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WALL MODEL EFFECTS ON TWO PHASE FLOWS AND PRESSURE DISTRIBUTION IN NANOCHANNELS

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ABSTRACT

Molecular simulations of single phase bounded nanoflows, especially at high density, showed discrepancies from the classical Navier Stokes solutions: the failure of predicting the slip value at the wall, stratification of the density close to the wall and excessive heating which affects the natural thermal fluctuations of the atomistic system (NVE ensemble). These discrepancies are a direct consequence of the importance of the surface effects for such scales as the surface to volume ratio increases dramatically at the nanoscale. To alleviate some of these observed phenomena, the modeling of the solid boundaries progressed from implicit mathematical wall models to explicit multi-layered atomistic structure including temperature/pressure control mechanisms and heat transfer exchanges. However, the wall models used in molecular simulations vary greatly in physical characteristics such as the wetting property (under static conditions) or momentum and heat exchange (under flow conditions) and consequently, the equilibrium and steady state conditions reached depend on the complexity of the model and the application it is developed for.

This work investigates the characteristics of different wall models found in the literature and compares their effects for the specific applications of single phase flows and nanojets (two-phase flows). It is found that the system thermodynamic pressure varies considerably depending on the parameters and complexity of the surface models and consequently alters both the flow and the jet behaviors. Assessments of these differences in terms of the system pressure, slip value at the surface and the injection velocity for different wall categories (atomistic, stochastic/diffuse and functional wall models) and parameters are provided. Another important consequence is the dependency of nanojet stability on the dense flow-surface interactions and liquid-gas-solid surface interactions.
A new integrated and sinusoidal wall model was developed to satisfy the requirements of our main application: two-phase flow injection. It provides agreement with thermodynamic data and flow profiles as well as injection velocity. Other numerical tools were also introduced to better serve this specific numerical experiment. A new Lennard-Jones modified potential for long range corrections and a preliminary pressure driven flow method were developed and implemented and promising results for pressure, energy and flow profiles are found.
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NOMENCLATURE

Roman

$a(t), A$  Acceleration vector, Atomistic or lattice site
$C$  Virial coefficient, Correlation function
$B$  Virial coefficient
$d$  Diameter, nearest neighbor distance in crystal lattice
$F, f_i, FF$  Force terms, Force field
$g$  Radial distribution function, Maxwell distribution
$k_b$  Boltzmann constant
$Kn$  Knudsen number
$L, l$  Length
$m, M$  Mass, number of atoms per molecule
$N, n$  Number of molecules, Number density
$P$  Pressure, Pressure tensor, Number of processors
$R, r_{ij}$  Radius, distance between particles, position vector
$r_c, r_s$  Cut off radius and Skin radius for force calculations
$T$  Temperature
$V$  Velocity magnitude $u^2 + v^2 + w^2$, Volume
$u(r), u$  Potential function, Potential energy
$v_i(t)$  Velocity vector
$w(r)$  Virial function, used in pressure and force calculations
$poly.$  Polynomial function
$<a>$  Statistical average of quantity $a$
$x, y, z, s$  Variables
Greek

\(\delta\)  
Displacement

\(\delta t\)  
Time step

\(\varepsilon\)  
Lennard-Jones potential well depth, Interactive potential strength

\(\sigma\)  
Lennard-Jones radius of minimum energy

\(\xi\)  
Langevin parameter

\(\eta\)  
Dynamic viscosity, Kolmogorov scale

\(\rho\)  
Density, Interatomic separation variable

\(\lambda\)  
Mean free path

\(a, \beta, \gamma\)  
Wall potential parameters or fitted constants

\(\phi\)  
Lennard-Jones potential

\(\mu\)  
Chemical potential

\(\tau\)  
Time period

Subscripts and Characters

Ar, Pt  
Argon, Platinum

LJ  
Lennard-Jones potential

f, liq  
Fluid or liquid property

sol  
Solid surface property

w  
Wall, fluid-wall property

g, gas  
Gas, fluid flow property

grav  
Gravitational or body force

\(i, j\)  
Indices to denote distinct particles \(i\) and \(j\).

m  
Molecule, Modified potential

v, vv  
Velocity or velocity correlation

corr  
Correction for long range interactions

0  
Target value

u, l  
Upper and lower levels

R  
Random force
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CHAPTER 1
INTRODUCTION AND FRAMEWORK

Two-phase flow injection simulation is one of the most important research fields in fluid mechanics and has been subject to numerous numerical studies (based on solving the Navier-Stokes equations). However, this multiscale, multiphase, transient, turbulent, non-linear problem is still not understood sufficiently to achieve significant improvement of the current technologies in various domains such as fuel injection, spraying and coating. Traditionally, most data on injection and mixing have come from wind tunnel tests, imaging (refractive and interferometric) techniques and probe and surface measurements. These experimental techniques are expensive, time constraining and in certain cases require further development in order to adapt for extreme test conditions.

With the rapid evolution of computing resources, numerical simulations became an affordable alternative to support and expand the understanding of jet flows and other aerodynamics problems.

Figure 1.1: Molecular and Continuum fluid Models
There are two ways for modeling a flow field (Figure 1.1). Either the fluid is a collection of particles or a continuum medium where the matter is assumed to be continuous. The former modeling can further be divided into deterministic and probabilistic methods while the latter is based on a set of non-linear differential equations for conservation of mass, momentum and energy. Basically the continuum models lead to fairly accurate predictions as long as the free mean path of the fluid is small enough by comparison to the flow characteristic dimension to ensure near thermodynamic equilibrium. This criterion which defines the Knudsen number is responsible for the following flow regimes: continuum, slip, transition and free molecular flows [1] as presented in Figure 1.2. Even when the continuum assumption is valid, computational fluid dynamics based on the differential equations can experience many problems. For example, issues related to grid size near boundary conditions and turbulence modeling are among the most serious issues affecting the accuracy of the results.

![Figure 1.2: Range of Knudsen Number for Gas Systems](image)

Moreover, in recent years, microscale and nanoscale devices [1] commonly called MEMS/NEMS (micro/Nano-electromechanical devices) involving fluid flows have seen a rapid increase in application, in a variety of industrial and medical fields. Micro heat exchangers for cooling of electronic circuits, accelerometers for automobile airbags, micropumps for ink-jet printing, blood analysers and pressure sensors for catheter tips are but a few examples of current usage. Fluid flow in such micro devices is expected, and was tested, was found to be different from conventional flow models provided by the Navier-Stokes equations. At these scales where the system sizes are comparable to the free mean path, the continuum theory based on the classical Navier-Stokes equations may
not hold since there is no account of the structure or the possible alignment of the fluid. The important increase of the surface to volume ratio ($\sim 10^6 m^{-1}$) is expected to substantially affect the transport of mass, momentum and energy and surface effects become dominant [1]. Functional characteristics of those nanodevices are to a large degree determined by the properties of material surfaces and their interactions with ambient or bulk media. One of the challenges is to understand how the interfacial characteristics statically and dynamically affect the performances of nanomechanical devices and thus determine their technological value. The understanding of the interfacial or wetting characteristics of a surface is fundamental to numerous other applications; for example, the wetting of porous media for oil recovery, printing, groundwater flow and detergency.

In this work, we use molecular dynamics simulations to investigate the specific application of single phase flows and two-phase jets, especially dense phases under confinement, at the nanoscale. Here the scale constraint is a direct consequence of the numerical method used. The long term objective is to construct large scale molecular simulations that allow bridging these numerical experiments to the macroscale and engineering analytical and experimental results. The focus of our research is then to acquire an understanding of how this numerical tool (molecular dynamics) and the consequent scale constraint (nanoscale) deviate from the macroscale data and at the same time provide an understanding for one and two-phase flows at the nanoscale. This bottom-up approach should allow us to construct numerically inexpensive, efficient and transferable models for flow simulations at the large scale.

Though numerous papers have already investigated similar fluids and flows under similar settings, the choice of surface models and its parameters for the confinement varied dramatically [2][3][4]. Qualitative agreement with macroscale results is usually reached for flow profiles while quantitative data (the slip value, the system pressure) are either omitted or stated as equal to the tabulated values [5][6]. The quantitative agreement in these cases is more challenging to reach not only because of the scale size or the dependency on the force field model and its parameters but also because of the interactions between the bulk phase and the surface at these scales. This aspect is usually
not studied and no comparison of the different surface models in molecular simulations for this application was published yet but for Abraham’s work [8] regarding the density distribution in nanochannels, even though jets’ stability is known to be sensitive to its initial conditions and the interfacial forces [9].

The objective of this study is to qualitatively and quantitatively investigate the effect of different wall models found in literature on single and two-phase nanoflows. The properties of interest for such comparison are the system pressure under quiescent conditions, the velocity slip value at the wall under flowing conditions and the injection velocity for two-phase flows. This constitutes the first work to assess and discuss the advantages and drawbacks of surface models and their characteristics on the above mentioned properties and provides a better understanding of their applicability for our application. Also, a newly developed wall model is introduced to better serve this application with low computational and ease of numerical implementation and transferability.

The thesis scope is as following: chapters 3 and 4 cover the tools necessary to set and model the relevant aspects of the numerical simulations. In chapters 5 and 6, results for single phase flows and two-phase flows are presented and discussed with respect to the different surface models.
CHAPTER 2
LITERATURE REVIEW

As stated in the introduction, the main framework for this research is the construction of a numerical experiment using molecular dynamics for the characterization of nanojets. The simulation of injection combined with molecular dynamics can be seen as a multi-component problem involving different aspects:

- Characterization of equilibrium states for fluids with discrete numerical methods.
- Bounded fluids: surface modeling/interfacial effect on single phase fluids.
- Bounded single phase flows: momentum and heat transfers at surfaces.
- Two-phase coexistence fluids: Equilibrium of liquid-gas interfaces.
- Two-phase injection: Nanojets.

Each of these components were subject of studies, separately or combined, for different engineering and scientific purposes [1] such as surface coatings for microdevices, cooling micropumps, ink jets for printing, drainage in porous structures, carbon dioxide entrapment….

In this chapter, we will cover the state of the art studies in some of these components and present the advances and challenges facing their molecular modeling. Other points will be discussed in the next chapters as we introduce our numerical tools and strategies.

2.1 Single Phase Flows

Molecular simulations offer alternate tools to simulate flows at different scales. They are considered ‘accurate’ methods to model the bulk flow since it relies on first principles such as the Newton’s equations of motion to determine the positions and/or velocities of the particles or the conservation of energy to solve for the particles
distributions. Molecular Dynamics simulations are deterministic methods where the trajectories and velocities of the particles are solved for.

The thermodynamic properties (temperature, pressure…) are statistical outputs of these simulations and allow the computations of higher order thermodynamic properties such as viscosity, surface tension, chemical potentials providing insights in the fluid and the flow behavior that are usually overlooked. However, this type of simulations forces the downsizing of the geometrical scale towards the nanoscale range, forcing new type of flow dynamics to appear that is not observed at the larger scale. The questions are then:

- Are those simulations accurate? Or is it a ‘new physics’ that is highlighted by those scales?
- How can we use them towards larger scales of wider engineering applications?

So far, it is easier to explore and improve our understanding of the first point. However, there is wide interest in the development of mesoscale methods such as coarse graining DPD [7], multi-scale methods [10] or hybrid methods combining particle based and grid based (continuum) methods [11] illustrated in Figure 2.1 [12] to fill the scale gap.

Figure 2.1: Hierarchical Multi-scale Models [5] (FF : Force Field)
2.2 Single Phase Flow: Non equilibrium Molecular Dynamics

Simple hydrodynamics problems have been extensively simulated using molecular dynamics method. Poiseuille or pressure capillary flow and Couette flow has been given much attention due to their non-homogeneous nature generating slip at solid surfaces as well as for their ease to numerically implement and compare to the classical Navier Stokes hydrodynamic theory. The slip is usually related to the flow momentum and is defined as the velocity difference between the fluid adjacent to the surface and the wall itself. An equivalent definition is also found for the heat flux proportional to the temperature jump between the solid surface and the flow next to it.

Previous studies including: Todd et al [13][18], Mansour et al. [15] and other published reviews [2][16][21] highlighted the importance of the fundamental research based on first principles in understanding the behavior of the fluid layers next to solid surfaces. The general view is that those layers in capillary flows develop characteristics different than the bulk flow which leads to different rates of transfer of particles, momentum and heat across the channels.

Poiseuille nanoflow simulations confirmed that the density is no longer constant across the channels and a layering effect appears especially near the boundaries. They also showed that for channels’ widths lower than 10-fluid diameters, the density, the velocity and the temperature profiles present a qualitative deviation from the continuum predictions [13]. For higher channel widths, qualitative [17] and quantitative [2] agreement with the slip-corrected Navier Stokes theory (originally derived by Maxwell for dilute gases) is found. However, Mansour et al. [15] showed that this is not always true depending on the Knudsen number. For a Knudsen number higher than 0.01 (but still in the continuum regime), the Navier Stokes theory fails to predict the local minimum in the temperature profile at the channel’s center and the non-constant pressure profile, both predicted by the kinetic theory and observed in numerical simulations [14][15].

More and more studies give special care is to the measurements [10] and numerical estimation of the slip values for microflows and nanoflows [5][19][20]. Consequently, surface modeling and their characteristics (wetting, roughness) are
investigated with respect to their direct effect on the slip values. The common observation is that the slip value is not only depending on the surface characteristics but also on the fluid nanostructuring which is due to the geometry, size and indirectly the surface model as well.

2.3 Wetting and Phase Transition: Importance of Surface Modeling:

Usually, the differences between the macroscale and nanoscale profiles occur close to the boundaries and are highly dependent on the wall models. The strength of the fluid-wall interaction (interfacial resistance) and the interface wettability play a major role in the momentum exchange (slip velocity estimation) and the energy exchange (temperature control) and have to be carefully modeled. Wall models can be classified into two categories:

- Implicit wall models: the solid boundaries are not simulated separately but their presence is implicitly imposed on the motion of the particles as a constraining force (specular reflecting wall model, perfectly diffuse reflecting wall model or analytical model [2][15][17][22]).

- Explicit wall models: a molecular structure is given to the wall and is simulated as part of the system. This allows the wall to interact with the flow and evolve in time and space which is a more realistic approach at these scales.

In the literature, a number of wall models falling into the latter category were used for confined nanoflows simulations. Branam [17] grouped atomistic wall models into three classes: one [2][13][23], two and three-zone [24] models depending on how different the treatment of the wall atomistic layers is. The one-zone models are the easiest to implement as all wall particles are treated the same way, interacting with the flow but not with each other. The two and three-zone models are more elaborate and more computational and have originally been developed in the chemistry field where surface effects (adsorption, wetting) and surface chemical reactions (abstraction, etching) are known to enhance reaction mechanisms [25].
The quality of the surface model is also important for capillary studies (fluid absorbed in narrow pores) or film spreading and coatings of materials in order to promote of inhibit flow motion. This type of studies looks for phase equilibrium of single phase fluid confined in nanometer scale pores. The resulting fluid retention is directly related to the layering or fluid sticking to the surface and the transition from a thin to thick wall films denotes a state transition from partial to complete surface wetting that can alter the adsorbate behavior [26].

2.4 Two Phase Coexistence Fluids and Flows in Molecular Dynamics Studies

This is one central research in molecular dynamics where understanding the dynamic behind interface equilibration is crucial for many applications such as phase change heat transfer, spread wetting or material processing.

Several studies involving different fluids, force fields and their characteristics are found in literature. Several works by Vrabec [27][28], Johnshon [29] covering correlations between the fluid equation of state and the computed data showed strong dependency on the conditions in the numerical simulations. Bulk phase pressure data were in general lower than the interface liquid-gas equilibrium data. Also, the equations of state are not indicative anymore of a given fluid but a given parameterized fluid such as a Lennard-Jones 2.5 argon. This is directly related to the pressure computation performed for the study of these interfaces [30][31]. Dependency on the cutoff value was found even though the simulation domains were unbounded. The reason is the existence of the thin interface (liquid-gas) where long range information and corrections vary as rapid and steep change density across the interface [32]. It is expected that bounded two-phase flows are more sensitive to pressure estimation and corrections.
2.5 Molecular Dynamics and Nanojets

Nanoinjection has been studied using molecular dynamics under subcritical conditions [6][17][23][33][35] and supercritical conditions [17][33][34]. Results from these simulations claim that the linear instability theory still holds at the nanoscale liquid flow with a free surface. They highlight that, unlike the macroflow jet breakup that is dynamically induced, thermally triggered fluctuations have a significant effect on the breakup characteristics of nanojets. Hence, it is expected that not only the inertial forces, the cohesive forces (surface tension) and viscous forces [9] do control the breakup regimes but also the interfacial forces (fluid-wall interactions).

So far, nanojet simulations using molecular dynamics are time dependent, hence depending on initial settings. The conditions of injection between published works vary with the different surface models and parameters and it is then hard to confirm and generalize observations [6][35]. Quantitative as well as predictive efforts are in general lacking in those studies because of the multiple “unknowns” that come with the simulations’ settings such as: the change of boundary conditions (usually from periodic boundaries to open, two-phase interfacial boundary), transient phases until steady state are reached and equilibrium can be attained, effect of the surface as well as fluid model and the combinations of multiple phases, introduction of thermostat. It is then crucial to establish a common basic knowledge of the effects of these modeling strategies on the two-phase injection which is the objective of this study.
CHAPTER 3

MOLECULAR SIMULATIONS FOR NANINOJECTION

Molecular simulation is a general term used to describe numerical methods used to solve problems at the molecular/particle level.

In fluid mechanics, this Lagrangian description contrasts with the widely used numerical methods based on solving the Navier-Stokes equations where the macroscopic fluid properties are the dependent variables while the independent variables are the spatial coordinates and time. Another alternative to computational fluid mechanics, to solve the conservation equations for momentum, mass and energy, the Lattice Boltzmann methods model the fluid consisting of fictitious particles, and such particles perform consecutive propagation and collision processes over a discrete lattice mesh. Due to its particulate nature and local dynamics, Lattice Boltzmann methods have several advantages over other conventional CFD methods, especially in dealing with complex boundaries, incorporation of microscopic interactions, and parallelization of the algorithm.

In molecular based models, the goal is to track the positions and/or velocities of the particles forming the fluid at all times. Different molecular simulation methods can be used depending on the application and the focus property chosen.

• Molecular dynamics (MD): a deterministic method that solves for future positions and velocities of the system based only on its current state. It is a very flexible method, easily applied for any geometry and fluid phase and structure (multi-atomic molecules). However, it has a much higher computational cost by comparison to the following methods and will be described in more detail later in section 3.2.

• Monte Carlo Method [36]: a stochastic method that relies on random sampling to compute results. Instead of trying to reproduce the dynamics of a system (positions and velocities), it generates states according to appropriate Boltzmann probabilities for energies by applying the popular Metropolis algorithm. The outcome of each trial move
depends only on its immediate predecessor contrasting clearly with the molecular dynamics philosophy. It is though a much more efficient alternative (computationally) to molecular dynamics though mostly suited to gas and rarefied gas applications and disordered materials.

- Dissipative Particle Dynamics (DPD) [7][37]: Similar to Molecular dynamics, this method does solve for the dynamics of the system. However, DPD is a coarse-grained version of molecular dynamics in which we have the possibility to simulate larger length and time scales. The coarse graining removes the hard core nature of the inter-particle interactions characteristic of molecular dynamics and responsible for the short time scales (~ fentosecond or fs) to ensure stability of the algorithm and replaces it by soft interactions where the interactive potential cannot exceed a maximum value. As a result, in DPD simulations, we lose the molecular details, but for adequate choices of the interactive forces, we are still able to capture physics at the molecular level. Further coarse graining will lead to the macroscale description of the fluid as illustrated in Figure 2.1.

![Figure 3.1: Schematic relationship between the different numerical methods.](image)

Each of these molecular based simulations techniques offers advantages and disadvantages for our application: Nanoinjection simulations. Because our focus will be on the high density phase interactions with the solid surface and the effects of the interactive potential from the wall on the state of the liquid, molecular dynamics is the best choice despite the computational cost induced. The molecular dynamics method remains the investigative tool of the nanoscale and the collective behavior of the particles especially at the interfacial regions and close to singularities.
Once the solid-liquid effects are well understood, it will be easier to transit to DPD simulations in order to reach large systems (higher Reynolds numbers) and longer simulations times (appropriate equilibration time). The advantage of the DPD method over molecular dynamics is relevant only if the simplifications in the physical model are compensated by the reduced number of simulated ‘particles’.

Molecular dynamics simulations are based on first principle laws (Newton equations of motion) where the ordinary differential equations in Eq. 3.1 and Eq. 3.2 are solved for:

\[
\frac{dv_i}{dt} = F_i = F_i^{ext} + F_i^{int} \quad \text{Eq. 3.1}
\]

\[
\frac{dr_i}{dt} = v_i \quad \text{Eq. 3.2}
\]

where \( r_i \) and \( v_i \) are respectively the position and velocity of the particle \( i \) within a collection of fluid particles \( N \). The forces that can be subjected to these particles are usually conservative forces and they are based on a theoretical model of the system. Those interactions are essentially pairwise interactions but three body forces are sometimes included. Pairwise interactions are either interactomic forces based on force fields already defined in the literature or external forces due to gravity, pressure gradients or electromagnetic forces. It can include bonded interactions such as harmonic and torsion forces or non-bonded interactions such as electrostatic and van der Waals forces [38]. The range of influence of these different forces can vary depending on its nature (covalent forces are the shortest versus the electrostatic forces that are the longest in range) consequently varying the computational cost. Because the focus of this work is the surface models on a given fluid, there is no need to introduce more degrees of freedoms due to a polyatomic fluid. The working fluid used here will be argon, not only because it is monoatomic in structure but also because it is one of the most widely studied fluids experimentally in comparison to molecular simulation work. As a result, the interactive potential between this fluid’s particles as well as its parameters are well documented as discussed in section 3.3.3. Sometimes, not all the atoms within a molecule have to be simulated. Particles can also represent a minimal number of atoms such as the United
Atoms model. For example, -CH3/-CH2 groups in polymers or hydrocarbons chains are represented as single united particles to alleviate a portion of the computational cost without affecting the physical outcome of the simulations.

Generally, molecular dynamics simulations contain a set of units intimately related to the theoretical model and that determine the thermodynamics properties for a given fluid. It is common to work with non-dimensional units (reduced units) molecular dynamics because of the transferability of the numerical results from one fluid to another.

Another advantage cited for such simulations is the fact that using dimensional ones involving very small numbers (which is the case for dimensions and scales at the molecular level), the round off errors could be important especially early on in the development of these numerical methods. Today, computer advancement offers higher precision for representing numbers which removes the accuracy issue. The codes developed for this work are dimensional.

### 3.1 Inter-Particle Interactions

As stated earlier, argon is chosen as the working fluid. The choice of argon is motivated by its simplicity to code (rare gas, no charges and single atom) and therefore lower computational cost and known properties (extensive experimental data). Besides, the form of the intermolecular potentials for argon has been one of the most studied since the argon atoms have the important attributes of spherical symmetry, almost classical behavior (minor quantum corrections are necessary for its properties) and availability for testing. Therefore, the argon parameters for many potential forms are well known [39] allowing us to focus our study only on the surface modeling and the discrepancies from one model to another while limiting the numerical deviation due to the simulation of a more complex working fluid.

In molecular simulations, van der Waals forces account for all interactions between the atoms for this rare gas and are responsible for all deviations from ideal gas behavior and existence of liquid and solid phases for argon. If those interactions were
studied experimentally (molecular beam experiment), the essential features for these interactions are: a negligible energy at large separation distances, a minimum at an equilibrium distance (0.38 nm for argon) and then a rapid increase of the energy as the distance continues to decrease. This behavior is usually considered to arise from a balance between attractive forces that are long-range and repulsive forces that are short ranged. The Drude model based on quantum studies \[36\] explaining the attractive component of the potential (considered to be a dispersive force) predicts that it varies as \(1/r^6\) for a first order approximation. The repulsive force also can be explained from quantum mechanics using the Pauli principle. The decay of energy varies as \(1/r\) at very short distances but changes to \(\exp(-2r/a_0)\) at larger distances with \(a_0\) is the Bohr radius.

Those dispersive and exchange-repulsive interactions between atoms and molecules can be represented by modeling the inter-atomic potential curve using simple empirical expression that can be rapidly computed. The most common potential representing pair-wise van der Waals interactions is the Lennard-Jones 12-6 potential for a soft sphere description of the particles as presented in both Eq. 3.3 and Figure 3.2.

\[
\phi(r_{ij}) = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] \quad \text{Eq. 3.3}
\]

\(\varepsilon_{Ar}\) is the depth of the well or the minimum energy of the potential corresponding to the equilibrium distance between two close atoms and \(\sigma_{Ar}\) is the hard sphere diameter (two spheres in contact), also called the collision diameter. The attractive component of this potential is consistent with the theoretical power law found by Drude. The repulsive representation though is not supported by strong theoretical arguments. The twelfth power term is found reasonable for rare gases but too steep for other systems such as hydrocarbons. This particular form of the Lennard-Jones potential is popular versus other lesser steep potentials such as LJ 10-6 or LJ 9-6, especially for big system simulations, because the repulsive branch is only a square of the attractive branch making it a rapid
calculation. The adjustable parameters \((\varepsilon_{Ar}, \sigma_{Ar})\) allow better correlations of the potential depending on the conditions of the working fluid used as discussed in 3.3.3.

Other potentials do include the exponential contribution at short distance such as the Buckingham potential but its drawback is it becomes steeply attractive at very short distances. An exponential representation of the energy decay is also a much more expensive operation numerically. The conservative inter-atomic force is defined as the gradient of the potential and is expressed in Eq. 3.4.

\[
F(\mathbf{r}_ij) = -\nabla \phi(\mathbf{r}_ij) = 24 \varepsilon \left[ 2 \left( \frac{\sigma}{\mathbf{r}_{ij}} \right)^{12} - \left( \frac{\sigma}{\mathbf{r}_{ij}} \right)^6 \right] \frac{\mathbf{r}_{ij}}{\mathbf{r}_{ij}^2}
\]

Eq. 3.4

It is important to note that for polyatomic systems, the determination of van der Waals parameters can be difficult and time consuming and so it is common to assume that parameters for cross interactions can be determined from parameters of the pure atoms using mixing rules. In the commonly used Lorenz-Berthelot mixing rules, the collision diameter is the arithmetic mean of the values of the pure species and the well depth is given by the geometric mean [38].

Figure 3.2: Lennard-Jones Potential Energy for soft sphere interaction.
3.2 Numerical Implementation of Molecular Dynamics

3.2.1 Integration Scheme for the Equations of Motion

As mentioned earlier, Newton’s equations are solved for in order to compute both positions and velocities of the particles and track their progress in time hence determining multiple system configurations. The choice of the time integration routine is therefore crucial in order to achieve different criteria: simplicity (ease to code), stability (long term energy equilibration), efficiency (rapid system progress without divergence) and reliability (handles a wide range of conditions and potentials). One extra characteristic the algorithm should also have is time reversibility.

For molecular dynamics systems, different algorithms satisfying these requirements were developed and can be classified into two categories: the Gear-Predictor-Corrector algorithms and the leapfrog algorithms. The accuracy produced by the Gear type of algorithms is higher than the one produced by the leapfrog type but this advantage in accuracy decreases as the time step size and the duration of the simulation increases. The most widely used integrator is the velocity Verlet algorithm that belongs to the leapfrog algorithms and provides a third order precision on the position calculation and second order on the velocity. The velocity Verlet algorithm \[41\] is a two step routine and is summed in Eq. 3.5:

\[
\begin{align*}
  r(t + \delta t) &= r(t) + \delta v(t) + \frac{1}{2} \delta^2 a(t) \\
  v(t + \delta t) &= v(t) + \frac{1}{2} \delta (a(t) + a(t + \delta t))
\end{align*}
\]

where \( r \) is the position, \( v \) is the velocity, \( a \) is the acceleration related to the computed force as following: \( a(t) = \frac{f(t)}{m} \) and \( \delta t \) is the time step.

In molecular dynamics, the stability of any algorithm is dependent on the choice of the time step which is in return dependent on the force field used. The time step must be smaller than the smallest time modeled by the force field. For example, short range
forces vary faster than long range forces and do need shorter time steps; the highest frequency vibrations are due to bond vibrations.

On one hand, if the time step is too small, the trajectories will cover only a limited proportion of the phase space. On the other hand, if the time step is too large, instabilities may arise from high energy overlaps between atoms (leading to program failures due to numerical overflow as well as loss of energy/momentum conservation). Previous work by Branam [17] showed that the range 2.5 fs up to 10 fs is stable and fairly accurate for the velocity Verlet algorithms for argon simulations. It is worth noting that the time step does not need to be the same for those two force categories; the forces can be computed at different frequencies.

3.2.2 Periodic Boundary Conditions

The periodic boundary conditions are adopted to overcome the difficulty to model surface interactions with the fluid in a given simulation. They also allow the study of bulk properties with molecular simulations with limited number of particles versus surface-influenced properties that are dominant at the nanoscale.

The implementation of the periodic boundary conditions requires only an initialization of fluid particles in a box and then, during the simulation, each particle interacts not only with particles inside the box (basic cell) but also with the duplicate particles existing in the images of the simulated box (Replicas) in the three directions (images are “created” by translation of the whole box in the three directions) as illustrated in Figure 3.3.
Periodic boundary conditions work well only for short range forces. The minimum size of the basic cell has to exceed the sphere of influence of the potential; otherwise particles’ effects would be counted twice in the integration process.

We note here that those boundaries can be applied for only one or more open dimension of the system and do not require the starting cell shape to be cubic. Actually, five possible shapes can be used to apply these boundaries (satisfy translation operations). The most used ones are: the cubic and the truncated octahedron. The choice of the starting cell has to be consistent with the underlying geometry of the simulated system such as a spherical droplet system is usually started with a truncated octahedron or a rhombic dodecahedron cell and not a cubic or rectangular cell.

3.2.3 Neighbor Lists

Another advantage of the use of short ranged potentials in molecular dynamics simulations is the use of neighbor lists [38]. Since the most time consuming part of a numerical simulation is the computation of non-bonded interactions (between every pair of atoms in the system), these short ranged potentials such as the Lennard-Jones 12-6 potential fall off very rapidly and reach only 1% of it value at a distance $2.5 \sigma_{Ar}$. Therefore, it is computationally efficient to only compute the forces within a non-bonded cutoff distance and disregard or correct for the long range effects if relevant. This feature combines well with the periodic boundary conditions though it requires the minimum size for the basic cell to be larger than twice the cutoff value (minimum image convention).
This by itself is not time saving since it still requires verifying if the distances between each two atoms of the system fall either beyond the cutoff distance or not. However, if we “knew” which atom’s neighbors fall within the cutoff range or range of influence, it is not needed to verify those distances for all particles every time step but only during a adequate choice of frequency or cycles (commonly every 10 to 20 time steps). Clearly, there will be a tradeoff between the size of the cutoff and the frequency of updating those lists as well as possible storage complications if the cutoff range is too large.

Arrays, also called Neighbor lists, storing the particles within the sphere of influence for each particle are then created and will be used to compute the forces every time step which still consists a very expensive part of a molecular dynamics codes. This allows the change of the force computation routine scaling from \( O(N^2) \) every time step to \( O(N) + \frac{1}{f} O(N^2) \) with \( N \) the number of particles in the system and \( f \) the number of cycles between Neighbor lists updates.

### 3.2.4 Parallelization

Molecular dynamics simulations are very convenient for the parallelization of their algorithms which is the reason behind the viability of these numerical methods. The most expensive task in those simulations is the forces’ computation and this task can be performed simultaneously over multiple processors.

As presented in the previous sections, using cutoff distances and neighbor lists are two ways to limit the force computational cost. Still, in order to reach larger systems and longer simulations times, the main task remains the computation of a force matrix represented in Figure 3.4.
Each term of the matrix corresponds to an interaction between a particle in the corresponding row and a particle in the corresponding column. A truncated potential means that most terms in the matrix are zeros. Clearly, the matrix is skew symmetric due to Newton’s third law for pairwise interactions.

Parallelizing a code does alleviate the *Computation* cost per processor, but does introduce a new cost: *Communication*. Communications between processors are necessary to synchronize and perform tasks that require information from other processors. The performance of a code on a cluster is hence depending on the number of processors, the capability of each processor and the bandwidth between the processors. Three possible ways to parallelize the codes can be used \([44]\) and each method has different computation, communication and memory costs and requirements.

The first and most straightforward method is the atom decomposition, AD, where the atoms are distributed evenly on the processors. Communications between the processors are very costly in this case, since it requires the broadcasting of the particles’ positions and sometimes flags to all processors in order to create the neighbor lists. Velocities are usually not needed to be communicated because the forces are computed independently of them (unlike the case in DPD).

The second method and the most complex to implement is the domain/space decomposition, SD. In this case, the physical domain is decomposed into volumes and each volume is attributed to a processor. This allows the limitation of the communication to only the particles of influence to the adjacent domains. This method is the most...
efficient in homogeneous fluid applications and short range interactions which is the case in most of molecular dynamics simulations of non charged particles. The homogeneity ensures the equal computational load between the processors.

The last method and the one used in our study is the force decomposition: FD. In this case, it is the force matrix that is decomposed into blocs of the size \( \frac{N}{P} \) and each processor is responsible for computing the forces for its block as represented in Figure 3.4. The communication load in this method is lower than the atom decomposition case. It requires the transfer of information between processors within one row and/or one column of the block matrix of the size \( \frac{N}{\sqrt{P}} \) instead of \( N \). However, the communication cost here is larger by comparison to the domain decomposition method. The net advantage of this method though is its equal load on all processors for all system configurations and all types of interactive forces. The differences in computational costs between these methods are gathered in Table 3.1 [44]. All these costs become even more important if longer ranged forces are included.

For the specific simulation of nanojets which is the objective of this work, where liquid, solid and gas phases are arranged inhomogeneously in space, densities can change dramatically from one region to another which makes the force decomposition the most computationally efficient method to implement.

<table>
<thead>
<tr>
<th>Algorithm</th>
<th>Computation</th>
<th>Communication</th>
<th>Memory</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>( \frac{N}{P} + N )</td>
<td>( N )</td>
<td>( N )</td>
</tr>
<tr>
<td>FD</td>
<td>( \frac{N}{P} + \frac{N}{\sqrt{P}} )</td>
<td>( 3 \frac{N}{\sqrt{P}} )</td>
<td>( 3 \frac{N}{\sqrt{P}} )</td>
</tr>
<tr>
<td>SD</td>
<td>( \frac{N}{2P} + 6r_s (\frac{N}{P})^{2/3} )</td>
<td>( 6r_s (\frac{N}{P})^{2/3} )</td>
<td>( \frac{N}{P} + 6r_s (\frac{N}{P})^{2/3} )</td>
</tr>
</tbody>
</table>

Table 3.1: Scaling Properties for the Parallelization Methods

It was observed though [58] that in a given number of processors, the top performance is achieved when we do not fully use all the processors in a node but
instead, we use more nodes. An example of this observation is shown Figure 3.5. This effect should be more pronounced as the number of processors increases.

Distribution of the Computational Time over 16 Processors

![Distribution of Computational Time](image_url)

Figure 3.5: Computational Time Variation with the Number of Cores per Node Used

The figure shows that for the same number of total processors used, the variation of the number of processors or cores per node does have no effect on the force and neighboring computational times but affects only the time needed to communicate the information between the processors. The clear trend is the lesser number of cores per nodes are used, the shorter the communication and consequently the overall time.

This effectively provides more memory bandwidth to each processor and improves the network latency experienced by each node/processor. Wise programming would use additional processors for non-network and low memory tasks.

In general however, running with fewer than maximum number of processors per node reduces overall throughput of a computer cluster and is not recommended. The cluster available to run this work includes 22 nodes of 4 CPUs of 1.8GHz (2 Dual Cores) with communications using a TCP/IP 1GB Ethernet.
3.3 Thermodynamic Properties and Model Parameters

3.3.1 General Thermophysical Properties

A wide variety of thermodynamic properties can be calculated from computer simulations; a comparison of experimental and calculated values for such properties is an important way in which the accuracy of the simulation and the model used can be quantified. Eventually, these simulations can enable predictions for thermodynamic properties of systems where no available experimental data.

According to statistical mechanics, as the simulations reach a steady state corresponding to equilibrium, thermodynamic properties such as temperature, internal energy and pressure can be computed from the following [38]:

- **Temperature:**
  \[ T = \frac{1}{3Nk_B} \left( \sum_{i=1}^{N} m_i \left( v_i - v_k \right)^2 \right) \]  
  Eq. 3.6

- **Internal energy:**
  \[ U = \frac{3}{2} Nk_B T + \left( \sum_i \sum_{j > i} \phi(r_{ij}) \right) \]  
  Eq. 3.7

- **Pressure:**
  \[ P = \frac{N}{V} k_B T - \frac{1}{6V} \left( \sum_{i \neq j} \sum \frac{\partial \phi(r_{ij})}{\partial r_{ij}} \cdot r_{ij} \right) \]  
  Eq. 3.8

The angle brackets indicate ensemble averages or expectation values; that is the average value over multiple replications/configurations of the ensemble produced by the simulation. Molecular dynamics is traditionally performed under conditions of constant number of particles \( N \), volume \( V \) and energy \( E \): the microcanonical/constant \( NVE \) ensemble. However, it can be modified to sample from other ensembles:

- **Canonical Ensemble:** constant \( NVT \)
- **Isothermal-isobaric Ensemble:** constant \( NPT \)
- **Grand Canonical Ensemble:** constant \( \mu VT \) with \( \mu \), the chemical potential.

For these ensembles, the thermodynamic properties such as temperature and pressure have the same expressions from one ensemble to another as they constitute a first order
derivative of the free energies. This becomes untrue for the second order derivative properties such as heat capacities with expressions depending on the ensemble considered. The temperature is defined from the particles kinetic energy. The internal energy corresponds to both the kinetic and potential energies (\( \phi(r_i) \) is the conservative potential).

The pressure is usually calculated in a computer simulation via the virial theorem of Clausius [36]. The virial is defined as the expectation value of the sum of the products of the coordinates of the particles and the forces acting on them. The virial theorem states that the virial is equal to \(-3Nk_B T\). In an ideal gas, the only forces are those due to interactions between the gas and the container and it can be shown that the virial in this case is equal to \(-3PV\). Hence, it is consistent with the equation of state for an ideal gas. Forces between the particles in a real gas or liquid affect the virial and thus the pressure. The first term of Eq. 3.8 corresponds to the kinetic contribution to the system pressure and the second term corresponds to the non-ideality contribution due to the inter-particle interactions. This shows that the definition of the pressure is intimately related to the form of the conservative potential. Another form of the pressure based on the pair distribution function: \( g(r) \) is shown in Eq. 3.9 and is equivalent to Eq. 3.8 for steady state.

\[
P = \frac{N}{V}k_B T - \frac{2}{3V}\pi N \rho \int_0^\infty r^2 \frac{\partial \phi(r)}{\partial r} g(r) dr \quad \rho \text{ is the number density} \quad \text{Eq. 3.9}
\]

The pair distribution function characterizes the fluid structure and corresponds to the probability of finding a pair of atoms a distance \( r \) apart relative to the probability expected for a completely random distribution at the same density.

As stated before, when the fluctuation-dissipation condition is used, the above definitions hold for molecular dynamic simulations [38]. Also, because of the pair-additive potential used, the virial formula holds whenever periodic boundary conditions are used which might become untrue (additional terms needed) once more complex force fields are used [57]. The virial equations are not suited for “inhomogeneous” fluids; that includes highly structured fluid in very narrow slits or fluids subject to external forces.
such as gravity forces [18]. In those cases, higher order virial terms have to be added to account for the rapid structural change in the system.

To summarize, the virial approach based on the internal interactions of the discrete atomic particle system correctly evaluates the macroscopic pressure; an external surface force acting on the continuum permeating the spatial region occupied by the system, only under three conditions [62]:

- The system is in steady motion: the system is in statistical equilibrium and no pressure waves (disturbances) reverberate in the molecular system (mathematically, this can be written as $\frac{d^2}{dt^2}(\vec{r}_i \cdot \vec{v}_i) = 0$).

- The pressure is to be interpreted in a time-averaged as well as volume-averaged sense: the fluctuations at the molecular level are assumed to average out over time and space.

- The pressure $P$ must be recognized as the average external force per unit area on the wall of a physical container holding the atomic system. This condition reflects that the virial theorem provides an effective measure of the structural interaction between the gas system and the external wall.

### 3.3.2 Cutoff Effect and Long-term Corrections

The introduction of a cutoff distance to limit the computational load is validated by the fact that most choices of interatomic potential (except the electrostatic potential) are effectively short ranged and decrease quickly as the interatomic distance increases. However, properties like energy and pressure/stress are affected by the loss of the contribution of faraway particles. Also, the cutoff does introduce a discontinuity in both the potential and the force near the cutoff value. For example, the effective, spherically truncated Lennard-Jones potential used has the form proposed in Eq. 3.10 and shows an abrupt change from a finite value of the potential to zero at the cutoff distance.
Mathematically, this potential should produce an impulsive force at the corresponding point. Therefore, the energy conservation is not satisfied and the molecular dynamic simulations results do not strictly represent the microcanonical ensemble.

\[
\begin{cases}
\phi_{\text{LJ}12-6}(r_{ij}) & r_{ij} < R_c \\
0 & r_{ij} \geq R_c
\end{cases}
\]  
Eq. 3.10

Several ways to counteract the effects of these discontinuities are found in literature. One way is the use of a shifted potential as shown in Eq. 3.11 or the use of the shifted potential and force as in Eq. 3.12. The additional term added in the second form of the potential is a constant that correspond to the Lennard-Jones 12-6 value of the potential at point \(r=R_c\) so that the potential at that point is continuous. This implies that the energy is conserved and no correction is needed. However, in molecular dynamic simulations, the forces remain discontinuous at the cutoff point and the dynamic of the system does not take into account the energy correction.

It is interesting to note though that unlike molecular dynamics simulations, the Monte Carlo method is based on the energy to define the distribution of particles each time. This means that the use of the shifted potential successfully restores the system configurations to the corrected energy level. Eq. 3.12 gives one example of a shifted potential and shifted force Lennard-Jones 12-6. The objective of such a form is to construct a potential that ‘smoothly’ goes to zero at the cutoff so that the system does not feel discontinuities/impulses. However, this shift makes the potential deviate from its “true” form and so any thermodynamic properties will be changed.

Another way to eliminate the discontinuity effects is the use of a switching function (usually polynomial) that multiplies the “real” potential over the whole or a
limited range of the potential. It has a value 1 for most of the range of influence of the potential and then goes “smoothly” to zero through a polynomial function.

In our work, we use mostly the unshifted potential. Therefore, long term corrections, mainly for the potential energy and the pressure, have to be introduced. This can be easily deduced from equation Eq. 3.9 if we assume that beyond the cutoff distance, the pair distribution function $g(r) \approx 1$ and the correction term is given by Eq. 3.13. These corrections are true for a bulk fluid description so that the radial distribution is of the order one assumed is valid. Also, these tail terms are density dependent and hence, for two or more phases, it is difficult to use these formulas to account for the long range effect locally [32]. In those cases, the long range corrections are not used and the cutoff distance becomes a “property” of the fluid in the numerical experiment [27].

$$E_{corr} = 2\pi N\rho \int_{rc}^{\infty} r^2 \phi(r) dr = \frac{8}{9} \pi \rho N \sigma^3 \left[ \frac{\sigma}{R_c} \right]^9 - 3 \left( \frac{\sigma}{R_c} \right)^3$$

$$P_{corr} = -\frac{2}{3V} \pi N\rho \int_{rc}^{\infty} r \frac{\partial \phi(r)}{\partial r} dr = \frac{32}{9} \pi \rho^2 \sigma^3 \left[ \frac{\sigma}{R_c} \right]^9 - 3 \left( \frac{\sigma}{R_c} \right)^3$$  \hspace{1cm} \text{Eq. 3.13}

$\rho$ : is the number density

Those thermodynamic corrections are numerical corrections that allow matching the full Lennard-Jones potential results starting with a truncated Lennard-Jones model. In molecular dynamics however, the corrections cannot be translated to the simulations themselves and do not affect the trajectories and distributions of the fluid particles and consequently the data averaged from the simulations remain those of a cut Lennard-Jones potential.

We will explore a new modified potential inspired by the switching function idea in order to “restore” the deficit of pressure due to long range contribution in the dynamic of the molecular dynamic systems simulated for dense phases section 4.3.
3.3.3 Model Parameters Determination

The parameters defining the strength of the conservative Lennard-Jones potential in the case of molecular dynamics simulations are intimately related to the thermodynamic properties of the working fluid.

Molecular dynamics simulations have a set of units that are inherently dependent on the property of the fluid and therefore they control the accuracy as well as the stability of the algorithm. The major sources of errors in the outcome of a molecular dynamics simulation is the choice of the cutoff, parameters of the Lennard-Jones potential, the integration time step in addition to the numerical errors introduced by the choice of the integration routine and the frequency of the updates of the neighbor lists. Any additional models introduced in the system will obviously affect the accuracy as well (in our work, wall models or modified potentials for fluid confinement).

The parameters for the Lennard-Jones potential are usually determined from experimental data to match the virial equation of state. In fact, the equation of state in virial form \([46][47]\) is expressed in Eq. 3.14
\[
P V = N R T \left[ 1 + B \left( \frac{N}{V} \right) + C \left( \frac{N}{V} \right)^2 + \ldots \right]
\]

\[\text{B : the second virial coeff.} \]
\[\text{C : the third virial coeff.} \]

Eq. 3.14

In this form, the pressure corresponds to a power function of the number density. Comparing Eq. 3.14 to Eq. 3.8, the relationship between the second virial coefficient \(B\) and the parameters defining the Lennard-Jones potential is easily seen. The experimental data are usually fit to a polynomial and then an estimate of the second virial coefficient is extracted. Thanks to mathematical approximation, the value of \(\varepsilon_{Ar}\) and \(\sigma_{Ar}\) are extracted. The value of \(\sigma_{Ar}\) is fixed to 0.34 nm. However, the well depth value lies in the range: \(\varepsilon_{Ar}/k_B = 119.8\ \text{K-125.2 K}\). The differences are due to the experimental data ranges (low temperature range or high temperature range), where the polynomial fit is done and the degree of the polynomial itself. Besides, at low pressure, effects like adsorption occur and corrections are made to account for this loss. The upper limit of the range accounts also for quantum effects and third order interactions.
The value we use (common in most publications) is $\epsilon_{Ar}/k_B = 121$ K corresponding to $\epsilon_{Ar} = 1.67 \times 10^{-21}$ J. The time step chosen for the simulation is 2.5 fs though for argon; it was showed that time steps up to 5 fs still gives stability and accuracy. The effect of cutoff will be studied later and results will be presented in Chapter 5.

### 3.3.4 Time Correlation and Sampling Rate

A molecular dynamics simulation provides data values at specific times. This enables the value of some property at some instant to be correlated with the value of the same (auto-correlation) or another property (cross-correlation) at a later time $t$. The resulting values are known as time correlation coefficients shown in Eq. 3.15

$$C_{xy}(t) = \langle x(t)y(0) \rangle$$  \hspace{1cm} Eq. 3.15

An autocorrelation function indicates the extent to which a system retains a ‘memory’ of its previous values. In general, a normalized correlation coefficient has an initial value of 1 and a zero value at long times. The time taken to lose the correlation (1->0) is called the relaxation time. Therefore, quantities with small relaxation times can be determined with greater statistical precision as it will be possible to include a greater number of data sets from a given simulation. Usually, transport properties such as shear viscosity or thermal conductivity have long correlation times and require large sampling intervals. Temperature, pressure and energy are sampled each 200/400 time steps during the production phase of the simulation for over 200,000 total time steps (depending on the system size). Production phase is the phase where the system reaches its equilibrium.
3.4 NVT ENSEMBLE: Thermostats Models

Molecular dynamics is by nature a microcanonical method; solving Newton’s equations of motion keeps the system at constant energy. Most simulations used in this work will be conducted in the NVE ensemble. Hence, temperature and pressure are thermodynamics properties we monitor to establish equilibrium conditions of the phases simulated. However, for example, if flowing conditions are simulated, energy is added to the system in the form of an acceleration to model the effect of a pressure gradient in a one direction which changes the global value of the energy which should not be the case. Therefore, extending molecular dynamics systems to NVT ensembles seems to be required especially when high accelerations are desired. Another advantage to the use of the temperature thermostat is avoiding the steady energy drift caused by the accumulation of numerical errors observed in molecular simulations (important for identification of stable molecules’ configurations)

The aim of the thermostat is to maintain a control on temperature and consequently the kinetic energy within the system. The way this control is maintained is critical in the way it may affect the dynamic behavior of the whole system. We present the most popular thermal control routines for molecular dynamics simulations and we will address their effects on our simulations in Chapter 5.

3.4.1 Velocity Rescaling

The easiest way to remove heat from the system and “force” the system to a prescribed temperature is to simply rescale the particles’ velocities to the targeted temperature. It just requires a frequent or systematic scaling of the velocity by the ratio of the target to the instantaneous temperatures and the associated change in temperature is as following:
Clearly, this control method is easy to code. However, this thermostat is too “crude” and does not correspond to any statistical ensemble since it does not allow temperature fluctuations for finite systems. It also alters the physical trajectories of the particles and this change is expected to be more pronounced for high acceleration cases.

### 3.4.2 Berendsen Thermostat

Another category of temperature control methods is the coupling of the system with an external thermal bath with fixed temperature $T_0$. For the Berendsen thermostat, the velocities are scaled at each step such that the rate of change of temperature is proportional to the difference in temperature [61] as following:

\[
\frac{dT(t)}{dt} = \frac{1}{\tau} (T_0 - T(t))
\]

with $\tau$ the coupling parameter which determines how tightly the bath and the systems are coupled together. This method gives an exponential decay of the system to the desired temperature. The change in temperature is hence given as:

\[
\Delta T(t) = \frac{\delta t}{\tau} (T_0 - T(t))
\]

In the limit of $\tau \to \infty$, the thermostat is inactive and the simulation samples a microcanonical ensemble. In the other hand, a value of $\tau$ too small will cause unrealistic low temperature fluctuations. The limit of $\tau$ equal to the time step $\delta t$ is the case of the velocity scaling (typical values are: $\tau \approx 0.1 \text{ps}$). This thermostat is also easy to implement and does prevent long time energy drift but it does not reproduce the canonical ensemble since fluctuations do not correspond to any statistical ensemble.
3.4.3 Andersen and Nose Hoover Thermostats

Two classes of methods for fixing the system temperature that produce fluctuations according to the canonical ensemble when properly implemented are the stochastic collisions method, Andersen thermostat, or the extended system method, Nose Hoover Thermostat. Both methods are based on the idea of a coupling with a heat bath. The idea behind the Andersen control \cite{36} is replacing at a certain frequency, the velocities of randomly chosen particles from a sampled value from a Maxwell Boltzmann distribution at the desired temperature. This represents stochastic collisions with a heat bath. The disadvantage of such a control is that this thermostat randomly de-correlates velocities and the dynamic is therefore not physical.

The Nose Hoover thermostat considers the bath to be part of the simulated system (hence the ‘extended system’) \cite{36}. Based on the extended Lagrangian approach in which an additional dynamic variable or degree of freedom, \( s(t) \), is added to the system Hamiltonian and for which an equation of motion can derived. The reservoir potential and kinetic energies are respectively given in Eq. 3.19 (\( f \) is the physical number of degrees of freedom = \( N_{df} \)):

\[
U = (f + 1)k_B T \ln(s) \quad K = \frac{Q}{2} (ds/dt)^2
\]

Eq. 3.19

\( Q \) is considered to be the mass of additional degrees of freedom. The magnitude of \( Q \) controls the coupling between the system and the reservoir and thus influences the temperature fluctuations:

- If this value is large, then the energy flow is small. The infinite limit is the NVE ensemble.
- If the value is small, the energy oscillates unphysically, causing equilibration problems.
The Modified algorithm for this extended system is as following [59]:

\[
\begin{align*}
    r(t + \Delta t) &= r(t) + \Delta t \dot{r}(t) + \frac{1}{2} \Delta t^2 \ddot{r}(t) - \dot{a}(t) \Delta t (a(t) - \dot{a}(t)) \\
    \dot{r}(t + \Delta t) &= \dot{r}(t) + \frac{1}{2} \Delta t \left( \ddot{r}(t) - \dot{a}(t) \dot{r}(t) + \dot{a}(t) \right) - \dot{a}(t) \Delta t \dot{r}(t) \\
    Ln(s(t + \Delta t)) &= Ln(s(t)) + \dot{\xi}(t) \Delta t + \left[ T(t) - T_0 \right] \frac{3 N_{df} k_B \Delta t^2}{2Q} \\
    \dot{\xi}(t + \Delta t) &= \dot{\xi}(t) + \left[ T(t) - T_0 \right] \frac{3 N_{df} k_B \Delta t}{2Q}
\end{align*}
\]

Eq. 3.20

The first step of the velocity Verlet algorithm can be carried out without any problem; however, the second step will not allow the velocities to be integrated exactly. Usually, the Nose Hoover thermostat will require the implementation of a predictor corrector scheme to complete the solution of this second step. The use of a Newton-Raphson scheme will provide rapid convergence of the algorithm with excellent accuracy and relative ease of coding.

This thermostat has the best ‘physical’ control of temperature with a minimum alteration of the physical trajectories. This thermostat would be implemented along with the velocity rescaling method for comparison purposes. It will also be used in the case of high acceleration flow systems.

### 3.5 Nanoinjection: System Configuration and Practical Aspects

As stated in the introduction, we set the objective of this work to be the exploration of how nanoinjection can be studied using molecular dynamics as well as understanding how the different models used would affect the jets’ dynamics, mainly its exit velocity. The desired system configuration to be simulated is presented in Figure 3.6 and corresponds to a liquid phase with an axial flow, directed into a larger, quiescent gaseous volume.
One major characteristic of the problem is the confinement of the different phases. Hence, in molecular modeling, this will require a modeling of the solid surfaces in contact with the different phases. The different wall models used from literature and developed for this work will be addressed in the next chapter. Their effects will be studied mostly for the liquid phase since it is confined in the smaller pores and it has the denser phase.

![Figure 3.6: Simulated Domains in the Injection Configuration.](image)

Usually, the starting configuration of a molecular dynamic simulation for a confined or non-confined fluid will require an initial ‘guess’ of the fluid positions and velocities. One conventional way to initialize the system is to start in an ordered, crystal-like distribution such as a cubic lattice or face-centered cubic lattice. The size of the lattices or number of particles is deduced from the desired density. The velocities on the other hand are sampled randomly from a Maxwell-Boltzmann distribution consistent with the desired temperature, Eq. 3.21. This initial setting will eliminate any initial energy divergence due to spatial overlaps of particles. Each phase is then allowed melting from the ordered phase into an equilibrated state monitored through the energy levels.

\[ g(v) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{mv^2}{2k_B T}\right) \]

Eq. 3.21

If a flow is needed, an external force or a pressure gradient will be imposed axially and the flow will also be allowed to equilibrate with the velocity reaching a steady value. Applying body forces is usually straightforward since it is only an additional term
to the computed inter-atomic forces in the axial direction. However, creating a pressure
gradient is a more challenging effort that will be detailed in the next chapter, in section
4.2. Both phases are equilibrated separately with periodic boundary conditions in the
axial direction. The initial thermodynamic conditions between the two phases are set to
match the liquid-gas coexistence point at that temperature of interest. The initial choice of
the coexistence points or orthobaric conditions is related to the use of body force induced
flow. It was motivated by the desire to control the jet injection velocity: if no initial
pressure difference exists between the phases, then any mechanical imbalance that would
appear will be induced either by the change of boundary conditions or by the exiting flow
field. Those statements will be readdressed in Chapter 5.
CHAPTER 4

NEW METHODS: WALL MODEL, PRESSURE DRIVEN FLOW AND PRESSURE CORRECTED POTENTIAL

As progress was made in this work, the need to investigate certain aspects of the different models implemented or properties assumed became evident. The major aspects reviewed were:

- The wall models and their effects on the dense phase properties, namely the pressure.
- The contribution of the long range correction towards the final jet velocity and the need to ‘reinject’ their contribution into the system.
- The need for the application of pressure driven flows instead of body force acceleration.

In this chapter, details of the implemented models from literature, their shortcomings for this application and the modifications made towards better fitted results are explained. Some of the explicative results will be referred to in the following chapters.

4.1 Wall Models for Molecular Dynamics Simulations: New Wall Development

Two wall models were initially implemented for the study of the effect of the confinement on the dense phase and later on the flow field and nanoinjection. Each model has its advantages and disadvantages either numerically or physically and hence the need for a development of a “tuned” wall model that will match the characteristics for our application. Those models will generally be applied for two geometries: planar and cylindrical (example in Figure 4.3) in order to partially assess the possible effects of the “degree” of confinement on the fluid.
4.1.1 Stochastic Wall Model

The ‘simplest’ wall model applied for mainly gaseous phases is to impose an implicit, perfectly diffusive boundary to the fluid. This so called “stochastic” boundary was developed by Ciccotti and Tenenbaum [3] and has the clear advantage of replacing a dynamic/static molecular wall with a smooth surface with the appropriate hydrodynamic conditions to replicate the scattering occurring from any rough, real surface. The diffuse effect of this wall model is shown in Figure 4.1 and the corresponding Newton’s equation to be solved for a particle rebounding from the wall is as following:

\[ m_i \frac{d^2 r_i}{dt^2} = - \sum_{i \neq j}^{j=1,N} \nabla \phi(r_{ij}) + f_w(r_i) \quad i = 1, N \]  

Eq. 4.1

where \( N \) is the molecular dynamics system size, \( \phi(r_{ij}) \) is the Lennard-Jones interatomic potential and \( f_w(r_i) \) is an impulsive, stochastic force acting on the particle only when it crosses the limiting boundary. The actual effect of this force is to move a particle that has traveled outside the desired physical domain back at its edge, at the point where it crossed as presented in Figure 4.1. This particle acquires a new velocity vector: the tangential component is sampled from a Maxwell Boltzmann distribution characteristic of the wall temperature and the normal component is sampled from a Rayleigh distribution at the same wall temperature to redirect the particle towards the fluid.

Figure 4.1: Schematic representation of a Stochastic Wall Model

This specific case where all particles change their tangential momentum if they intercept the wall boundary corresponds to the extreme case of perfectly reflective surface. Usually, the parameter controlling the proportion of molecules selected to undergo the thermalization process is called the tangential momentum accommodation
coefficient $f$ and varies between 0 and 1. If $f=1$ (this case), then 100% of the particles colliding with the surface are thermalized and all linear momentum is removed of the fluid at the wall. This however does not insure the no-slip value of the velocity at solid boundaries as known from continuum fluid mechanics because of the local effect of the surface on the fluid.

This wall model was used to study thermodynamic properties for a single phase fluid and proved efficient to thermalize simple systems to the targeted temperature with low computational costs. Since the gaseous phase corresponds to a relatively low density phase with no momentum, the stochastic boundary is successful in achieving equilibration at the desired temperature. Besides, this region is chosen to be significantly larger so that the solid boundaries do not affect the coexistence region. Therefore, from the computational point view, the stochastic boundary is the best model for the confinement of the gaseous phase. The implementation of the stochastic boundary in the algorithm is very straightforward. It requires a geometrical shift in the particles coordinates back at the edge of the domain along the incoming direction and a sampling of velocity as explained earlier.

Though very easily implemented with little cost over the simulation run, this model shows physical limitations. Under flowing conditions, this model showed its limit at predicting the velocity slip values at the wall especially for dense fluid where the momentum is higher close to the wall [2]. Besides, this wall model is unable to remove excess heat produced by a body force under flowing conditions.

4.1.2 Atomistic Wall Model

A more realistic approach to wall modeling is to explicitly incorporate a molecular structure to the wall. The molecular wall model chosen in this work includes three zones [24]:
• A reactionary zone that interacts with the fluid molecules using a Lennard-Jones solid-fluid inter-atomic potential.

• A stochastic zone that maintains the wall temperature using a 3D Langevin thermostat developed by Tully [40].

• Finally, a stationary zone that imposes the geometry and the size of the structure in which the particles are fixed into their lattices.

The molecules in both the reactionary and stochastic zones are allowed to vibrate around their original lattices using harmonic forces to connect them (illustration in Figure 4.2). Other interatomic potentials can be used instead of a spring potential such as a Lennard-Jones potential but for moderate temperatures, the spring potential was shown to be efficient numerically and computationally. Two geometrical representations of the atomistic wall model as set up numerically are presented in Figure 4.3 using the visualization software VMD for a flat and axisymmetric configurations.

The stochastic and stationary zones do not directly interact with the fluid but are crucial in maintaining the system to the constrained geometry through the fixed outer layer and the desired temperature through the Langevin thermostat. The equation of motion for each wall particle in this model has the form:

\[
\frac{dp_i}{dt} = -5p_i(t) + f(t) + F_R(t) \quad i = 1..N
\]  

Eq. 4.2

where the first term on the right hand side corresponds to the damping effect and the third term is the random force. Those two forces act only on the stochastic zone particles.
(second or thermal wall layer). The second term corresponds to the interaction forces combining the harmonic forces between the neighboring solid particles and the Lennard-Jones forces corresponding to the fluid particles acting only on the reactionary zone particles. The random force is sampled from a Gaussian distribution with zero mean value and a standard deviation \( \sigma = \sqrt{2 \xi k_B T_w / \delta t} \). \( T_w \) is the targeted temperature for the wall, \( k_B \) is Boltzmann constant \( \delta t \) is the integration time step and \( \xi \) is the damping factor or Langevin parameter. The concept behind these two zones is that the excess/loss of energy from the fluid is transmitted to the reactionary zone and then to the thermal zone through lattice vibrations (harmonic forces). The dissipated energy from the reactionary zone is then balanced by the fluctuating force in order to maintain the desired temperature in the reactionary layer. Therefore, the choice of the spring constant and the Langevin parameter coupling the damping and the random forces are depending on each other through the fluctuation-dissipation principle in order to reach the target temperature \( T_w \).

![Figure 4.3: Cylindrical and Planar Geometries for the Atomistic Wall Model. The three set of layers are color coded: Blue for reactionary layers, Grey for stochastic layers and Red for fixed layer.](image)

This wall model, including three zones, has many advantages. In fact, it is a realistic description of the wall model that has the same "accuracy" as the fluid model. The wall is an incorporated component of the system to simulate and its dynamic is allowed to evolve due to the presence of the fluid. Also, instead of a non-physical
thermostat based on the rescaling of the particles’ velocities, the Langevin model allows one to adjust the wall parameters to remove excess heat especially at elevated accelerations of the flow. Besides, the fluid particles are not directly influenced by the Langevin model since the random and damping forces act only on the external layers of the wall which preserves the physical nature of the interfacial interactions between the liquid and the solid boundary. The major obstacle in using this model is the computational cost that is involved in tracking the dynamics of the particles within the higher density solid wall model. Usually, in molecular dynamics simulations, the computational resources have to be awarded towards the focus application of the study which is, in our case, the single and two phase flow behavior. This model will be used to improve our understanding of the surface effects on the flow field but is not viable for the cases of larger system simulations.

The atomistic wall, through its interactive solid-fluid potential, can exhibit either wetting or non-wetting properties depending on the choice of its parameters. Wetting characteristics is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. The degree of wetting (or wettability) is determined by a force balance between adhesive (solid-fluid forces) and cohesive forces (fluid-fluid forces). From Eq. 4.3, the Lennard-Jones potential is modified with the introduction of two parameters: $\alpha$ and $\beta$. Decreasing the value of $\alpha$ decreases the strength of the interfacial interaction by comparison to the fluid-fluid interaction. However, decreasing the parameter $\beta$ weakens the attractive portion of the potential and the repulsive part becomes dominant leading closer to a non-wetting surface. Wetting surfaces produce undersaturated density profiles (average density value is higher than the centerline density across the channel). This observation provide a visual test to check if the fluid-wall parameters/model correspond to a wetting or non-wetting surface.

The wettability of the surface will have dramatic effects on the fluid state in confined configurations and consequently on the two-phase nanoflows. Those model parameters will be adjusted in order to satisfy the desired fluid state for quiescent conditions.
From a practical point of view, the atomistic wall is used only to confine the liquid phase. The implementation of the atomistic wall is comparable to the molecular dynamics’ fluid simulation. The wall molecules are chosen as platinum \( \left( \frac{3.25 \times 10^{28}}{m} \right) \) and are initially placed in an FCC(100) configuration with a lattice size set to \( \frac{10^{-77}}{m} \). The reactionary zone includes 3 layers of atoms so that there are enough wall atoms in the cutoff sphere of the closest argon particle to the wall. The stochastic zone includes 2 layers of atoms and the stationary zone only one layer (Figure 4.2). The Langevin parameter controls both the friction and the fluctuating forces and is set to: \( \xi_p = 1.613 \times 10^{13} /s \) as defined by Tully[40].

Because of the interactive forces between the solid and liquid particles, the first layer of solid particles has to be initially placed properly (at \( a_{sep} \) from the outer layer of fluid as seen in Figure 4.4) in order to avoid numerical divergence and to achieve the target system density. Depending on the potential parameters, the initial separation distance \( a_{sep} \) varies between \( a_w / \sqrt{2.5} \) and \( a_w / \sqrt{3} \) [16]. Figure 4.4 is obtained after equilibration of the dense phase inside a channel with an atomistic boundary and it shows how the fluid equilibrates to a random configuration versus the solid that stays in a more ordered structure with atoms only vibrating around their initial sites.

\[
\phi_{liq-sol}(r_{ij}) = 4 \alpha_{liq-sol} \left[ \left( \frac{\sigma_{sol-liq}}{r_{ij}} \right)^{12} - \beta \left( \frac{\sigma_{sol-liq}}{r_{ij}} \right)^{6} \right]
\]

Eq. 4.3

\[
\text{with } \left\{ \begin{array}{l}
\sigma_{liq-sol} = 0.894 \times 10^{-21} J \\
\sigma_{sol-liq} = 3.085 \text{nm}
\end{array} \right.
\]

Figure 4.4: X-Y Plane of the Domain. The outer particles represent the solid atomistic layers (color coded) and the fluid in the “average” volume.
Finally, the spring constant is adjusted to satisfy the targeted temperature. If the spring constant is too high, then the wall structure is too stiff, and the heat transfer to the stochastic layers would be limited: the Langevin thermostat is inefficient. A lower limit can be fixed by applying the Lindemann rule [42] for melting shown in Eq. 4.4. It states that the mean square displacement of the wall particles should be smaller than a critical value to keep the wall in its crystal-like state.

\[
\frac{\langle u^2 \rangle}{R_0^2} < 0.023
\]

Eq. 4.4

where \( \langle u^2 \rangle \) is the vibrational mean square displacement and \( R_0 \) is the nearest-neighbor distance in the crystal (\( R_0 = a_w / \sqrt{2} \)).

It is to be noted that simpler atomistic wall models are also used such as a static atomistic model with the fluid particles interacting only with the fixed sites of the solid structure. Another version can allow the dynamics of the solid structure but does not include the outer thermalizing layer.

To summarize the differences between those two wall model categories, we have the following:

- The stochastic boundary acts only on the thin layer of fluid in contact with the solid boundary. The atomistic wall however influences the particles within the cutoff radius of the Lennard-Jones potential.
- The atomistic wall allows the possibility of temperature control by adjusting the model parameters. This is not possible with the stochastic wall.
- Because of its implicit nature, the stochastic wall adds no significant computational load to the simulations. The atomistic model in general and a three-zones model in particular, have a significant computational cost.
- Finally, the stochastic wall model has a non-wetting characteristic since there is no attraction of the fluid to the wall. However, its repulsive contribution acts only on one component of the velocity (normal component is reversed) which could be described as a ‘soft’ repulsion. For example, hydrophobic or non-wetting surfaces exhibit plug flows instead of Poiseuille profiles for moderate flow rate. The
stochastic wall model does capture the quadratic profile for high flow rates though at the expense of higher slip values. Non wetting surfaces also produce oversaturated density profiles. This means that the density at the channel centerline region is higher than the average density in the volume which is the case when using the stochastic wall model.

These observations lead us to look for another category of wall models. We look for an implicit wall model, where the interactive fluid-surface force is analytical so that the computational cost is reasonable. Also, the wall effect can extend to a wider range within the fluid with a more realistic repulsive/attractive description that provides the capability of surface wettability.

4.1.3 Analytic Wall Models

This category of wall models is an intermediate description of the wall models that would allow interactions between the wall and the fluid without involving the molecular structure of the surface. In the literature, multiple models were introduced to reproduce the physical short range repulsion-longer range attraction of the surface. All the parameters for these models will be compared to the reference taken here as the atomistic solid boundary described for the FCC, Platinum wall in order to allow comparison between the models. However, this analysis should hold for other type of solid wall structures.

- **Morse Potential**

The first functional wall model examined is a Morse potential [4] that has the form expressed in Eq. 4.5 and shown in Figure 4.5 (a).

$$U_w(R_{sep}) = \varepsilon_{af} \left( e^{-2\alpha R_{sep}} - 2e^{-\alpha R_{sep}} \right)$$

Eq. 4.5
where $R_{sep}$ corresponds to the normal distance to the wall and the inverse of $\alpha$ determines the extent of the range of interactions. It is used commonly as a short-range attractive potential to approximate the bond vibrational energy in molecules. Here, it is actually combined with the diffuse boundary of section 4.1.1. Because this potential is constructed as attractive, the diffuse boundary provides the repulsive effect, though local, necessary for the confinement of the volume. Also, this potential acts only on the normal component of the momentum leaving the tangential component unaffected by “collision” with the walls. The diffuse boundary does therefore allow momentum exchange that becomes indispensable under flowing condition.

Another form of this potential was also explored and is presented in Figure 4.5 (b). It is actually a combination of two Morse potentials with different parameters and opposite signs. This allows a more ‘wider’ effect of the repulsive forces from the potential and preserves the attractive portion of the potential. Unfortunately, the velocity rescaling and reversing at the boundary is still needed since the repulsive force goes to zero at the surface allowing some particles to cross the wall and the interaction is purely normal to the wall surface.

![Combined Morse Potential](image)

**Figure 4.5:** Morse Potential for multiple choices of parameters (solid-fluid strength and region of influence): (a) Purely Attractive (b) Combined Repulsive/Attractive.
• **Integrated Lennard-Jones Potential**

Contrary to the Morse potential with no theoretical arguments to support its use as the interactive surface-fluid potential, this model is based on a continuous approximation of the actual atomistic surface. The model developed originally by Steele [50] describes the surface as a continuum of density which is infinite in extent and assumes that each particle of the fluid interacts with a unit volume in the solid through a Lennard-Jones 12-6 potential (the parameters of the potential for fluid-fluid and fluid-solid are different). The resulting solid-fluid potential is equivalent to the sum of the pair wise energies over all fluid particles or, because of the continuous assumption, to the integration over the continuous variable \( \rho \) as shown in Eq. 4.6 in the case of a flat surface:

\[
U_{wf}(z) = \sum_i \Phi_{LJ_{12-6}}(\rho_i) = \int_{\text{solid}} \phi_{LJ_{12-6}}(\rho) n \, dV
\]

\[
= 4n \varepsilon_{wf} \int_{0}^{\infty} \left( \frac{\sigma_{wf}}{\rho} \right)^{12} - \left( \frac{\sigma_{wf}}{\rho} \right)^{6} \pi \, dS \, dZ \quad \text{Eq. 4.6}
\]

with \( \rho_i \) : discrete variable ; \( \rho = \sqrt{(z + Z)^2 + X^2 + Y^2} \) and \( S = X^2 + Y^2 \)

where \( X, Y, Z \) are the coordinates of the unit volume of the solid wall, \( n \) is the number density of the solid and \( z \) is the normal distance of a particle away from the \( X-Y \) solid surface. This form is integrated in two times. Firstly, over the variable \( S \) providing a useful surface potential; it represents the interactions with a single plane of atoms parallel to the local surface and has the following form (Eq. 4.7):

\[
U_{wf}(z) = 2n \pi \varepsilon_{wf} \int_{0}^{\infty} \left( \frac{2 \sigma_{wf}^{12}}{5(z + Z)^{10}} - \frac{\sigma_{wf}^{6}}{(z + Z)^{4}} \right) dZ \quad \text{Eq. 4.7}
\]

Secondly, for an infinitely thick wall, over the variable \( Z \) providing the total interacting, volume potential of the form Lennard-Jones 9-3:

\[
U_{wf}(z) = \frac{2}{3} n \pi \sigma_{wf}^{3} \varepsilon_{wf} \left( \frac{2 \sigma_{wf}}{z} \right)^{9} - \left( \frac{\sigma_{wf}}{z} \right)^{3} \quad \text{Eq. 4.8}
\]
The degree to which this approximation is an accurate representation of the sum given in Eq. 4.6 depends on the distance between the fluid particle and the surface, becoming more accurate at large distances as well as the relative sizes of the atoms of the fluid to the atoms of the solid. Comparison of these analytical results to numerical experiments by direct summation of a fluid particle over a flat surface with a finite thickness, infinite extent in the X-Y directions and a (100) FCC structure provide the typical result shown in Figure 4.6. Along with the ‘summed’ curves denoted by A, S and SP, the integrated surface and volume potentials are plotted.

![Figure 4.6: Comparison between the ‘Summed’ and Integrated Lennard-Jones Potentials for the various sites of the FCC lattice: A, S and SP.](image)

Two main observations have to be made. First, the discrete nature of the wall appears in the form of the multiple curves denoting the different sites of the FCC lattice in X-Y plane. For the short distance to the surface, the fluid particle ‘senses’ a different potential depending on the site it is facing. At larger distances, all curves collapse on top of each other since the continuous assumption is most accurate. It is important to note that those three curves are only representative of three remarkable sites of the lattice. All intermediate positions between these sites should provide a potential curve situated...
between the extreme sites $A$ (lowest probability adsorption site) and $S$ (highest probability adsorption site). Second, there seem to be a difference between the integrated potentials and the numerically summed curves. The reason comes from the fact that at close distances, the continuous assumptions does not hold and therefore, the integrated form of the potential is a poor representation of the summed one at short separation distances. In contrast, the ‘partially’ integrated or surface potential in the form of a Lennard-Jones 10-4 provides a better approximation to the true curves. A better fit for this potential curve is given by Eq. 4.9 and it includes the thickness of the wall by introducing a summation over multiple layers which will have a direct effect of increasing the well depth of the overall potential.

$$U_w(R_{sep}) = 2\pi n_i \epsilon_{nf} \sum_{i=1}^{k} \left( \frac{2 \sigma_{nf}^{12}}{5 R_{sep}^{10}} - \beta \frac{\sigma_{nf}^6}{R_{sep}^4} \right)$$  

Eq. 4.9

This form of the potential and other modified versions were used in multiple studies. Abraham [8] used the form of Eq. 4.9 to compare the effects of the wall model on the density distributions in channels. Other works used the shifted and cut Lennard-Jones 9-3 [51] to study the phase behavior of a film over a surface and in presence of two phase droplets. Examples of modified potential form used are: a Lennard-Jones 10-3 [52] to study capillary condensation and a Lennard-Jones 10-4-3 [53] to simulate binary fluids in pores where the additional tail to the power 3 accounts for a multi-layered surface.

However, this potential has some shortcomings. It still does not represent the ‘structure’ of the wall but corresponds to an average potential between the extremes potentials of $A$ and $S$. Another major issue with this potential is its dependence only on the normal position of the particle reducing its effect to the normal component of position and momentum. This is a direct consequence of ‘smoothing’ out the surface and by symmetry; the surface force should only act in the normal direction. Clearly, this will prevent the use of such a wall model in this form to simulate flowing conditions.

Also, we will show in the next chapter that the system geometry has also a significant effect of the conditions of the confined fluid. The integration of the molecular potential provided a fairly simple expression because of the planar surface considered.
The main reason for the modified versions of the proposed potentials is the common use of pores versus planar channels in numerical and experimental settings. The same applies for our work where cylindrical channels are adopted for the injection experiment. Studies provided exact integration of the Lennard-Jones 12-6 potential in a cylindrical capillary [54][55][56]. All computed potentials have a complex form that either require local evaluation of integrals whenever a fluid-wall interaction occurs or require evaluation of summation or tabulated functions such as the hypergeometric functions. This makes the numerical implementation complex as well as computationally demanding besides the fact that the final potential is still an average form that does act only on the normal momentum component. Interestingly though, the expressions have the controlling power function of the type $1/r^{10}$ and $1/r^4$.

It is important to note that Steele [50] did provide an approximated analytic form of a potential that takes into account the structure of the surface at short range distances. His development was based on integrating a periodic Lennard-Jones potential. The periodicity is given by the type of lattice structure used for the simulation. The result was found and expressed in terms of Bessel functions of order 2 and 5. This form however does have a dependence on the three space variables making this potential act on both the normal and tangential components of the momentum. However, the form of the potential is dependent on the lattice structure (not transferable) and requires the evaluations of the Bessel summations.
4.1.4 New Wall Model: Sinusoidal Lennard-Jones Potential

Clearly, the closest description to the atomistic structure of the wall is the integrated form introduced by Steel. The idea is to implement the structure of the wall into an analytical form by fitting a given form of a Lennard-Jones potential to the numerically summed potentials. We expect this potential to evolve as a Lennard-Jones 10-4 potential. Effectively, a fluid particle will ‘sense’ the force as directly summed from the potential and therefore the fit is a realistic representation of the force and not a mathematical representation of the potential. It has the advantage of taking into account the numerical experiment as it is set into the simulation: size effect, lattice structure, thickness of the wall, cutoff effects and effective wall radius. The potential is summed over all pairwise forces acting from all particles from the solid on a single fluid particle moving away from the surface (Figure 4.7). The potential is then plotted versus the distance $R$ denoting the normal separation distance from the surface of the wall to any particle in the fluid. The zero reference for this normal distance or consequently the effective summed wall radius is one of the crucial parameters to determine for a given potential and will be discussed later in this section. Examples of the summed potential curves and the effects of certain initial settings on the potential form are represented in Figure 4.8. It is easily seen that the number of layers included in the wall does increase the well depth and vice versa. This is a consequence to the increase of number of atoms in depth which has an overall attractive effect. Adopting a cutoff value for the fluid-wall interactions will remove energy from the system while preserving the symmetry of the system because of its spherical action. Finally, Figure 4.8 shows that for a given choice of $R_{\text{wall}}$, the computed curves cross the zero energy level at the same position of separation distance. However, a shift in the $R_{\text{wall}}$. 

Figure 4.7: Schematic Representation of the Numerical Summation.
value (a larger value here) will dramatically move the characteristic separation distance for a zero energy level.

![Numerically Summed Potential](image)

**Figure 4.8**: Effect of the Problem Settings on the Summed Potential: Wall thickness, Cutoff, Wall position

Clearly, one can choose any initial value for the effective wall radius around the value of the geometrical radius of the problem. A natural choice would be the position of the first layer of solid atoms in contact with the fluid. A different value will provide the same profile but shifted along the axial direction: A bigger value of the radius would shift the potential to the left and a smaller value will shift the potential to the right. This feature is displayed in Figure 4.11 where the 2nd and 5th curves represent the potential for two solid layers at different positions but having the same shape with a shift in the axial axis. Even when the potential is fitted for the given choice of $R_{\text{wall}}$, the equilibrated configuration does not correspond to the equilibrated configuration realized using the equivalent atomistic wall model. The main difference can be seen in the distribution of the density across the channel and the total volume occupied by the fluid. Both distributions do fit only for an optimum value of the ‘effective’ $R_{\text{wall}}$ as can be seen in Figure 4.9. By contrast, another choice of channel size such as the surface position
provides a different fluid structure that can be seen with the ‘out of phase’ density stratification.

The distribution of the fluid in the channel has a direct effect on the system pressure as it will be discussed in the next chapter.

This optimal value $R_{wall}$ is actually deduced in a reverse fashion. Because the position of the zero energy level is directly related to the ratio of coefficients in front of the repulsive and attractive branch of the Lennard-Jones potential as well as the choice of the ‘effective’ wall position, it is found that the optimal value for $R_{wall}$ that provides the matching density profiles. It is however important to notice that the continuous wall model always has a higher peak at the wall (higher fluid adsorption) than the atomistic value and the difference will be stronger for denser fluids.

Figure 4.9 shows the numerically summed potentials over the three remarkable sites of the FCC lattices for the 2 geometries considered here: flat and cylindrical geometries. The integration is done over one surface layer of atoms at a time.
Clearly, the potentials are sensitive to the geometry of the surface over which the fluid particle is moving even though the spatial configuration is still symmetric.

![Graph showing LJ12-6 Integration over an Atomistic wall (2 Geometries)](image)

Figure 4.10: Numerically Integrated Lennard-Jones Potential for 2 Geometries.

The planar geometry provides the most consistent curves versus the cylindrical configuration and that complicates the fitting procedure as well as finding the optimal $R_{wall}$ for the latter. One possible reason for this difference is the way the atomistic cylinder is set. It is basically created by ‘carving’ a pore inside a box and even though there is an effort to smooth the surfaces, there are still indentations and spikes on the surface that might affect the summed potentials.

Therefore, the fitting procedure will be done for the planar geometry and then we explore extending this wall function to the cylindrical geometry. As seen in Figure 4.11 , the flat geometry summed potentials show a similar shape profile that depends only on the value at which it crosses the zero energy level and the well depth value. As we change the layer position (moving deep in the solid), the profiles are repeated exactly.
These numerically summed potentials can be approximated by a single analytical form presented in Eq. 4.10. This potential, combined with the optimal $R_{\text{wall}}$, is well represented by the Lennard-Jones potential $10^{-4}$ which is consistent with our previous settings.

$$\phi_{LJW}(R) = 2\pi \varepsilon_w \alpha \left( \frac{2}{5} \left( \frac{R}{\sigma_w} + k \right)^{10} - \left( \frac{R}{\sigma_w} + k \right)^{-4} \right)$$

$$\alpha = \beta \left( 1 + \gamma \cos \left( \frac{2\pi y}{a_w} \right) \right)$$

$$k = \Delta \left( 1 - \cos \left( \frac{2\pi y}{a_w} \right) \right) + \frac{(n - 1) a_w}{2\sigma_w}$$

Eq. 4.10

Figure 4.11: Fitted Potential for a Flat Geometry.
However, this simplified form has extra terms: two cosine waves depending on the axial position $y$. Normally, both the $x$- and $y$- directions have equal effects. However, it is a necessary choice in our case to create the variation in the $y$-variable because under flowing conditions, the momentum will be produced along that direction and this choice will allow the surface to interact with the flow and exchange momentum with it. And since the effect is similar in both directions, it is unnecessary to create a variation in the $x$-direction as well.

These waves are placed so that they modulate the points where the potential crosses the zero energy level: $k$ and the well depth: $\alpha$. It is also important to note that the integer $n$ denoting the multi layered surface acts only on the $k$ function which is consistent with our previous observations. The numerical value of $n$ is actually found to be 5 although we are using a three-layered wall. This is resulting from a direct comparison of the numerically summed potential over a three-layered atomistic wall versus an analytical summation of the formula in Eq. 4.10 and varying until properly matching both well depths. It can be assumed that it is a correction to the periodicity of the wall in both the $x$- and the normal directions. The numerical values of the other different parameters are directly deduced from the fitted curves for a given geometry and are dependent essentially on the wall volume initially considered. We will discuss those parameters with respect to our application when we focus on computing the pressure in the dense phases in the next chapter.

4.2 Particle Generation Method: Pressure Driven Flow

4.2.1 Generation in Two Phase Flows

Usually, molecular dynamics simulations involve systems of a finite number of particles. However, in applications like injection or even Poiseuille flow, we want to simulate a continuous incoming flow of liquid particles into a gaseous domain at the same inlet conditions (density, temperature and pressure). To overcome the ‘loss’ of
particles from the liquid domain into the gaseous domain, Branam [17] implemented the particle generation method to compensate partially for the loss. It consists in duplicating each particle crossing into the gaseous volume and adding it at the inlet of the liquid channel. The challenge is to be able to introduce the new particles into the liquid phase at the same rate as they are injected into the gas without creating numerical divergences. Numerical divergences are usually due to particles getting suddenly placed too close to each other.

Computationally, this technique is implemented as illustrated in Figure 4.12:

- At the inlet of the equilibrated liquid channel, two ‘Generation’ planes composed of FCC sites are placed where new particles can be stored. Those sites do not interact with the system of particles.
- If a particle from the liquid tube crosses a plane placed close to the tube exit, a new particle is stored in one of the free generation sites.
• For a particle to be included into the physical system, it needs to be tested so that no numerical divergence occurs (neighboring particles too close). The generation sites that have particles will be tested each time step so that the maximum number of particles can be included.

• The newly injected particle has a random velocity sampled from a Maxwell Boltzmann distribution based on the targeted liquid temperature. To accelerate the motion of the newly, non-guided particles, an axial body force acts on the new particles at a higher acceleration level to promote the particle departure from the generation sites.

This technique allows us to start the injection simulations using shorter tubes, hence speeding the simulation run times. This allows the conditions in the flow channel to reach a steady state and maintain a constant density flowing into the gaseous chamber. By contrast, if no generation is produced, the closed volume of flow initially set to flow into the chamber will progressively loose particles into the gaseous domain that cause changes and new property gradients to appear in the dense phase that will not be steady over time. In the literature, another way to limit this decaying trend is to push slabs of fluid (piston-like force) one after the other into the gaseous domain [35]. This should create a pulsating behavior that might interact with the jet physical times and induce unrealistic jet breakup.

4.2.2 Generation and Parallelization Requirements

The challenge in implementing this technique for the injection case using the force decomposition method is the constant change in the number of particles of the system. When the force matrix changes in size, the whole setting of the method has to be updated so that no communication errors occur. In this decomposition method, each processor creates its own neighbor lists. Therefore, the generation sites have to be split on the processors as well so that only one new particle can be distributed per generation site. Unfortunately, this means that certain particles cannot be injected into the system at given
time steps even though certain generation sites are free. This might create a cross sectional variation of the density that can be avoided if the sites are randomly redistributed over the processors often during the simulation in order to even out the number of generated sites per processor.

Once a particle is allowed in a generation site, all settings have to change in the generation processor first, then a new communication subroutine: *Update Parallel* will change the communication parameters over the processors in the same column and the same row so that the regular positions and forces communications can proceed properly. Because this communication is low cost (not involving arrays), the new subroutine is not computationally extensive, however an extra call to ‘fold’ the newly formed position vectors have to be executed afterwards.

### 4.2.3 Generation for Pressure Driven Flows

Pressure driven flows are induced by an initial gradient of pressure imposed between both ends of the flow volume. Taking advantage of the generation technique, we implement this method for a quiescent fluid volume and this time, unlike the case for body force based injection where the conditions are set to be at the orthobaric values (see 3.4), the adjacent domain can either be void or gaseous. The advantage of this application (by comparison to the injection) is that the focus is the flow in the channel and not the two phase behavior. Therefore, we can disregard the mechanisms of the outer regions and maintain a constant number of particles in the complete system (actual simulated system+stored particles). Hence, the idea is to reinject any particle that crossed towards the lower density region (due to pressure difference) into the inlet region which will maintain itself at higher density as the system reaches a steady level. Snapshots of this axially induced motion is shown in Figure 4.13:
In this figure, the colored particles are coded with respect to the number of rotations around the tube done during the total simulation run. Interestingly, this shows that during the early stages (time 1 and 2) the flow particles are moving unidirectional and almost produce a uniform front that can be visually resolved. However, towards the end of the simulation, at steady level of the velocity (time 3) particles from different rotations constitute the equilibrated phase due to the slowing down of particles at the solid walls versus the much accelerated centerline velocities: the flow is fully developed.

To equilibrate the flow, we need to extend the length of the tube to three regions: the inlet region with the higher density portion, a middle section that keeps an average constant density and an outlet region that has a lower density value. The separation of the regions is possible for longer channels. In this work, we take a first look at these types of flows. The drawback of this method is the inability to maintain the initial density level in the section of interest. This is a direct consequence of the numerical limitation to reinject all particles if no generation sites are not found (possible particles overlaps).
4.3 Modified Lennard-Jones Potential for Pressure Computation

As stated in the previous chapter, Lennard-Jones potentials are considered short ranged pairwise potentials which means that the potential decays quickly as the separation distance between particles increases. However, the potential does not reach a zero value which leaves a tail of energy (or other properties) that is not accounted for in the system. There are three ways to modify the complete potential (Black Curve) in order to implement the effective influence range in the potential as displayed in Figure 4.14:

- **Truncation (Eq. 3.10)** does not provide the correct system energy but the error can be limited by increasing the cutoff distance. Yet, it does introduce a discontinuity in the energy and therefore an impulse in the force which is non-physical (Red Curve).

- The **shifted potential and/or shifted forces (Eq. 3.11 and Eq. 3.12)** does remove any discontinuities in the functions but in expense, it does modify the energy values over a large range of the interatomic distances that are not supported physically either (Green Curve).

- The **switch function idea (Blue Curve)** is to preserve most of the potential as the original one and then switch on a function, usually a piecewise function involving a higher order polynomial over a finite interval \([R_l, R_u]\), that will bring the potential smoothly (or not) to zero. An example [36] of such a function is given in Eq. 4.11:

\[
U'(r) = U_{LJ2-6}(r) \cdot S(r)
\]

with

\[
S(r) = \begin{cases} 
1 & r < R_l \\
(R_u - r)/(R_u - R_l) & R_l < r < R_u \\
0 & R_u < r 
\end{cases}
\]

**Figure 4.14**: Modified Cutoff Potentials
The new function can either bring the potential to zero or both the energy and the force to zero. Usually, the criteria to find the coefficients for the polynomial function is a set of conditions on the continuity of the potential \( S(r) \) itself, on the force (first derivative of \( S(r) \)) or even on the curvature (second derivative of \( S(r) \)) for the integrating algorithm to work properly. However, there is no information as to how the new deformed potential will affect the true total energy. Besides, these cutoff potentials still do require corrections in order to compare to the full Lennard-Jones potential data; those corrections do not affect the physical system as explained in 3.3.2.

Then, the idea is to use the fact that the modified potential does affect the true energy but this time, we want to quantify this modification and equate it to the tail energy. This way, the correction is physically changing the system back to the energy level of the complete Lennard-Jones potential. This has to be carefully done however, since the forces are controlling the dynamic of the system (and not energy distributions) and therefore the equilibrium states are sensitive to the gradient’s modifications of the potential. Hence, the alteration of the potential has to occur on a region with less stiffer gradients; in other words with reasonably high cutoff values (>2.5\( \sigma \)).

The modified potential will have the form expressed in Eq. 4.12. The complementary potential function is chosen to be polynomial and acts only on a finite interval \([R_L, R_u]\) while the remainder of the potential is the truncated Lennard-Jones 12-6. The form of the potential is still conservative and reversible. Depending on the number of conditions required, the order of the polynomial potential can be determined. It is also interesting to consider that the values \( R_L \) and \( R_u \) can be part of the unknowns to be determined in order to satisfy the set of conditions, which in return decrease the order of the polynomial function by 2. This option has two disadvantages: one to constrain the number of parameters that can be modified in the new potential in order to compensate for condition changes (bigger molecules, complex geometries) or to track the accuracy and two, if a second order polynomial or higher is used, quadratic or cubic equations will have to be solved for in order to ‘close’ the problem.

\[
\phi_m(r) = \phi_{LJ \, 12-6}(r)_{cut \mid R_u} + \phi_{poly}(r)_{[R_L,R_u]} \tag{4.12}
\]
The set of conditions required for this problem is:

1. Continuity of energy at \( R_l \):
   \[
   \phi_m (R_l) = \phi_{LJ\ L2-6} (R_l) \quad \text{Eq. 4.13}
   \]

2. Zero energy at \( R_u \):
   \[
   \phi_m (R_u) = 0 \quad \text{Eq. 4.14}
   \]

3. Continuity of the Force at \( R_l \):
   \[
   -\frac{\partial \phi_m}{\partial r} (R_l) = F_{LJ\ L2-6} (R_l) \quad \text{Eq. 4.15}
   \]

4. Zero Force at \( R_u \):
   \[
   \frac{\partial \phi_m}{\partial r} (R_u) = 0 \quad \text{Eq. 4.16}
   \]

5. Equal Potential Energy:
   \[
   \int_{vol}^\phi_m g(r) dv = \int_{vol}^\phi_{LJ\ L2-6} g(r) dv \quad \text{Eq. 4.17}
   \]

6. Equal Virial Pressure:
   \[
   \int_{vol} r \frac{\partial \phi_m}{\partial r} g(r) dv = \int_{vol} r \frac{\partial \phi_{LJ\ L2-6}}{\partial r} g(r) dv \quad \text{Eq. 4.18}
   \]

Therefore, for this case, the complementary function added to the truncated potential is a polynomial of order 5. If only interested to correct only the system energy, then it not necessary to consider all those six conditions but only the three conditions: 1, 2 and 4 which provides lower order polynomial functions. In this case, the system energy is corrected to match the full Lennard-Jones values even though the pressure is also consequently changed since the system relaxes to a different energy state. An example of a second order polynomial derivation is presented in Eq. 4.19 and a full derivation can be found in Appendix A.

\[
\begin{bmatrix}
R_l^2 & R_l & 1 \\
R_u^2 & R_u & 1 \\
\Delta_5/5 & \Delta_4/4 & \Delta_3/3
\end{bmatrix}
\begin{bmatrix}
a \\
b \\
c
\end{bmatrix}
= \begin{bmatrix}
0 \\
-\phi_{LJ\ L2-6} (R_u) \\
E_{corr}/2 \pi \rho N
\end{bmatrix} \quad \text{Eq. 4.19}
\]

\( a, b \) and \( c \) are the coefficients of the polynomial. \( E_{corr} \) is the energy correction as defined in Eq. 3.13 and \( \Delta_k \) is any term of the form \( (R_u^k - R_l^k) \). The matrix and the RHS of the equation are constants (independent of the position \( r \)), hence the system can be inverted numerically once using a LU-decomposition and the polynomial can be defined without any extra computational cost. For this set of conditions, the energy should be conserved and the system is slightly changed in order to account for the long range changes. This can be seen in Figure 4.15 where a comparison of the system potential energy is shown.
for a system with the analytical energy correction versus a system with the complimentary polynomial potential for the case of a box with periodic boundary conditions with two different cutoff distances at 120K and 1205kg/m³. For all cases, the energy reaches a steady state with fluctuations less than 2% of the total energy. The system pressure is given by the thermodynamic tables as 7MPa. We can see that both modified potentials provide comparable energy levels as the Lennard-Jones cut and corrected potential. The pressure values are: 4.01MPa, 4.4MPa and 5.2MPa respectively for the Lennard-Jones cut and corrected potential, the 5th order polynomial and the 2nd order modified potentials. Hence, the modified potentials are consistent with the full Lennard-Jones potential and not the thermodynamic data. The 2nd order polynomial has a different pressure value due to an energy fitting procedure only, though it is lower than the simply cut potential since it does incorporate some long range forces.

![Potential Energy for 3D PBC Box](image)

**Figure 4.15**: Polynomial Potential for Energy Conservation for the different Lennard-Jones, cut, cut and corrected and modified form.

This potential was tested in a bulk phase placed in a box with periodic boundary conditions in the three dimensions as well as confined configurations for the case of the higher order polynomial since our focus property is the pressure.
CHAPTER 5
SINGLE PHASE FLOW RESULTS

In this section, we present the numerical results for molecular dynamics simulations of single phase fluids. The majority of the results cover the surface effects on the quiescent and flowing fluid. Comparison between bulk behavior and the different wall models detailed in the previous chapter will be showed as well as various parameter effects on the pressure computation. Preliminary results for the developed modified potential and pressure driven flow will also be presented in this chapter.

5.1 Wall Model Effects on Pressure Computations

We use dimensional molecular dynamics simulations to study quiescent liquid argon phase where the temperature and system density are fixed. The system is allowed to relax and the equilibration is conducted in either an NVE or NVT ensemble. Once equilibration is reached, the pressure of the system is computed using the virial formula from Eq. 3.8. For this section, the pressure is corrected for the long range interactions using the term in Eq. 3.13. Hence, the simulated data correspond to equilibrium data for a Lennard-Jones fluid. No flow was applied whenever the virial pressure is computed consistent with the statements in section 3.3.1. The simulated system pressure is then compared to the thermodynamic data. Usually, those data are properties of the fluid and are related by the equation of the state. However, at these nanoscales, the surface effect through its interaction with the fluid can have a dramatic effect on the state of the fluid making its wetting characteristics an important parameter to be addressed to define the state of a confined phase. All our results will be compared to the macroscale thermodynamic data since the gaseous simulated phases to be used in the two phase cases do reproduce those data.
As explained in section 3.3.3, the Lennard-Jones potential parameters are set to match different focus properties such as pressure data [46] from tabulated values (Source: NIST website). This type of correlation is valid over limited ranges of temperature (85 K-124 K) and range of densities (gaseous argon). It is then expected that liquid phases, especially close to the critical point, might be subject to greater deviations than gases and these deviations can be amplified by the density structuring that is characteristic of such scales. We will be looking at two isotherms: 120 K and 145 K (close to the critical point 150.89 K) and a wide range of densities starting as low as the orthobaric value for each isotherm. We start by simulating the bulk phase in an “infinite” volume of fluid placed in a 3D box with periodic boundaries. These cases constitute the basis of our comparison of pressure data with the cases of confinement.

5.1.1 Periodic Boundary Cubic Volume

We start by investigating the effects of the cut, unshifted Lennard Jones potential model and its parameters on pressure in the bulk phase. The system is simulated until steady state and equilibrium is reached. Figure 5.1 and Figure 5.2 respectively show the system potential energy (kinetic energy is kept constant by using a velocity scaling thermostat) and the velocity autocorrelation function (allows the computation of the diffusion coefficient). The energy level reaches steady state with fluctuations less than 2% and the correlation function shows the “cage effect” observed for dense phases as the coefficient takes negative values [36].
Figure 5.1: Steady State Conditions - Potential Energy for PBC configuration at 120K.

Figure 5.2: Velocity Auto-correlation Function for 120K and 1245kg/m3.
The pressure results are presented in Figure 5.3 for both isotherms of interest and two different values of the cut off distance: $2.5 \sigma_{Ar}$ and $4.0 \sigma_{Ar}$. The number of particles simulated is \( \sim 4500 \) and the pressure spans a 40 MPa range with the lowest point corresponding to the othobaric coexistence point for the given temperature. The box’s length \( L \) is chosen so that the cutoff distance is \(< L/2 \).

For the value of well depth used in most papers, the computed pressure agrees with the thermodynamic values mainly at the higher density range. This is more pronounced for the 120 K isotherm by comparison to the 145 K where the thermal fluctuation is lower. However, close to the coexistence point, the computed pressure is underestimated and in cases is a non-realistic, negative value. The cutoff distance has little effect over the whole density range and this observation allows eliminating the added pressure correction term as responsible for the observed deviations between the computed and the experimental data. The results above were generated by fixing the box size and changing the number of particles. Also, Figure 5.4 shows the results when the number of particles was kept constant instead. It shows that the deviations in the computed pressures are not due to statistics once a sufficient number of particles are simulated.

Figure 5.3 shows multiple curves for different potential well depths for the 145 K isotherm. It proves that better pressure fits could only be achieved for limited density ranges and that the governing factor for each fit is the corresponding value of the well depth, the lower the value of the well depth, the better the fit for lower density ranges.
Figure 5.3: Virial pressure values in a 3D periodic, cubic volume.

Figure 5.4: Statistical effect on the computation of the Pressure data.
5.1.2 Stochastic Wall Effect on the Pressure

Now, the fluid is confined within a cylindrical tube with the stochastic radial boundary as the wall model (purely diffuse wall model) and periodic boundaries are applied in the axial direction. Contrary to the periodic boundary box where the volume is ‘infinite’ and the size has no effect on the pressure if chosen properly, the tube radius becomes a parameter that has to be studied as well.

Figure 5.5 shows the steady state value of the potential energy when an average value is reached with ~ 1.5% fluctuations. When the equilibrium is reached (>4000000 steps), the sampling for the pressure data starts and the sampling rate is chosen to be every 500 timesteps.

Figure 5.5: Potential Energy for Bounded fluid (4nm channel) using a Stochastic wall model.

The results for the 145 K isotherm are given in Figure 5.6 for two cutoff distances and two tube radii (2nm and 4nm). The error bars correspond to the standard deviation of the sampled pressure data in time.
Again, all cutoff distances and radii have a comparable behavior at high densities and the differences occur as the density decreases. The computed pressure is higher than the thermodynamic data for all cases for densities lower than ~1175 kg/m$^3$ and only the combination of 4nm-$R_c=2.5 \sigma_A$ gives a good agreement over the complete range of densities. If we look in detail at the fluid structure for a low density case (Figure 5.7) and a high density case (Figure 5.8), we observe that the effective volume seen by the fluid is different depending on the combination tube radius and cutoff distance for the low density case. For the 2nm-$R_c=4.0 \sigma_A$ case, the fluid particles are pushed towards the centerline. Therefore, the effective volume seen by the particles is smaller which explains the high pressure values. This means that for this combination the fluid-fluid interactions are not strong enough to overcome the repulsive action exerted by the wall and to spread into the whole volume. The case 4nm-$R_c=2.5 \sigma_A$ seems to have the right balance (size and cutoff) for this temperature (145 K) to successfully fit the thermodynamic data.
The high density case exhibits the same structure independently of the tube size or the Lennard Jones cutoff distance and hence all computed pressure curves collapse around the same values. It is also interesting to observe that for the smaller radius cases, around the density value \( \sim 1175 \text{ kg/m}^3 \), there is a distinctive transition denoting a change in the fluid environment. This can be explained by the higher structuring at the wall that ends up creating an attractive net potential towards the surface. This behavior is more pronounced for the wider channels making the transition smoother though it is still observed. These curves support the fact that fluids with the same structure across the channel have the same pressure data even if size and cutoff are different as clearly shown for the higher density cases as well as the low density cases for the cases 4 nm-\( R_c=4 \sigma_{Ar} \) and 2 nm-\( R_c=2.5 \sigma_{Ar} \).

Figure 5.7: Density Profiles for the diffuse wall case close to the coexistence point. Effect of the channel Radius and the cutoff distance.
Another interesting observation is that smaller cut off distances seem to provide better experimental correspondence. We would expect that higher cutoff distances would include more interactions within the system accounting for longer range interaction but consequently, for confined systems, it would include more effects of the non homogeneous density close to solid boundaries. Consequently, in confined geometries, higher cutoff distances would deviate more from the bulk data making the analytical pressure corrections more questionable.

Now we take a look at the 120 K isotherm. We test the orthobaric coexistence point for different tube radii and the cutoff value of $R_c=2.5\sigma_{Ar}$. It is seen in Figure 5.9 that, for the system to relax to the desired pressure, we need to use either a 6 nm or 8 nm radius tube to match the thermodynamic data with good accuracy. The same figure illustrates also the stronger fluctuations for pressure computation due to their higher sensitivity to long range settings.
Hence, for stochastic wall modes, smaller tube radii achieve higher pressure values and higher cutoff distances lead to even higher computed values. Higher cutoff distance means lower contribution of the pressure correction term and more contribution of the long range attractive portion of the virial. The fact that we end up with higher values means that the structure of the fluid is different as the cutoff increases and the change is towards a more compact fluid in the center leading to an increase in the repulsive virial component instead of the attractive one. Intuitively, one would run lower densities in order to achieve a lower average pressure. Two different densities were tested for the 2 nm radius and we still end up with high pressure values. Figure 5.10 illustrates the behavior of the fluid moving away from the wall if no balance between the fluid-fluid interactions and the wall-fluid interactions is found. This clearly displays the non-wetting characteristic of the stochastic boundary. The centerline densities are usually higher than the average value (as displayed with the density profiles) and in those cases, the system is called ‘oversaturated’.

Figure 5.9: Diffuse wall: Average Pressure vs. Radius at the Coexistence Point. 120 K-1160 kg/m³ -1.2 MPa.
Finally, the radial profiles for the pressure and density as well as the different contributions to the simulated pressure (kinetic contribution, the virial term and the correction) are plotted in Figure 5.11. The figure shows that the pressure and mainly the virial component are strongly influenced by the density distribution across the tube and consequently the fluid structure. The density and pressure are ‘out of phase’ for their oscillations because the correction term is proportional to the square of the density.

Figure 5.10: Diffuse wall: Particle Distribution into the volume for different density values for 2 nm radius channel and $R_c=2.5 \sigma_{Ar}$ (120 K).

Figure 5.11: Radial distribution of the density and the virial pressure components (120 K -1160 kg/m$^3$ -Radius=6 nm - $R_c=2.5 \sigma_{Ar}$)
5.1.3 Atomistic Wall Model Case

In this section, we change the radial solid wall to an atomistic model and we investigate the pressure of the confined fluid for different sizes of the tube radius and different cutoff distances. In order for the system to equilibrate at the target temperature (in this case: 145 K), the spring wall constant needs to be changed for the different run cases. The trend is to increase the spring constant as the density decreases for the given $\varepsilon_{\text{sol-liq}}$. Figure 5.12 presents the potential energy with its fluctuations lower than 1% of the average value which is statistically better than the stochastic bounded case.

Figure 5.12: Potential Energy for a 4nm channel using the Atomistic wall Boundary.

The results are presented in Figure 5.13. It is interesting to see that the data for the confined flow using the atomistic wall seem to behave in the same way as observed with the stochastic wall:
All data seem to have better agreement with the thermodynamic values at higher densities.

For a wide range of densities, especially close to the coexistence point, the computed pressure is higher that the expected value.

The combination 4 nm-Rc=2.5σ gives the best fit over the wider range of densities.

However, the deviation of the data from the experimental values is more pronounced with this model. All the curves seem to level to a constant value as the density decreases towards the coexistence point; density changes do not influence the computed virial. This behavior typically describes a phase change.

Again, it is of interest to observe the fluid structure for this wall model at high and low densities respectively is shown in Figure 5.14 and Figure 5.15. For the high density case, the fluid structure is quasi independent of the size and the cutoff distance. In fact, the oscillations have the same period σ and both channel sizes exhibit four distinctive peaks. The density ordering is however more important for smaller tubes and proportionally, do extend more towards the channel center. In the low density case, the
fluid structure becomes different from one case to another with a stronger deviation for the case 2 nm-\(R_c=4.0 \sigma\) consistent with the previous stochastic wall model. This is then a consequence of the fluid confinement and not the surface model itself.

![Density Profiles for the atomistic wall case for a high Density. Effect of the channel Radius and the cutoff distance](image)

However, unlike the stochastic model where the fluid moves away from the wall and the density concentrates in the center, the atomistic model, thanks to its attractive interactions, forces the fluid to coat the solid boundary instead. The density is lower than the average value and is the lowest for the case 2 nm-\(R_c=4.0 \sigma\). Those centerline densities are liquid-like (not liquid or gaseous) and no clear two-phase coexistence can be identified. The fluid-fluid interactions are then not strong enough to counterpart the attraction of the solid boundary leading to the fluid sticking to the boundary and the virial to stagnate. The fluid is highly structured into a solid-like state close to the boundaries. This displays the wetting characteristic of the atomistic wall model. The system is then called ‘undersaturated’.
The advantage of using an atomistic wall model is the possibility to control the strength of the solid-liquid interactions. Intuitively, the previous wall characteristic was too strong for the lower densities to reach a proper balance between the interfacial forces and the interatomic forces. Therefore, for a lower value set to $80\% \varepsilon_{\text{sol-\text{liq}}}$ ($\alpha = 80\%$ in Eq. 4.3), we can have a better fit for the computed pressure data over a wide range of densities as shown in Figure 5.16.

Figure 5.15: Density Profiles for the atomistic wall case close to the coexistence point. Effect of the channel Radius and the cutoff distance.
To summarize this section, the pressure of confined fluids modeled using a cut Lennard Jones potential is dependent on the size of the system and the value of the cutoff distance. The dependency on the cutoff distance indirectly questions the use of the analytical pressure correction terms. If the diffuse wall is used to model the solid boundary, the experimental orthobaric conditions are reached for a combination of size and cutoff that varies with the system temperature and density. The atomistic wall allows the adjustment of the wall parameters in order to find an optimum solid-fluid interaction strength so that for a given size and temperature, we achieve good agreement with the experimental values over the entire density range.

It is also interesting to see that the nature of the wall model itself (purely repulsive model versus attractive model) and its wetting property play a dominant role in defining the thermodynamic state of the fluid. Hence, the model of the surface most likely has to be representative of ‘real’ interactions in order to account for good pressure data agreement at these scales and phases.

Figure 5.16: Atomistic Wall: Pressure data for a fluid-wall interaction at 80% $\varepsilon_{\text{sol-liq}}$. 

![Pressure vs Density for Atomistic Wall](image)
5.1.4 Analytic Wall Model Case

In this section, we investigate the effect of the analytical wall models detailed in the previous chapter on the pressure computation. We will limit our study to the case of a 4 nm channel radius or half width and a cutoff distance of $R_c = 2.5 \sigma_{Ar}$. We will cover results for both isotherms, 120 K and 145 K, and also for both flat and cylindrical geometries in the case of the integrated Lennard Jones wall model since the best fitted potential was done for the flat configuration (see section 4.10.4). Our effort is to reproduce similar behavior as the results obtained with the atomistic wall model: preservation of the wetting characteristic, good thermal control, same equilibrated volume occupied by the fluid and a wide thermodynamic pressure fit. Hence, velocity scaling was used for all cases and only undersaturated fluids were generated since they do account for the existence of surface wetting. In general, oversaturated systems provide an easier fit because the wall model effects are “limited”. The effect of the configuration, thermostat and isotherms will be addressed in the next section.

It is important to note that various wall model parameters can provide simulated pressure fit for limited density ranges, especially the low density cases. This is however not as accurate as we would like to think since it is one, inconsistent with the atomistic wall model and two, the data are within the statistical error around the numerical average making it not a significant “numerical measurement”.

5.1.4.1 Morse Potential

The first wall model we implemented is the Morse attractive potential; either combined with the stochastic boundary or including a repulsive component of the same form. The results for the simulated system pressure are presented in Figure 5.17 for the 145 K isotherm.

The curves are the best fit we get for the various parameters of the analytical form in Eq. 4.5. The combination stochastic boundary and attractive potential model has high
density structuring next to the wall because of the local action of the repulsive component of this model. The combination repulsive and attractive Morse potential has an extended effect on the fluid and a balance can be established between the fluid-fluid and fluid-wall interactions that can match the thermodynamic data mainly at low and medium density values. The higher density cases (starting at 1150 kg/m$^3$) are not matched and the deviations from the thermodynamic data become more pronounced as the density increases.

### 5.1.4.2 The Integrated Constant Lennard-Jones Model

Next, we implement the constant Lennard-Jones potential as given in the literature and present the simulated pressure data for the cylindrical channel and the 145 K isotherm in Figure 5.18.
Different forms of the potential were implemented: the LJ9-3 potential for the volumetric integration, the single layered LJ10-4 as well as the multilayered potential. The common observation is the inability of the fluid-wall potential to adjust to higher densities and generate an equilibrated configuration that can match the thermodynamic pressure. All pressure computed at higher densities seem unaffected by the change of the potential form itself or its parameters (lower solid-fluid strength $\alpha$ or lower attractive effect $\beta$). In reality, the changes are much slower for such high densities to react to them and only dramatic changes in the wall model or its parameters will induce an effective pressure changes as it will be shown later (section 5.1.).

The pressure values are generally under-estimated mostly for the higher range densities. This reflects an effective fluid density that is actually lower than the average value; there is a “density loss” towards the coating layers over the solid wall that becomes extreme and overcomes the fluid-fluid and fluid-wall balance established for lower densities. The densities at the wall for the continuous potential wall surfaces are usually higher than in the atomistic case and this added layer changes the wall properties as seen by the fluid. In an attempt to limit the ordering effect of the wall potential, a
softer potential, LJ6-3, is used and it does effectively provide better simulated values. Still, this potential does not reproduce the similar equilibrated volume plus it has no physical support to its use.

The lower density cases are strongly dependent on the potential used to bound the system. An example of such a dependency is shown in Figure 5.19 where the simulated system pressure is computed for the orthobaric point at 145 K for different fluid wall strengths in the case of an LJ9-3 model. The reference value of the fluid-wall strength is the atomistic value used in the previous section. The figure shows that the wall can successfully reproduce the exact pressure for two values of this wall model: one for an oversaturated system and the other for an undersaturated one.

Figure 5.19: Effect of Wall-Fluid Strength on Pressure and Density Distribution (Cylindrical Configuration).

Figure 5.20 shows the effect of the fluid-wall interactions on different density levels using another constant Lennard-Jones wall potential: LJ10-4. Two conclusions can be made from this figure. First, the lower density case does not provide only two values for the targeted pressure but a wide range of values that are within the statistical error of the numerical pressure average which make low density data unreliable to decide the
physical “quality” of a wall model. The second conclusion is the inability of the constant Lennard Jones potential to provide a wide fit for a single choice of parameters because of the slow changes of pressure values at high density.

![Figure 5.20: Effect of Wall-Fluid Strength on the Pressure for Various Density Levels Flat LJ10-4 Wall Model.](image)

The continuous description of the wall model as a Lennard Jones potential with constant parameters is not only ineffective for simulating flows since it does not promote momentum exchange as discussed in 4.10.3, it is also unable to reproduce the correct density distributions within the channel consequently failing to reproduce the correct pressure values of interest.

5.12.4.3 The Sinusoidal Lennard-Jones Model

The main difference between the atomistic wall model and the continuous Lennard-Jones model is the atomistic wall’s non-homogeneous nature due to the discrete sites of the crystal lattice forming the solid surface. The potential energy is presented here
in Figure 5.21 with a steady state reached with fluctuations of the order of 1% of the average value of the energy.

![Potential Energy for 4nm channel with Lennard Jones Wave Boundary.](image)

**Figure 5.21:** Potential Energy for Bounded fluid (4nm channel) using a Lennard-Jones Wave wall model.

!["Wave" and Uniform LJW10-4](image)

"Wave" and Uniform LJW10-4
Flat Config. - 120 K Width =8 nm - Rc=2.5σ

**Figure 5.22:** Lennard Jones Sinusoidal Wall Model Potential
The sinusoidal wall developed here does integrate part of that discrete property from the atomistic wall and the corresponding simulated pressure data are presented in Figure 5.22. The figure shows data from two geometries, to compare to the constant Lennard Jones wall for the 120K isotherm. The parameters used for the flat wall model from Eq. 4.10 are presented in Table 5.1 below. Those parameters are all direct fits of the potential curves but for the parameter ∆ related to the position of the ‘effective’ wall boundary. It was multiplied by a factor 3 to 5 depending on the geometry to account for the extra variation with respect to the secondary directions as well as the motion of the solid surface in the atomistic model. Again, all data were fitted against the FCC platinum configuration but the procedure holds for any structure and any type of surface.

<table>
<thead>
<tr>
<th>β</th>
<th>γ</th>
<th>∆</th>
<th>n</th>
<th>a_w</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.45</td>
<td>0.143</td>
<td>0.021</td>
<td>5</td>
<td>2.77E-10m</td>
</tr>
</tbody>
</table>

The data for the flat geometry present an excellent agreement with the thermodynamic data for a wide range of densities validating the importance of the surface and here, its discrete and wetting characteristics in reordering dense phases in confined environments. This wall model does also provide the same density ordering across the channel as presented earlier in Figure 4.9 and the same equilibrated, occupied fluid volume which validates the equivalence between this derived wall model and the original atomistic wall.

The same model was used for the cylindrical configuration with higher value of ∆ consistent with the wider distribution within the structural sites in Figure 4.10. The data present good agreement for medium density values but they are more sensitive to the variations of the potential for the lower and higher levels. A better potential for this configuration might need to include the variation in the tangential direction because of the higher degree of confinement in this case.
5.1.5 Effect of Other Parameters on Pressure

In this section, we reconsider methods that we used in our previous simulations and that might or might not affect the pressure computation within the confined environment.

1. Temperature and Geometry:

Figure 5.23 displays the pressure data for the atomistic wall model for the isotherm 120 K and both the axisymmetric and flat geometries. The data fit is still in very good agreement for the cylindrical geometry by comparison to the earlier Figure 5.16 but for the lower value of the global fluid-wall strength (65% $\varepsilon_{\text{sol-liquid}}$).

The planar geometry does affect the data since it reduces the isotropy of the fluid environment by reducing the solid confinement to only one direction. This induces two consequences: higher fluid-solid strength is needed to achieve similar fluid confinement as the axisymmetric channels and the simulated pressure will deviate at the higher densities even though it is still within the statistical numerical error.

![Geometry Effect - Atomistic wall 120K Isotherm](image)

Figure 5.23: Atomistic Wall: Effect of Geometry on the Pressure Computation.
2. **Temperature Thermostat:**

Another tool used in our simulations is the thermostats to constrain the system to relax around the target isotherms. All thermostats change the particle trajectories and we would like to investigate if those changes influence the simulated pressure data.

Firstly, we test the different thermostats versus no scaling configurations in a bulk phase for a 3D periodic boundary box and the results are shown in Figure 5.24. The thermostats have little effect on the computed pressure data for most density levels but the higher range even though the data are still within the value’s statistical variation. Hence, the coupling with the thermostat does reflect the correct thermodynamic state of the full Lennard-Jones fluid.

![Effect of Thermostat on Pressure 145K Isotherm](image)

Figure 5.24: Thermostat Effect in a Bulk Phase

Fifty, we test the different thermostats versus no scaling configurations in a bulk phase for a 3D periodic boundary box and the results are shown in Figure 5.24. The thermostats have little effect on the computed pressure data for most density levels but the higher range even though the data are still within the value’s statistical variation. Hence, the coupling with the thermostat does reflect the correct thermodynamic state of the full Lennard-Jones fluid.

Figure 5.25 shows the resulting pressure data for these thermostats interacting with the fluid in the confined geometry. Clearly, the velocity scaling allows the system to relax to the proper thermodynamic state. Though this thermostat is generally very crude, it provides better pressure data than the Nose Hoover thermostat. For this thermostat, if we take a look at the average velocity inside the confined volume as seen in Figure 5.26, the component normal to the solid surface exhibits a strong system oscillation. This oscillation decays rapidly from its initial phase but still modulates the system during the
simulation. Hence, the virial formula fails then to estimate the system pressure under such circumstances. The velocity rescaling however removes any natural system oscillation leading to a better pressure estimate.

Figure 5.25: Effect of Thermostat for Confined Geometries

Figure 5.26: Velocity Variation Normal to the Flat LJ wall Model.
Nose Hoover Thermostat for 120 K isotherm.
5.2 Wall Model Effects on Poiseuille Flows

Now, we impose a flow in the simulated system by adding an axial body force parallel to the solid surface. Here, we plot the velocity profiles after equilibration for the different wall models for systems having the same average velocities. The velocity profiles are shown in Figure 5.27 for a flat configuration with the atomistic, the sinusoidal Lennard Jones and the stochastic wall models. As stated previously, the constant Lennard Jones potential cannot exchange momentum with the fluid making it inaccurate for this application. The atomistic wall provides the least slip at the solid surface yet it is still in good agreement with the sinusoidal developed wall model.

It is also important to note that for cases of high flow accelerations, the forces at the wall cannot handle the directional momentum and flatter profiles are produced until the system becomes unstable as shown in Figure 5.28.

![Velocity Profiles](image)

**Figure 5.27:** Non Dimensional Velocity Profiles for Different Wall Models. The quadratic analytical profile is fitted for an apparent Knudsen number of 0.35.
5.3 Modified Potential for Pressure Correction

Figure 5.28: Velocity instabilities for high driving forces.

Figure 5.29: Modified Potential with 6th order Polynomial
The 5\textsuperscript{th} order polynomial modified potential used to simulate fluid-fluid interaction (shown in Figure 5.29) is tested first in the bulk phase for the pressure data and is compared to the 3\textsuperscript{rd} order polynomial as well the full Lennard-Jones potential simulation data for the isotherm 120 K. The corresponding results are presented in Figure 5.30. The simulated pressure data show that the 6\textsuperscript{th} order polynomial addition is a closer fit to the full Lennard-Jones potential, unlike the 3\textsuperscript{rd} order polynomial potential that fits closer to the thermodynamic data. This shows the difference between modeling the system energy versus modeling the inter-atomic forces. The system relaxes towards the proper equilibrium energy and for which the correct thermodynamic pressures are produced.

We implement this modified potential in the case of confined fluids for a flat and cylindrical configuration for the sinusoidal wall model. The results are presented in both Figure 5.31 and Figure 5.32. Again, the potential does provide similar results as the truncated and corrected Lennard-Jones potentials reproducing the long range corrections and preserving the fluid state equilibrium. Slight deviations at the lower and higher densities are observed; the fluid with the modified potential is forced to take into account the bulk phase information while evolving in a confined system. This potential is a promising tool to incorporate long range corrections or bulk phase behavior with little computational cost and without the need to implement large cutoff distances.
Figure 5.30: Bulk Phase Pressure for the Modified Potential with no Correction.

Figure 5.31: Confined Phase Pressure for the Modified Potential with Sinusoidal Lennard Jones Wall Model – Cylindrical Configuration at 120 K
It is also important to note that the choice of the lower cutoff radius for which the modified potential is applied has to be large enough in order to reproduce the proper energy and equilibrium state.

![Fluid-Fluid Modified Potential](image)

**Figure 5.32**: Confined Phase Pressure for the Modified Potential with Sinusoidal Lennard Jones Wall Model – Flat Configuration at 120 K

### 5.4 Pressure Driven Flows

This is a preliminary presentation of pressure driven results. The method implemented is based on putting a dense phase in contact with a void medium and allowing the system to reach steady state values. The fluid is simulated in a cylindrical channel of 2 nm radius with a sinusoidal Lennard-Jones wall model and the isotherm 120 K and 1250 kg/m³ initial density. We first present the dependency of the average fluid velocity with the surface-fluid strength which has an indirect dependency on the differential pressure driving the flow (Figure 5.33).
The dependency is clearly linear but switches slope at a low value of the wall-fluid strength. This is due to an increase of pressure in the system as the fluid switches from an undersaturated to oversaturated configuration and the wall becomes non-wetting. For higher pressure differential, the velocity becomes uniformly constant and the wall tangential forces cannot slow down the flow at the wall. This linear dependency is not transposed to the velocity variation with respect to the pressure difference. Unlike the macroscale, the wall model becomes a parameter that enhances the functional change of average velocity with the pressure difference.

The velocities achieved so far are quite high since the pressure in the simulated systems are high. An example of velocity profiles is presented in Figure 5.34. The profile can still be fitted to a quadratic form however the apparent Knudsen number allowing the Poiseuille flow fit is quite high denoting a large slip at the wall. This again is due to the inability of the wall to handle high momentum and acceleration in the channel. The density profile in Figure 5.35 displays the structuring close to the solid surface characteristic of the nanoscale.
One major drawback of such method is the decrease of the system initial density. In fact, due to the high initial system pressure (without correction), the system starts with high momentum and particles fluxes that cannot be compensated for at the inlet. The system density changes consequently force the system temperature to increase. This effect is undesirable since one of the reasons behind implementing this method is the elimination of heat induced by the work of body forces, and hence the use of thermostats.

Figure 5.34: Pressure Driven Flow: Example of Velocity Profile
Figure 5.35: Pressure Driven Flow: Example of Pressure Profile
CHAPTER 6

TWO PHASE INJECTION RESULTS

6.1 Wall Models Effects on Injection

Now that we have a quantitative understanding of the conditions in confined liquids for the different wall models, we can proceed to test them on the injection behavior. The starting conditions are for quiescent liquid in contact with a quiescent gaseous volume, both set at the same pressure and temperature. In absence of any flow, the bulk phases should remain in their respective domains if the thermal, mechanical and chemical potential are the same at the liquid-gas interface. The purpose of this test is to investigate the effect of the models as designed and discussed earlier on the exit velocity of the simulated liquid nanojets.

The desired conditions for these test runs are the coexistence points, where for the same temperature and pressure, we can equilibrate two different phases. The gaseous conditions are easier to establish to match the liquid phase conditions (pressure and temperature). A more careful equilibration process has to take place for the liquid phase for each wall model. The conditions for the injection test are kept mostly the same and are as following:

\[ T_{\text{liq}} = 145K, \begin{cases} R_{\text{liq}} = 4\text{nm} \\ L_{\text{liq}} = 10\text{nm} \end{cases}, R_c = 2.5\sigma_{Ar}, \rho_{\text{liq}} = 865kg/m^3, P_{\text{simulated}} = 3.8MPa \]

\[ T_{\text{gas}} = 145K, \begin{cases} R_{\text{gas}} = 14\text{nm} \\ L_{\text{gas}} = 20\text{nm} \end{cases}, R_c = 2.50\sigma_{Ar}, \rho_{\text{gas}} = 275kg/m^3, P_{\text{simulated}} = 3.8MPa \]
The wall model for the liquid phase confinement is chosen to satisfy the target pressure on average in order to satisfy the mechanical balance. The parameters are chosen consistently to produce comparable density distributions between the different wall models if possible (the diffuse wall is inherently a non-wetting wall). Velocity scaling is used as a thermostat to satisfy the thermal balance. The chemical balance for the mono-atomic argon is assumed. The chemical potential effect is directly related to producing defined interfaces. We care mostly about a directional momentum flux and not the interface mixing.

The fluid-fluid potential is the truncated Lennard-Jones potential and the system pressure is actually the corrected value set to match the conditions stated above. What we learned from the simulated pressure data is that the pressure values in the system are actually on average higher than the actual corrected one since the long range correction accounts for an expansion term that is negative. Even so, we will use wall parameters that fit the full Lennard-Jones potential data for better transferability between cutoff distances or other potentials such as the modified potential developed later.

We look to achieve the same objectives as for pressure data; reproduce the behavior of the atomistic wall model test run with a lower computational cost. From the previous chapter, the sinusoidal wall model seems to be the most appropriate model for the single phase fluid and we would like to verify its effects in this two-phase-fluid configuration. Actually, the following results retrace our chronological wall implementation, testing and eventual development.

Snapshots for each of the test runs presented in Figure 6.1 to Figure 6.10 represent test cases for different wall models. In all tests, we compare the injection velocity at the start of transient stage of injection as the two domains are put in contact. This initial stage puts in display the differences between the surface models and consequently controls the initial conditions of the jet. For better reproducibility of jet simulations using molecular dynamics, it is important to understand those conditions and ensure that they are similar.
In the diffuse wall case, two stages can be distinguished in the injection process:

- Though no initial velocity is present in the dense phase (blue particles), a jet-like behavior is observed and the liquid penetrates the gaseous domain with a narrow cone angle up to 450ps.

- Afterwards, the jet decelerates and it starts evaporating and mixing within the gaseous volume. The density in the tube starts to redistribute homogeneously. The process becomes diffusive. A net flux of liquid particles is maintained throughout the simulation run.

The first step of fast penetration of the liquid causes a rapid decrease of density in one end of the tube generating a gradient of density and pressure within the liquid channel. Figure 6.2 shows the average axial velocity at different sections of the channel highlighting the rapid increase of velocity up to 40 m/s in the region in contact with the gaseous phase and then a leveling to a constant value of 20 m/s.
Figure 6.2: Diffuse Wall Model: Axial Velocity

Figure 6.3: Test Run-Atomistic Wall Model: Interface Mixing
In the case of the atomistic wall model (Figure 6.3), particles are exchanged through the liquid/gas interface. This exchange is not balanced however: more net liquid particles cross into the gaseous volume. Hence, as shown in Figure 6.4 (undersaturated case), an average axial velocity is maintained through a first stage. As time progresses, the system evolves towards equilibrium by exchanging particles between both domains. This balance is reached when the dense fluid adjusts to the abrupt change of axial boundary conditions (periodic boundary condition) and the interfacial forces between the solid and liquid close to the gaseous domain are responsible for slowing down the flow back to zero. The striking difference distinguishing the atomistic case from the previous injection-like behavior is the presence of gaseous particles (red particles) in the tube as well.

Figure 6.4: Average Axial Velocity for the Atomistic Wall Model Test Run.

Originally, this observed difference in the jet behavior between the two test runs instigated the work on identifying the simulated pressure for each medium. Clearly, the nature of the wall model, as it is the only difference between the test runs and specifically the wettability characteristics, is the primary factor for creating the flow in one case and inhibiting the directional motion in the other. Therefore, it is expected that the new wall model needs to include an attractive component that is strong enough to resist any axial motion or instability and reproduce the atomistic wall behavior.
Firstly, we eliminate the difference in section size between the two mediums as a possible reason for creating an inflow due to the geometric expansion. Figure 6.5 shows the same test run realized with liquid phase (blue) having the same section size as the gaseous phase (red). Both phases are bounded using the diffuse wall model. Clearly, the initial interface position moves towards the gaseous domain due to a differential pressure created by the combination dense phase and stochastic wall model.

![Figure 6.5: Diffuse Wall: Test run with Constant Section.](image)

Now, we continue implementing the analytical wall models for the test run. Respectively, the Morse potential wall model, the continuous Lennard-Jones 6-3 wall model as well as a multi-layered Lennard-Jones 10-4 model and the sinusoidal wall model injection results are shown in the following figures.

![Figure 6.6: Test Run-Strong Attractive Morse Potential + Stochastic Boundary.](image)
Figure 6.7: Test Run-Attractive + Repulsive Morse Potential.

Figure 6.8: Test Run- Continuous Lennard Jones 6-3 Potential
Figure 6.9: Test Run - Multi Layered Continuous Lennard Jones 10-4 Model

Figure 6.10: Test Run - Sinusoidal Lennard Jones Wall Model
The test run results for the different wall models provide the following observations:

- A wall model that has an attractive component and is equilibrated to fit the right thermal and mechanical conditions is not enough to inhibit a jet-like behavior. The most pronounced injection actually occurs for the Lennard-Jones 6-3 (Figure 6.8) which has a weaker repulsive branch and has a better pressure data fit than the Lennard Jones 10-4 or 9-3. The fluid in the channel cannot reach equilibrium and moves completely towards the adjacent domain. A similar behavior is reproduced by the LJ10-4 model.

- The Morse potential combined with the diffuse boundary provide a similar behavior to the atomistic wall model for an elevated fluid-wall interactive value even though it has difficulties adjusting to the proper thermodynamic pressure data (Figure 6.6). If the repulsive Morse potential replaces the action of the stochastic boundary, the result becomes similar to a strong injection-like behavior.

- The sinusoidal wall model produces a less pronounced jet-like behavior though it is not sustained as the previous Lennard-Jones model. Yet, it is also unable to equilibrate back to zero directional motion (Figure 6.10).

- For all these wall models, including the atomistic model, the liquid phase has a higher effective pressure than the gaseous phase. This difference is the same for all models since the tail correction is based on the fluid-fluid potential parameters, the liquid density and the cutoff value. This imbalance does probably explain any initial onset of the flow but ultimately it is the surface model that will promote or inhibit the instability to evolve.

A common point between the wall models that promote the flow injection is the limited or zero effect of the attractive or wetting characteristic of the surface. But as seen in the case of LJ10-4 this is not sufficient even with very strong attractive forces. The other common point that turns out to be equally important to stabilize the jet velocity, is the inability of these surface to exchange lateral momentum with the fluid. If present, this effectively will allow the attractive characteristic to act upon any momentum instability to limit its growth. This is displayed in the two cases of the Morse potentials; one that is
combined with the diffuse wall which does exchange momentum and the other coupled with a repulsion potential that only acts normally on the fluid particles.

Another conclusive remark to this work is the importance of the mechanical balance towards the equilibrium balance in confined media. This mechanical balance however is not defined anymore between the two phases as the pressure or stresses acting on the interface but also the balance between all interfacial surfaces including the solid surfaces.

The sinusoidal wall model presents both characteristics: Wetting surface and lateral momentum exchange. However, it seems to be not enough to dissipate the instability as a net inflow of liquid particles continue to cross towards the gaseous medium as the simulation progresses (the same as for the Morse+diffuse wall model). One major difference existing in our all atomistic simulations and the modeled wall cases is that the wall acts only on the particles normal to the surface (even if coupled with a lateral momentum exchange). The atomistic description based on the Lennard-Jones potential act on a sphere around each particle allowing the atoms constituting the solid surface from the wall region to extend their action towards the gaseous particles which undoubtedly has a stabilizing effect on the interface and can be the reason for the drop of the axial average velocity towards zero (Figure 6.4). Hence, we would like produce a similar effect by extending the action of the attractive wall on the interface liquid-gas and investigate if such action would promote the interface equilibrium.

6.2 Effect of the Transitional Section on Nanojets

Two ways are considered in order to extend the action of the modeled surface from the liquid domain towards the interface liquid-gas and even the gaseous domain. A schematic representation of the numerical implementation is given in Figure 6.11. The key issue here is to create a uniform transition from one domain to the other without creating numerical divergence due to particles moving too close to the surface without previous information of its repulsive action. The idea is actually to include the corner in this 2D representation (the complete circle in the 3D code) as a point potential for which
all particles are either attracted or repulsed in a continuous manner form the first region’s channel (dotted arrows). Consequently, the wall model acts locally on the interface liquid-gas with the same or an enhanced potential (in order not to block the jet later on). It is more realistic also to include a wetting characteristic for the lateral wall separating the two regions and the wall model can be easily extended as shown through the solid arrows.

![Figure 6.11: Schematic Representation of the Lateral Wall Action including the Corner Effect](image)

A combination of these corner and lateral potentials are implemented along with the sinusoidal wall model for the test run and snapshots of the two phase injection is shown in Figure 6.12 as well as the average axial velocity distribution along the channel versus time in Figure 6.13.

The initial non-equilibrium stage is observed, consistently with the previous test runs and the velocity peak is of the same order for all tests denoting an independence of the wall model and a dependence on the interfacial characteristics: change of boundaries combined with the same differential pressure. However, the second stage is now inhibited thanks to the extended model to the intersectional wall allowing the velocity to be brought back to zero.
Figure 6.12: Test Run-Sinusoidal Wall + Interactive Transitional Section

Figure 6.13: Axial Velocity with Simulated Corner Effect
CHAPTER 7

CONCLUSIONS AND FUTURE WORK

7.1 Concluding Remarks

Numerical simulations of nanoscale fluids and flows using molecular dynamics were performed in order to assess the importance of the liquid-surface and liquid-gas-surface on nanojet behavior. At these scales, the models implemented to describe different phases can have detrimental effects that can alter the thermodynamic equilibrium state; essential to validate statistical results of these particle-based simulations.

The confidence in the numerical outcomes of these simulations and their viability is dependent on several factors:

- Good statistical representation: long runs, good sampling rate and large systems to produce accurate statistical averages.
- Models based on realistic and physical representation of the phenomena at the molecular level.
- Reproducible and consistent results for a wide range of conditions.
- Transferability of these models for larger and more complex systems.

In this work, we investigated existing surface models and their effects on nanoflows and nanojets. Some models were not designed to handle flows such as the normal wall models, some were not designed to control the system pressure such as the stochastic model and others cannot transfer to large systems such as the atomistic wall for computational reasons.

The developed wall model satisfies our need for a wetting surface that handles momentum exchange with flows and allows control over the system pressure and nanojet stability. It is also an analytical model based on the physical description of an atomistic
surface structure and can be applied for different geometries and larger systems with no extra computational costs entailed to its use. Hence, we successfully developed a surface numerical model that satisfies the requirements of our application and can be extended for a broader range of applications such as porous surface effects on nanoflows, wetting transitions or alkane flows in nanopores.

The developed Lennard–Jones modified potential also satisfies our preliminary requirements for handling long range corrections without altering equilibrium states of the system. The transferability of this potential to complex geometries (planar and cylindrical) was proven in this work but it has still to be tested for more complex molecules with more complex base force fields.

### 7.2 Future Work

Based on what we learned in this work, we can further some aspects of the numerical models developed and extend the use of others towards different applications. Here are some immediate directions to follow up this work:

- The modified Lennard-Jones can be applied to confined fluids hence suppressing the initial pressure difference. This would allow associating any characteristic jet behavior directly to the fluid-surface interactions of the dense phase.

- The focus of our surface modeling was satisfying the system thermodynamic pressure. The lack of such a control was originally the reason thought to be behind the existence of a jet-like behavior. However, we learned that the pressure differential at these scales is only half the reason. The stability of the jet is directly related to the surface stresses in the confined dense phase. Hence, the wall parameters should actually be designed to satisfy stronger stresses at the wall or in other words lower slip values to match the Knudsen numbers for these scales.

- The pressure driven method has to be improved for better control of the system density and temperature. This is related to finding better ways to reinsert the fluid particles in the system. The generation sites should not be limited to planes situated at
one end of the channel but a compressive lateral force (same idea as pressure barostat) can be applied at one section of the tube and the generated particles should be reinjected in the freed volume. The compressive forces should be proportional to the new density within the ‘generation’ volume formed of both existing and new particles.

- From a macroscopic point of view, turbulence is characterized by 3D, multiscale, irregular structures occurring at relatively high Reynolds numbers (Re $>$ 2300 for pipe flows). The scales for the turbulence structures range from: the large eddies carrying energy (scales as the channel diameter $l$) to the kolmogorov microscale $\eta$ where the energy is dissipated ($\frac{\eta}{l} \approx \text{Re}^{-3/4}$). It is assumed that though microscopic scales are involved in turbulence, continuum theory holds as these scales are larger than the molecular dimensions. Numerical simulations based on NS equations require careful modeling of the nonlinear terms and are dependent on the choice of the grid size especially in bounded configurations where the flow interactions with the solid boundary are crucial.

Molecular dynamics simulations of flows are limited in system sizes which limit the Reynolds numbers considerably. However, different experiments conducted by Mala [64] and Hsieh [63] observed transitions from laminar to turbulent flows at $Re_{cr} = 500$, $Re_{cr} = 260$ and $Re_{cr} = 200$ respectively. The latter work investigated a flow through a rectangular channel of height of 115 $\mu$m with a surface roughness of 0.6 $\mu$m. These values for Re numbers are dependent on the working medium and different operating conditions but they agree that the transition to turbulence occurs at the microscale for lower Reynolds numbers than predicted for the macroscale results. Another study from Ransing et al. [60] and reported in Figure 7.1 shows a remarkable average flow velocity change with the increase in the acceleration value driving the fluid. This denotes of the possibility of two distinctive regimes and a transition to turbulence is observed. Similar simulations can be performed taking advantage of the low cost wall model and the implemented Nose-Hoover thermostat for temperature control.
Figure 7.1: Flow Velocity Dependency on the Driving Body Forces


APPENDIX A

MODIFIED LENNARD-JONES POTENTIAL FOR PRESSURE CORRECTION

The details of the development of the modified Lennard-Jones potential: $\phi_m$ are presented here. The total potential in Eq. A.1 has two parts:

$$\phi_m = \phi_{LJ12-6}(r)_{\text{cut}} + \phi_{\text{poly}}(r)$$

Eq. A.1

The first corresponds to the regular truncated Lennard-Jones 12-6 potential and the second part is a polynomial of order 5 chosen to solve for the set of conditions proposed in section 4.3. The procedure is the same for any number of conditions and order of polynomial.

The polynomial is written in Eq. A.2 and we want to solve for the vector in Eq. A.3.

$$\phi_{\text{poly}}(r) = ar^5 + br^4 + cr^3 + dr^2 + er + f$$

Eq. A.2

$$\begin{bmatrix} a & b & c & d & e & f \end{bmatrix}$$

Eq. A.3

The first step is to convert the conditions in Eq. 4.13 to Eq. 4.18 so that they are applied directly on the polynomial function which gives the new set of conditions:

Potential Continuity:

$$\phi_{LJ12-6}(R_l) + \phi_{\text{poly}}(R_l) = \phi_{LJ12-6}(R_l) \Rightarrow \phi_{\text{poly}}(R_l) = 0$$

Eq. A.4

Potential Truncation:

$$\phi_{LJ12-6}(R_u) + \phi_{\text{poly}}(R_u) = 0 \Rightarrow \phi_{\text{poly}}(R_u) = -\phi_{LJ12-6}(R_u)$$

Eq. A.5

Force Continuity:

$$\frac{\partial \phi_{LJ12-6}(R_l)}{\partial r} + \frac{\partial \phi_{\text{poly}}(R_l)}{\partial r} = \frac{\partial \phi_{LJ12-6}(R_l)}{\partial r} \Rightarrow \frac{\partial \phi_{\text{poly}}(R_l)}{\partial r} = 0$$

Eq. A.6

Force Truncation:

$$\frac{\partial \phi_{LJ12-6}(R_u)}{\partial r} + \frac{\partial \phi_{\text{poly}}(R_u)}{\partial r} = 0 \Rightarrow \frac{\partial \phi_{\text{poly}}(R_u)}{\partial r} = -\frac{\partial \phi_{LJ12-6}(R_u)}{\partial r}$$

Eq. A.7
Applying simple polynomial integration and derivatives, the final form of the system to be solved is as following:

\[
\frac{N}{2} \int_0^\infty \phi_m g(r) 4\pi \rho r^2 dr = \frac{N}{2} \int_0^\infty \phi_{LJ12-6} g(r) 4\pi \rho r^2 dr
\]

\[
\Rightarrow \int_0^{R_u} \phi_m g(r) r^2 dr = \int_0^{R_u} \phi_{LJ12-6} g(r) r^2 dr \quad \text{since } \phi_m \text{ vanishes after } R_u
\]

\[
\Rightarrow \int_0^{R_u} \phi_{LJ12-6} g(r) r^2 dr + \int_{R_l}^{R_u} \phi_{poly} g(r) r^2 dr = \int_0^{R_u} \phi_{LJ12-6} g(r) r^2 dr + \int_0^{R_u} \phi_{LJ12-6} g(r) r^2 dr
\]

Approximating \( g(r) \approx 1 \), for \( r \geq R_l \) \( \Rightarrow \int_{R_l}^{R_u} \phi_{poly} r^2 dr = \int_{R_l}^{R_u} \phi_{LJ12-6} r^2 dr = E_{corr} / 2\pi \rho N \)

Pressure Conservation: (Same as Eq. A.9)

\[
\Rightarrow \int_{R_l}^{R_u} r^3 \frac{\partial \phi_{poly}}{\partial r} dr = 3P_{corr} / 2\pi \rho^2 \quad \text{Eq. A.10}
\]

Applying simple polynomial integration and derivatives, the final form of the system to be solved is as following:

\[
\begin{bmatrix}
R_i^5 & R_i^4 & R_i^3 & R_i^2 & R_i & 1 \\
R_u^5 & R_u^4 & R_u^3 & R_u^2 & R_u & 1 \\
5R_i^4 & 4R_i^3 & 3R_i^2 & 2R_i & 1 & 0 \\
5R_u^4 & 4R_u^3 & 3R_u^2 & 2R_u & 1 & 0 \\
\Delta_8 / 8 & \Delta_7 / 7 & \Delta_6 / 6 & \Delta_5 / 5 & \Delta_4 / 4 & \Delta_3 / 3 \\
5\Delta_8 / 8 & 4\Delta_7 / 7 & \Delta_6 / 2 & 2\Delta_5 / 5 & \Delta_4 / 4 & 0 \\

\end{bmatrix}
\begin{bmatrix}
a \\ b \\ c \\ d \\ e \\ f \\
\end{bmatrix}
= \begin{bmatrix}
0 \\ -\phi_{LJ12-6} (R_u) \\ 0 \\ -\frac{\partial \phi_{LJ12-6}}{\partial r} (R_u) \\ E_{corr} / 2\pi N \rho \\ 3P_{corr} / 2\pi \rho^2 \\
\end{bmatrix}
\quad \text{Eq. A.11}
\]

with \( \Delta_k = (R_u^k - R_i^k) \)

This system is solved numerically using a LU decomposition of the 6x6 matrix and the forward/backward substitution to define the polynomial constants. It is preferred to implement this method in a non-dimensional form so that the higher power terms of very small quantities (here is the intermolecular distance) can be evaluated properly and are not subjected to round off or numerical errors. The dimensional value can be recovered when the force is evaluated and added to the Lennard-Jones potential.
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