asynchronous. The basic idea of the Gear Predictor-Corrector is to make a Taylor expansion at time $t + \Delta t$ of positions, velocities, accelerations (and higher order derivatives depending on the order of the algorithm) in the predictor step. These values must then be corrected in the corrector step, calculating the accelerations obtained using the equations of motion on the predicted positions. Because in the correcting step the equation of motion can be implemented with all the constraints this method is particularly useful for NEMD (see section 2.6) or where geometrical constraints (like rigid bonded molecules) are present. To generate our results we used a fourth order Gear Predictor-Corrector. For the prediction step we have for the position:

$$r_i^p(t + \Delta t) = r_i^p(t) + \Delta t r_i^p(t) + \frac{1}{2} \Delta t^2 r_i^p(t) + \frac{1}{6} \Delta t^3 r_i^p(t) + \frac{1}{24} \Delta t^4 r_i^p(t),$$

$$r_i^p(t + \Delta t) = r_i^p(t) + \Delta t r_i^p(t) + \frac{1}{2} \Delta t^2 r_i^p(t) + \frac{1}{6} \Delta t^3 r_i^p(t),$$

$$r_i^p(t + \Delta t) = r_i^p(t) + \Delta t r_i^p(t) + \frac{1}{2} \Delta t^2 r_i^p(t),$$

$$r_i^p(t + \Delta t) = r_i^p(t) + \Delta t r_i^p(t). \quad (2.4)$$
similarly for the velocity:

\[
\begin{align*}
\mathbf{v}_0(t + \Delta t) &= \mathbf{v}_0^p(t) + \Delta t \mathbf{v}_1^p(t) + \frac{1}{2} \Delta t^2 \mathbf{v}_2^p(t) + \frac{1}{6} \Delta t^3 \mathbf{v}_3^p(t), \\
\mathbf{v}_1(t + \Delta t) &= \mathbf{v}_1^p(t) + \Delta t \mathbf{v}_2^p(t) + \frac{1}{2} \Delta t^2 \mathbf{v}_3^p(t) + \frac{1}{6} \Delta t^3 \mathbf{v}_4^p(t), \\
\mathbf{v}_2(t + \Delta t) &= \mathbf{v}_2^p(t) + \Delta t \mathbf{v}_3^p(t) + \frac{1}{2} \Delta t^2 \mathbf{v}_4^p(t), \\
\mathbf{v}_3(t + \Delta t) &= \mathbf{v}_3^p(t) + \Delta t \mathbf{v}_4^p(t),
\end{align*}
\]

(2.5)

where in \( r_j^p \) and \( v_j^p, \) \( j \) refers to the order of the time derivative. To estimate the errors for Eqs. (2.4) we compute the difference:

\[
\Delta \mathbf{r} = \mathbf{v}_0(t + \Delta t) - \mathbf{r}_1^p(t + \Delta t),
\]

(2.6)

while for Eqs. (2.5):

\[
\Delta \mathbf{v} = \mathbf{a}(t + \Delta t) - \mathbf{v}_1^p(t + \Delta t).
\]

(2.7)

The acceleration \( \mathbf{a}(t + \Delta t) \) is computed from the force evaluation based on the predicted positions \( r_0^p(t + \Delta t) \). For the correction step we have, for the positions:

\[
\begin{align*}
\mathbf{r}_0(t + \Delta t) &= \mathbf{r}_0^p(t + \Delta t) + c_0 \Delta \mathbf{r}, \\
\mathbf{r}_1(t + \Delta t) &= \mathbf{r}_1^p(t + \Delta t) + c_1 \Delta \mathbf{r}, \\
\mathbf{r}_2(t + \Delta t) &= \mathbf{r}_2^p(t + \Delta t) + c_2 \Delta \mathbf{r}, \\
\mathbf{r}_3(t + \Delta t) &= \mathbf{r}_3^p(t + \Delta t) + c_3 \Delta \mathbf{r},
\end{align*}
\]

(2.8)

and for the velocities:

\[
\begin{align*}
\mathbf{v}_0(t + \Delta t) &= \mathbf{v}_0^p(t + \Delta t) + c_0 \Delta \mathbf{v}, \\
\mathbf{v}_1(t + \Delta t) &= \mathbf{v}_1^p(t + \Delta t) + c_1 \Delta \mathbf{v}, \\
\mathbf{v}_2(t + \Delta t) &= \mathbf{v}_2^p(t + \Delta t) + c_2 \Delta \mathbf{v}, \\
\mathbf{v}_3(t + \Delta t) &= \mathbf{v}_3^p(t + \Delta t) + c_3 \Delta \mathbf{v}.
\end{align*}
\]

(2.9)

A convenient choice for the coefficients \( c_j \) has been discussed by Gear [Gea71] and it depends on the order of the differential equations and of the algorithm.

It is also possible for equilibrium simulations to use only Eqs. (2.4) and (2.8),
using $\mathbf{r}_0$ and $\mathbf{v}_0$ as the actual position and velocity of the particles, in this case the error estimation is given by

$$
\Delta \mathbf{r} = \mathbf{a}(t + \Delta t) - \mathbf{r}_2(t + \Delta t).
$$

(2.10)

In homogeneous synthetic nonequilibrium simulations however, in which both equations of motion are modified, this choice is inconvenient (see section 2.7).

### 2.3 Potentials

The level of complexity of the potential describes the level of precision in the interactions between particles. The simplest and first model to be implemented was obtained considering rigid spheres, equivalent to an infinite step potential on a sphere. In this case there is no need of solving the equations of motion, because all that is needed is to compute the angle of collision in between the free flight of the particles. In spite of its simplicity this model has been able to produce many interesting results and it is still widely used for dynamical systems studies, see for example [MHB87, TM06a, TM03, EFPZ05a, SBJ06, AW57]. However atoms have several properties, such as attractive interactions, repulsive interactions and many body interactions, which can be accounted for to be able to reproduce real physical phenomena. The interactions are simplified and broken into separable pieces to make the problem more tractable: dividing them in 2, 3, 4, etc. body interactions, short range and long range, etc. One can use quantum mechanics to determine the forces on the atoms due to all others, and when this is used in combination with molecular simulations it is referred to as ab-initio molecular dynamics. In theory, this would provide very accurate results as model potential energy surfaces do not need to be constructed. However the quantum mechanical calculations are very time-consuming, and in practice approximations to solutions of the Schroedinger equation have to be made. The drawback of this approach is clearly the complexity and computational cost that makes it unfeasible for the purpose of following the trajectories of thousands of particles for long times. In this work we use simple
pairwise additive intermolecular potentials that produce the main features of the systems to be described.

The two main characteristics when describing atomic interactions are repulsion (overlapping of electronic clouds at close distances) and attraction (van der Waals forces and electrostatic effects due to electronic correlations at long distances). The most common potential to be developed to capture these characteristics in noble gases is the Lennard-Jones 12-6 potential

\[ \Phi_{LJ} = 4 \epsilon \left( \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right), \]  

where \( r_{ij} = |\mathbf{q}_i - \mathbf{q}_j| \) with \( \mathbf{q}_i \) being the laboratory particle position, \( \sigma \) is the value of \( r_{ij} \) for which the LJ interaction potential is zero, and \( \epsilon \) is the well-depth of the LJ potential, usually a cutoff of \( r_{\text{cut}} \sim 2.5 \sigma \) is used and \( \Phi_{LJ} \) is set to 0 when \( |r_{ij}| > r_{\text{cut}} \). For simplicity of data manipulation all the physical units are expressed in reduced units where the unit of mass is the particle mass \( m \), the energy unit is the parameter \( \epsilon \), the length unit is \( \sigma \) and the time unit \( t \), expressed in terms of the previous defined units, is \( \sqrt{m\sigma/\epsilon} \). In our work we set \( \epsilon = \sigma = m = 1 \). This makes it possible to adapt results to different molecular/atomic systems just by scaling with respect to the appropriate parameters and avoid managing very large or small physical quantities as the atomic masses and energies.

If we take the LJ potential to model liquid argon then in real units we would have [Rap95]:

\[
\begin{align*}
\text{Length} & \quad \sigma = 3.4\text{Å,} \\
\text{Energy} & \quad \epsilon/k_B = 120\text{K,} \\
\text{Mass} & \quad m = 66.904265 \times 10^{-24}g, \\
\text{Time} & \quad t = 2.161 \times 10^{-12}\text{s.}
\end{align*}
\]

This potential is still used today despite its simplicity, and is capable of capturing phase transitions. For modeling more complex structures such as carbon nanotubes or obtain high accuracy it is preferable to use many-body potentials that capture
quantum mechanical effects such as the Brenner potential [Bre90]. An even simpler potential than the LJ is the Weeks-Chandler-Anderson (WCA) potential [WCA71, HO06], which is a truncated and shifted form of the LJ potential and which neglects the attractive component of the interatomic force (repulsive only), mainly capturing the characteristic of low density gases:

$$\Phi_{WCA} = \begin{cases} 
4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] + \epsilon, & r_{ij} \leq 2^{\frac{1}{6}}\sigma, \\
0, & r_{ij} > 2^{\frac{1}{6}}\sigma,
\end{cases}$$

(2.13)

So the cutoff, $$r_{cut} = 2^{\frac{1}{6}}\sigma \simeq 1.122\sigma$$. In all the results presented in this work we used the WCA potential, because the attractive interactions were not relevant for the properties we were interested in. For example in the framework of dynamical systems, the chaos in multiparticle systems is due to the convex nature of the particles, well represented by the repulsive potential part. The theory is therefore unaffected by the use of the WCA potential over the LJ and we don’t expect any significant change to the simulation results. Furthermore when testing new algorithms (as in our case with planar mixed flow) it is preferable to save computation time, having a smaller cut-off, while ensuring no discontinuity in mechanical properties. Both potentials are two-body potentials. It is possible to include three-body terms into the computation but this would decrease the speed and it is not relevant for our purposes [MTS01b, MTS01a, ZT04].

2.4 Periodic Boundary Conditions

Periodic boundary conditions originate from the necessity to describe bulk regions of fluids with finite systems. The thermodynamic limit requires the number of particles to go to infinity, $$N \to \infty$$, however this requirement is clearly not practical, since the computation effort required grows in the worst case scenario as $$O(N^2)$$ [Rap95]. We therefore require a method to simulate a relatively small number of particles limited in a fixed volume but that could represent our ensemble. The most trivial way to achieve this is to place the particles in a rigid container. Unfortunately this would
also introduce surface effects. For macroscopic systems of the order of Avogadro’s number, and for not too low densities, the fraction of molecules close to the walls could easily be discarded [Rap95], however in normal MD simulation where the numbers are typically of the order of thousands, the interaction with the container would become important. A way to solve this issue is to use periodic boundary conditions (PBCs) where a unit cell is considered in an infinite, periodic lattice. Then, as a particle leaves the unit cell, another re-enters from the opposite side with the same velocity vector. As a result the total number of particles, volume/density and energy are conserved, forming a microcanonical ensemble. In reality the PBCs introduce additional constraints of which one needs to be aware. In the above situation for example the PBCs conserve not only the energy, but also the linear momentum and the position of the centre of mass. This of course decreases the degrees of freedom accessible to the system, influencing the temperature for example [SBJ06]. These will also have effects on the dynamics, which we analyze with the Lyapunov exponents.

The unit cell can be chosen to have different shapes according to the system’s specific requirements. The most common and intuitively easy figure is the square (in 2 dimensions) or cube (in 3 dimensions). However the need for PBCs are not confined to molecular dynamics. Many areas of physics require the use of specific PBCs (e.g. quantum field theories in curved space-time), hence the study of PBCs in hyperbolic geometries [ST07]. In the discussion that will follow, for simplicity of treatment we will consider 2 dimensional boxes. In fact, the nonequilibrium flows we are interested in are planar, meaning that two dimensions are directly involved, and therefore we simplify our analysis by considering a 2 dimensional system.

2.5 Periodic Boundary Conditions: Equilibrium case

In this section we analyze the PBCs for equilibrium systems, developed for the study of a fluid’s bulk phases. At equilibrium as shown in Fig. 2.1, one square box (that represents the particles simulated in the computer) is replicated an infinite number of times to represent an infinite system. This simplification allows us to think of the
prime primitive cell as a part of the whole. If the range of interactions were infinite this would not be a useful simplification because every particle would feel the interaction of an infinite number of replicas

\[ U_{i}^{TOT} = \sum_{j} U_{ij}, \]  

(2.14)

where \( U_{i}^{TOT} \) is the total potential energy felt by particle \( i \) and the index \( j \) includes also the copies of particle \( i \) [FS02]. However we usually deal with short-range interactions so that the minimum image convention (each particle interacts only with the nearest images of the other particles) is particularly useful. Loosely speaking we draw a cell centered around the particle we want to compute the forces on, and we consider the interparticle potential due to the enclosed particles (including the periodic images).

In specific cases in which long-range interactions are present, e.g. electromagnetic, one can use particular methods as the Ewald summation [Ewa21].
Figure 2.1: Schematic representation of equilibrium periodic boundary conditions, the primitive 2D cell box is at the center (solid lines) and its periodic images (dashed lines) are surrounding it.

Topologically speaking the usual PBCs are an equivalence relation between points \((x, y)\) and \((x', y')\) in a Euclidean space (remember we are considering a two dimensional space for simplicity)

\[
\begin{align*}
    x' &= x + L \, n_x, \\
    y' &= y + L \, n_y,
\end{align*}
\] (2.15)

where \(L\) is the length of the box and \(n_x, n_y\) are integers. The quotient space [Tal01] associated is a 2 dimensional torus \(T^2\). In a 3 dimensional simulation we would have a 3 dimensional torus \(T^3\). This relation however, does not imply any particular tessellation choice, \(i.e.\) the simulation cell can be chosen of any shape.
as long as the tiling is space-filling. This means that alternatively to the square (cube in 3 dimensions) one could choose a hexagon (octahedron in 3 dimensions) if searching for a shape to optimize the volume to surface ratio [FS02]. The sphere would obviously be the best choice in this regard, but it is not, unfortunately, space-filling, with consequences that will be discussed in Appendix A.

As already introduced in the previous section, PBCs can introduce unphysical effects. For example there could be unwanted correlation effects if the cell size is small compared to the dimension of the system to study. This is particularly evident studying phase transitions where fluctuations of wavelengths usually longer than cell sizes are expected to be important (and the maximum wavelength can only be $\lambda = L$), when dealing with polymer melts or proteins, whose length could cause one end of the chain to interact with the other end of the same chain, or in crystalline structure where the development of sound waves could be enhanced by resonance effects. Unfortunately it is very difficult to quantify these effects in general and they must be evaluated on a case to case basis.

2.6 Canonical Ensemble

When evolving a system by Newton’s equations of motion we automatically conserve its energy, generating the phase space distribution of the $(N, V, E)$ ensemble. A change in energy can be caused by performing mechanical work on the system or if another system is put in thermal contact so that heat transfer can occur. Therefore, if we want to change our system’s temperature, to best mimic nature, we should also simulate a surrounding bath, with a heat capacity large enough to not be influenced by heat exchanges. This of course places practical problems due to the limited computation time. A workaround that allows us to perform simulations in an $(N, V, T)$ ensemble is to directly modify the equations of motion (however the same procedure can be extended to other ensembles, e.g. $(N, P, T)$). This is of course an artifact that does not have an equivalent in nature and alters the dynamics. It allows however, successful reproduction of the physical behavior of a thermostatted system. We need to be aware of the consequence of this technique however, to be
able to quantify significant physical deviations.

Many different types of thermostats have been derived. We will present in some
detail three of them: Gaussian, Nosé-Hoover and Configurational (only the first two
have been used in this work). These thermostats are able to preserve the deter-
ministic nature of the Newtonian dynamics. Their use has allowed a number of new
relationships for systems far from equilibrium to be obtained without introduction of
stochasticity. For example they were essential to obtain steady states in a deter-
ministic, reversible way and therefore to obtain fluctuation relations, nonlinear response
theory and to understand relaxation of a system to an equilibrium canonical state
[ES02, SPWS08]. An extensive discussion on the role of thermostats in chaos and
transport theories for nonequilibrium systems is presented in Ref. [Kla07].

2.6.1 Gaussian Thermostat

This thermostat is based on Gauss’ principle of least constraint, derived by Gauss
in 1829 [Gau29] which states that a mechanical system with constraints will evolve
such that the quantity
\[ C = \frac{1}{2} \sum_i m_i \left( \ddot{r}_i - \frac{F_i}{m_i} \right)^2 , \]  
(2.16)
is a minimum. For this work the constraint fixes the temperature at all times. We
can use this principle for both holonomic and nonholonomic constraints, but we are
interested only in the nonholonomic case because our constraint depends on the
velocities. Using this condition and the Lagrange multipliers [EM90] we can obtain
modified equations of motion
\[ \dot{q}_i = \frac{p_i}{m_i}, \]
\[ \dot{p}_i = F_i - \xi p_i, \]  
(2.17)
The Lagrange multiplier, also called friction coefficient, because it acts as a viscous
force on the velocities, is
\[ \xi = \frac{\sum_i p_i/m_i F_i}{\sum_i p_i^2/m_i} , \]  
(2.18)
The same procedure can be applied to fix the total energy [HLM82] instead of the kinetic energy [EHF+83]. An important characteristic is that the kinetic energy is identically conserved at each time step, and no fluctuations are allowed. Therefore it creates an isokinetic ensemble whose distribution function assumes the form

\[ f_G(\Gamma) = \frac{e^{-\beta \phi(\Gamma)} \delta(K(\Gamma) - K(\Gamma_0))}{\int d\Gamma e^{-\beta \phi(\Gamma)} \delta(K(\Gamma) - K(\Gamma_0))}, \quad (2.19) \]

where \( \Gamma \) is the phase-space vector representing the microscopic state of the system, \( \beta = dN/2K_0 \), \( \phi(\Gamma) \) is the potential energy, \( K(\Gamma) \) the kinetic energy (\( K(\Gamma_0) \) is the kinetic energy of the initial state). It is easy to see that the kinetic degrees of freedom follow a microcanonical distribution while the configurational degrees are canonical. Although the isokinetic dynamics is not able to generate a canonical distribution it is able to preserve it [EM90]. The fact that the system is evolving on a hypersurface at constant kinetic energy will have important consequences in terms of Lyapunov spectra, and it will be discussed in further detail in Chapter 5. We also note that an Hamiltonian formulation of the Gaussian thermostat has been derived by Dettmann and Morriss [DM96a].

### 2.6.2 Nosé - Hoover Thermostat

The Nosé - Hoover thermostat was originally proposed by Nosé [Nos84], and relies on an extended Hamiltonian which includes an additional degree of freedom which mimics an external reservoir

\[ H_N(q, p, s, p_s) = \sum_i \frac{p_i^2}{2m_i s^2} + \phi(q) + \frac{p_s^2}{2Q} + (g + 1)k_B T \ln s, \quad (2.20) \]

where \( g \) is related to the number of degrees of freedom, \( s \) is the additional degree of freedom \( d \), \( p_s \) its momentum, \( Q \) its mass, and \( (g + 1)k_B T \ln s \) its potential energy chosen such that the dynamics generates a canonical ensemble. The equilibrium distribution function in this extended phase-space is microcanonical, however with a convenient change of variables \( q' = q \), \( p' = p/s \), we can obtain a canonical distribution over the new scaled variables \((q, p')\).
From a practical point of view the method in this formulation is rather difficult to handle (also due to a non-Galilean interpretation of the time). Hoover [Hoo85] simplified the problem introducing a time transformation $dt' = dt/s$ and considering only the variables $\mathbf{q}, \mathbf{p}', t'$. With this new set of variables the equations of motion become (dropping the primes)

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m_i},$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \xi \mathbf{p}_i,$$
(2.21)

where

$$\dot{\xi} = \frac{1}{Q} \left[ \sum_i \frac{p_i^2}{m_i} - gNk_BT \right].$$
(2.22)

The extended distribution function at equilibrium is canonical

$$f_N(\mathbf{\Gamma}, \xi) = \frac{e^{-\beta(H_0 + \frac{1}{2}Q\xi^2)}}{\int d\mathbf{\Gamma} d\xi e^{-\beta(H_0 + \frac{1}{2}Q\xi^2)}},$$
(2.23)

where $H_0$ is the $N$-particle Hamiltonian (in the derivation it is assumed that the dynamics is ergodic). Because the friction coefficient evolves according to its time derivative this thermostat follows an integral feedback mechanism, as opposed to the Gaussian thermostat that follows a differential feedback mechanism. It is known, however, that when the system is small or stiff, and the resulting dynamics is not ergodic [CJ92, LLM07, LLM09], the thermostat fails to reproduce the canonical ensemble [Hoo85, TO90]. Even though solutions have been proposed (see, for example, [KBB90, Ham90, Win92, MKT92, KBB90]), the systems studied in this work did not fall into these cases and the original form of the Nosé-Hoover thermostat has been used.

## 2.6.3 Configurational Thermostat

The thermostats presented above, in spite of different traits, share in common the same idea, altering the velocities. A somewhat innovative approach is followed by the configurational thermostat, that as the name suggests, uses the particle positions to
control the temperature. The importance of this method can be better appreciated when dealing with nonequilibrium systems where a correct and precise determination of the streaming velocity is a major issue. Its introduction in a tractable form was due to Rugh [Rug97], however it is possible to find mention of it in the earlier books by Tolman and Landau and Lifshitz [LL58, Tol79]. Rugh described how to derive the temperature in a microcanonical ensemble in a dynamical way and by geometric (in an Euclidean phase-space) considerations from the Hamiltonian of the system. Loosely speaking the idea relies on the inverse proportionality between the temperature and the change in energy due to displacements orthogonal to the Hamiltonian hypersurface (that in Eq. (2.24) is given by the divergence of the gradient on the r.h.s.)

\[
\frac{1}{k_B T} = \left\langle \nabla \cdot \nabla H \right\rangle \frac{1}{|\nabla H|^2} + O(N^{-1}),
\]

(2.24)

where \( H = H(\Gamma) \) and \( \Gamma = (q_i, p_i) \) is the phase-space vector. This expression was later generalized by Jepps et al. [JAE00]. Its use as a thermostat was first propose by Butler et al. [BAJE98] as a check for Monte Carlo algorithms, where the temperature cannot be computed in a dynamical fashion but only by looking at the particle positions. If we consider only the configurational phase-space we obtain for the temperature this operational expression

\[
\frac{1}{k_B T_{\text{conf}}} = \left\langle \nabla \cdot \nabla U \right\rangle \frac{1}{|\nabla U|^2},
\]

(2.25)

where in this case \( U = U(\Gamma_q) \) and \( \Gamma_q = (q_i) \) is the phase-space vector of the particles’ position only. It was later applied to molecular dynamics and many studies have been published either for atomic or molecular fluids [BT05, DE01c, LE00]. It is for the latter category that its use was more promising because of the implicit contribution of all degrees of freedom (e.g. vibrational and rotational) to the temperature [LJDE02, TB06, DE01a, DE01b]. However because its implementation requires the second derivative of the potential, computation time issues arise for systems with complex many-body potentials and a possible solution is to use finite difference methods or potential energy tabulations [TB06]. Two main formulations exist, one due to
Delhomelle and Evans [DE01b], that uses the gradient of the temperature for the dynamics of the friction coefficient, and one by Braga and Travis [BT05] whose derivation leads to a Nosé-Hoover type of thermostat

\[
\dot{q}_i = \frac{p_i}{m_i} - \xi \frac{\partial U}{\partial q_i}, \quad \dot{p}_i = F_i, \tag{2.26}
\]

where

\[
\dot{\xi} = \frac{1}{Q} \left[ \sum_i \left( \frac{\partial U}{\partial q_i} \right)^2 - k_B T \sum_i \frac{\partial^2 U}{\partial q_i^2} \right]. \tag{2.27}
\]

Like the kinetic Nosé-Hoover thermostat, the canonical distribution can be obtained if the system is ergodic. We also note that this time the friction coefficient acts on the position and not on the velocity. We implemented a modified version of the configurational thermostat at an early stage when analyzing thermostatting mechanisms for confined fluids (because of the confinement, density variations have to be accounted for [DE01c]) (see Chapter 3). However, the results for this type of thermostat are not reported because it was found to be unstable for the system with rigid walls and high external fields, where collisions becomes particularly “stiff”.

### 2.7 Nonequilibrium Molecular Dynamics

What we have presented in the previous sections is valid at equilibrium. If one wants to perform nonequilibrium simulations specific changes need to be made. In this section we give a general introduction to the two main ways to realize nonequilibrium simulations, namely syntethic and nonsyntethic algorithms.

Nonequilibrium is obtained when, applying a perturbation to the system, quantifiable changes in macroscopic quantities, e.g. fluxes in mass, temperature, energy, pressure etc. can be detected. We can perturb the system mechanically using boundaries (nonsyntethic algorithms) and external force fields or by appropriately modifying the Hamiltonian or the equations of motion (syntethic algorithms).
The most general form of the equations of motion to generate nonequilibrium conditions is

\[
\dot{q}_i = \frac{p_i}{m_i} + C_i F^\text{ext}_i(t), \quad (2.28a)
\]

\[
\dot{p}_i = F_i + D_i F^\text{ext}_i(t) - \xi p_i. \quad (2.28b)
\]

By choosing appropriate values for the coupling terms \(C_i, D_i\) and the external force \(F^\text{ext}_i\) it is possible to realize both homogeneous and inhomogeneous NEMD.

For inhomogeneous NEMD, physical boundaries can be obtained choosing non-zero values for \(C_i\) and \(D_i\) if the particle \(i\) is to be part of the wall, and an appropriate form for the external force \(F^\text{ext}_i\) to link the wall particles together or to a virtual lattice (as it has been done in this work). Nonequilibrium can then be induced either by driving the walls in a particular direction (\(F^\text{ext}_i\) must be modified accordingly) or using \(C_i\) and \(D_i\) to couple the fluid to an external field, e.g. electric field or gravity.

In homogeneous synthetic NEMD all particles are identified as fluid (even though they can be of different species) and \(C_i, D_i\) and \(F^\text{ext}_i(t)\) are chosen as to mimic the response of the system to the transport process of interest (e.g. SLLOD for shear viscosity [EM84a], color field algorithm for self diffusion [EHF+83], thermal conductivity algorithm [Eva82]).

The use of thermostats is necessary to reach a steady state. The viscous heat produced by performing work on the system is compensated by a thermostat, so that the macroscopic properties (density, temperature, streaming velocity, etc.), after a transient initial period, do not change in time. The form of the thermostatting term will depend on the type of thermostat and on how the equations of motions are modified. The Gaussian term, for example, requires the kinetic energy to be constant and \(\xi\), in the homogeneous case, assumes the form

\[
\xi = \frac{\sum_i p_i / m_i \cdot (F_i + D_i F^\text{ext}_i(t))}{\sum_i p_i^2 / m_i}. \quad (2.29)
\]

The Nosé-Hoover term instead does not change because it only requires the knowledge of the peculiar velocities’ sum. The term “peculiar” refers to the fact that the
velocities only include thermal fluctuations and not components due to streaming (collective) motions.

Integrators and periodic boundary conditions must also be modified accordingly (PBCs will be addressed in details in chapter 4). If we use a NEMD algorithm that includes external forces only in Eq. (2.28b), no change is needed for the integrators, in fact the forces can easily be added to the acceleration during the force evaluation step. However if we want to implement a synthetic homogeneous algorithm (e.g. SLLOD), in which both Eqs. (2.28a) and (2.28b) are modified, it is much simpler to use a Gear PC integrator. The Leapfrog, in fact, updates velocities and accelerations at different time steps and *ad hoc* modifications are necessary. Using the Gear PC, the additional terms in Eqs. (2.28a) and (2.28b) can be easily inserted at correction step respectively in $r_p(t + \Delta t)$ (Eq. 2.6) and $a(t + \Delta t)$ (Eq. 2.7).

Because in NEMD we do not sample the $(N,V,E)$ ensemble, one of the advantages of the Leapfrog (*i.e.* symplecticity) is no longer applicable. However, new symplectic-like integrators have been realized to obtain the $(N,V,T)$ ensemble by means of operator splitting techniques [Can91, FR90, GNS94, MA92, Suz92, Yos90] and applied to nonequilibrium dynamics simulations with Gaussian [ZSE +99] or Nosé-Hoover thermostats. Although these algorithms can be highly stable and eliminate drift in conserved quantities, provided that small enough time steps and good enough schemes are used, *ad hoc* corrections to ensure that numerical errors do not destroy conserved quantities can give results that are just as accurate, and this is what is most often done in numerical simulations.
Chapter 3

Simulation of confined fluids and boundary driven nonequilibrium systems

3.1 Introduction

Inhomogeneous algorithms allow the container to be modelled explicitly, with an appropriate set of Eqs. (2.28a) and (2.28b) to describe the walls. This set could include harmonic potentials to model solid crystals or complicated many-body potentials. In inhomogeneous systems the walls themselves could drive the fluids away from equilibrium or (as for homogeneous systems) the forces necessary to create a flux in the fluid region (gravity, magnetic, etc.) could be added directly into the fluid equations of motion. Also for inhomogeneous systems compatible PBCs must be realized so that unphysical effects are not introduced. For homogenous systems this non-trivial issue will be discussed in the next chapter.

We mentioned in section 2.1 two types of flow particularly common in engineering applications: Couette and Poiseuille flows. Both flows are generated when the fluid is trapped between two confined walls and a force is applied to drive the system away
from equilibrium. For Couette flow, homogeneous algorithms capable of reproducing
the velocity profile and modeling part of the bulk system are available (SLLOD), but
for Poiseuille flow the walls are a necessity, as the friction between the fluid and the
confining walls’ surface is required to be able to reproduce the velocity profile typical
of this flow. However there are cases in which the walls themselves are the case of
study, in particular with the growing interest in nanotechnology and nanofluidics.
Theory of transport in nanochannels, slip, chemical reactions in porous materials,
etc. have boosted the interest in the area in the last 10 years [AK08, BC10, LBS07].
In nanodevices as well as in biological systems where the scale becomes small and
continuum theories break down, new and interesting phenomena can be observed
and the need for new theories is increasing, for example when the channel size
becomes of nanometer length scales, pressure gradients are not feasible for driving
the fluid and interface-driven methods need to be developed. In turn this requires a
better understanding of interface phenomena, slip conditions [BB07], and transport
theory that in nanofluidics behaves differently, due to the significant influence of the
walls and the small number of molecules involved [SvdBE10, BN07, BN08a, BN08b,
LBNN10, NB09].

In the case of confined geometries, PBCs can be employed, exploiting the symme-
tries of the system. For example, carbon nanotubes could be seen as cylinders which
are periodic along the main axis. It is therefore straightforward to consider only a
section of the tube and “glue” the two ends together so that particles going out
from one end enters from the other. In this way the PBCs are only in one direction
and the fluid is trapped in a “donut” (topologically speaking because the fluid does
not experience any space curvature). For planar Poiseuille flow and planar Couette
flow, instead of pipes we have confining plates and therefore the PBCs are in two
directions, and the plates may be regarded as infinite.

The wall can be realized in several ways depending on the complexity of the model.
Empirical many-body potentials have been realized to originally reproduce the chem-
ical bonds in hydrocarbons [Bre90, Ter88a, Ter88b] and are used for instance when
modeling carbon nanotubes. These potentials allow for the reproduction of experi-
mental results on crystalline structures but can be time consuming for big systems.
Often Lennard-Jones or WCA particles that are linked to a lattice by a harmonic potential are sufficient to capture the physics of interest, and this is the case in this thesis.

3.2 Thermostatting Driven, Confined Fluids

In intensive computations carried out in nanopores, as in the case of flows of water in carbon nanotubes, molecules in porous media, lubrication films between surfaces, etc. where the channel diameter can be of the order of a few nanometers, the appropriate use of the thermostatting mechanism could become a major issue. Ideally one would apply a thermostat to the walls and let the heat dissipate through them, leaving the dynamics of the fluid unaltered. However fluid models are often very complex and computation time could be saved by neglecting the dynamics of the walls particles, or the amount of heat produced could be too high for the walls to be able to extract it. For such reasons uniform thermostats are often applied to the fluid. The walls can either be modeled by vibrating particles [LC05, SNQ01, KSDG05], or by ‘frozen’ particles, fixed in their equilibrium positions [SNQ02, TM08, TM09, KWK04, HN06a, HN06b, JA08, JHT07], sometimes also as a continuum cylindric potential [LBR96] or as continuum potentials representing slit pores [Ste73, Ste78]. It is also possible to avoid resolving the wall dynamics and at the same time extract the heat at the boundaries using the so-called stochastic boundary thermostats. The walls are in this case represented as hard surfaces and particles’ momenta changes, upon collisions, according to special rules [WKN99]. We also note that a chaotic analysis has been conducted for these types of systems [Wag00]. In nanopores the fluctuations in density become important, making the use of simple uniform thermostats inappropriate. Depending on the purpose of the simulation, this may not be a primary concern, and the influence on the results negligible. However in other situations in which precise measurements are being attempted, the results could be significantly affected by inappropriate thermostatting.

The thermodynamic, or entropic, temperature is defined by the following differ-
and for a system at equilibrium it is equivalent to the kinetic temperature, defined as
\[ T_K(t) = \frac{\sum_i m_i v_i(t)^2}{dNk_B}, \] (3.2)
where \( N \) is the number of particles, \( d \) the Cartesian dimension, \( k_B \) the Boltzmann constant, \( m_i \) the mass per particle, \( \mathbf{r}_i \) and \( \mathbf{v}_i \) are the position and laboratory velocity respectively of particle \( i \). This equivalence holds also for a confined fluid at equilibrium. The presence of material boundaries, in fact, only changes the structure and arrangement of the particles close to the surface, making the system spatially inhomogeneous but leaving the equipartition of energy unaffected.

The definition of temperature for nonequilibrium systems is still an open problem [CVJ03, JCSCV05, AK03, BDD04, CG04, PH07]. The thermodynamic expression for the temperature is in fact linked to the definition of the entropy, which for nonequilibrium steady states, is still under debate [Rue99, Gal99, ER02, Cro07, Gal06, Rue03, LJCV08]. However it is commonly accepted that the majority of the systems under study satisfy the local thermodynamic equilibrium postulate [dGM84]. This is true if the inhomogeneities both in space and time are small enough to be ignored on a microscopic scale.

For driven inhomogeneous systems, because of the strong density fluctuations in space, the local thermodynamic equilibrium postulate can only be valid if considering slices of the simulation cell in which the variation in density is negligible (however for very high external fields, even this assumption is no longer true). Thus a proper thermostat that is applied to the fluid will have to account for this inhomogeneity.

For a nonequilibrium system, the kinetic temperature is defined as
\[ T_K(t) = \frac{\sum_i m_i [\mathbf{v}_i(t) - \mathbf{u}(\mathbf{r}_i, t)]^2}{dNk_B}, \] (3.3)
where \( \mathbf{u}(\mathbf{r}_i, t) \) is the instantaneous streaming velocity. In nonequilibrium systems, as a result of the external force, different areas of the fluid move at different ve-
3 Simulation of confined fluids and boundary driven nonequilibrium systems

velocities. These are collective velocities and must be neglected when computing the thermal motion. The correct evaluation of the streaming velocity is also not an easy task [LC92], especially in nanoconfined systems where few molecules are physically present in any point in time and at any region in space. The determination of the streaming velocity is a delicate point because its incorrect evaluation could cause a thermostat, which makes use of this definition, to induce a non-physical behavior on the particles. An example is the production of a string phase for homogeneous Couette flow [EM86]. The most commonly used deterministic thermostats for simulation of nonequilibrium systems are the Gaussian iso-kinetic [EHF+83] and Nosé-Hoover [Hoo85] thermostats. Both have the characteristic of being deterministic and time reversible, both facilitating analysis by dynamical systems theory. For the production of our results we have used the Nosé-Hoover thermostat (because it is able to reproduce the canonical distribution function at equilibrium [Hoo85]) unless explicitly stated. The thermostatting devices presented in this thesis are the profile biased thermostat (PBT) and profile unbiased thermostat (PUT) [EM90]. A profile biased thermostat is a thermostat that makes assumptions on the streaming velocity of particles. Its use was first explored by Evans and Morriss [EM86] to explain the formation of the so-called string phase for homogeneous shear systems observed by Erpenbeck in 1984 [Erp84]. It is particularly common in modeling planar Couette flow to assume that the streaming velocity profile is linear. This is, however, not always the case, especially for high strain rates and high Reynolds numbers or for very highly confined fluids. If the streaming velocity differs from the expected values the thermostat will interpret this difference as if the system was heating up, suppressing the formation of secondary flows. For boundary driven Couette flow the streaming velocity at the boundary will not be linear and therefore a PUT should always be the preferred choice. For the PBT we consider the case in which the fluid is treated as homogeneous (see Fig. 3.2). The PUT does not need this distinction, in fact the variation in density is automatically accounted for during the instantaneous evaluation of the streaming velocity (see Fig. 3.3). For both PBT and PUT with a vibrating wall, the Nosé-Hoover thermostat has been applied also to the wall, to avoid the fluid acting as a thermal reservoir for the wall particles.
3.3 Confined System Model

In this thesis, a two-dimensional system confined by a channel of a width of the order of a few atomic diameters has been used for the study of Lyapunov exponents and thermostatting mechanisms. The channel is periodic in the $x$ direction and the walls are composed of particles with the same mass and interparticle pair-potential potential as that of the fluid (see Fig. 3.1). The particles (both fluid and wall particles), interact with each other by the Weeks-Chandler-Anderson potential [WCA71, HO06].

In addition to their WCA interactions, the wall particles are subject to a harmonic potential, which tethers each of them to a virtual lattice site, leaving them free to oscillate as a consequence of interactions.

$$
\Phi_H(|q_i^W - q_i^L|) = \frac{1}{2} k_w |q_i^W - q_i^L|^2,
$$

where the superscripts $W$ and $L$ indicate the wall particle and its lattice site, re-
spectively. The harmonic spring constant \( k_w \) has been set to 150, a common value in the literature (see for example Travis et al. [TTE97a]). A shift of the lattice sites drives the wall particles in the case of Couette flow:

\[
\Delta q_{iL}^L = \pm \frac{1}{2} \dot{\gamma} L_y \Delta t, \tag{3.5}
\]

where \( q_{iL}^L \) is the \( x \) coordinate of the lattice site, \( \dot{\gamma} \) is the strain rate, \( L_y + \sigma \) is the distance between the two walls, as defined in Fig. 3.1, and \( \Delta t \) is the time step. The sign in equation (3.5) is positive if the particle is in the top wall and negative if it is in the bottom wall.

### 3.3.1 Density, Temperature and Stress Profiles

We compute most fluid properties as a function of the distance from the wall, in bins of width \( \Delta \). In the bin method we divide the pore into several slabs aligned with the wall direction and compute the averages for every slab/bin of the quantity of interest. This method is very easy to implement but the bin dimension has to be chosen carefully. If it is too wide the resolution will be poor, while if it is too small, few particles will be found in the bin at any time, resulting in poor statistics. An alternative ‘method of planes’ technique (that is exact) can also be used to avoid this ambiguity [DTT96]. Formally, the presence in a bin of a particle at \( r_i \), can be expressed by integrating a Dirac delta function \( \delta(r - r_i) \), over all positions, \( r \), within the bin. We now introduce the microscopic density and the momentum density used for computation of the streaming velocity and the temperature at a chosen position in the system. The mass density in the position \( r \) and time \( t \) is defined as

\[
\rho(r, t) = \sum_i m_i \delta(r - r_i(t)), \tag{3.6}
\]

and the momentum density as

\[
J(r, t) = \rho(r, t) u(r, t) = \sum_i m_i v_i(t) \delta(r - r_i(t)), \tag{3.7}
\]
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where \( u(r, t) \) is the streaming velocity

\[
\mathbf{u}(r, t) = \sum_i m_i \mathbf{v}_i(t) \delta(r - r_i(t)) \over \sum_i m_i \delta(r - r_i(t)).
\]  

(3.8)

and \( \delta(r) \) is the Dirac Delta function. In a simulation, the channel is divided into slabs (or bins) of finite size, \( \Delta = 0.05 \), aligned with the wall direction and the averages for every slab are computed for the quantities of interest. Defining \( B(y_{\text{bin}}) \) as the value of the phase variable, \( B \), in a bin centered at \( y_{\text{bin}} \) we have

\[
B(y_{\text{bin}}, t) = \int \int_{y_{\text{bin}} - \Delta/2}^{y_{\text{bin}} + \Delta/2} dxdy B(r, t)/(\Delta \cdot L_x),
\]  

(3.9)

where \( L_x \) is the bin dimension in the \( x \) direction. We compute the streaming velocity in each bin as a running average during the simulation. This definition gives good results as we will see in the result discussion.

The kinetic temperature has been computed in each bin as \[TE97\]

\[
\langle T(y_{\text{bin}}) \rangle = \frac{\sum_{i \in \text{bin}} N_{\text{bin}} [\mathbf{v}_i(t) - \mathbf{u}(y, t)] [\mathbf{v}_i(t) - \mathbf{u}(y, t)]}{\langle 2N_{\text{bin}} \rangle},
\]  

(3.10)

where \( v_i(t) \) is the laboratory velocity of particle \( i \) at time \( t \) and \( N_{\text{bin}} \) is the number of particles in any particular bin. Because of the reduced dimension of the system and the difficulty in defining an instantaneous streaming velocity for each bin at each time step, a running average of the streaming velocity has been used. For the PUT discussed in section 3.2, each slab is associated with a friction coefficient, which accounts for density fluctuations across the channel.

The equations of motion for the wall particles connected to the virtual lattice by
3 Simulation of confined fluids and boundary driven nonequilibrium systems

Figure 3.2: Schematic representation of a system with vibrating walls and profile biased thermostat.

a Hookean potential are:

\[
\begin{align*}
\dot{q}_w^i &= \frac{p_w^i}{m_w^i}, \\
\dot{p}_w^i &= F_w^i - \bar{\xi}_w^i p_w^i, \\
\dot{\bar{\xi}}_w &= \frac{1}{Q} \left[ \sum_i \frac{p_w^{i2}}{m_w^i} - g N_w k_B T \right],
\end{align*}
\]

(3.11)

where \( g \) represents the Cartesian degrees of freedom (2 in this case), and the superscript \( w \) identifies wall particles. \( F_w^i \) includes the term due to the spring potential as well as the interactions with other wall atoms and the fluid.

When the wall atoms are frozen there are no equations of motion and their position changes according to Eq. (3.5) where this time \( q_L^i \) has to be substituted with the real particle coordinates.

The fluid particles for the wall thermostatted system move according to Newton’s
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Figure 3.3: Schematic representation of a system with “frozen” walls and profile
unbiased thermostat.

equations of motion:

\[
\begin{align*}
\dot{q}_i^f &= \frac{p_i^f}{m_i^f}, \\
\dot{p}_i^f &= F_i^f,
\end{align*}
\]

(3.12)

while if the fluid is thermostatted:

\[
\begin{align*}
\dot{q}_i^f &= \frac{p_i^f}{m_i^f}, \\
\dot{p}_i^f &= F_i^f - \xi_i^f p_i^f,
\end{align*}
\]

(3.13)

where the friction coefficient \(\xi_i^f\) and the term \(p_i^f\) take different forms depending on
the thermostat device type (PUT, PBT). The differences depend on the definition
of the streaming velocity in the \(x\) direction to obtain the peculiar velocity.
For the PBT thermostat the velocity gradient is assumed to vary linearly across the channel:

\[ v_x(y) = \dot{\gamma} y \]  

(3.14)

where \( \dot{\gamma} \) is the shear strain rate. This assumption is good for low shear rate and homogeneous fluids (as in the SLLOD algorithm), however for highly confined systems it is not valid anymore, at least in the region close to the wall.

For the computation of the pressure tensor, we employ the method of planes [TED95] mentioned above. The pressure tensor can be split into a kinetic and a potential part, \( P = P^U + P^K \). The channel is divided into planes equally spaced, and the velocity of the particles crossing the planes and the force between the particles on opposite sides of the planes are used to generate the potential and kinetic components of the pressure tensor respectively:

\[
P^U_{\alpha y}(y) = \frac{1}{4A} \sum_{ij} F_{\alpha ij} [\Theta(y_i - y)\Theta(y - y_j) - \Theta(y_j - y)\Theta(y - y_i)], \quad (3.15a)
\]

\[
P^K_{\alpha y}(y) = \lim_{\tau \to \infty} \frac{1}{A\tau} \sum_{0 < t_i, m < \tau} \sum_{i} p_{\alpha i}(t_i, m) \text{sgn}[p_{yi}(t_i, m)], \quad (3.15b)
\]

where \( i \) and \( j \) are the particle indices, \( \alpha \) is any of the \( x, y \) or \( z \) components in the force and momentum vectors, \( \Theta \) is the Heaviside step function and \( m \) indexes the times at which the particle crosses the plane. This method allows a high resolution because, unlike the bin method, the separation of the planes does not influence the statistical precision of the pressure tensor [TED95]. The method of planes has been used exclusively for the computation of the pressure tensor as we do not need that level of precision for the determination of the other quantities we consider.
As a further check we computed the velocity and speed distribution to see if they followed Maxwell-Boltzmann statistics. We considered only the $x$ component (direction of the flow) for the velocity distribution. The two distribution functions are computed for each slab across the channel:

$$f(v_x, y_{\text{bin}}) = \sqrt{\frac{m(y_{\text{bin}})}{2\pi k_B T(y_{\text{bin}})}} \exp \left[ -\frac{m(y_{\text{bin}})v_x^2(y_{\text{bin}})}{2k_B T(y_{\text{bin}})} \right], \quad (3.16a)$$

$$f(v, y_{\text{bin}}) = \left( \frac{m(y_{\text{bin}})}{k_B T(y_{\text{bin}})} \right) v(y_{\text{bin}}) \exp \left[ -\frac{m(y_{\text{bin}})v^2(y_{\text{bin}})}{2k_B T(y_{\text{bin}})} \right]. \quad (3.16b)$$

We do not show the plots however, because the results are in good agreement for all systems.
Chapter 4

Algorithms and Periodic Boundary Conditions for Homogeneous Flow

4.1 Introduction

In this chapter we describe the implementation of periodic boundary conditions for nonequilibrium homogeneous fluids. In sections 4.2 and 4.4, we give a theoretical and historical background for the PBCs that have been developed until the present time for planar Couette and elongational flow and in the remaining parts we introduce our new algorithm to implement a PBC scheme for mixed flow, that is a mixture of elongational and planar Couette flow. Results from calculations of viscosities determined using these new PBCs will be presented at the end of this chapter.
4.2 Periodic Boundary Conditions: Nonequilibrium case

Homogeneous nonequilibrium molecular dynamics (NEMD) techniques have been successfully employed to characterize the rheology of many classes of simple and polymeric fluids because they allow one to study bulk properties by means of synthetic algorithms combined with appropriate periodic boundary conditions (PBCs). PBCs have to be compatible with each particular type of flow one wants to simulate so as not to introduce any spurious dynamics. Finding PBCs for every type of flow is still an open problem. Standard flows can be divided into shear and shear-free flows according to the value of the off-diagonal components of the strain-rate tensor (shear-free flow corresponds to the case of zero off-diagonal components). We will concentrate our attention on planar flows. Many studies have been done on planar shear flow (planar Couette flow, PCF) and fewer on planar elongational flow (PEF), because they are simple to characterize, efficient simulation techniques have already been implemented and they are present in almost every real flow situation. Even if these flows represent idealised situations, their study has proven to be useful in understanding many industrial processes such as extrusion, injection molding and sheet casting, but also in biological systems such as DNA chain dynamics [WS03].

We present here not only the PBCs necessary to perform NEMD simulation of PCF and PEF but also the algorithms necessary to reproduce such flows. The development of the algorithms follows both a practical and a theoretical approach, ensuring it works as intended but also establishing a statistical mechanics connection. This connection does not require PBCs as an infinite system can be considered. The implementation of appropriate PBCs is instead merely a practical way to allow simulations to be performed with a small number of atoms to represent many.

For now we concentrate our attention on how to modify the equations of motion to generate the desired flux. Such methods are called synthetic because they try to induce the same physical effect without reproducing the natural experimental settings. They are successful in computing transport coefficients valid in the limit of
applied zero field. Of course, this can be done using EMD. However NEMD also gives us the opportunity to observe structural changes that occur when a field is applied and that can be important in complex molecular systems such as polymer melts or DNA filaments. Synthetic methods also allow us to treat systems in the nonlinear regime, and allows us to use the transient time correlation function formalism (see Eq. (1.8)) which enables properties to be determined in the nonlinear regime even when statistical noise is large.

We are going to present here the SLLOD equations [EM84b] whose name comes from their relationship with a previous set of equations named DOLLS [HEH+80]. The DOLLS equations can be derived from a Hamiltonian:

\[ H = H_0 + \sum_i q_i p_i \cdot \nabla u^T \]  

from which follows the equations

\[ \dot{q}_i = \frac{p_i}{m_i} + q_i \cdot \nabla u, \]
\[ \dot{p}_i = F_i - \nabla u \cdot p_i. \]

The SLLOD equations of motion differ from the DOLLS only in the momenta

\[ \dot{q}_i = \frac{p_i}{m_i} + q_i \cdot \nabla u, \]
\[ \dot{p}_i = F_i - p_i \cdot \nabla u, \]

where the term in the strain rate tensor \( \nabla u \) is transposed, and means they are not derivable from a Hamiltonian. The strain rate tensor \( \nabla u \) is

\[ \nabla u = \begin{pmatrix}
\frac{\partial u_x}{\partial x} & \frac{\partial u_y}{\partial x} & \frac{\partial u_z}{\partial x} \\
\frac{\partial u_x}{\partial y} & \frac{\partial u_y}{\partial y} & \frac{\partial u_z}{\partial y} \\
\frac{\partial u_x}{\partial z} & \frac{\partial u_y}{\partial z} & \frac{\partial u_z}{\partial z}
\end{pmatrix}, \]

where \( u(r,t) \) represents the macroscopic flow field. However they are correct in the linear regime and unlike the DOLLS equations they do not show errors in physical
properties of quadratic order in the strain rate [EM90]. They are correct also in
the nonlinear regime, unlike DOLLS [DT06]. The SLLOD equations of motion have
been demonstrated to be the appropriate equations of motion for any homogeneous
flow [EM84a, DT06]. Other sets of equations have been proposed at different times
[BEKC05b, BEKC05a, ED01, TMBK96], but they have all been found to be deficient
in some aspects [DT06, TD07]. Many homogeneous flows can be studied using
Eqs. (4.3), depending on the form of the strain rate tensor (in conjunction with
appropriate boundary conditions).

We analyze the form that the strain rate tensor assumes for three flows, planar
Couette, planar elongation and planar mixed flows. For the last one (linear combi-
nation of the previous two flows) we also derive for the first time, to our knowledge,
appropriate PBCs. Couette flow can be thought of as being generated from the
movement in opposite directions of two plates, exerting therefore a shear force on
the fluid, see Fig. (4.1). The strain rate assumes the form:

\[
\nabla \mathbf{u} = \begin{pmatrix}
0 & 0 & 0 \\
\dot{\gamma} & 0 & 0 \\
0 & 0 & 0
\end{pmatrix},
\]

and the equations of motion become

\[
\begin{align*}
\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m_i} + \hat{x}\dot{\gamma}y_i, \\
\dot{\mathbf{p}}_i &= \mathbf{F}_i - \hat{x}\dot{\gamma}p_{gi},
\end{align*}
\]

where \(\hat{x}\) is the unit vector in the \(x\) direction. The additional terms in Newton’s
equations are equivalent to superimposing a linear velocity profile at time \(t = 0\), and
if the system is assumed to be infinite this velocity profile will not decay. Of course
the viscous forces will heat the system, therefore a thermostat must be added to
Eqs. (4.6) to achieve a steady state. The issue of how to properly thermostat fluids
in molecular simulation has been discussed in chapters 2 and 3.

These equations present some properties which have some influences on the phase
space distribution. It must be noted that in general they will not preserve total
4 Algorithms and Periodic Boundary Conditions for Homogeneous Flow

momentum and centre of mass unless they are set to zero in the beginning of the simulation [TD07]. We note however that this is the case also for the centre of mass in unthermostatted EMD, and for the centre of mass and total momentum in thermostatted EMD. This is easy to see considering the evolution of the centre of mass

\[ \dot{X}(t) = \frac{P_x(t)}{M} + \dot{\gamma} Y(t), \]
\[ \dot{Y}(t) = \frac{P_y(t)}{M}, \]
\[ \dot{Z}(t) = \frac{P_z(t)}{M}, \]

and total momentum

\[ \dot{P}_x(t) = -\dot{\gamma} P_y(t), \]
\[ \dot{P}_y(t) = 0, \]
\[ \dot{P}_z(t) = 0, \]

where \( M = \sum m_i \) is the total mass of the system, \( \mathbf{R}_\alpha(t) = \sum i m_i \mathbf{r}_{\alpha i}/M \) with \( \alpha = x, y, z \), \( P_\alpha(t) = \sum_i p_{\alpha i} \), and we have used Newton’s third law \( \sum_i F_{\alpha i} = 0 \). However because of machine finite numerical precision we are never able to set the initial condition to zero exactly. This is not a problem for shear flow due to the linear growth of the error in time. As we will see the situation is different for PEF and PMF.

The SLLOD equations for planar shear flow (PSF) were the first to be developed, even if the strain rate tensor can assume many forms and represent many flows. This may be because the flow is fairly simple to generate and also to reproduce with moving boundaries as one would do in experiments. This made it possible to compare the algorithm with other simulation techniques [HHP08, LBC92].

As the flow is homogeneous, every point in space has to experience the same strain, this means that when a particle crosses the upper/lower boundaries it has to re-enter the lower/upper boundary shifted as in Fig. (4.2) so that the strain rate is infinitely propagated.

The PBCs presented in Fig. (4.2) are the well known Lees-Edwards PBCs [LE72]. They were the first to be developed for homogeneous Couette flow and they were
even used to create a shear flow by the action of the boundaries alone. However that method suffered from two major drawbacks: the system took time to establish the correct profile (and this clearly increases with system dimension and complexity) and lacked the connection with response theory [TD07]. The shift in the x-coordinate of a particle when it is re-imaged into the unit cell after crossing the top or bottom boundary is determined by the strain rate and the time since the start of the simulation (when boxes were aligned). The boxes are shifted with respect to each other by $\pm(L_y \dot{\gamma} t)_{\text{mod}L}$, where $L_y$ is the length of the cell in the $y$ direction, $t$ is the total simulation time and the modulus operation ensures that the particles re-enter the primitive cell. These PBCs are simple to implement and easy to visualize, however they can only be applied to shear flow. What one would like in principle, is a general procedure to derive PBCs able to follow any type of flow. One way to achieve this is to let the simulation box evolve according to the streamlines of the flow (for Couette flow see Fig. (4.1)). This operation acts, of course, at a macroscopic level, just like a colored dense patch of liquid would evolve immersed in a river (leaving out the dynamics of the constitutive molecules). The streamlines are determined just by the strain rate tensor, neglecting the particle thermal motion,

$$\dot{L}_k(t) = L_k(t) \cdot \nabla u,$$

where $k = 1, 2, 3$ indicate the 3 basis vectors that generate the box.
For PCF that gives

\[ L_{kx}(t) = L_{kx}(0) \gamma t, \]  
\[ L_{ky}(t) = L_{ky}(0), \]  
\[ L_{kz}(t) = L_{kz}(0), \]

where the change in Eq. (4.10a) represents the same amount of shifting \( \pm (L_y \gamma t) \) expressed in the Lees-Edwards PBCs, however now it is not only the upper boundary that slides but every \( xz \) plane, depending on its \( y \) position, (see Fig. 4.3).

The PBCs in Fig. (4.3) are known as Lagrangian-Rhomboid (as opposed to the Eulerian description) and as can be seen in the figure this method is equivalent to that of Lees-Edwards. After a certain time it is possible to take a right-angled
triangle region on the right of the cell, cut it, and past it to the left side, so that we recover the initial square shape. In this way, the simulation can be extended indefinitely, *i.e.* it is possible to perform a mapping of the cell such that the initial configuration is periodically recovered (without causing any discontinuity in physical properties). This is not a necessary condition for Lagrangian-Rhomboid PBCs, however if it is not met the simulation comes to a stop as soon as the cell shape, due to deformation, is not compatible with the system or, as in the PSF case, the linear dimension of the box becomes too large. Finding the conditions for the remapping to occur is easy for PSF, for which the conditions for the remapping optimization have also been derived [BCC96], but is quite involved for PEF. We present here for the first time how to derive the PBCs for PMF, but for other flow geometries they might not even exist (as in the case of uniaxial and biaxial extensional flows [KR92]). The question of whether or not a cell may be remapped into its original shape after a fixed amount of time, can be addressed by applying results from the theory of lattices (an extensive description of lattice properties can be found in Refs. [AB85, AZB85]).
To do this one represents the 4 corners of the box (in 2 dimensions) by 4 points. These points, plus the ones coming from the periodic cells, form an infinite lattice that univocally represents the primitive cell and its copies (see Fig. 4.4).

![Figure 4.4: Representation of lattice reproducibility for PSF after a time \( t = \tau_p \) (in blue). In red, the lattice at time \( t = 0 \).](image)

Therefore if at any time during the simulation the evolving lattice will overlap with the original lattice a time \( t = 0 \), it means that the lattice is reproducible and with some “cut and paste” is possible to recover the original box. In Fig. 4.4 we show how a lattice at time \( t = 0 \) (in red), evolves and becomes reproducible at a time \( t = \tau_p \). As outlined above, the lattice represents the primitive cell and its copies, however if we arbitrarily chose to represent a section whose shape is the same as the cell box, then due to self similarity the outmost lattice points could represent a “scaled” version of the simulation box. As already mentioned for Lagrangian-Rhomboid PBCs applied to shear, simple geometric considerations were sufficient to determine the angle between \( \mathbf{L}_1 \) and \( \mathbf{L}_2 \) for which a remapping is possible, and many simulations are performed at \( \theta = 45^\circ \) and mapped back at \( \theta = -45^\circ \) to reduce the mappings [BCC96].

For the remapping to take place (for general lattices), two conditions have to be met simultaneously: the underlying lattice, from which the cell box is generated, has to be both compatible and reproducible. Compatibility means that there is a finite minimum spacing between lattice points; reproducibility means that the lattice can, at two different times, be generated by two equivalent basis vectors, i.e. the lattice
points at two different times occupy the same positions in space [AB85]. This has been shown for PCF (Lagrangian-Rhomboid PBCs) and for PEF by Kraynik and Reinelt [KR92], but for other geometries it can be difficult, if not impossible.

We now consider PEF and the Kraynik and Reinelt (K-R) PBCs, the understanding of which is of importance in the derivation of PMF PBCs as well.

For planar elongational flow (PEF) the strain rate assumes the form

\[
\nabla \mathbf{u} = \begin{pmatrix}
\dot{\epsilon} & 0 & 0 \\
0 & -\dot{\epsilon} & 0 \\
0 & 0 & 0
\end{pmatrix}, \tag{4.11}
\]

Figure 4.5: Planar elongation flow streamlines.

This flow can be described as shown in Fig. 4.5, a material stretched along the \( x \) axis and squeezed in the \( y \) direction with a stagnation point in the origin.

The SLLOD equations of motion in this case take the form [TD98]

\[
\dot{q}_i = \frac{p_i}{m_i} + \dot{\epsilon}(x_i \hat{x} - y_i \hat{y}), \\
\dot{p}_i = F_i - \dot{\epsilon}(p_{xi} \hat{x} - p_{yi} \hat{y}). \tag{4.12}
\]
As for shear SLLOD, these equations too present some interesting characteristics that will have some repercussions in our chaotic analysis of PMF. These equations do not conserve total linear momentum and centre of mass, unless we set them both to zero at the time origin. For the centre of mass we have

\[
\dot{X}(t) = \frac{P_x(t)}{M} + \dot{\varepsilon}X(t),
\]

\[
\dot{Y}(t) = \frac{P_y(t)}{M} + \dot{\varepsilon}Y(t),
\]

\[
\dot{Z}(t) = \frac{P_z(t)}{M},
\] (4.13)

and for the momentum

\[
\dot{P}_x(t) = -\dot{\varepsilon}P_x(t),
\]

\[
\dot{P}_y(t) = -\dot{\varepsilon}P_y(t),
\] (4.14)

\[
\dot{P}_z(t) = 0.
\]

Solving the equations we find an exponential growth of the total momentum and centre of mass velocity for finite precision numerics. Unlike for shear SLLOD, where the growth was linear, this time we could experience problems in time spans comparable with an average NEMD simulation length. These stability problems can be resolved easily, by resetting these quantities to be zero at each time step without altering the physics behind the flow [TD00]. We stress in fact that these errors are only due to the finite precision of the machine we use. If it was possible to have infinite precision this problem would not exist. The exponential increase is due to the hyperbolic characteristic streamlines of the flows.

If we apply Lagrangian-Rhomboid PBCs to PEF in the same way we proceeded for PSF, we would have a very short simulation. As shown in Fig. 4.6 the cell would become so small in the \( y \) direction that the particles would start to interact with their own periodic images. Two ways to overcome time limits in PEF have been attempted at different times: by means of the transient time correlation function technique (TTCF) [Tod98] and by using frequency dependent strain rate techniques [DT98, TD97]. The first approach allows one to improve statistics for NEMD algorithms with a limited simulation time, while the latter allows the extrapolation of properties of interest at the zero frequency limit. Neither method has been employed for mixed

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flow to our knowledge. However, recently a hybrid MD-MC coarse-grained method that does not rely on the implementation of periodic boundary conditions has been devised and tested for short chain systems for various flow geometries in the weak field limit [IOK09]. Like all such schemes, it is unsuitable in the strongly non-linear regime.

As outlined above the best solution comes from a lattice representation of the periodic cells. Kraynik and Reinelt [KR92] provided, for the first time, the conditions necessary for both reproducibility and compatibility of arbitrary lattices for planar extensional flow with respect to multiphase flows. Their results were used by Todd and Daivis [TD98] and Baranyai and Cummings [BC99] to independently realize NEMD PBCs for planar extensional flow. More recently, Hunt and Todd [HT03] showed that the Kraynik-Reinelt PBCs are related to the Arnold cat map, and derived much simpler mathematical rules to find the necessary conditions for the remapping. Furthermore Matin et al. [MDT03] provided a new cell list algorithm to reduce the computation time for large systems.
4.3 Kraynik and Reinelt Periodic Boundary Conditions

Following the lattice representation of Adler and Brenner [AB85, AZB85] and the procedure of Kraynik and Reinelt [KR92] a general lattice can be written at time \( t = 0 \) as a set of points

\[
\mathbf{L}_i(0) = n_1\mathbf{l}_1(0) + n_2\mathbf{l}_2(0) + n_3\mathbf{l}_3(0),
\]

where \( n_p \) is a set of integers and \( \mathbf{l}_i(0) \) are linearly independent lattice vectors. The time evolution for the lattice is given by

\[
\mathbf{L}_i(t) = \mathbf{L}_i(0) \cdot \mathbf{A},
\]

where \( \mathbf{A} = \exp(\mathbf{D} t) \), \( \mathbf{D} \) is the diagonal PEF strain rate tensor and \( \det\mathbf{A} = 1 \).

The lattice is reproducible only if for some \( N_{ij} \)

\[
\mathbf{L}_i(t = \tau_p) = \mathbf{L}_i(0) \cdot \mathbf{A} = N_{i1}\mathbf{l}_1(0) + N_{i2}\mathbf{l}_2(0) + N_{i3}\mathbf{l}_3(0) = \mathbf{L}_i(0),
\]

where \( \tau_p \) is the reproducibility time.

We can rewrite Eq. (4.17) as an eigenvalue problem

\[
(N - \lambda_i \mathbf{I})\mathbf{c}_i = 0,
\]

where \( \mathbf{N} \) is an integer tensor, \( \lambda_i = \exp(\mathbf{D}_i t) \) and \( \mathbf{c}_i \) contains the \( i \)th component of the basis vectors \( \mathbf{l}_j \). Solving for \( \lambda \) one obtains the following:

\[
\lambda_1 = \frac{k + (k^2 - 4)^{1/2}}{2}; \quad \lambda_2 = \lambda_1^{-1} = \frac{k - (k^2 - 4)^{1/2}}{2},
\]

with \( k = 3, 4, 5, 6, \ldots \). Note however that even if \( k \) can assume infinite values, only some of them are allowed to give reproducible lattices. One then proceeds to find a set of basis vectors for the lattice and their orientation with respect to the direction of extension and contraction (which we choose to be aligned with the \( x \) and \( y \) axes respectively).
We are interested in square lattices (other shapes are possible and conditions have been derived for hexagonal lattices [KR92]) and this simplifies the problem. The orientation of the lattice is defined by the angle $\theta$ as shown in Fig. 4.7.

Figure 4.7: Schematic representation of the square primitive cell for K-R PBCs whose edges are defined by four contiguous lattice points.

Figure 4.8: Representation of lattice reproducibility for PEF with K-R PBCs, after a time $t = \tau_p$ (in blue). In red is the lattice at time $t = 0$. 

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This algorithm has proven to be very useful and several works have been done even on complex fluids \cite{DMT07, FT07, HT09b, HT09a, BEKC05c, BEK+06, IBe+06, KJ09} where the possibility of extending simulations without physical limitation is a key component. This is true also for planar mixed flow for which until now an algorithm for indefinitely extending the simulation was absent. In the next section we present a novel procedure to derive a reproducible and compatible lattice for PMF. Once the lattice has been found, the simulation will proceed until a time $t = \tau_p$ such that the total Henky strain is $\varepsilon_p = \dot{\varepsilon}\tau_p = \ln\lambda_i$, at which time one can map the cell back into its original shape at time $t = 0$ as can be seen in Fig. 4.8. Todd and Daivis \cite{TD99} also found a way to optimize the remapping and the wrapping of the atoms between the boundaries.

Figure 4.9: Initial configuration for a lattice (black dots) undergoing planar elongational flow and corresponding streamlines (red lines). The contracting and expanding axes are orthogonal.
4.4 Arnold cat map

It is interesting to note that the mapping introduced by Kraynik and Reinelt is actually related to the Arnold cat map [AA89]. Both describe in fact a mapping of the torus $T^2$ into itself, and constitute a subset of Anosov diffeomorphisms [Ano70](characterized by a differential map with hyperbolic structure).

The Arnold cat map is given, in 2D, by the following operation

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} \mod (1)$$

(4.20)

The map described by Eq. (4.20) has two eigenvectors, along which we have contraction and expansion, mimicking the action of the elongational flow on K-R lattices. The eigenvectors are however inverted, that is, what is the expanding direction in K-R is the contracting direction in the cat map and vice versa. The modulo operation maps everything into the original square, an action performed by the PBCs in the K-R procedure (see Fig. 4.10). This connection is not only interesting per se. The cat map is in fact chaotic (and ergodic despite the fact that the rational points $(p/q, r/s); p, q, r, s \in \mathbb{Z}$ are periodic [KH95]), meaning that it has positive Lyapunov exponents, and therefore the K-R PBCs describe an inherently chaotic macroscopic flow independently of the dynamics of the microscopic constituents [Tod05]. It also offers a more practical (and of easier derivation) means to obtain the parameters for the K-R PBCs. That procedure is in fact algebraically involved [KR92]. This is described in details in [HT03] and the derivation roughly goes as follow. One starts from the Anosov mapping (in 2 dimensions) given by the matrix

$$\mathbf{M} = \begin{pmatrix} m_1 & m_2 \\ m_2 & m_3 \end{pmatrix}$$

(4.21)

which is area preserving, $\det(\mathbf{M}) = 1$ (we consider only the positive case which preserves orientation) and symmetric with $m_i \in \mathbb{Z}$. We then obtain the eigenvalues

$$\lambda = \frac{(m_1 + m_3) \pm [(m_1 + m_3)^2 - 4]^{1/2}}{2},$$

(4.22)
the Henky strain is again $\varepsilon_p = \ln(\lambda)$. It is easy now to compute the eigenvectors as

$$e_1 = \left( \begin{array}{c} s \\ \frac{s}{\lambda_1 - m_1} \\ \frac{s}{m_2} \end{array} \right), \quad e_2 = \left( \begin{array}{c} s \\ \frac{s}{\lambda_2 - m_1} \\ \frac{s}{m_2} \end{array} \right), \quad (4.23)$$

where $s$ is a real number that can be set to unity for convenience. From the eigenvectors we obtain the orientation angle (between the expanding direction and the $\hat{x}$ axis)

$$\theta = \cos^{-1} \left( \frac{1}{\|e_1\|} \right), \quad (4.24)$$

Figure 4.10: The Arnold cat map. (a) The original image; (b) after the one iteration. The circular cat muzzle is deformed into an ellipse along the contracting and expanding eigenvector directions and wrapped into the original square frame by the modulo operation.
4.5 Periodic Boundary Conditions for Nonequilibrium Systems: Planar Mixed Flow

For simple planar Couette flow (PCF), the Lees-Edwards PBCs [LE72] make it possible to extend a simulation for an arbitrary amount of time. Unfortunately it is not possible to generalize them to other flow geometries. A general PBC procedure, applicable to every flow, requires the deformation of the simulation box to follow the streamlines of the flow. However, the simulation can be extended indefinitely only if it is possible to perform a mapping of the cell such that the initial configuration is periodically recovered (without causing any discontinuity in physical properties). For the remapping to take place, two conditions have to be met simultaneously: the underlying lattice, from which the cell box is generated, has to be both compatible and reproducible. Compatibility means that there is a finite minimum spacing between lattice points; reproducibility means that the lattice can, at two different times, be generated by two equivalent basis vectors, i.e. the lattice points at two different times occupy the same positions in space [AB85]. This has been shown for PCF (Lagrangian-Rhomboid PBCs) for which the conditions for the remapping optimization have been derived [BCC96] and for PEF by Kraynik and Reinelt [KR92], but for other geometries it can be difficult, if not impossible. An extensive description of lattice properties can be found in Refs. [AB85, AZB85].

In what follows work we show how to derive compatible and reproducible PBCs for planar mixed flow (PMF). As previously stated, fluids in real situations can simultaneously show a combination of several types of flows, hence the importance of developing techniques that extend the range of flows that can be characterized.

Until now simulations of fluids undergoing mixed flow were performed through an irreversible deformation of the cell box [BC95], bringing the simulation to an end when the minimum distance requirements were broken. This clearly restricted the available length of the simulations, and the complexity of the systems which could be studied.

Brownian Dynamics techniques alternatively can be used for the characterization
and study of single molecular chains in solution [DC03, HS07, WS03] undergoing any kind of flow, however, because of the impossibility of simulating interactions among multiple units, they are not suitable for dense fluids.

The idea for indefinitely extended PBCs for mixed flows relies on the possibility of finding reproducible lattices for any homogeneous and isochoric flow with a diagonalizable velocity gradient tensor [KR92]. The application of this idea to NEMD simulations of mixed flow has already been outlined in the Ph.D. thesis of Hunt [Hun08], but in this thesis we now complete the derivation and implement the specific NEMD algorithm to achieve indefinite simulations of mixed flow.

4.6 Theory

The algorithm we present in this section makes use of results concerning both lattice reproducibility and compatibility, some of which were outlined in the previous section [KR92].

For clarity we rewrite the time evolution for a lattice

\[ L_i(t) = L_i(0) \cdot A, \]  

(4.25)

where \( A = \exp(\nabla u \cdot t) \) and \( \det A = 1 \). This time however we do not have constraints on \( \nabla u \), while for PEF the velocity gradient \( \nabla u \) was constant, traceless and diagonal.

The lattice is reproducible only if for some \( N_{ij} \)

\[ L_i(t = \tau_p) = L_i(0) \cdot A = N_{i1}l_1(0) + N_{i2}l_2(0) + N_{i3}l_3(0) = L_i(0), \]  

(4.26)

where \( \tau_p \) is the reproducibility time. However, Kraynik and Reinelt noted that \( \nabla u \) can be replaced by any diagonalizable constant matrix with real eigenvalues and zero trace. In fact, if \( \nabla u = S \cdot D \cdot S^{-1} \) with \( D \) a diagonal matrix, a new set of basis vectors

\[ l_i'(0) = l_i(0) \cdot S^{-1}, \]  

(4.27)
exists which is reproducible under the flow generated by $\nabla \mathbf{u}$. The tensor $S^{-1}$ represents therefore a mapping necessary to make the old basis $l_i(0)$ reproducible in the new flow geometry. If a diagonalization can be performed:

$$A = \exp(\nabla \mathbf{u} \ t) = \exp(S \cdot D \cdot S^{-1} \ t) = S \cdot \exp(D \ t) \cdot S^{-1},$$

it follows that

$$L'(t = \tau_p) = L'(0) \cdot A = L(0) \cdot S^{-1} \cdot S \cdot \exp(D \ t) \cdot S^{-1} = L(0) \cdot \exp(D \ t) \cdot S^{-1}$$

$$= N_1 l_1(0) + N_2 l_2(0) + N_3 l_3(0). \quad (4.29)$$

This expression is equivalent to Eq. (4.26) but in the new basis $l_i'(0)$.

For the development and testing of our algorithm we consider a velocity gradient tensor of the form

$$\nabla \mathbf{u}^c = \begin{pmatrix} \dot{\varepsilon} & 0 & 0 \\ \dot{\gamma} & -\dot{\varepsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (4.30)$$

that we call ‘canonical’ and in which the expanding/contracting directions are respectively along the $x$ and $y$ axes, with elongational field strength $\dot{\varepsilon}$, and shear gradient $\dot{\gamma}$ along the $y$ direction. We note that other parameterizations for the velocity gradient are possible, see for example Refs. [FL81, Lar99]. The canonical velocity gradient tensor can be diagonalized as follows:

$$\nabla \mathbf{u}^c = \begin{pmatrix} \dot{\varepsilon} & 0 & 0 \\ \dot{\gamma} & -\dot{\varepsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ \dot{\gamma} / 2\dot{\varepsilon} & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon} & 0 \\ 0 & 0 & \dot{\gamma} / 2\dot{\varepsilon} \end{pmatrix} = S \cdot D \cdot S^{-1}. \quad (4.31)$$

The diagonal matrix $D$ is the velocity gradient for PEF, for which Kraynik and Reinelt [KR92] had already identified a set of orthogonal, reproducible and compatible basis vectors $l_i(0)$. We can therefore apply the mapping of Eq. (4.27) and obtain a reproducible lattice under mixed flow:
\begin{align}
I_1'(0) &= l_1(0) \cdot S^{-1} = (\cos \theta, \sin \theta, 0) \cdot S^{-1} = (\cos \theta - \frac{\dot{\gamma}}{2\dot{\epsilon}} \sin \theta, \sin \theta, 0), \\
I_2'(0) &= l_2(0) \cdot S^{-1} = (-\sin \theta, \cos \theta, 0) \cdot S^{-1} = (-\sin \theta - \frac{\dot{\gamma}}{2\dot{\epsilon}} \cos \theta, \cos \theta, 0), \\
I_3'(0) &= l_3(0) \cdot S^{-1} = (0, 0, 1) \cdot S^{-1} = (0, 0, 1), \\
\end{align}

(4.32)

where $\theta$ is the angle between the simulation box basis vector along the $x$ direction and the extension direction for PEF (see Fig. 4.9). Only certain values of $\theta$ give reproducible lattices and we choose, for our simulations, the value of $\theta \approx 31.7^\circ$ already used in the literature.

The lattice generated by the vectors $I_i'(0)$ in Eqs. (4.32) is reproduced after a period of time $\tau_p$, that is, when the system has experienced a total ‘Hencky’ strain of $\epsilon_p = \dot{\epsilon} \tau_p = \ln(\lambda)$, where $\lambda$ is the eigenvalue of the map $\nabla u_{\text{elongation}}$[HT03]. The reproducibility time $\tau_p$ is the same for both PEF and PMF. As can be seen in Eq. (4.29), the shear field changes the PEF basis vectors (i.e. the tensor $S^{-1}$), but the evolution of the lattice is due to the PEF velocity gradient alone (i.e. the tensor $D$).

Figure 4.11: Schematic representation of the vectors $r_i(t)$ identifying the three vertices of the simulation box and used to verify the compatibility condition.

We now need to verify the compatibility of the lattice with our flow geometry. Kraynik and Reinelt demonstrated that reproducibility guarantees compatibility, i.e.
4 Algorithms and Periodic Boundary Conditions for Homogeneous Flow

the distance $D(t)$ among the lattice points never falls below a minimum and finite value $D_m$ such that the lattice points do not overlap. However we need to ensure that $D_m$ is large enough for our purposes, i.e. is not less than the interatomic potential diameter. We are interested in the evolution of the lattice only in the $xy$ plane, therefore we set one corner of the cell box as the origin, and express $D(t)$ in turn as the modulus of the three vectors $r_i(t)$, $i = 1, 2, 3$, representing the other three vertices of the cell box in the $xy$ plane (see Fig. 4.11).

We start from the equation for the streamlines for the mixed flow, both in parametric form,

$$
\begin{align*}
    x(t) &= \frac{\dot{\gamma}}{\dot{\epsilon}} y(0) \sinh(\dot{\epsilon} t) + x(0) \exp(\dot{\epsilon} t), \\
    y(t) &= y(0) \exp(-\dot{\epsilon} t),
\end{align*}
$$

and in non-parametric form,

$$
\dot{\gamma} y^2 + 2\dot{\epsilon} xy = c,
$$

where $c$ is a numeric constant and $x(t)$, $y(t)$ are in turn the coordinates of the three corners of the cell. Using the above expressions and solving the equation

$$
\frac{d}{dt}(r(t) \cdot r(t)) = 2(\dot{x} \dot{y} + y \ddot{y}) = 0,
$$

we calculate the time $t_m$ at which the distance $r(t)$ is a minimum, substitute it into $y(t)$ and $x(t)$, and find the distance $D_m$:

$$
\begin{align*}
    t_m &= \frac{1}{4\dot{\epsilon}} \ln \left( \frac{\dot{\gamma}^2 y_0^2 + 4\dot{\epsilon}^2 y_0^2}{(\dot{\gamma} y_0 + 2\dot{\epsilon} x_0)^2} \right), \\
    y(t_m) &= y_0 \exp(-\dot{\epsilon} t_m), \\
    D_m &= \sqrt{x(t_m)^2 + y(t_m)^2} = \sqrt{\left(\frac{c - \dot{\gamma} y(t_m)}{2\dot{\epsilon} y(t_m)}\right)^2 + y(t_m)^2},
\end{align*}
$$

where $x_0 = x(0)$ and $y_0 = y(0)$. The results show compatibility for all the cases we evaluated.
Figure 4.12: (a) Initial configuration of a lattice (black dots) undergoing planar mixed flow and corresponding streamlines (red lines). The contracting and expanding axes are non orthogonal. (b) Schematic representation of how the angle $\psi_{\text{canonical}}$ varies for different values of shear field keeping the elongational field constant.
4.6.1 Non-Canonical Mixed Flow

For canonical mixed flow, the expanding and contracting axes are determined by the directions of the velocity gradient’s eigenvectors and the field strength by their modulus. For the velocity gradient in Eq. (4.30) we have the following eigenvalues

\[ \lambda = \pm \dot{\varepsilon}. \]  

(4.37)

A possible choice of eigenvectors is:

\[ u_1 = (1, 0, 0), \quad u_2 = \left( -1, \frac{2\dot{\varepsilon}}{\dot{\gamma}}, 0 \right). \]  

(4.38)

The angle between them is therefore

\[ \psi_{\text{canonical}} = \cos^{-1} \left( -\frac{\dot{\gamma}}{\sqrt{\dot{\gamma}^2 + 4\dot{\varepsilon}^2}} \right). \]  

(4.39)

From Eqs. (4.31), (4.39) and Fig. 4.12 we can see that changes to \( \dot{\varepsilon} \) and \( \dot{\gamma} \) result in a change of the angle between the axes of expansion and contraction, however the field along these axes assumes always the values \( +\dot{\varepsilon} \) and \( -\dot{\varepsilon} \) respectively.

As expressed in Fig. 4.12, if \( \dot{\gamma} = 0 \), \( \psi_{\text{canonical}} = \frac{\pi}{2} \pm n\pi \), while if \( \dot{\gamma} \to \infty \), \( \psi_{\text{canonical}} = \pm n\pi \) with \( n \) an integer. This means that for the canonical mixed flow the contraction axis always lies on a slope \( y = -ax \) with \( a \in \mathbb{R}^+ \).

We now consider a general (non-canonical) matrix \( \nabla u^{nc} \), where extension and contraction are along the \( x \) and \( y \) axes respectively, but with a shear gradient oriented along an arbitrary direction:

\[ \nabla u^{nc} = \begin{pmatrix} 
  g \cos(\phi) \sin(\phi) + e & -g \sin(\phi)^2 & 0 \\
  g \cos(\phi)^2 & -g \cos(\phi) \sin(\phi) - e & 0 \\
  0 & 0 & 0 
\end{pmatrix} \]  

(4.40)

where \( \phi \) is the angle between the contracting (\( y \) in this case) axis and the velocity gradient (negative towards the first Cartesian quadrant and positive towards the
second, (see Fig. 4.13). $g$ and $e$ are the shear gradient and the elongational field strengths respectively (we use different symbols to avoid confusion between the two representations).

We now show that, when the non-canonical strain-rate tensor in Eq. (4.40) is able to generate a mixed flow, it can be expressed in a canonical form in a rotated frame. To our knowledge this is the first time that this equivalence is shown and it means that the canonical form is able to parameterize any planar mixed flow. The expansion and contraction directions are given by the eigenvectors of the $\nabla u^\text{nc}$ matrix; if for a given choice of $[g, e, \phi]$ we are able to find a pair $[\dot{\gamma}, \dot{\epsilon}]$ such that the angles between the eigenvectors in both canonical and non-canonical forms are the same, the two representations will be equivalent up to a rotation. For the non-canonical system we have the eigenvalues

$$\lambda = \pm \sqrt{e^2 - 2e g \sin(\phi) \cos(\phi)},$$

(4.41)

and the following eigenvectors:

$$w_1 = \left(1, \frac{g \sin(\phi) \cos(\phi) - e + \sqrt{2e g \sin(\phi) \cos(\phi) + e^2}}{g \cos(\phi)^2}, 0\right),$$

(4.42)

$$w_2 = \left(-1, \frac{g \sin(\phi) \cos(\phi) - e - \sqrt{2e g \sin(\phi) \cos(\phi) + e^2}}{g \cos(\phi)^2}, 0\right).$$

(4.43)

Therefore the angle between them is:

$$\psi_{\text{non-canonical}} = \cos^{-1} \left( -\frac{g}{\sqrt{4e^2 - 8e g \cos(\phi) \sin(\phi) + g^2}} \right).$$

(4.44)

For $\phi = 0$ we fall into the canonical case. For any given set $[g, e, \phi]$ it is always possible to find a pair $[\dot{\gamma}, \dot{\epsilon}]$ such that $\psi_{\text{non-canonical}} = \psi_{\text{canonical}}$ if the non-canonical eigenvalues are real, i.e.

$$\sin(2\phi) < \frac{e}{g}.$$  

(4.45)

If the eigenvalues are 0 the flow reduces to pure shear flow, while if they are imaginary, the flow becomes elliptical. The condition given by Eq. (4.45), visualized
in Fig. 4.13(b), is equivalent (for any chosen values of $g$ and $e$) to drawing a cone around the slope $y = -x$; this is easy to see plotting $\sin(2\phi)$ against $\phi$. If the shear gradient falls inside the cone the flow becomes elliptical. We note that there is one specific case in which the flow is a pure rotation. This happens when $\phi = 45^\circ$ and $g = 2e$, that is when the matrix $\nabla \mathbf{u}^{nc}$ is antisymmetric. Any shear flow can, in fact, be decomposed as the sum of an elongational flow plus a pure rotation. Therefore if the shear flow component of the non-canonical mixed flow can be separated into a rotational and an elongational part, and the two elongational fields so obtained cancel each other out, what remains is just pure rotational flow.

Figure 4.13: (a) Schematic representation of the non-canonical flow with the strain-rate gradient tensor of Eq. (4.40) when varying the parameter $\phi$. (b) The blue cone represents the range of shear gradient axis orientations for which the non-canonical flow of Eq. (4.40) degenerates into an elliptical flow.

4.7 Algorithm

Methods that perform an irreversible squeezing of the simulation cell require a careful choice of $\dot{\varepsilon}$ to ensure the achievement of a steady state before the box dimension in the contracting direction reaches $2r_c$, where $r_c$ is the cut-off distance for the potential
energy function. Our algorithm does not suffer from such a drawback. We cannot however, arbitrarily choose the simulation box dimensions. The map $S^{-1}$ in Eqs. (4.32) is not volume preserving but has determinant $\det(S^{-1}) = \frac{-2\hat{\epsilon}}{\hat{\gamma}}$. This map, as already pointed out, changes the PEF basis vectors, making them reproducible under PMF, but while the basis vectors that generate the PEF box are equal in modulus and orthogonal, the basis vectors that generates the PMF box depend (in both modulus and direction) on the ratio between elongational and shear fields:

$$
|l'_1(0)| = \sqrt{1 + \frac{\hat{\gamma}^2}{4\hat{\epsilon}^2}\sin^2\theta - \frac{\hat{\gamma}}{\hat{\epsilon}}\cos\theta\sin\theta},
$$

$$
|l'_2(0)| = \sqrt{1 + \frac{\hat{\gamma}^2}{4\hat{\epsilon}^2}\cos^2\theta + \frac{\hat{\gamma}}{\hat{\epsilon}}\cos\theta\sin\theta},
$$

$$
I'_1(0) \cdot I'_2(0) = -\frac{\hat{\gamma}}{2\hat{\epsilon}}\cos2\theta + \frac{\hat{\gamma}^2}{4\hat{\epsilon}^2}\sin\theta\cos\theta,
$$

This must be taken into account when setting up the system at the beginning of a simulation. We want to stress however, that the volume of the cell box does not change with time during a specific simulation (we are in fact considering only isochoric flows). The orientations of the basis vectors are field dependent and will not in general be orthogonal. It may be convenient however, to start a simulation from a rectangular parallelepiped to be able to arrange particles on usual lattices. To recover a rectangular parallelepiped we utilize the fact that the Hencky strain does not depend on the choice of the origin along the time axis. This means that $L'_i(t^* + \tau_p) = L'_i(t^*)$ for arbitrary $t^*$. Therefore, if a time $t_\perp$ exists at which the basis vectors for mixed flow in Eq. (4.47) are orthogonal, we can set $t^* = t_\perp$ as the new time origin. To obtain $t_\perp$ we impose the basis orthogonality condition, $I'_1(t^*) \cdot I'_2(t^*) = 0$, and solve for $t^*$. Because $I'_1(0)$ and $I'_2(0)$ depends on both $\hat{\gamma}$ and $\hat{\epsilon}$, $t_\perp$ varies for different mixed flow fields.

The remainder of the implementation of the PBCs follow the same procedure outlined by Todd and Daivis [TD99]. Each time step the simulation cell is rotated so as to align the cell box with the laboratory $x$ axis, making the PBC and the minimum image distance calculation much easier and improving the computational
4 Algorithms and Periodic Boundary Conditions for Homogeneous Flow

efficiency. This procedure is applied only to perform the PBCs and does not affect the particle dynamics. Once in the rotated frame, we compute the displacement of the boundaries applying Eqs. (4.33) for the streamlines to the rotated primitive lattice vectors:

\[
\begin{align*}
L'_{kx}(t) &= \frac{\dot{\gamma}}{\epsilon} L'_{ky}(0) \sinh(\dot{\epsilon} t) + L'_{kx}(t) \exp(\dot{\epsilon} t), \\
L'_{ky}(t) &= L'_{ky}(0) \exp(-\dot{\epsilon} t), \\
L'_{kz}(t) &= L'_{kz}(0),
\end{align*}
\]

(4.48)

where the index \(k = 1, 2, 3\) defines the lattice vectors and the primed variables refer to the rotated vectors. The angle by which the simulation box must be rotated evolves as \(\Theta(t) = \arctan(L'_{1y}(t)/L'_{1x}(t))\), (see Fig. 4.14).

In order to implement our mixed flow algorithm, we use the corresponding SLLOD equations of motion for the particle dynamics [TD07],

\[
\begin{align*}
\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla \mathbf{u} = \frac{\mathbf{p}_i}{m_i} + \dot{\epsilon} (x_i \hat{x} - y_i \hat{y}) + \dot{\gamma} y_i \hat{x}, \\
\dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{u} = \mathbf{F}_i - \dot{\epsilon} (p_{x_i} \hat{x} - p_{y_i} \hat{y}) - \dot{\gamma} p_{y_i} \hat{x} - \xi \mathbf{p}_i,
\end{align*}
\]

(4.49)

coupled with a Nosé-Hoover thermostat [Hoo85].

4.8 Results for Mixed flow

To test the validity of our algorithm we compare our viscosity data with those found in Baranyai and Cummings [BC95]. We simulate an atomic system interacting by the Weeks-Chandler-Anderson potential (WCA) [WCA71] at a temperature \(T = 0.722\) and density \(\rho = 0.8442\). We use a time step of \(\Delta t = 0.001\). To reach steady state, the system is equilibrated for \(t = 1000\) time units and a further \(t = 3000\) time units are used for data collection. The viscosity values and standard errors plotted in Table 4.1 correspond to an averaging over 5 independent runs. All physical quantities are expressed in reduced units where the unit of mass is the particle mass \(m\), the energy unit and the length unit are the WCA parameters \(\epsilon\) and \(\sigma\), which are all set to unity.
From the relation between the heat production rate per unit volume and the second scalar invariant of the strain rate tensor $II = \dot{\gamma} : \dot{\gamma}$, Hounkonnou et al. [HPR92] derived a general expression for the viscosity of an isotropic fluid undergoing isochoric flow:

$$\eta = (\sigma : \dot{\gamma})/(\dot{\gamma} : \dot{\gamma}), \quad (4.50)$$

where $\sigma$ is the stress tensor and $\dot{\gamma}$ is the strain-rate tensor. It is then possible to obtain a viscosity for the mixed flow which can also be expressed in terms of PCF and PEF viscosities ($II = 2\dot{\gamma}^2$ for PCF and $II = 8\dot{\epsilon}^2$ for PEF):

$$\eta_{\text{mixed}} = \frac{-2\dot{\epsilon}P_{xx} + 2\dot{\epsilon}P_{yy} - 2\dot{\gamma}P_{xy}}{8\dot{\epsilon}^2 + 2\dot{\gamma}^2} = \frac{(8\dot{\epsilon}^2\eta(\text{PEF}) + 2\dot{\gamma}^2\eta(\text{PCF}))}{8\dot{\epsilon}^2 + 2\dot{\gamma}^2}. \quad (4.51)$$

We note that the formula in Eq. (4.51) reported in Ref. [BC95] contains some typographical errors.
In Table 4.1 we report only the PEF and PCF viscosities defined as

\[ \eta_{PEF} = \frac{P_{yy} - P_{xx}}{4\dot{\epsilon}}, \quad \eta_{PCF} = \frac{P_{xy}}{\dot{\gamma}}, \] (4.52)

and we report the general viscosity \( \eta_{\text{mixed}} \) in Fig. 4.15 to easily compare the results. Our viscosities agree very well with those computed by Baranyai and Cummings (see Table 4.1). Finally we note from Fig. 4.15 that the elongational field affects the viscosity more than the shear field. The viscosity thinning is more pronounced when the elongational field increases and the shear field is kept constant rather than the other way around.
Table 4.1: Elongational viscosity and shear viscosity results for an atomic fluid undergoing mixed flow with different combinations of field strengths. The fluid is thermostatted at a reduced temperature of $T = 1.0$ and the density is set at $\rho = 0.8442$. The errors, in brackets, are twice the standard error of the mean of 5 independent runs. We also report the viscosities obtained by Baranyai and Cummings [BC95] where a comparison is possible.

<table>
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<tr>
<th>PEF ($\dot{\varepsilon}$)</th>
<th>PCF ($\dot{\gamma}$)</th>
<th>$\eta_{\text{PEF}}$</th>
<th>$\eta_{\text{PCF}}$</th>
<th>$\eta_{\text{PEF}}$</th>
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<td>2.155 (0.009)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.5</td>
<td>2.068 (0.001)</td>
<td>1.972 (0.001)</td>
<td>2.12 (0.04)</td>
<td>1.96 (0.04)</td>
</tr>
<tr>
<td>0.2</td>
<td>0.5</td>
<td>1.970 (0.001)</td>
<td>1.918 (0.001)</td>
<td>1.97 (0.04)</td>
<td>1.95 (0.04)</td>
</tr>
<tr>
<td>0.3</td>
<td>0.5</td>
<td>1.901 (0.001)</td>
<td>1.857 (0.001)</td>
<td>1.91 (0.04)</td>
<td>1.87 (0.04)</td>
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<td>0.4</td>
<td>0.5</td>
<td>1.846 (0.001)</td>
<td>1.808 (0.001)</td>
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<tr>
<td>0.5</td>
<td>0.5</td>
<td>1.804 (0.000)</td>
<td>1.759 (0.001)</td>
<td>1.80 (0.04)</td>
<td>1.75 (0.04)</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>1.804 (0.001)</td>
<td>1.760 (0.002)</td>
<td>1.77 (0.04)</td>
<td>1.70 (0.04)</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>1.756 (0.001)</td>
<td>1.692 (0.001)</td>
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<td></td>
</tr>
<tr>
<td>1.5</td>
<td>1.0</td>
<td>1.682 (0.000)</td>
<td>1.591 (0.002)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.5</td>
<td>1.694 (0.001)</td>
<td>1.563 (0.000)</td>
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</tbody>
</table>
Figure 4.15: Plot of the viscosity defined in Eq. (4.51) for an atomic fluid undergoing mixed flow with different combinations of field strengths. The fluid is thermostatted at a reduced temperature of $T = 1.0$ and the density is set at $\rho = 0.8442$. The error bars are not reported because they are smaller than the symbols. (a): Viscosity for different values of elongational field (on the $x$ axis) at fixed shear fields. (b): Viscosity for different values of shear field (on the $x$ axis) at fixed elongational fields.
Chapter 5

Many Particle Dynamical Systems and Lyapunov Spectra

5.1 Chaos

NEMD simulation techniques have attracted much interest for the study and characterization of many particle dynamical systems, which in this work is carried out through the analysis of the Lyapunov spectra. Lyapunov exponents are one of the main tools for the characterization of chaos, providing a quantitative measure. Lyapunov spectra have been computed for several many particle dynamical systems in the past either for equilibrium or nonequilibrium steady states, see for example [PH06a, Mor88, BD95, BDC+96, BP10, DM96b, WB04a, WB04b, DLB98, EFPZ05b, GB02, LBD97, MP09, MP02, Mor02a, MT09, PH98, PH06b, RK02, RM08, TPDM02, TM06b, ZBD98, ZB02] and references therein. They have proven to be a particularly useful tool for the characterization and theoretical analysis of systems far from equilibrium in thermostatted steady states. Furthermore, it is possible to use the exponents to derive an expression for quantifying the probability of observing violations of the Second Law of Thermodynamics, Fluctuation Theorems (FTs) [ECM93, ER02, JES04], and assisting to explain Loschmidt’s Paradox which questions the possibility of obtaining irreversibility from time-reversible dynamics.
The study of the Lyapunov spectra also provides a link between dynamical systems theory and statistical mechanics. It has been shown that many transport properties of fluids are related to Lyapunov exponents [GN90, Gas98]. More precisely, for thermostatted systems in nonequilibrium steady states the rate of entropy production can be related to the sum over the Lyapunov exponents and to the transport coefficients [EM90, ECM90]. This is true for a wide range of systems and is valid even for nonlinear processes far from equilibrium [Coh95, SEM92]. In particular the viscosity determined from the SLLOD equations of motions can be expressed in terms of the sum of the system’s Lyapunov exponents [Coh95]. Furthermore, if the system respects the Conjugate Pairing Rule (CPR) only the knowledge of the maximum and minimum exponents is required. In this work we used Lyapunov spectra and vector analysis extensively:

- to characterize the chaoticity of anisotropic confined systems in nonequilibrium steady states;
- to better understand how thermostats affect the particle dynamics when the fluid is highly confined;
- to characterize the phase space of planar mixed flow, also in view of previous studies on its constituent flows (PSF and PEF).

The theoretical background presented in this chapter will therefore focus on aspects of dynamical system related to these systems.

### 5.2 Lyapunov Exponents

The measurement of chaos in dynamical systems quantitatively translates the concept of sensitivity to initial conditions introduced by Lorenz [Lor63]. Essentially, if a system subjected to small perturbations evolves towards a microscopic state considerably different from the initial one, this indicates the presence of chaos. Lyapunov exponents describe the rate of exponential growth or contraction of nearby phase...
space trajectories, and the presence of a positive exponent indicates that the system is chaotic.

The phase-space of a multiparticle system is $2dN$ dimensional, where $N$ is the particles number, $d$ the Cartesian dimension and the factor 2 accounts for positions and momenta [Gol50, Arn99]. A point in the phase-space at time $t$ is $\Gamma(t) = [q_1(t) \ldots q_n(t), p_1(t) \ldots p_n(t)]^T$ and the equations of motion describing its evolution are given by:

$$\dot{\Gamma} = G(\Gamma, t).$$  \hfill (5.1)

Let us consider a displacement vector $\delta\Gamma$ that represents the distance between two close points in the phase-space $\delta\Gamma = \Gamma_1 - \Gamma_2$. If a system is chaotic then the separation of nearby points in phase will on average increase exponentially in the long time limit, with a rate given by the maximum Lyapunov exponent, $\lambda^1$. Furthermore, infinitesimal hypervolumes of dimension $m$ will grow exponentially with a rate given by the sum of Lyapunov exponents $1, \ldots, m$.

Formally if we take the vanishing limit of the displacement $\delta\Gamma \to 0$, we can solve its evolution in the tangent space

$$\dot{\delta\Gamma}(t) = T \cdot \delta\Gamma,$$  \hfill (5.2)

where $T$ is the Jacobian or Stability matrix $T \equiv \partial\dot{\Gamma}/\partial\Gamma$.

The solution for the tangent vector is therefore

$$\delta\Gamma(t) = L(t) \cdot \delta\Gamma(0),$$  \hfill (5.3)

where $L(t)$ is the propagator defined as

$$L(t) = \exp_L \left( \int_0^t ds T(s) \right),$$  \hfill (5.4)

and $\exp_L$ is the left-ordered exponential (meaning that in its expansion later times appear on the left).
The multiplicative theorem of Oseledec assures that matrix

$$\Lambda = \lim_{t \to \infty} \Lambda(t) = \lim_{t \to \infty} \left[ L^T(t) \cdot L(t) \right]^{1/2},$$

exists and is limited.

The Lyapunov exponents can be defined \cite{ER85} as

$$\lambda_i = \lim_{t \to \infty} \frac{1}{2t} \ln(\text{eigenvalues}(L^T(t) \cdot L(t))).$$

This result in practice is not very convenient for evaluation of Lyapunov exponents using MD simulation. Computing the exponents operatively following Eq. (5.6) means that one has to compute the matrix $L^T(t) \cdot L(t)$ that grows quickly even after a few time steps \cite{SEI97}. A more useful expression is given by

$$\lambda_i = \lim_{t \to \infty} \lim_{\delta\Gamma \to 0} \frac{1}{t} \ln \left( \frac{|\delta\Gamma_i(t)|}{|\delta\Gamma_i(0)|} \right),$$

where $|\delta\Gamma_i(t)|$ is the length of the $i$th orthogonal displacement vector at time $t$, and $i = 1, \ldots, 2dN$ in two dimensions. We note that this expression will give the full spectrum only if $\delta\Gamma_i(0)$ is an eigenvector of $(L^T(t) \cdot L(t)) \forall i$, and if this is the case, in the long time limit Eqs. (5.6) and (5.7) are equivalent. Eq. (5.7) will always give the correct maximum Lyapunov exponent $\lambda_1$, and in practice the vectors $\delta\Gamma^i$ can be constrained to be orthogonal in a hierarchical fashion.

Benettin et al. \cite{BGGS80a, BGGS80b, SN79} used this definition to implement a “classic” algorithm that can be adapted to NEMD, where a set of $2dN$ displacement vectors $\delta\Gamma_i$ is generated at time $t = 0$ and evolved forward in time with the use of the Jacobian matrix. Because of the instability of the dynamics, the vectors rapidly grow or shrink, rotating in the phase space and aligning themselves into the direction of maximum expansion. To avoid this and maintain the vectors orthonormal, a Gram-Schmidt procedure is performed on a fixed number of time steps $n\Delta t$. The average in time of the logarithm of the change in modulus then gives the Lyapunov exponents.
An alternative but equivalent method is the one proposed by Hoover and Posch [HP85] and also developed independently by Goldhirsch et al. [GSO87] which introduced the rescaling of the displacement vectors directly into the equation of motion by means of constraint forces (Lagrange multipliers) whose time average are the Lyapunov exponents. The main difference of this method with respect to the Benettin algorithm, from a computational point of view, is that instead of considering the dynamics in the tangent space one has to solve the dynamics of $2dN$ copies (Daughters) of the original system (Mother), each one with a displacement in a different direction of the phase-space (that is a small increase in the particles’ positions and momenta). This algorithm results in being slightly slower because of the computation time needed to evolve all the Daughters. For this reason, in this research, it has been implemented (using the approach proposed by Sarman et al. [SEM92]) only at an early stage to have a term of comparison with the Benettin method.

The matrix $\Lambda$ is defined only for infinite time and, if the system is ergodic, the Lyapunov exponent can be considered an intrinsic property of the dynamical system, independent of the initial point in the phase space taken. Being also positive semidefinite, its eigenvalues are real and non-negative. Furthermore if the dynamical system is Hamiltonian the Jacobian matrices are symplectic and the $2dN$ eigenvalues can be organized in conjugate pairs $(\nu^i, 1/\nu^j)$, while the Lyapunov exponents can also be organized in conjugate pairs $(\lambda^i, -\lambda^j)$. This means that the sum of the whole spectra will be zero. This reflects the general property of Hamiltonian systems of being volume preserving. In general in NEMD simulations, because work is performed on the system a thermostat needs to be applied to maintain a steady state. As a result the system is not Hamiltonian anymore, but under certain conditions it is still possible to have conjugate pair structures in the Lyapunov spectra [SEI98]. An exact proof of conjugate pairing for thermostatted systems (either Gaussian and Nosé-Hoover thermostat) was obtained by Dettmann and Morriss [DM96b, DM97]. The pairs of exponents in this case will sum to a constant negative number. This is called the Conjugate Pairing Rule (CPR) and it turns out to be a very useful result even from a practical point of view. If the conjugating-pairing rule holds it is possible to extrapolate quantities of interest computing only two exponents, usually the maximal $(\lambda^{max}, \lambda^{min})$ because they are the easiest to compute. The calculation...
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Figure 5.1: Representation of a typical Lyapunov spectra for an equilibrium 2D system of 19 particles at a reduced density $\rho = 0.6$ and temperature $T = 1.0$. The blue circles represent the Lyapunov exponents and the red diamonds represent the sum of the ordered pairs.

of the entire spectra is in fact a computationally heavy task to perform: for an $N$-body system, with short ranged forces, the computation time goes as $O(N^2)$ at best [SEI98]. In Fig. 5.1 we show the typical shape of a Lyapunov spectra for an homogeneous equilibrium system (19 particles interacting via a WCA potential and with PBCs in all directions). On the $y$ axis is reported the value of the exponents and on the $x$ axis the pair index, which is maximum for the maximum (in absolute value) Lyapunov exponents. Exponent pair index $= M/2 − 1 + i$, where $M$ is the phase space dimension of the system. This representation will be used throughout the thesis. Because the system is Hamiltonian, the sum of the pairs is zero. We also note the presence of six vanishing exponents associate with conserved quantities. This issue will be addressed in detail in the next chapter.

A connection has been proven between the Lyapunov spectra and transport properties in NEMD simulations of many-particle systems [SEM92][ECM90], which makes the computation of the exponents worthwhile for practical applications. The
connection derives from the fact that for a wide range of non equilibrium thermostatted systems at steady state, the sum of the Lyapunov exponents matches the total entropy production rate (connected in turn with the transport coefficients).

The Liouville equation expresses the rate of change of a distribution \( f(\Gamma, t) \) in the phase-space [EM90]:

\[
\frac{df}{dt} = \partial_t f + \dot{\Gamma} \cdot \partial f = -f \partial f, \quad (5.8)
\]

where \( \dot{\Gamma} = [\dot{q}_1, \ldots, \dot{q}_n, \dot{p}_1, \ldots, \dot{p}_n] \) is the phase point velocity. Equation (5.8) is the equivalent in the phase space of the continuity equation of hydrodynamics for the density of a fluid \( \rho \) in the physical space. The element \( \partial f / \partial \Gamma \cdot \dot{\Gamma} \) is called the phase space expansion factor and it is easy to show that for a system generated by a Hamiltonian

\[
\Lambda(\Gamma) = \sum_{i=1}^{N} \left( \frac{\partial}{\partial q_i} \cdot \dot{q}_i + \frac{\partial}{\partial p_i} \cdot \dot{p}_i \right) = 0, \quad (5.9)
\]

where \( q_i = \frac{\partial H}{\partial p_i} \) and \( p_i = -\frac{\partial H}{\partial q_i} \). This is true even when the system is driven away from equilibrium by external fields. However, as a result of the field performing work on the system, it heats up and it has to be thermostatted. As discussed above, in NEMD simulations, this is usually done by modifying the equations of motion of the system by adding a constraint force. In the presence of a thermostat the phase-space compressibility is not null and will be proportional in general to the friction coefficient of the thermostat multiplier \( \alpha \) and the degrees of freedom thermostatted, \( g \), that in turn is equal to the entropy production rate.

The Gibbs entropy is defined as

\[
S = -k_B \int d\Gamma f(\Gamma, t) \ln f(\Gamma, t). \quad (5.10)
\]

Taking the time derivative, and using the properties of the distribution function, we can derive the expression for the irreversible entropy production [Hol86, Eva85]
\[
\dot{S}/k_B = -\frac{d}{dt} \int d\Gamma \ f \ln f \\
= - \int d\Gamma \ \frac{\partial}{\partial t} (f \ln f) \\
= - \int d\Gamma \ (\ln f + 1) \frac{\partial f}{\partial t} \\
= - \int d\Gamma \ ln f \frac{\partial f}{\partial t} \\
= - \int d\Gamma \ fn f \left[ -\frac{\partial}{\partial \Gamma} \cdot \left( f \dot{\Gamma} \right) \right] \\
= - \int d\Gamma \ f \dot{\Gamma} \cdot \frac{\partial \ln f}{\partial \Gamma} \\
= - \int d\Gamma \ \dot{\Gamma} \ \frac{\partial f}{\partial \Gamma} \\
= - \int d\Gamma \ f \frac{\partial f}{\partial \Gamma} \cdot \dot{\Gamma} \\
= \langle \Lambda \rangle
\] (5.11)

If the equation of motion are thermostatted with a kinetic thermostat (the kind used in this work) the differential equation for the momentum evolution become

\[
\dot{p}_i = F_i - \xi p_i,
\] (5.12)

and the term \( \frac{\partial}{\partial p_i} \cdot \dot{p}_i \) is nonzero due to the explicit dependence of \( \dot{p} \) on \( p \)

\[
\Lambda = \sum_i \frac{\partial}{\partial p_i} \cdot \dot{p}_i = dN \xi,
\] (5.13)

where we have omitted \( O(1/N) \) corrections.

In this work a Nosé-Hoover thermostat has been employed when dealing with confined systems and a Gaussian thermostat was used when studying the phase-space of planar mixed flow for consistency with previous studies [FST06, FST08]. The Nosé-Hoover thermostat is not a common choice when computing Lyapunov exponents because it increases the phase space dimension by one for each friction term. In fact the equations of motion contain the additional differential equation for the
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evolution of $\dot{\xi}$. This will not change the phase space expansion because $\frac{\partial}{\partial \xi} \cdot \dot{\xi} = 0$ but has important consequence on the phase space characterization.

Considering the evolution of a hypervolume in the space-phase

$$\delta V_{2dN}(\Gamma, t) = \delta V_{2dN}(\Gamma, 0) \exp \left[ \left( \sum_{i=1}^{2dN} \lambda^i \right) t \right]$$

(5.14)

with $\delta M$ phase points inside, we can rewrite the change in time of the distribution function $f(\Gamma, t) = \delta M/\delta V_{2dN}(\Gamma, t)$ as

$$\frac{df}{dt} = -f \frac{d}{dt} \ln \delta V_{2dN}(\Gamma, t) = -f \Lambda(\Gamma, t) = -f \sum_{i=1}^{2dN} \lambda_i = -f dN \xi,$$

(5.15)

then, taking the ensemble average

$$\langle \Lambda(\Gamma, t) \rangle = \sum_{i=1}^{2dN} \lambda_i = dN \langle \xi \rangle.$$  

(5.16)

Eq. (5.16) relates the Lyapunov exponents’ sum to the entropy production rate, and this can be related to the transport coefficients. In particular, it has been shown [ECM90] that the viscosity described by the SLLOD equations of motion can be expressed in terms of the sum of its Lyapunov exponents (for a review, also see Ref. [Coh95]). As discussed in Ref. [FST06], this relationship becomes a proportionality between the viscosity and the sum of the Lyapunov exponents in the thermodynamic limit. Furthermore, if the system respects the CPR, only the knowledge of the maximum and minimum exponents is required. The relationship between the sum of the Lyapunov exponents and the viscosity has already been tested in previous works for simple fluids under shear and elongational flows [ECM90, FST06] and we now extend it to PMF. It is worth noting that the proof for this relation was first derived for PSF SLLOD equations, Eqs. (4.6), for an isoenergetic system in the thermodynamic limit [ECM90]. The same result applies to isokinetic systems.

For PMF we can follow the same steps. We impose the time derivative of the
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internal energy to be zero

\[
\frac{dH_0}{dt} = \sum_i \left( -\dot{\varepsilon}p_{ix}^2 + \dot{\varepsilon}p_{iy}^2 - \dot{\gamma}p_{ix}p_{iy} - \dot{\varepsilon}F_{ix}q_{ix} + \dot{\varepsilon}F_{iy}q_{iy} - \xi_{pi} \cdot p_i \right) = 0, \tag{5.17}
\]

and obtain the friction coefficient

\[
\xi = -\dot{\gamma}V P_{xy} - \dot{\varepsilon}V (P_{xx} - P_{yy}) \sum_i p_i \cdot p_i, \tag{5.18}
\]

where \( V \) is the cell box volume, and \( P_{ij} \) are the elements of the pressure tensor. We can express the friction coefficient in terms of the viscosities for PEF and PSF (see Eqs. (4.52)),

\[
\xi = V(\dot{\gamma}^2 \eta_{PSF} + 4\dot{\varepsilon}^2 \eta_{PEF}) \sum_i p_i \cdot p_i, \tag{5.19}
\]

and now using the expression for the PMF viscosity (Eq. 4.51), a linear combination of PEF and PSF viscosities, and Eq. (5.16) we can establish the connection with the Lyapunov exponents’ sum. For PSF and PEF we have respectively:

\[
\eta_{PSF}(\dot{\gamma}) = -\frac{k_B T_{SS}}{\dot{\gamma}^2 V} \sum_{i=1}^{2dN} \lambda_i, \tag{5.20}
\]

\[
\eta_{PEF}(\dot{\varepsilon}) = -\frac{k_B T_{SS}}{4\dot{\varepsilon}^2 V} \sum_{i=1}^{2dN} \lambda_i, \tag{5.21}
\]

where \( k_B \) is the Boltzmann constant and \( T_{SS} \) is the temperature at the steady state. For PMF we have:

\[
\eta_{PMF}(\dot{\varepsilon}, \dot{\gamma}) = -\frac{k_B T_{SS}}{(4\dot{\varepsilon}^2 + \dot{\gamma}^2) V} \sum_{i=1}^{2dN} \lambda_i, \tag{5.22}
\]

which, as said, is exact in the limit of large \( N \). Comparing viscosity values from NEMD runs, we will see that the above equation for PMF is already satisfactory when \( N = 32 \).

The phase space reflects the symmetries of the system and these are in turn reflected in the Lyapunov spectra. We already mentioned how for Hamiltonian systems the sum of the exponents is zero and the ordered couples form two symmetric “arms” around the \( x \) axis. The growth/contraction of the hypervolume in Fig. 5.2 is quantified by the exponents’ sum and this means that when energy is conserved the volume is conserved, even if it can deform.
There are however other symmetries reflected by the values of specific exponents associated with particular directions in the phase space. For a (2 dimensional) system at equilibrium, purely Newtonian and with PBCs in all direction, the conservation of linear momentum, center of mass in all Cartesian dimensions, the conservation of energy and the autonomous character of the equations of motion gives rise to six zero Lyapunov exponents. Their vectors associated with directions perpendicular to the hypersurface cannot grow nor shrink but remain constant. For homogeneous nonequilibrium systems it is still possible to have peculiar exponents (that will not be necessarily zero) due to the symmetries of the SLLOD equations. The origin of these exponents for PSF and PEF has been explained at length in a previous paper [FST06], therefore we only present a brief explanation. Their numerical value can be obtained exactly in the low density limit, when the interatomic forces become negligible and the particle dynamics just follows the streamlines. Practically this means solving the evolution of displacements given by $\delta \mathbf{q}$ and $\delta \mathbf{p}$ according to the underlying SLLOD equations of motion neglecting $\mathbf{F}_i$ terms. Because we are dealing with dense systems and high force fields, the potential energy cannot be ignored, therefore the exact value of these exponents is sometimes hard to determine. Five of the six trivial exponents result from properties conserved by the dynamics (temperature, center of mass and total momentum). Displacements orthogonal to the isokinetic constraint hypersurface give exponents of value 0 (PSF) or close to zero.
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Displacements in $q_i$ result in two exponents of value 0 for PSF and of value $\dot{\epsilon}$ and $-\dot{\epsilon}$ for PEF; and displacement in $p_i$ gives two exponents of value $-\langle \xi \rangle$ and $-\langle \xi \rangle$ for PSF and $\dot{\epsilon} - \langle \xi \rangle$ and $-\dot{\epsilon} - \langle \xi \rangle$ for PEF. Here $\langle \xi \rangle$ is the average value of the Gaussian constraint for the flow considered. In both cases there is an additional exponent due to displacements in the direction of flow, which is non-zero due to the non-autonomous nature of the equations of motion (the box boundaries change in time). Consideration of Eq. (4.49) shows that the trivial exponents for PMF will have the same form as those for PEF due to the dominating exponential growth along the expanding and contracting directions.

It is worth stressing the effects that a Nosé-Hoover thermostat has on the dynamics compared to those of a Gaussian thermostat (which has been more commonly used in simulations of Lyapunov exponents) to avoid any confusion later. We have in fact used both at different stages during this work, and we recall that the Nosé-Hoover has been used when dealing with confined systems, while a Gaussian when looking at homogeneous systems.

A Gaussian thermostat restricts the dynamics to an isokinetic hypersurface, decreasing the accessible phase space dimension by one. This in turn generates a zero exponent associated with the direction perpendicular to the hypersurface. A Nosé-Hoover thermostat however, does not create a hypersurface, instead it uses an integral feedback mechanism that leaves the temperature free to oscillate around the mean value. There are no vanishing exponents associated with this constraint. The dynamics of its friction coefficient, however, is generated by a 1st order ODE, that coupled to the particles’ ODEs, increasing the phase space dimension by one. The perturbation vector parallel to this additional direction will generate an extra Lyapunov exponent and our calculations, showed in the next chapter, indicate that its associated Lyapunov exponent has a value close to zero. Depending on the Lyapunov spectrum we were looking at (for confined systems), a thermostat has been applied either to the fluid, to the walls or both. When the walls where thermostatted, the two walls confining the fluid were thermostatted independently, therefore the dimension of the phase-space is incremented by two, creating two additional almost vanishing Lyapunov exponents.
5.3 “Subsystem” Lyapunov Exponents

When characterizing the phase space for confined fluids, we have two sets of equations of motion, one for the wall particles

\[ \dot{q}_W^i = p_W^i, \]
\[ \dot{p}_W^i = F_W^i - \xi_W^i p_W^i, \]
\[ \xi_W^i = \frac{1}{Q} \left[ \sum_i \frac{p_W^i}{m_W^i} - N_f k_B T \right], \]

(5.23)

whose dynamics is thermostatted and where phase space contraction occurs and one for the fluid particles

\[ \dot{q}_F^i = p_F^i, \]
\[ \dot{p}_F^i = F_F^i + F_E, \]

(5.24)

where \( F_E \) is the external force (present only for Poiseuille flow). These equations generate a Newtonian dynamics with no phase space expansion in this subspace.

In addition to the full Lyapunov spectrum defined above, it is therefore of interest to consider how different parts of the system contribute to the spectrum. Our technique differs from a previously attempted way to achieve such splitting which involved projecting the whole phase space onto the low dimensional Hamiltonian phase space [PH04]. In the system studied here, the natural division of the full system into a wall and fluid region, where the dynamics is quite different, suggested consideration of the behavior of sub-system specific exponents. In order to do this, we define displacement vectors \( \delta \Gamma_{i...j}^n = [\delta q^n_i, \delta p^n_i, ..., \delta q^n_j, \delta p^n_j] \) where \( \delta \Gamma_i^n = [\delta q_i^n, \delta p_i^n] \) gives the components of the \( n \)th displacement vector associated with the \( i \)th particle and the displacement vectors associated with all other particles are set to zero. Therefore, we define the subsystem Lyapunov exponents as:

\[ \lambda_{W/F}^n = \lim_{t \to \infty} \lim_{\delta \Gamma_{i...j} \to 0} \frac{1}{t} \ln \left( \frac{|\delta \Gamma_{i...j}(t)|}{|\delta \Gamma_{i...j}(0)|} \right), \]

(5.25)

where the particle indices \( i...j \) are the wall particles for \( \lambda_W^n \) and the fluid particles...
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Physically, this can be interpreted as looking at the evolution, in phase space, of the full displacement vector, subject to the constraint that it remains in the reduced space of the subsystem. Note that the dynamics of the subsystem of interest is fully coupled to that of the rest of the system. In this paper we will show how the Lyapunov exponents determined by Eq. (5.7) are related to those of the subsystem.

To further investigate how the exponents can be associated with distinctive parts of the system, we consider the so-called localization width, as introduced by Taniguchi and Morriss [TM03]. In this case, instead of looking at the Lyapunov exponents, we consider the corresponding Lyapunov vectors. If the Lyapunov vectors are localized in the phase space, it is possible to say how many and which type of particle contribute to each exponent. In our case ‘type’ refers to the different type of dynamics to which the particle is subjected - wall or fluid dynamics.

If $\lambda^n$ is the $n$th exponent, the contribution of particle $'i'$ to the generating Lyapunov vector at time $t$ would be $\delta\Gamma^n_i(t)$ where $i$ is the particle index. We can now introduce the normalized amplitude $\gamma_i^n(t)$ of the Lyapunov vector $\delta\Gamma^n_i(t)$ [TM03]

$$\gamma_i^n(t) \equiv \frac{|\delta\Gamma^n_i(t)|^2}{\sum_{j=1}^{N} |\delta\Gamma^n_j(t)|^2}. \tag{5.26}$$

As a consequence of this definition, the following conditions are satisfied

$$\sum_{i=1}^{N} \gamma_i^n(t) = 1, \tag{5.27}$$

$$0 \leq \gamma_i^n(t) \leq 1. \tag{5.28}$$

Following Taniguchi and Morriss [TM03], we can also introduce an entropy like quantity $S^n$ defined as

$$S^n \equiv -\sum_{i=1}^{N} (\gamma_i^n(t) \ln \gamma_i^n(t)), \tag{5.29}$$
where $\gamma_j^n(t)$ is treated as a distribution function. The quantity $W^n$

$$W^n \equiv \exp(S^n), \quad (5.30)$$

is the localization width of the $n$th Lyapunov exponent $\lambda^n$ [TM03]. One property of the localization width which helps to clarify its physical meaning is that

$$1 \leq W^n \leq N. \quad (5.31)$$

The situation $W^n = 1$ only occurs when a single $\gamma^n_i(t)$ is equal to one and all others are zero, while $W^n = N$ occurs when all the $\gamma^n_i(t)$ have the same value of $1/N$. It is clear at this point that the localization width quantifies the number of particles contributing to a particular Lyapunov vector and the corresponding Lyapunov exponent.

### 5.4 Lyapunov Vectors and Modes

As we stated above, Lyapunov exponents quantify the amount of separation/contraction to which nearby trajectories are subjected in phase-space, but we lose information about the direction along which the separation/contraction occurs. These directions are given by the Lyapunov vectors that are the eigenvectors of the matrix $\Lambda$. These vectors rotate in space and are difficult to characterize due to the high dimensionality of the space in which they exist. It is for this reason that only recently they have become a subject of study. In particular, the vectors associated with the small (in absolute value) exponents show interesting properties. The maximum Lyapunov exponents are associated with the fast dynamics happening in the system while the minimum exponents to the slowest. This is because the maximum Lyapunov exponents, associated to the most chaotic events, are, in a multiparticle system, due to the repulsive collisions between convex particles. In practical terms this means that at any instant the Lyapunov vectors associated with the maximum exponents are dominated by components associated with the colliding particles and have one large component along one direction in the phase space but zero along the others.
Many Particle Dynamical Systems and Lyapunov Spectra

For the small exponents all the components contribute in a similar amount. It turns out that the way these components are distributed and oriented in space is not random, but form delocalized structures. We refer to these exponents as Lyapunov modes. Lyapunov modes are usually associated with symmetries in the system due to conserved quantities (energy, linear momentum, centre of mass, etc.) to which all particles contribute, therefore they are associated with a delocalization property.

![Figure 5.3: Stepwise structure of the Lyapunov modes for a quasi-one dimensional system of 100 particles; full Lyapunov spectrum in the top-right insert. Figure source: [TM05], Copyright (2005) by The American Physical Society.]

If we consider only one of the two symmetric branches of the Lyapunov spectra (see Fig. 5.1), then we can identify the modes in the stepwise structure found in the smallest exponents (see Fig. 5.3). A particular mode can be conveniently visualized as a vector field, plotting the vector component (that can be a positional or momentum perturbation) of each particle against its physical position in real space (see Fig. 5.4). In the case of particles in a 2 dimensional box, they are characterized by a wave vector $\mathbf{k}$ with wave number

$$k_{nx, ny} = \sqrt{\left(\frac{2\pi}{L_x} n_x\right)^2 + \left(\frac{2\pi}{L_y} n_y\right)^2},$$  \hspace{1cm} (5.32)
where periodic boundary conditions are assumed. They have first been observed for hard-dumbbell fluids [MPH98a, MP02], then studied for hard-disks [EFPZ05a, FHPH04] and then for soft core potentials [FP05]. In recent years they have been the object of extensive studies [TM07], also trying to improve and extend the connection between dynamical systems theory and statistical mechanics [HPF+02]. The modes can be divided into two types, stationary modes and time oscillating modes which propagate at one third the speed of sound and whose oscillating period is twice as long as the period of the longitudinal momentum autocorrelation function. There has also been some recent work that tried to relate them to the Goldstone modes (for example hydrodynamic modes and phonons in crystals) [WB04a]. The stationary modes are transverse, that is their wave vectors are orthogonal to the axis of the corresponding perturbation (perturbations in the $x$ components of the modes are orthogonal to the $x$ axis), where the oscillating modes are longitudinal. The stepwise structure is due to the degeneracy consequence of periodic box symmetry and the phase shift of $\pi/2$ in sine and cosine periodic patterns consistent with the same wave number $k$. 
Figure 5.4: Time averages for the $x$ and $y$ components of the Lyapunov mode relative to exponent no. 195 of Fig. 5.3. Figure source: [TM05], Copyright (2005) by The American Physical Society.
5.5 Localization of Lyapunov exponents across the channel

To understand if and how the dynamics is altered by the use of the thermostat in the confined systems, we compute the spectra of subsystem Lyapunov exponents of the fluid and which part of the channel contributes the most to a particular exponent. It is important to underline that the spectra considered here do not involve all the degrees of freedom of the system (fluid, walls and thermostat degrees of freedom). Following the same technique described in section 5.3 we consider only the dynamics of the fluid phase space. We note that the fluid subsystem Lyapunov exponents approach the true Lyapunov exponents in the limit of zero coupling with the walls.

To compute the spectral density of the subsystem Lyapunov exponents inside the channel we use the Lyapunov vectors $\delta \Gamma^n$ associated with the exponents. These vectors indicate the direction in which expansion/compression in phase space occurs for each Lyapunov exponent at an instant in time. If the vectors are ortho-normalized we can write the normalized amplitude (see Eq. 5.26) [TM06a]

$$\gamma^n_i = (\delta q^n_i)^2 + (\delta p^n_i)^2,$$  \hspace{1cm} (5.33)

such that

$$0 \leq \gamma^n_i \leq 1 \quad \text{and} \quad \sum_i \gamma^n_i = 1.$$  \hspace{1cm} (5.34)

This quantity tells us how, for each exponent $n$, the contributions are distributed among the particles $i$. After computing $\gamma^n_i$ every selected number of time steps $\Delta t_j$, we localize the particle $i$ in the real space across the channel and, at this position, sum the contributions for each exponent. This will give us the exponent localization

$$\Upsilon^n(y_{\text{bin}}) = \sum_{\Delta t_j} \sum_{i \in \text{bin}} \gamma^n_i,$$  \hspace{1cm} (5.35)

where $N_{\text{bin}}$ is the number of particles in any particular bin. We consider the localization only for the $y$ direction using the same resolution of 0.05 as for the mechanical properties.
Chapter 6

Results

6.1 Introduction

Because of the range of topics introduced and discussed in this work, the results will be presented in the order they have been obtained and organized as self concluding topics, with the exception of the results regarding planar mixed flow which has already been presented (see chapter 4) and validated. The discussion will therefore be organized as follows:

• The first section covers the study of Lyapunov spectra for particles in confined geometries, with particular emphasis on the phase space characterization for both confining walls and fluid.

• The second section considers the role that thermostatting mechanisms have in properly reproducing the physics of confined nanofluids, both from a dynamical (using Lyapunov spectra analysis and Lyapunov vector localization in real space) and a mechanical point of view.

• In the third and last section, we present the chaotic analysis performed on planar mixed flow, also in light of the extensive studies already done on the two flows whose linear combination is the basis of PMF, namely planar Couette flow and planar elongational flow.
6 Results

6.2 Lyapunov Spectra for Confined fluids

The results presented in this section pertain to a 2 dimensional simulation box of 18 fluid particles at a density $\rho_F = 0.6$ and two walls delimiting a channel of width $L_y = 6.826$. The length of the simulation box along the $x$ axis is $L_x = 4.180$. Each wall is formed by two layers of 4 atoms arranged in an fcc lattice and at a density of $\rho_W = 0.8$. Since we desire an equivalent contribution to the Lyapunov spectra from the fluid and dissipative wall dynamics, we used a similar number of fluid and wall particles. Also, because of the intensity of the computation task, we had to keep the system size low. Note that while the computation time for a molecular dynamics simulation increases as $O(N)$ (at best) where $N$ is the number of particles, in the case of a calculation of the Lyapunov spectrum, the increase is $O(N^2)$ at best. The kinetic temperature is kept at a fixed value of $T = 1.0$. The timestep applied was $\Delta t = 10^{-3}$, a simulation time of $t = 100,000$ (that is considerably longer than the thermalization time) has been used before data production and a further $t = 10,000$ for collecting the data, for a total simulation time of $t = 110,000$, corresponding to around $10^8$ time steps. The two flows, Couette and Poiseuille, have been simulated using three values of driving field. For Couette flow, strain rates of $\dot{\gamma} = 0.5$, $\dot{\gamma} = 1.0$ and $\dot{\gamma} = 2.0$ have been used while for Poiseuille flow external forces of $F_e = 0.15$, $F_e = 0.3$ and $F_e = 0.9$ have been employed. For each pair of systems, the total dissipation is similar. These strain rates and field strengths are all quite large [MDC07], and this resulted in observable anisotropy between the $x$ and $y$ temperature components, that in the worst case scenario is around $12\%$. However this work focuses on the properties of Lyapunov spectra and high values of the dissipated energy make the phase-space characterization easier.

Since the velocity gradient is not constant for sliding boundary (SB) Couette flow near the wall and Poiseuille flow, it is not possible to use the second scalar invariant of the strain-rate tensor to compare the flows at equivalent state points, as has previously been done for Couette and elongational flows [BAH87, DMT03].
Instead we use the entropy production rate that we rewrite for convenience as

\[
\dot{S}(t)/k_B = - \sum_i \lambda_i = g\langle \xi \rangle > 0.
\] (6.1)

This relation has been shown to hold for homogeneous systems in nonequilibrium steady-states. The fact that the average phase-space expansion is always positive for nonequilibrium steady-states is a key factor for understanding the irreversible behaviour of such systems. A positive phase-space expansion means that the phase-space collapses onto a multifractal strange attractor [ESH+98]. Values of \( \dot{\gamma} \) have been chosen for the Couette system to be consistent with previous values used in the literature [FST06, SEM92], and values of \( F_e \) have then been selected to maximize the agreement in entropy production. The entropy production is an average quantity, obtainable only once the steady state has been reached, and it cannot be imposed at the beginning of a simulation. This makes it difficult to achieve exactly the same average values. Furthermore, the relation between external force and thermostating coefficients is not linear. However, the absolute difference between Poiseuille and Couette flows never exceeds 6\% in entropy production. Values of interest for the systems considered are shown in Tables 6.1 and 6.2.
Table 6.1: Summary of the results for the wall phase-space for Couette and Poiseuille flow at different values of strain rate and external force. The fluid obeys Newtonian dynamics and the walls are thermostatted at $T = 1.0$. The errors, in brackets, are twice the standard error of the mean of ten independent runs. The value of $D_{KY}$ cannot be defined for large fields because the maximum subsystem exponent is negative.

<table>
<thead>
<tr>
<th>Flow type</th>
<th>Ext. Field</th>
<th>$\langle \dot{S} \rangle$</th>
<th>$- \sum_n \lambda_n^W$</th>
<th>$D_{KY}$</th>
<th>$\lambda^{max}$</th>
<th>$\lambda^{min}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Couette</td>
<td>$\dot{\gamma} = 0.5$</td>
<td>4.061 (0.003)</td>
<td>4.049 (0.006)</td>
<td>57.82 (0.01)</td>
<td>0.474 (0.001)</td>
<td>-0.602 (0.001)</td>
</tr>
<tr>
<td>Couette</td>
<td>$\dot{\gamma} = 1.0$</td>
<td>17.400 (0.007)</td>
<td>17.41 (0.02)</td>
<td>31.27 (0.02)</td>
<td>0.370 (0.001)</td>
<td>-0.914 (0.001)</td>
</tr>
<tr>
<td>Couette</td>
<td>$\dot{\gamma} = 2.0$</td>
<td>100.20 (0.03)</td>
<td>100.34 (0.05)</td>
<td>-0.366 (0.001)</td>
<td>-2.450 (0.001)</td>
<td></td>
</tr>
<tr>
<td>Poiseuille</td>
<td>$F_e = 0.15$</td>
<td>4.133 (0.005)</td>
<td>4.13 (0.01)</td>
<td>58.66 (0.02)</td>
<td>0.551 (0.001)</td>
<td>-0.684 (0.001)</td>
</tr>
<tr>
<td>Poiseuille</td>
<td>$F_e = 0.3$</td>
<td>16.500 (0.007)</td>
<td>16.50 (0.01)</td>
<td>36.20 (0.02)</td>
<td>0.465 (0.001)</td>
<td>-0.991 (0.001)</td>
</tr>
<tr>
<td>Poiseuille</td>
<td>$F_e = 0.9$</td>
<td>105.46 (0.03)</td>
<td>105.68 (0.06)</td>
<td>-0.199 (0.001)</td>
<td>-2.855 (0.001)</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.2: Summary of the results for the extended wall-fluid-friction coefficient phase-space for Couette and Poiseuille flow at different values of strain rate and external force, respectively. The fluid obeys Newtonian dynamics and the walls are thermostatted at $T = 1.0$. The errors, in brackets, are twice the standard error of the mean of ten independent runs.

<table>
<thead>
<tr>
<th>Flow type</th>
<th>Ext. Field</th>
<th>$\langle S \rangle$</th>
<th>$- \sum \lambda^n$</th>
<th>$D_{KY}$</th>
<th>$\lambda_{max}$</th>
<th>$\lambda_{min}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Couette</td>
<td>$\dot{\gamma} = 0.5$</td>
<td>4.060 (0.002)</td>
<td>4.055 (0.002)</td>
<td>136.841 (0.001)</td>
<td>3.513 (0.001)</td>
<td>-3.513 (0.001)</td>
</tr>
<tr>
<td>Couette</td>
<td>$\dot{\gamma} = 1.0$</td>
<td>17.389 (0.009)</td>
<td>17.399 (0.014)</td>
<td>133.590 (0.003)</td>
<td>4.167 (0.001)</td>
<td>-4.169 (0.001)</td>
</tr>
<tr>
<td>Couette</td>
<td>$\dot{\gamma} = 2.0$</td>
<td>100.4 (0.2)</td>
<td>100.9 (0.5)</td>
<td>113.5 (0.2)</td>
<td>5.92 (0.01)</td>
<td>-5.94 (0.01)</td>
</tr>
<tr>
<td>Poiseuille $F_e = 0.15$</td>
<td>4.132 (0.004)</td>
<td>4.121 (0.008)</td>
<td>136.784 (0.002)</td>
<td>3.404 (0.001)</td>
<td>-3.405 (0.001)</td>
<td></td>
</tr>
<tr>
<td>Poiseuille $F_e = 0.3$</td>
<td>16.486 (0.007)</td>
<td>16.482 (0.017)</td>
<td>133.433 (0.006)</td>
<td>3.803 (0.001)</td>
<td>-3.805 (0.001)</td>
<td></td>
</tr>
<tr>
<td>Poiseuille $F_e = 0.9$</td>
<td>105.40 (0.04)</td>
<td>105.8 (0.2)</td>
<td>109.68 (0.03)</td>
<td>5.306 (0.002)</td>
<td>-5.328 (0.002)</td>
<td></td>
</tr>
</tbody>
</table>
The two tables refer to the same system composition and state points (same number of fluid and wall particles, and same temperature and density). Table 6.1 however reports results for the wall particles’ phase-space only, while in Table 6.2 the whole phase-space (fluid, wall and friction coefficients) has been taken into account. As expected from theory, Eq. (6.1), the sum of the Lyapunov exponents is equal in magnitude to the phase space expansion factor, with opposite sign. This is observed when the full system is considered as well as when the wall subsystem is considered. However a phase-space expansion is present in both cases. A measure of this contraction is the Kaplan Yorke (KY) dimension [KY79]. This dimension has been conjectured by Kaplan and Yorke (1979) as the effective measure of the attractor in the phase-space (loosely speaking it is the dimension of a volume in the phase-space that neither shrinks nor grows):

\[ D_{KY} = M + \frac{\sum_{i=1}^{M} \lambda_i}{|\lambda_{M+1}|}, \]  

(6.2)

where \( M \) is the largest integer such that \( \sum_{i=1}^{M} \lambda_i > 0 \). Clearly, the ratio of the KY dimension and the ostensible dimension (66 for the wall phase-space and 138 for the total phase-space for the wall thermostatted system) decreases as the driving force increases, and more heat is removed to maintain the steady state. The value of the maximum Lyapunov exponent in Table 6.2 increases as the external force increases, reflecting a more chaotic dynamics. This result might be thought to be in contrast with other studies where the maximum Lyapunov exponent was shown to be insensitive to the field’s changes [Mor89, SEM92]. In billiard systems, for example, the external force is thought to have a focusing effect, leaving nearly unchanged the collision rate, and hence the maximum exponent, but increasing contraction. This effect may be dependent on density, field strength and the length of the free flight (due to the scatterers’ geometry) on which the field can act [MDI96, BR09]. In our system however, the geometry is very complex and many factors can influence the dynamics of the particles, but what ultimately leads to an increase of the maximum exponents is probably the temperature, that rises (in the middle of the channel) as the field is increased. What is also interesting is that the minimum exponent has the same absolute value, to within statistical error, as the corresponding maximum.
exponent. As we shall explain later this is due to the more complex dynamics of the fluid and to its Newtonian dynamics reflected in the second half of the spectra (with respect to the pair index). It is also interesting to note that in Table 6.1, where we present subsystem Lyapunov exponents, rather than real Lyapunov exponents, for the two highest values of external field, $\dot{\gamma} = 2.0$ and $F_e = 0.9$, the maximum subsystem exponents are negative and $D_{KY}$ cannot be defined. This result can be attributed to the extremely high external fields in conjunction with the fact that these exponents, as previously explained, are not a global property of the system.
Figure 6.1: Couette profiles, strain rate $\dot{\gamma} = 2.0$. (a) BLUE TRIANGLES: cross section density profile; RED CIRCLES: $xy$ component of the pressure tensor $P_{xy}$ (the big squares indicate the pressure values at the wall); (b) BLUE TRIANGLES: streaming velocity; RED CIRCLES: temperature. The system consists of 18 fluid particles at a density $\rho_F = 0.6$ in a channel of width $L_y = 6.8\sigma$ (reduced units) and 16 wall particles at a density $\rho_W = 0.8$. Walls are thermostatted at $k_B T = 1.0$. 
Figure 6.2: Poiseuille profiles, external force $F_e = 0.3$. (a) BLUE TRIANGLES: cross section density profile; RED CIRCLES: $xy$ component of the pressure tensor $P_{xy}$ (the big squares indicate the pressure values at the wall); (c) BLUE TRIANGLES: streaming velocity; RED CIRCLES: temperature. The system consists of 18 fluid particle at a density $\rho_F = 0.6$ in a channel of width $L_y = 6.8\sigma$ (reduced units) and 16 wall particles at a density $\rho_W = 0.8$. Walls are thermostatted at $k_B T = 1.0$. 
In Figs. 6.1 and 6.2, we show the shear stress, density, temperature and streaming velocity profiles for Couette and Poiseuille flow, respectively, for $\dot{\gamma} = 2.0$ and $F_e = 0.3$. The shear stress ($xy$ component of the pressure tensor) is constant along the channel for Couette flow and roughly linear for Poiseuille flow, and the velocity profiles show slip close to the walls. The densities oscillate close to the walls revealing fluid packing, but the oscillations decrease in a region of 2 to 3 $\sigma$ in the middle of the channel. The temperature profile for Poiseuille flow, however, does not show a quartic profile, a physical effect due to the channel being narrow with few particles inside it [TTE97a]. Further tests on widening the pore showed profiles in agreement with classical predictions.

![Figure 6.3: BLUE TRIANGLES: Lyapunov spectrum for an equilibrium (NVE) system composed of 18 fluid and 16 wall particles. RED CIRCLES: subsystem Lyapunov spectrum for the 18 confined fluid particles only. For both spectra the fluid density is $\rho_F = 0.6$ and temperature $T = 1.0$.](image)

In Fig. 6.3 we show Lyapunov spectra for a confined system at equilibrium (microcanonical for the system composed of walls and fluid). Only one pair of exponents vanishes. These are associated with the time-translational invariance of the system.
and, as a consequence, the conserved total energy. There is no conservation of total momentum and center of mass because of the walls. The total sum of the exponents is zero and the CPR is satisfied. It is possible to distinguish a region (low pair index) where the exponents are small (in absolute value) and a region where the exponent values increase more rapidly. As we demonstrate below, this is due to the different dynamics of the wall and fluid particles. Wall particles are tethered to a lattice and thus their behavior is less chaotic than the fluid particles, which have a wider range of accessible velocities and are free to mix in space. In Fig. 6.3 we also show the subsystem Lyapunov spectrum computed using Eq. (5.25) for the fluid particles. This has been obtained by only evolving the displacement vectors associated with the fluid phase-space and thereby implicitly constraining the Lyapunov vectors on that phase-space. The interactions felt by the fluid by means of the wall particles are in some ways akin to an external force field, and if the coupling of the fluid and wall dynamics was removed (force field becomes independent of the dynamics of the fluid), this would be exact. In Fig. 6.3 we note that the part of the full Lyapunov spectrum with exponent index greater than 32 is very similar to the subsystem Lyapunov spectrum, indicating that those exponents are largely determined by the dynamics of the fluid. One should not expect however a perfect match because the dimensionality of the phase space generating the two spectra is different and contributions to the fluid exponents caused by tangent vectors involving displacements of the wall particles are prevented in the fluid exponent calculations. In recent preliminary studies we found that the spectra generated by the fluid looks similar to the case in which the wall is implemented as a rigid structure without any degrees of freedom. This interesting result however, needs to be studied further.

In Fig. 6.4 we show how the spectrum changes once subjected to an external field (or sliding boundaries) and where a thermostat is applied to the walls to reach the steady state. Two exponents with values close to zero are directly associated with two thermostat multipliers (see Frascoli et al. [FST08]) and are not shown in this figure or subsequent figures unless explicitly stated. Clearly the spectra are not symmetric and do not satisfy the CPR. We observe two different regions, one characterized by negative pair sum and one characterized by zero pair sum. Figure 6.4 also shows that there is not a large difference between Couette and Poiseuille
flows, both from a qualitative and quantitative point of view: maximum exponents are slightly higher in absolute value for Couette flow. However, this could be due to the different value in entropy production (see Table 6.2): a higher entropy production for Couette flow means a more chaotic spectrum than the one for Poiseuille flow.

The system is composed of particles to which a thermostat is directly applied, and others that are not, and both a dissipative and conservative dynamics are observed, hence the exponents with negative sum are largely determined by the dynamics of the wall region (the thermostatted region) while the exponents with zero sum belong to the fluid (Newtonian dynamics region). This is not trivial for two reasons: i) the maximum Lyapunov exponents are due to the repulsive collisions (the most chaotic events) and even the wall particles could contribute when colliding with the fluid, and ii) the contraction could be distributed along all directions in the phase-space. To understand the reason for such a separation we have to consider the evolution of the displacement vector and the stability matrix.

If we consider splitting the system into wall and fluid sections, and ignore the possibility of contributions from the thermostat multipliers, the phase-space displacement vector is

$$\delta \Gamma = (\delta q^W, \delta p^W, \delta q^F, \delta p^F).$$  \hspace{1cm} (6.3)

Its evolution is determined by the Jacobian matrix $T$:

$$
\begin{pmatrix}
\frac{\partial \dot{q}^W}{\partial q^W} & \frac{\partial \dot{q}^W}{\partial p^W} & \frac{\partial \dot{q}^W}{\partial q^F} & \frac{\partial \dot{q}^W}{\partial p^F} \\
\frac{\partial \dot{p}^W}{\partial q^W} & \frac{\partial \dot{p}^W}{\partial p^W} & \frac{\partial \dot{p}^W}{\partial q^F} & \frac{\partial \dot{p}^W}{\partial p^F} \\
\frac{\partial \dot{q}^F}{\partial q^W} & \frac{\partial \dot{q}^F}{\partial p^W} & \frac{\partial \dot{q}^F}{\partial q^F} & \frac{\partial \dot{q}^F}{\partial p^F} \\
\frac{\partial \dot{p}^F}{\partial q^W} & \frac{\partial \dot{p}^F}{\partial p^W} & \frac{\partial \dot{p}^F}{\partial q^F} & \frac{\partial \dot{p}^F}{\partial p^F}
\end{pmatrix}
$$  \hspace{1cm} (6.4)

where $W$ and $F$ refer to the wall and fluid particles respectively.
The Jacobian matrix can be divided into four blocks, relative to the wall dynamics (block 1), fluid dynamics (block 4) and wall-fluid interaction (blocks 2 and 3):

\[
\begin{pmatrix}
1 & 2 \\
3 & 4
\end{pmatrix}
\]

where blocks 2 and 3 are null except for the terms \( \frac{\partial \dot{p}_W}{\partial q^F} \) and \( \frac{\partial \dot{p}_F}{\partial q^W} \). These elements are generally small compared to the terms in blocks 1 and 4, and in the case that the wall and fluid particles were uncoupled they would become zero. Therefore, the Jacobian matrix can be approximated by a symmetric block matrix. The eigenvalues of such a matrix are the collection of the eigenvalues of the diagonal blocks computed separately: this means that the spectrum is the collection of the exponents associated with the wall particles plus the ones associated with the fluid particles.

This is an interesting result because it shows the decoupling of the different dynamics occurring in the system, Newtonian for the fluid and dissipative for the walls. Unfortunately it also means that the results from the CPR and the complete characterization of the dynamics via the Lyapunov spectra, cannot be achieved for an inhomogeneous system such as the confined fluid system considered here.
Figure 6.4: (a): Lyapunov spectra for Couette flow with $\dot{\gamma} = 1.0$; (b): Lyapunov spectra for Poiseuille flow with $F_e = 0.3$. Both systems consist of 18 fluid particles at a density $\rho_F = 0.6$, 16 wall particles at a density $\rho_W = 0.8$, channel width $y = 6.8\sigma$ and walls thermostatted at $T = 1.0$. The red squares represent the exponents’ pair sum. The two zero-valued exponents associated with the thermostat multipliers are not plotted.
Figure 6.5: Lyapunov spectra for a Couette flow system composed of 18 fluid particles at a density $\rho_F = 0.6$, 16 wall particles at a density $\rho_W = 0.8$ with channel width $y = 0.8\sigma$, strain rate $\dot{\gamma} = 2.0$ and walls thermostatted at $T = 1.0$ (reduced units). (a) Lyapunov spectrum computed for the whole phase-space (fluid and wall, triangles); the circles are the exponents computed for the wall and fluid phase-space independently. The two zero-valued exponents associated with the thermostat multipliers are not plotted; (b) Lyapunov spectrum computed for the wall phase-space; (c) Lyapunov spectrum computed for the fluid phase-space. The red squares represent the exponents’ pair sum.
Figure 6.6: Localization width for a system of 18 fluid particles and 16 wall particles. Only half of the spectrum is considered, from $\lambda^1$ to $\lambda^{2N}$. Walls are thermostatted at $T = 1.0$, $\rho_F = 0.6$ and $\rho_W = 0.8$. The contribution of the fluid particles (BLUE TRIANGLES) is maximum for high pair index exponents ($n/2N \simeq 0.2$) and minimum for low pair index exponents ($n/2N \simeq 1$); the opposite behaviour is instead observed for the wall particles (RED SQUARES). This demonstrates that the fluid’s dynamics is associated with the largest (in absolute value) exponents that sum to zero, while the wall dynamics generates the lower (in absolute value) exponents.

To test this further we now look at the full Lyapunov spectrum, the wall subsystem Lyapunov spectrum and the fluid subsystem Lyapunov spectrum for Couette flow at $\dot{\gamma} = 2.0$ in Fig. 6.5. Here the region of mixing is clearer, as the phase-space expansion is larger. If we consider the separate contributions to the spectrum from the fluid and the wall, we see that the maximal pair index exponents for the fluid and the minimal pair index exponents for the wall have approximately the same values as the maximal and minimal pair index exponents respectively for the total spectrum. Their union could give an approximation for the total spectrum, with the exception of the middle region where coupling of the dynamics has a large effect. This can be attributed to the quasi-zero off-diagonal terms in blocks 2 and 3 of Eq. (6.4) being non-zero.

Let us now consider the localization width for the total spectrum of the same system. We consider only the upper part of the “bell” curve that forms the Lyap-
punov spectrum (for symmetry reasons). The localization width provides us with a quantitative measure of the contribution of each particle species (wall or fluid) to each exponent. In the plots in Fig. 6.6, the $x$ axis refers to the exponent index, 0 refers to $\lambda_1$ and 1 to $\lambda_2^N$. The localization width ($y$ axis) has been normalized such that the sum of all contributions is equal to 1. A localization width close to 0 means that just a few particles are providing almost all of the contributions to the normalized vector associated with that particular exponent. In the plot, the triangles refer to the fluid particles’ contribution that, as we can see, is maximum for high pair index exponents and minimum for low pair index exponents. The opposite behaviour (minimum contribution for high pair index exponents and maximum contribution for low pair index exponents) is instead observed for the wall particles (square symbols in the plot), which confirms our interpretation of the results.

We now analyze the case of the wall particles’ equations of motion being Newtonian and the fluid being thermostatted. This is physically an unrealistic thing to do, but it demonstrates some points more clearly. We use a profile biased thermostat (PBT) [EM90], so that we do not have to compute the dynamics of several friction coefficients that would have been present using a profile unbiased thermostat (PUT). To obtain the presumed streaming velocity, we simulate the same system thermostatted with a PUT applied to the fluid. The streaming velocity profile has been extrapolated from the linear region ($\sim 3\sigma$) in the middle of the channel, with an effective value of $\dot{\gamma} = 0.63$. Four plots are presented: the two in Fig. 6.7 are, from top to bottom, the subsystem spectrum computed separately for the wall and fluid phase-space respectively. In Fig. 6.8 the spectrum computed for the whole phase-space is shown on the top and the subsystem exponents for the fluid and wall of Fig. 6.7, combined together and reordered, on the bottom. Again the match is impressive, showing that the Lyapunov spectrum indeed reflects the two different dynamics, regardless of the particle species thermostatted. The exponents’ sum is also in agreement in both cases: for the reordered spectrum $\sum \lambda = -38.32 \pm 0.18$ while for the whole system $\sum \lambda = -37.94 \pm 0.45$. The exponents for the wall sum to zero as expected. It is also interesting to note the step-like structure of the spectrum due to equal contributions from the walls, since they are not in contact with each other and are thermostatted independently.
Figure 6.7: (a): Lyapunov spectrum for 16 wall particles. (b): Lyapunov spectrum for 18 fluid particles. Sliding boundary method with a PBT applied to the fluid, whereas the walls are not thermostatted. Temperature $T = 1.0$, density $\rho_f = 0.6$ and $\rho_w = 0.8$, $\dot{\gamma} = 2.0$. The expected linear streaming velocity profile used in the thermostat $\dot{\gamma} = 0.63$ has been extrapolated from the velocity profile of a system at the same state point with a PUT applied to the fluid. The red squares represent the exponents’ pair sum.
Our final results refer to a Couette flow ($\dot{\gamma} = 2.0$) in which fluid and walls have been thermostatted together with a PUT, shown in Fig. 6.9. For this purpose the simulation box has been divided into 8 bins. Because each bin has a distinct friction coefficient due to the different streaming velocity and density, the number of bins has been chosen to not excessively increase the phase-space dimension, but still account for the anisotropy of the system. The difference between the two figures is only that the exponents associated with the friction terms have not been considered in Fig. 6.9(a), while in Fig. 6.9(b) the whole phase-space has been accounted for. The CPR is in this case obeyed because the contraction is distributed along all the directions in the phase-space. It is interesting to see that the exponents that can be attributed to the thermostatting term in Fig. 6.9(b) almost vanish (indicated by the arrow), similarly to what was observed by Frascoli et al.[FST08] for homogeneous isobaric systems. We refer to section 5.3 for a more comprehensive explanation.
Figure 6.8: (a): Lyapunov spectrum computed for the whole phase-space of 18 fluid and 16 wall particles. (b): Lyapunov spectrum obtained from collecting and reordering the separate contributions of wall and fluid spectra in Fig. 6.7, at the same state point. The squares represent the exponents’ pair sum. The zero-valued exponents associated with the thermostat multipliers are not plotted.
Figure 6.9: Lyapunov spectra for a Couette flow system with 18 fluid particles at a density $\rho_F = 0.6$ and 16 wall particles at a density $\rho_W = 0.8$. Channel width $y = 6.8\sigma$ and strain rate $\dot{\gamma} = 2.0$. The whole system is thermostatted by a PUT dividing the simulation cell in 8 bins. (a): Lyapunov spectrum computed for the fluid and wall phase-space. The exponents associated with the thermostat multipliers are not plotted. (b): Lyapunov spectrum computed for the fluid, wall and friction coefficient phase-space. The arrow indicates the exponents associated with the friction coefficients. The red squares represent the exponents’ pair sum.
6.3 Thermostatting devices

In this section we consider the difference in properties obtained using homogeneous and wall thermostats.

The system, used to analyze the effects of different thermostatting devices, is composed of 45 fluid particles and 40 wall particles, 20 for each wall organized in two layers of 10 atoms each. The wall particle density has been set to $\rho_w = 0.8$ and the fluid at $\rho_f = 0.6$. The channel is $L_y = 6.82$ wide and $L_x = 11.18$ in length. The number of particles is small because the computation of the Lyapunov spectra is computationally intensive. However we stress that the purpose of the present thesis is not to provide meaningful rheological results to compare with real experiments, but rather to show the effects related to the use of different thermostatting devices.

The mechanical properties in the case of the wall-only thermostatted system (WT) have been computed for a system with 250 fluid particles and no significant changes in the off-diagonal pressure, density, temperature and streaming velocity profiles have been detected. The results are organized such that for every thermostatting device, the plots relative to the profiles (for density, temperature, streaming velocity and $xy$ component of the pressure tensor across the channel) for vibrating and frozen walls are superimposed.
Figure 6.10: Wall-only thermostatted system, for Couette flow with applied shear rate $\dot{\gamma} = 1.0$. (a) Cross section profile of density; (b) $xy$ component of the pressure tensor $P_{xy}$ (the blue circles indicate the pressure values at the wall), the plot inserted on the top right corner is a zoom of the pressure. The system consisted of 45 fluid particles at a density $\rho_f = 0.6$ in a channel of width $L_y = 6.82$ and 40 wall particles at a density $\rho_w = 0.8$. Walls thermostatted at $T = 1.0$. 
Figure 6.11: Wall-Only thermostatted system, for Couette flow with applied shear rate $\dot{\gamma} = 1.0$ as with Fig. 6.10. (a) streaming velocity; (b) temperature (circle represent data points, while the dashed line is a quadratic fit to the data).
We start by examining the properties of the WT systems that, mimicking real experiments, will be our reference system (Figs. 6.10 and 6.11). The applied shear rate is set at the wall to $\dot{\gamma} = 1.0$. For a sliding boundaries Couette flow this is a high value [RBCP88, LBC92], however to make possible a comparison between the Lyapunov spectra for the SB (sliding boundary) systems and the homogeneous system (SLLOD), a high value of shear rate is necessary. We can observe that the mechanical properties show sensible profiles: the streaming velocity is linear in a region of $3\sigma$ in the middle of the channel with an effective strain rate of $\dot{\gamma}_{\text{eff}} = 0.55$, the density shows packing close to the walls but the oscillations decrease rapidly away from the boundaries. The shear stress is constant inside the channel, with a value of $P_{xy} \approx 0.59$, and the temperature shows a quadratic profile, as predicted by the hydrodynamic equations:

$$\rho \frac{\partial u_x}{\partial t} = \rho F_e - \frac{\partial P_{xy}}{\partial y},$$  \hspace{1cm} (6.5)

$$\rho F_e = 0,$$  \hspace{1cm} (6.6)

and because at steady state $\frac{\partial u_x}{\partial t} = 0$

$$\frac{\partial P_{xy}}{\partial y} = 0 \implies P_{xy} = \text{constant}.$$  \hspace{1cm} (6.7)

For the temperature we have

$$\lambda \frac{d^2 T}{dy^2} = -\eta \left( \frac{\partial u_x(y)}{\partial y} \right)^2,$$  \hspace{1cm} (6.8)

from which we obtain

$$T(y) = -\frac{\eta \dot{\gamma}^2}{2\lambda} y^2 + Cy + D,$$  \hspace{1cm} (6.9)

with $C$ and $D$ being constants of integration. The average temperature of the fluid is $T = 2.5$.

The speed and velocity distributions are in good agreement with the theoretical curves relative to the temperature inside each bin (i.e. Eqs. (3.16a) and (3.16b)).

In all the systems in which the thermostat is directly applied to the fluid, the
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temperature, for both wall and fluid, has been set by taking the average value of the temperature across the channel for the wall thermostatted system. This is to ensure that when a comparison between the systems is attempted they are at an equivalent state point and to avoid temperature gradients at the wall-fluid interface. However, this is not a common practice. In fact, exactly what is the right average temperature of a fluid is something that cannot be known in advance from the knowledge of the boundary conditions. A trial simulation would be required, undoing the advantage of a simulation performed by thermostating the fluid. A set of simulations with wall and fluid temperature kept at $T = 1.0$ has also been performed. The results show a higher disagreement even with respect to the system with the temperature set at $T = 2.5$. Such disagreement can be summarized by a more accentuated packing close to the walls and layering across the channel, a quantitative difference in shear stress due to the lower kinetic component of the pressure tensor, and slightly shifted values of speed distributions toward smaller velocity values.
Figure 6.12: Profile unbiased thermostatted system (PUT), for Couette flow with applied shear rate $\dot{\gamma} = 1.0$. (a) Cross section profile of density; (b) $xy$ component of the pressure tensor $P_{xy}$. The system consisted of 45 fluid particles at a density $\rho_f = 0.6$ in a channel of width $L_y = 6.82$ and 40 wall particles at a density $\rho_w = 0.8$. BLUE (dashed line and diamond symbols): fluid thermostatted at $T = 2.5$ and wall at $T = 1.0$. RED (solid line and triangle symbols): fluid thermostatted at $T = 2.5$ and ‘frozen’ walls.
Figure 6.13: Profile Unbiased Thermostatted system (PUT), for Couette flow with applied shear rate $\dot{\gamma} = 1.0$ as with Fig. 6.12. (a) streaming velocity; (b) temperature.
We now look at the PUT system (Figs. 6.12 and 6.13). The density for the vibrating wall system shows typical fluctuations, however for the frozen wall system the peaks at the boundaries and in the middle of the pore are higher than for the vibrating wall system, indicating a more pronounced layering. This situation is also present in the PBT systems that is discussed later in this section. In the frozen wall system the channel is slightly narrower than for vibrating wall systems because the fluid pushes the vibrating wall particles away. In fact, apart from the harmonic potential, no other constraints have been used to keep the wall layers in place, to avoid the introduction of spurious dynamics. The shear stress for the vibrating wall system is roughly correct in value but shows a slightly parabolic profile. This means that a pressure gradient is present across the fluid even if the system has reached a steady state. This is in contrast with the hydrodynamic predictions and means that the fluid shows unphysical properties. For rigid walls the parabolic profile is more strongly emphasized and furthermore the value shows a net increase, which is significantly different to that for the vibrating wall.

![Figure 6.14: Schematic representation of the effect that a ‘frozen’ wall has on the slip with respect to a vibrating wall.](image)

The streaming velocities are, for both vibrating and frozen walls, comparable with the wall thermostatted system. However the induced strain rate for frozen walls is slightly higher, $\dot{\gamma} \simeq 0.62$, while for vibrating walls it is $\dot{\gamma} \simeq 0.51$. This means that the slip for rigid walls is lower than for vibrating walls. This has been verified by performing a set of simulations in which only one wall was allowed to shear, keeping the opposite one stationary. The stationary wall was in turn allowed to vibrate or kept frozen. The slip, defined as the value of the linear interpolation of
the streaming velocity at the intersection with the steady wall, has been computed for different values of wall density and strain rate (the strain rates were of the order of $10^{-2}$ to avoid temperature gradients across the channel and keep the velocity profile roughly linear even close to the wall). What we observed was a slip for the vibrating wall systems ($slip \simeq 0.06$), double the value for the rigid wall ($slip \simeq 0.03$). However, if the wall density exceeded a value of $\rho_w \simeq 1.2$ (in two dimensions this implies a quasi-smooth surface) the trend was reversed. This can be explained by considering the geometry of the wall (Fig. 6.14). Let us consider for simplicity a hard sphere potential, and a fluid particle coming towards the wall at a 45° angle with respect to the normal to the wall surface. When the wall is frozen it behaves like an array of hard scatterers and the chances for the fluid particle to be reflected back are high (this decreases the slip), whilst, when the wall is able to vibrate, the wall particle will partly absorb the fluid momenta and, shifting backward, allows the fluid particle to keep moving towards the same direction thus increasing the slip. The temperature profile in the PUT system is constant across the channel as imposed by the thermostat.
Figure 6.15: Profile Biased Thermostatted system (PBT) (the thermostat does not account for density fluctuations), for Couette flow with applied shear rate $\dot{\gamma} = 1.0$. (a) Cross section profile of density; (b) $xy$ component of the pressure tensor $P_{xy}$. The system composition is the same as for Figs. 6.12 and 6.13. BLUE (dashed line and diamond symbols): fluid thermostatted at $T = 2.5$ and wall at $T = 1.0$. RED (solid line and triangle symbols): fluid thermostatted at $T = 2.5$ and ‘frozen’ walls.
Figure 6.16: Profile Biased Thermostatted system (PBT) (the thermostat doesn’t account for density fluctuations), for Couette flow with applied shear rate $\dot{\gamma} = 1.0$ as with Fig. 6.15. (a) streaming velocity; (b) temperature.
For the PBT (Figs. 6.15 and 6.16), we impose a linear profile with a strain rate obtained by interpolation from the PUT instead of the WT system. This is to avoid imposing a profile that would be unnatural for a thermostatted fluid. The density and streaming velocity profiles for either the vibrating or frozen walls are qualitatively and quantitatively the same as for the PUT. The shear stress however shows two opposite profiles, a concave parabolic profile for the vibrating wall system, whilst convex for the rigid wall system and a significant difference between the two of $\simeq 0.1$. The temperature for the vibrating walls system is roughly constant in the center of the channel but increases at the wall interface where there is a steep density increase and the velocity gradient differs from the assumed value. When the walls are frozen we observe an accentuated parabolic profile, higher temperature close to the walls and lower in the center of the channel. Such erratic and unphysical profiles can lead to wrong conclusion in studies where thermal properties are involved. Also evident are kinks in the temperature, due to the steep density gradients that the homogeneous thermostat is not able to account for. For the PBT system with frozen walls we also checked if an independent control of the temperature in the $x$ and $y$ directions would improve the mechanical response, due to the temperature anisotropy present in a strongly driven fluid. However the mechanical properties did not show any significant difference.

The last system simulated was a PUT (Fig. 6.17) in which the temperature imposed across the channel was parabolic and obtained by quadratic interpolation from the wall thermostatted system, i.e. the temperature in each bin is thermostatted to the equivalent temperature in each corresponding bin in the WT system. As one would expect for the system with vibrating walls, the profiles are the same as for the WT system, however for rigid walls the streaming velocity shows a higher velocity gradient and the pressure again displays the irregular and slightly parabolic profile.

We now analyze the effect of the thermostats on the subsystem Lyapunov spectra of the confined system and the Lyapunov spectrum of the homogeneous system. All the spectra plotted refer to the exponents for the phase space generated by the fluid particles only. We show four spectra, one for the WT system and one for a SLLOD system at the same average state point as the WT (together in Fig. 6.18), and two
for the PUT system in Fig. 6.19 (either vibrating or frozen wall). The SLLOD spectrum has six characteristic exponents that we omit from Fig. (6.18) because they are related to conservation properties that do not exist for the confined fluid. Four exponents are related to the momentum and center of mass conservation in the $x$ and $y$ direction for the SLLOD algorithm, one exponent is related to kinetic energy conservation and has a value of zero, and the last one to the non-autonomous character of the dynamics [SEM92]. The first five exponents are identically zero. In Fig. 6.18 we can see that, because the chaoticity of the fluid is determined mainly by the actual velocity gradient inside the fluid and its density and temperature, the spectra of the two systems look basically the same with comparable maximum Lyapunov exponents. The confinement does not seem to affect the spectra’s shape (see a discussion in [PH89]), which is influenced for the most part by the overall fluid density that determines the collision rate. The only appreciable difference is in the sum of the exponents, which is 0 for the fluid subsystem exponents in the confined system and $\simeq -0.2$ for the homogeneous system. This is not surprising and is a natural consequence of the dissipative character of the SLLOD equations of motion [SEM92, Coh95, FST06, Mor02b] (Eqs. 4.6,4.8). The phase space contraction for Eqs. (4.6 and 4.8) is strictly connected with the entropy production and heat dissipation (Eq. 6.1). The equations of motion of the fluid for the confined system Eqs. (3.12), however, do not show explicitly the thermostat’s friction coefficient, which is included only in the wall equations of motion. Note that if the Lyapunov spectrum of the confined system was calculated (i.e. the full spectrum which includes both the walls and fluid), rather than the fluid subsystem exponents, the sum of the exponents would also be expected to be negative (see Ref. [23]). This is why the negative pair sum appears only in the Lyapunov spectra for the SLLOD system.

In Fig. 6.19, we display the fluid subsystem Lyapunov spectra for a PUT system with vibrating walls. Because the thermostat acts independently in every bin the number of friction coefficients is equal to the number of bins, so the above relation, Eq. (6.1) should account for a sum over the bins $\sum_{i}^{\text{bin}} \xi_i$. The PUT in Fig. 6.19 however, shows a higher dissipation than the equivalent SLLOD system. This could be due to the fact that to obtain the same velocity gradient, the walls have to perform more work on the fluid particles and thus even the heat absorbed by the
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thermostat is higher. This, according to Eq. (6.1), would result in a more negative pair sum. This spectrum is indistinguishable from the spectrum computed for a PUT system with ‘frozen’ walls and the PBT system with either vibrating and ‘frozen’ walls. The specific implementation of the wall does not seem to affect the exponents. Their value reflects the mixing of the fluid particles in the coordinate and velocity spaces. The mixing is determined mainly by temperature, number density and velocity gradient, therefore, these quantities being equal, the spectra will look the same. Several wall implementations have been tested, including a repulsive potential wall, and the spectra did not show any appreciable difference.

The last results presented in Fig. 6.20 refer to the Lyapunov localization. The Lyapunov spectra characterizes the system as a whole. However because the system is inhomogeneous we want to examine where, inside the channel, the chaotic nature of the fluid receives its largest contributions. Using Eq. (5.33) we quantify these contributions, and we do this for the whole Lyapunov spectrum.

The largest Lyapunov exponents quantify the fastest dynamical events happening in the system (i.e. particle collisions). For large systems with conserved quantities (e.g. energy) and spatial symmetries (PBCs), the smallest Lyapunov exponents represent the particles’ collective behaviours that manifest themselves with periodic structures present in the perturbations associated with the smallest exponents, called Lyapunov modes [MPH98b, FP05, EFPZ05a]. However, because our system is small, confined and thermostatted, the small exponents do not organize themselves into modes, even if they can still be regarded as characterizing the system’s global properties. Our interest is in the Lyapunov localization inside the channel and therefore we only consider the phase space generated by the fluid. This allows us also to compare the Lyapunov localization for exponents characterized by the same dimensionality. Fig. 6.20(a) shows the localization for the fluid subsystem exponents in the WT system, while Fig. 6.20(b) shows the localization for the PBT system with frozen walls. In Fig. 6.20(a) we purposely choose to exclude the phase space generated by the wall while in Fig. 6.20(b), the wall particles, not having any degrees of freedom, do not add dimensionality to the phase space. The localization exponents have been normalized with respect to the largest (of both systems, WT
and PBT) exponent contribution. In this way a quantitative comparison between the two systems is also possible. For both the WT or PBT systems the fluctuations across the channel show a strong correlation with the density, in fact, the more a particular area of the channel is populated, the more it is likely to contribute to chaos. This effect is simply because there are more particles there. Consideration of the deviations of the localization from the density profile indicate that the maximal exponents have a reduced contribution in the region near the walls, and the contribution is fairly uniform elsewhere. Conversely, when considering the smallest exponents, the particles near the wall have a considerably enhanced contribution. In fact, as we approach the smallest exponents, the more the localization is enhanced near the walls. Comparing the WT and PBT systems shows both a quantitative and qualitative change: for the WT system the change in the contribution as we go from the maximum to the minimum exponent assumes the shape of ‘braces’ while for the PBT system a bell shape is observed with a significantly high contribution from the minimum exponents. This result shows that the presence of a thermostat in the fluid coupled with a rigid wall distorts the dynamics, especially near the walls.
Figure 6.17: Parabolic Temperature Profile thermostatted system (the thermostat accounts for density fluctuations), for Couette flow with applied shear rate $\dot{\gamma} = 1.0$. (a) Cross section profile of streaming velocity; (b) $xy$ component of the pressure tensor $P_{xy}$. The system composition and state point are the same as for Figs. 6.12 and 6.13.
Figure 6.18: (a): Fluid subsystem Lyapunov spectra for “Wall-Only” thermostatted system, 45 fluid particles at a density $\rho_f = 0.6$, 40 wall particles at a density $\rho_w = 0.8$, channel width $y = 6.82$, Couette flow with effective velocity gradient $\dot{\gamma} = 0.55$, walls thermostatted at $T = 1.0$ (reduced units). (b): Lyapunov spectra for a SLLOD system, 50 fluid particles at a density $\rho_f = 0.6$, velocity gradient $\dot{\gamma} = 0.55$, temperature $T = 2.5$. 
Figure 6.19: Fluid subsystem Lyapunov spectrum for Couette flow with a PUT and vibrating walls. This spectrum is, within limits of error, indistinguishable for both PBT and PUT systems, either with vibrating walls or ‘frozen’ walls. The system composition and state point are the same as for Figs. 6.12 and 6.13.
Figure 6.20: (a): Fluid subsystem Lyapunov exponent localization for a Couette flow fluid thermostatted through conduction to the walls. 40 fluid particles at a density $\rho_f = 0.6$, strain rate $\dot{\gamma} = 0.55$, wall thermostatted at $T = 1.0$ (reduced units). (b): Fluid subsystem Lyapunov exponent localization for a Profile Biased Thermostatted fluid (PBT) with 'frozen' walls (from which comes no contribution).
6.4 Lyapunov Spectra for Mixed Flow

Let us now present and discuss the results for PMF Lyapunov spectra. For consistency with previous studies on pure shear and elongational flows, the same system specifications are used: 32 particles, at a density $\rho = 0.3$ and at a temperature $T = 1.0$. Simulations have been performed at different state points, depending on the values of field strengths $\dot{\varepsilon}$ and $\dot{\gamma}$, and ordered according to the second scalar invariant of the strain rate tensor ($II = 2, 4, 8, 10, 16$). The precision of $\dot{\varepsilon}$ and $\dot{\gamma}$ used in the computations are of the 5th decimal place, as reported in Table 6.3, however in the results section, when reported, their values are given to 2 decimal places. Equations of motion are integrated via a fourth order Gear predictor-corrector method, with a time step $\Delta t = 0.001$. An initial simulation time of $5 \times 10^6$ time steps was carried out to ensure that the system had reached a steady state, which was then followed by data production for $6 \times 10^6$ time steps. Results for exponents and sums are averaged over 10 independent runs. Throughout the discussion, we define the exponent pair index as $M/2 - 1 + n$, such that it is maximum for the maximal (in absolute value) Lyapunov exponents. Before showing spectra, we remark that particles in nonequilibrium steady flows generally give rise to six trivial exponents. These are omitted from the plots, since they are not to be considered when evaluating the CPR. They are however considered when calculating the results presented in Table 6.3.

In Figs. (6.21a) and (6.21b) we plot the Lyapunov spectra and the ordered pair sum respectively for pure elongation, pure shear and three rates of mixed flow, all characterized by $II = 2$. For PMF, two systems have a dominant elongation contribution. This is also true for Figs. (6.22a) and (6.22b) to be discussed later. As expected, the spectra for PSF looks qualitatively different from PEF. The coupled exponents show a larger separation for PEF. It is interesting that the PMF spectra show a transition between the two pure flows, according to which flow geometry is dominant ($\dot{\gamma} > \dot{\varepsilon}$ or $\dot{\varepsilon} > \dot{\gamma}$). In the two cases when $\dot{\varepsilon}$ is higher, the PMF spectra almost completely overlap with the PEF spectra, while when $\dot{\gamma}$ is higher, the spectrum sits in between the PEF and PSF spectra. Clearly, this reflects the stronger contribution of the elongational component in the total balance of $II$, which is four
Figure 6.21: Results for a system of 32 particles in an isokinetic ensemble, with density $\rho = 0.3$ and temperature $T = 1.0$. Five different values of the pair $\{\dot{\epsilon}, \dot{\gamma}\}$ are considered, all at $II = 2$. (a): Lyapunov spectra, (b): Lyapunov pair sums.
times larger than the corresponding component for shear.

Looking at the maximum exponents in Table 6.3, we can notice that pure shear flow is consistently smaller. This result needs a careful interpretation. In fact, although it might seem to suggest that PSF is less chaotic than PEF, and to certain extent PMF, we need to consider the heat dissipation, also consistently smaller for PSF. The PSF lower average exponent sum and lower average thermostat multiplier with respect to PEF and PMF (also reflected in the values of the Kaplan-Yorke dimension and Kolmogorov-Sinai entropy), is probably due to the approximation of the heat production rate per unit volume, i.e. II (obtained by macroscopic continuum mechanics considerations) is not exactly reproduced in these small systems by the average of the thermostat multiplier. If the equivalence between II and heat production rate were exact, the values of the average thermostat multiplier would match for all flows. However, if we now consider the maximum exponents for pure PSF at $\dot{\gamma} = 2.0$ and PMF at $\dot{\gamma} = 1.0$ and $\dot{\varepsilon} = 0.5$, we see that the former is smaller. This time II and the heat dissipation for PSF is twice that of PMF, therefore even if the maximal exponents value are too close for definitive conclusions to be made, this is an indicator that the exponents respond differently to the two flows.

In general, the action of each separate flow on the degrees of freedom of the system does not appear homogeneous. This can also be confirmed, in a more general way, by looking at the rest of the spectrum in Fig. 6.21a. The exponents with maximal absolute values are known to be associated with the fastest events happening in the system (i.e. particle collisions), whereas the smaller couples are indicative of global and delocalized aspects of the dynamics. If we consider only the positive half of the spectra, we can see that exponents for PSF are always below those for PMF for low couple numbers, similarly, the PMF exponents are below the PEF exponents. As we move towards larger exponent pair indices, the differences between PSF, PMF and PEF drastically diminish. All this shows that the collective particle behaviour of planar shear is markedly different from planar elongation and both seem to provide a lower and upper limit respectively for planar mixed flow depending on the ratio of the fields. Collisions, being mostly controlled by state variables such as temperature and density, are less sensitive to the type of flow considered at small and high values
of $II$ (see also Figs. 6.22a and 6.22b), and seem to occur with similar frequencies and energy exchanges in all the flows.

The ordered pair sum in Fig. 6.21b looks qualitatively analogous for PEF and PMF, and different from PSF. Sums for PEF and PMF share the same trend, and their average absolute value increases as the elongational/shear component is increased/decreased. This suggests that the CPR is only sensitive to the value of the strain rate, and not the value of $II$. However, the fact that deviations from CPR are smaller in PMF with respect to PSF and more sensitive to the value of the strain rate is not surprising, as it is the shear flow that is responsible for the deviations. These irregularities, which show a distinctive kink for low pair indices, are in fact the expected deviations from CPR for non-Hamiltonian shear-SLLOD [FST06, SEI98]. Note that the small deviations from CPR in PEF are due to $O(1/N)$ effects [FST06].

If we now inspect Figs. 6.22a and 6.22b where $II = 8$, we can better appreciate how qualitatively different the spectra are. In particular, notice how for PEF and PMF, around pair index 25, a hump divides the bell-shaped spectra into two parts: one with a slightly different slope than PSF, and one, at small pair indices, with a much smoother parabolic end. PEF and PMF have similar spectra, as in the previous Figure. Note that the differences between exponents of pure shear, mixed and pure elongational flows remain large and constant for a longer part of the spectrum than those in Fig. 6.21a, where $II$ is smaller. This indicates that differences among flows increase as $II$ is increased, and they tend to persist over a larger range of time scales. Only fast collisions (i.e. the end of the spectrum), are relatively insensitive to the type of flow considered. The degree of similarity between PSF and PEF, instead, does not seem to be affected overall by changes in $II$.

From Fig. 6.22b, it is now clear that CPR does not hold for shear-SLLOD while much smaller deviations exist for PEF, whose sums display once more very strong similarities and satisfy CPR within less than 1%. An interesting fact that is more evident in Fig. 6.22b is that the non-Hamiltonian character in PMF due to PSF has a quantitative influence on the quality of conjugate pairing for PMF. The initial part of the kink that PSF displays for the sums of lower index is in fact mimicked by the shear dominated PMF: as we increase the rate of $\dot{\gamma}$, a jump appears. Its amplitude
Figure 6.22: Results for five different values of the pair \( \{\dot{\varepsilon}, \dot{\gamma}\} \), with \( II = 8 \), for the same system described in Fig. 6.21. (a): Lyapunov spectra, (b): Lyapunov pair sums.
depends directly on the value of the rate, making the divergence from CPR higher when the shear component is made larger. Also, the asymmetry between low and high pair numbers in Fig. 6.22b with respect to the average value of the sums is more prominent for stronger shear rates in PMF.

To better understand the effect of $\dot{\gamma}$ on the sums for PMF, in Fig. 6.23 we plot the difference between the ordered pair sum and the expected CPR value, computed as $(\sum_i \lambda_i)/2N$ for different fields. We can clearly see how an increase in $\dot{\gamma}$ pushes deviations in the CPR to higher values, up to about 4% when the shear rate is doubled. Instead, when the weight of elongation is increased, keeping $\dot{\gamma} = 1.0$, the conjugate-pairing does not worsen. Interestingly, the most pathological sums tend to occur both at one third and two thirds of the spectrum, rather than concentrate at its ends or in the middle. This indicates that the way dissipation takes place in PSF, and therefore PMF, shows that less dissipation is produced by couples of exponents associated with collective particles dynamics and vice versa for couples of exponents associated with short time-scale dynamics. As said, this imbalance is also evident in the spectra in Figs. 6.21a and 6.22a.
Figure 6.24: Results for three different values of the pair \( \{ \dot{\varepsilon}, \dot{\gamma} \} \), for the same system as in Fig. 6.21. A pure shear flow and a pure elongational flow both at \( II = 8 \) are directly summed to give a mixed flow with \( II = 16 \). (a): Lyapunov spectra, (b): Lyapunov spectra shifted with respect to the average conjugate-pairing values. Error bars are omitted because too small to be resolved.
Figure 6.25: Results for three different values of the pair \( \dot{\varepsilon}, \dot{\gamma} \), for the same system as in Fig. 6.21. A pure shear flow and a pure elongational flow both at \( II = 8 \) are directly summed to give a mixed flow with \( II = 16 \). (a): Lyapunov pair sums (error bars are omitted because too small to be resolved), (b): Difference between Lyapunov pair sums and expected CPR value.
In Figs. 6.24a, 6.24b and Figs. 6.25a, 6.25b we compare PMF with \( \dot{\gamma} = 2.0 \) and \( \dot{\varepsilon} = 1.0 \) with PSF with \( \dot{\gamma} = 2 \) and PEF with \( \dot{\varepsilon} = 1 \). \( II \) for PSF and PEF are the same, but lower than that of PMF. This will result in a significantly different conjugate pair sum for PMF due to the much higher heat dissipation, and therefore to aid the comparison, the spectra in Fig. 6.24b are shifted so that they are all centred about 0. From an analysis of Fig. 6.24b we see that PMF and PEF are nearly overlapping for low pair indices up to about 15, where the arms of the spectra for PMF separate from those of pure elongation. This shows that the elongational component dominates the collective dynamics in PMF even when the shear component generates similar heat dissipation, whereas larger effects tend to appear in high indices: at large \( II \), collisions in PMF are quantitatively affected by the presence of a \( \dot{\gamma} \neq 0 \). Fig. 6.24a shows that this change is not absolute, since the differences between maximal exponents for PEF and PMF are small, but rather a relative effect with respect to CPR, i.e. with respect to the average dissipation of all degrees of freedom in the system. This increase in the importance of collisions in the distribution of energy events in the system may indicate either that collisions are more frequent and/or that the energy exchanged per particle is larger. Finally, in Figs. 6.25a and 6.25b, the contribution to violations in CPR due to the non-Hamiltonian character of the shear component in PMF are, once again, directly evident. In Fig. 6.25b, similarly to what already observed in Fig. 6.23, at constant \( \dot{\gamma} \) the deviation from the expected CPR does not change with changes in \( \dot{\varepsilon} \).

Finally, from Table 6.3, we can observe that PMF viscosities, obtained using the sum of all Lyapunov exponents, are in good agreement with the NEMD viscosities, the accuracy of which has already been tested in Chapter 4.
Table 6.3: Summary of the results for PEF, PSF and PMF, ordered according \( II \). The system is composed of 32 particles at a density \( \rho = 0.3 \) and temperature \( T = 1.0 \). \( \lambda^{\max} \) and \( \lambda^{\min} \) are the maximum and minimum Lyapunov exponents respectively, \( \sum \lambda^i \) is the sum of the whole spectra, \( D_{KY} \) is the Kaplan-Yorke dimension, \( \eta_{\text{NEMD}} \) and \( \eta_{\text{Lyap}} \) are the viscosities computed using NEMD and the Lyapunov exponents relation respectively, \( \langle \xi \rangle \) is the time average of the Gaussian multiplier. The errors, in brackets, are twice the standard error of the mean of ten independent runs. When uncertainties are of the order of \( 10^{-4} \) for \( \eta_{\text{NEMD}} \) and \( \eta_{\text{Lyap}} \), they have not been indicated.

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Chapter 7

Conclusions

In this thesis we presented new and interesting results that shed light on many aspects of homogeneous and inhomogeneous nonequilibrium molecular dynamics simulations of atomic fluids. Some of them improve our understanding of the dynamics helping us to establish connections between statistical mechanics and dynamical system theory, while other results were of a more immediate use, like the detailed examination of thermostats in highly confined fluids, (currently a prominent topic with many studies on transport in nanotubes and porous biological systems) or the development of a new algorithm to enable the simulation of fluids under mixed flow.

We compared the Lyapunov spectra of inhomogeneous systems at non-equilibrium steady states, for two types of flow, namely Couette and Poiseuille. It is the first time to our knowledge that all the degrees of freedom of such dynamical systems (walls and fluid) were taken into account in this type of study. The results clearly showed that, for inhomogeneous systems in steady states, the Lyapunov spectra are highly asymmetric and the CPR is not satisfied. The spectra shows two distinct regions, one in which there is a negative sum of the pairs and one which tends to a zero sum. The first can be identified by the region of thermostatted particles, that are responsible for the reduction in dimensionality of the phase-space, and the second by a purely Newtonian region. The existence of a few non-zero off-diagonal terms in the Jacobian matrix (due to the weak coupling between the dynamics of
the fluid and wall particles) is the reason for the smooth mixing between the two zones.

Couette and Poiseuille flows show qualitatively the same spectra, reflecting similar chaotic properties in spite of a different distribution function. Two regions can also be distinguished in the plot of a confined fluid at equilibrium (see Fig. 6.3): the characteristic “bell” shape of the Lyapunov spectra is very narrow for the first half of the pair indices, indicating a small increase in the absolute value of the exponents, while the second half shows a steeper increase (the “bell” becomes wider), reflecting a much more chaotic dynamics. The narrow region can easily be identified with the wall atoms, experiencing a constrained motion since they are linked to the wall lattice, whilst the wider region pertains to the fluid particles where the collisions give rise to spatial reordering and mixing.

Another study has considered projected Lyapunov exponents [PH04]. In contrast to the case when the full Lyapunov spectrum is determined and projected, we propagate a projected vector, keeping it constrained to the subspace of interest and define a subsystem Lyapunov exponent. This allows us to obtain subsystem spectra which give an approximation to the full spectrum. Using this approach, the part of the Lyapunov spectrum associated with the fluid (and the chaoticity of the fluid) can be determined by simply considering the evolution of displacement vectors in this subspace, which is feasible for fluids consisting of few particles such as in highly confined systems, and not concerning the, possibly very large, thermostatting region which could be computationally, or experimentally, impossible to determine. We note however that the splitting in phase space between the two regions is possible due to the small amount of coupling between wall and fluid. In case of strong coupling the off-diagonal blocks in the Jacobian matrix given in Eq. (6.4) would not be negligible.

We make the point that our results are independent of the particular choice of thermostatting mechanism used. In fact, we obtained very similar results for the Lyapunov spectrum of the fluid using several thermostatting schemes, including a variant of the Müller-Plathe algorithm [MP99, BMP02], where only the walls are used to induce the flow and no thermostat is used.
We next presented results concerning the use of thermostating devices for a highly confined fluid. The purpose was to cast light on the effects that a thermostat mechanism can have when applied directly on the fluid particles instead of using it on the channel’s walls, as in real experiments, to allow the heat produced in the fluid by the external force field to dissipate through them. We examined how a number of properties change, either from a mechanical point of view, showing what happens to the shear stress, streaming velocity, density and temperature across the channel, or from a dynamical point of view by comparing the Lyapunov spectra for the fluid phase space.

From the analysis of these systems we conclude that, independent of the type of thermostat device used, the mechanical properties show significant variations, and all together they are never comparable to the wall-only thermostatted system, in which case the profiles show good agreement with hydrodynamic predictions. The values of pressure and shear rate are lower, the density shows stronger fluctuations, and the velocity distribution functions are not always in agreement with the theoretical curve (if the temperature is not chosen carefully). Thermostatting the fluid improperly also gives rise to a different dynamics as can be seen from the analysis of the Lyapunov localization, the greatest difference being for the smallest Lyapunov exponents and close to the walls. The main conclusion to be drawn is that thermostatting a confined fluid can lead to significant unpredictable and unphysical material properties and underlying dynamics. Thermostatting a strongly driven confined fluid should always be done by the action of the walls, mimicking nature as close as possible. Furthermore, freezing the walls (hence by necessity requiring one to thermostat the fluid) should also be avoided to remove such artificial material and dynamical properties. Our results therefore suggest caution in interpreting the results of recent NEMD studies on confined systems, such as flows inside carbon nanotubes, in which the carbon nanotube atoms are frozen and the fluid molecules are thermostatted.

Next we derived and implemented an algorithm for indefinite NEMD simulation of fluids under mixed flow, a linear combination of planar elongational flow and planar shear flow. To accomplish this we used results from the theory of lattices. Similarly
to PEF simulation techniques [TD98, TD99], the cell box deforms according to the flow streamlines and is remapped to its original shape after a fixed amount of time without discontinuities in physical properties. Statistics are therefore improved and a broad range of fluids, such as dense alkanes or polymer melts, can be investigated. Our viscosity results are validated with previous data [BC95] obtained with a finite-time algorithm. To conclude we have also shown (for the first time, to our knowledge) that a mixed flow in which the shear and elongation axes are not orthogonal is equivalent to one in which they are orthogonal, for an appropriate choice of field parameters.

Thanks to this new algorithm we could extend the analysis of the chaotic structure to planar mixed flow. The Lyapunov exponents are in fact properly defined only in the infinite time limit, therefore with the simulation technique previously available it was impossible to maintain the steady state long enough to extract Lyapunov spectra. Our algorithm clearly solves this problem (giving the possibility to perform simulations indefinitely). We concentrated our attention on the compliance of PMF to the conjugate-pairing rule. Since the equations of motion for PMF are non-Hamiltonian, due to the PSF contribution (also non-Hamiltonian), a breaking of conjugate-pairing rule is expected. The most interesting point in this regard is the quantitative dependence of the Hamiltonian character to the shear rate. The higher the value of $\dot{\gamma}$ the larger the non-Hamiltonian contribution, and therefore a worse abidance of the CPR. The elongation component is however important in determining the degree of chaoticity of the system. Also from a qualitative point of view, the PMF spectra resembles the PEF spectra’s shape, suggesting a similar phase-space distribution function. The collective behavior of the particles is mainly due to the flow streamlines. The streamlines of PMF and PEF are qualitatively similar [HBT10], in fact the only action of the shear flow in PMF, is to change the angle between the expansion and contraction axes, leaving the elongational field along them the same.

As often happens in physics, the making of steps forward in understanding opens the path to new questions and new ways to address them. The discovery of new PBCs allowing for homogeneous flow characterization is a continuous challenge. In
the Appendix we present a possible way to simulate homogeneous rotational and elliptical flows. However, lattices reproducible under uniaxial and biaxial extensional flows are not possible to derive [KR92], therefore other ways to overcome this problem must be developed. We also note that lattices, despite their conceptual simplicity, still play a main role in the understanding and modeling of many areas of statistical mechanics, e.g. the study of chaotic diffusion in Lorentz gas [MS10], magnetism in the Ising model [HRL07] and computational fluid dynamics, e.g. Lattice Boltzmann methods [TYH11, MI11].

Lyapunov vectorial space analysis, as well as the localization of chaos in physical space and Lyapunov modes (at the moment developed only for simple equilibrium systems), could help broaden and deepen our understanding of dynamical process in narrow geometries. These are only a few examples of possible directions worth considering to extend our physical knowledge by means of NEMD.
Appendix A

Elliptical Flow

A.1 Introduction

In Chapter 4 we presented the concepts behind lattice reproducibility and compatibility necessary to derive periodic boundary conditions for planar mixed flow. In this Appendix we introduce a simple algorithm to produce nonequilibrium molecular dynamics simulation for rotational and elliptical flows with appropriate periodic boundary conditions. We note that rotational flow is a particular case of elliptical flow in which the off-diagonal components of the velocity gradient tensor are equal in modulus. We therefore present a general derivation for elliptical flow and consider the rotational flow as a special case. Some formulas and concepts presented herein resemble closely the ones obtained by Adler and Brenner [AB85, AZB85] for spatially periodic suspensions. Starting from the most general parameterization for two dimensional homogeneous flows derived by Kao et al. [KCM77], they analyzed the conditions for reproducibility and compatibility also for elliptical flows. Their treatment, however, aimed at a quasistatic dynamical analysis, and is somewhat abstract when applied to NEMD techniques and PBC implementations. These flows are encountered in many real situations, from engineering applications (e.g. polymer flows) to biofluids studies (e.g. blood cells flows and DNA chain dynamics). Their characterization is mainly carried out by means of Brownian dynamics simulations
on dilute solutions [HS07, WS03, DC03], therefore without implementing PBCs, or
experimental/simulation studies by means of 4-roller mill [MME95, FL81] and 4-roll
mill devices [DKSS09].

A.2 Periodic Boundary Conditions

A possible parameterization for the elliptical flow velocity gradient tensor in two
dimensions is

$$\nabla \mathbf{u}^\varphi = \begin{pmatrix} 0 & -\dot{\gamma}_2 \\ \dot{\gamma}_1 & 0 \end{pmatrix}. \quad (A.1)$$

Rotational flow is obtained if we set $\dot{\gamma}_1 = \dot{\gamma}_2$. We consider a two dimensional planar
flow for simplicity and a square primitive cell to start with. The equations for the
streamlines are

$$x(t) = x(0) \cos(\sqrt{\dot{\gamma}_1 \dot{\gamma}_2} \ t) - y(0) \frac{\dot{\gamma}_1}{\sqrt{\dot{\gamma}_1 \dot{\gamma}_2}} \sin(\sqrt{\dot{\gamma}_1 \dot{\gamma}_2} \ t),$$

$$y(t) = x(0) \frac{\sqrt{\dot{\gamma}_1 \dot{\gamma}_2}}{\dot{\gamma}_1} \sin(\sqrt{\dot{\gamma}_1 \dot{\gamma}_2} \ t) + y(0) \cos(\sqrt{\dot{\gamma}_1 \dot{\gamma}_2} \ t). \quad (A.2)$$

In Fig. A.1 we show 6 frames for the evolution of a lattice under elliptical flow.
It is clear from the nature of the flow that the lattice is periodic with a period
$\tau_p = \frac{2\pi}{\sqrt{\dot{\gamma}_1 \dot{\gamma}_2}}$ and therefore reproducible.
Figure A.1: Snapshots representing the evolution of a lattice under elliptical flow. Lattice points in blue, streamlines in red. In the last (f) frame the lattice reproduces itself (a).
Following the same procedure as for mixed flow we can check compatibility ensuring that the distance between the vertices of the simulation box does not become less than the interatomic potential diameter. We consider the equation
\[
\frac{d}{dt}(r(t) \cdot r(t)) = 2(x\dot{x} + y\dot{y}) = 0,
\] (A.3)
and derive the time at which we have a minimum
\[
t_m = \frac{1}{2\sqrt{\gamma_1\gamma_2}} \arctan \left( \frac{2x_0y_0\sqrt{\gamma_1\gamma_2} - 2x_0y_0\sqrt{\gamma_1\gamma_2}}{x_0^2 \left( \gamma_1\gamma_2 - 1 \right) + y_0^2 \left( \gamma_1\gamma_2 - 1 \right)} \right),
\] (A.4)
where \(x_0 = x(0)\) and \(y_0 = y(0)\). If we set one corner of the cell as the origin, we need to check this time only for the remaining three corner coordinates, substituting them, in turn, in \(x_0\) and \(y_0\). We successively replace the time \(t_m\) in the equations for the streamlines, thus finding \(x(t_m)\) and \(y(t_m)\), and compute the minimum distance
\[
D_m = \sqrt{x(t_m)^2 + y(t_m)^2}.
\] (A.5)

The analytical expression is however quite involved and we can use simple geometry to find an easier solution. As shown in Fig. A.2, each corner of the cell lies on different streamlines (excluding the one centred at the origin). If the simulation starts with the box sides aligned with the major and minor ellipse’s axes, the maximum contraction/expansion will be at an angle \(\varphi = \sqrt{\gamma_1\gamma_2} t = \pi\). At this time the cell side (indicated as \(a\) in Fig. A.2) contracts of a factor \(\sqrt{\frac{\gamma_1\gamma_2}{\gamma_1}}\) determining the minimum lattice distance.

The dynamics can evolve according to the SLLOD equations of motions
\[
\begin{align*}
\dot{r}_i &= \frac{p_i}{m_i} - y_i\gamma_1 \hat{x} + x_i\gamma_2 \hat{y}, \\
\dot{p}_i &= F_i + p_y\gamma_1 \hat{x} - p_x\gamma_2 \hat{y} - \xi p_i,
\end{align*}
\] (A.6)
with the Gaussian isokinetic thermostat

\[ \xi = \frac{\sum_i \mathbf{F}_i \cdot \mathbf{p}_i + p_{y_i}^2 \dot{\gamma}_1 - p_{x_i}^2 \dot{\gamma}_2}{\sum_i \mathbf{p}_i \cdot \mathbf{p}_i}. \]  

From Fig. A.1 we can note two things:

- First, if we consider the limiting case of rotational flow, the simulation box does not deform at all, while rotating in the laboratory frame. From a practical point of view this means that one needs to implement only the SLLOD equations of motion, and treat the primitive cell as for equilibrium.

- Second, the more pronounced are the elliptic streamlines, the more rectangular the box will become. This will of course affect some physical properties such as energy, because at \( \tau_p/2 \) the particles will be pushed together in the \( x \) direction. This effect could be reduced by a careful choice of the box initial dimensions and diminishing the value of \( \dot{\gamma}_1 \) and \( \dot{\gamma}_2 \), while leaving constant their ratio, so to give to the particles more time for relaxation and rearrangement. A possible way to solve the latter issue could be to follow the example given by rotational flow, and noticing that if we choose an elliptical box, delimited by one of the streamlines, its shape would not change in time. In this way we could treat the box as in the equilibrium case. Again the only thing affecting the particles...
would be the homogeneous SLLOD equations of motion.

An elliptical cell opens however new questions on how to implement PBCs in a non space-filling tailing of the Euclidean space. One possible solution would be to “glue” the margin of the cell box together obtaining what is known as the crosscap, i.e. a two-dimensional differentiable and compact manifold which is not orientable (see Fig. A.3). From a topological point of view this means that the particles would be able to travel on both sides of a closed surface, as opposed to normal PBCs where they would only visit one side. To better explain the idea we look at the quotient space for the square box. The quotient space is, loosely speaking, what we obtain when gluing surfaces according to their borders’ orientation. For normal PBCs, where the cell box is space filling, opposite corners have same orientation (see top of Fig. A.4), therefore after gluing them (so that the orientation is preserved) we obtain a torus, with two distinct sides. A particle travelling on one side wouldn’t be able to access the other one. If however opposite corners have opposite orientation (see Fig. A.4), when gluing them (again being careful to preserve the orientation) we obtain what is known as Klein bottle, a surface with only one side. A particle would be able to travel everywhere, “inside” and “outside”. The crosscap is topologically equivalent to the Klein bottle where instead of a square we use a circle to delimit the surface. This has practical consequences in NEMD simulations, in that the system

Figure A.3: Schematic image of an “open” cross-cap. The self intersection of the 2D surface is is due to its embedding in 3D. It would not occur if the embedding were in 4D. Cross-cap image source [WK0a].
would not conserve linear momentum and center of mass each time a particle would cross the boundaries, but would conserve the total angular momentum.

Preliminary tests with atomic and molecular systems have been carried out for the case of a “deforming” square cell. The oscillations in physical quantities do not necessarily represent a problem, and can be averaged out similarly to what has been done by Todd and Daivis [TD97], who presented an algorithm for computing frequency dependent elongational viscosities for PEF and USF/BSF extrapolating them to zero-frequency. The algorithm involved a periodic squeezing and extending of the cell box, according to the flow type, such that

\[ L_\alpha(t) = L_\alpha(0) \exp \left[ \dot{\varepsilon}_{\alpha\alpha} \omega^{-1} \sin(\omega t) \right], \quad (A.8) \]

where \( L_\alpha \) represents the corners of the cell box, \( \alpha = x, y, z \), and the frequency \( \omega \).
must be chosen such that the box is compatible in the contracting direction. This periodic contraction and expansion is equivalent to what happens to the cell’s corners in elliptical flow.
Bibliography


A BIBLIOGRAPHY


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