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Drag properties of graphene coatings: atomistic simulations

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Contents

1	Intoduction	8
2	Theory of fluid-solid interface phenomena	11
2.1	Origin of Fluid-Surface Drag Force	11
2.1.1	The Operative Definition of Drag Coefficient	11
2.1.2	The Role of Bulk hydrodynamics	12
2.1.3	Couette flow	14
2.1.4	Poiseuille flow	15
2.1.5	Couette flow: link with interface properties	16
2.2	Nanofluidics: Microscopic origin of drag force	16
2.2.1	The role of transport phenomena	17
2.2.2	Hydrodynamic limit of validity	18
2.2.3	Green-Kubo relation for interface properties	21
3	Molecular dynamics: A simulation method	26
3.1	Atomistic simulations	26
3.2	Basics of Molecular dynamics	26
3.2.1	Integrating the equation of motion: finite difference methods	28
3.2.2	Simulate other ensembles	29
3.2.3	The holonomic constrain	30
3.2.4	The holonomic constrain: SHAKE algorithm	30
3.3	NEMD: Non equilibrium molecular dynamics	32
3.3.1	Flow driven simulations: Method and Techniques	33
3.3.2	Challenges on NEMD nanofluidics simulations	35
4	Simulation approach and protocols	37
4.1	System modeling	37
4.1.1	SPC/E Water model	37
4.1.2	Graphene model	39
4.2	Fixed-velocity method	39
4.2.1	Simulation protocol	41
4.3	Method validation: free-flow	43
4.3.1	EMD: Conservation of energy and correlation time	44
4.3.2	NEMD and EMD comparison: Radial density function and velocity distribution	46
4.3.3	Profile measurements	48
5	Results	50
5.1	Slip length and slip velocity calculations	51
5.1.1	Temperature drift	56
6	Conclusions	59
A	Additional tables	62

name	symbol	definition
Freestream Dynamic Pressure	q_∞	$\frac{1}{2}\rho_\infty U_\infty^2$
Drag Coefficient	C_D	$\frac{D}{q_\infty S}$
Skin Friction Coefficient	c_f	$\frac{\tau_w}{q_\infty}$
Shear Rate (or Strain Rate)	$\dot{\gamma}$	$\frac{\partial u_x}{\partial y}$
Friction local coefficient	λ	$\tau_w = \lambda v_s$
Dynamical Viscosity	μ	-
Slip Length	b	μ/λ
Slip velocity	v_s	$b \left(\frac{\partial u_x}{\partial y} \right)_{y=0}$

Table 1: Table with the more important definition used into the thesis.

Sommario

In questo lavoro di tesi abbiamo affrontato il problema del calcolo della resistenza (drag) per un flusso d'acqua su grafene mediante simulazioni atomistiche, nell'ambito di un progetto più ampio in cui è coinvolto un gruppo del Dipartimento di Fisica (*Atomistic Simulations of damaGe, Adhesion and dRag reDuction of graphene-based coating* - ASGARD, Innovation Grant del Centro Nazionale di Ricerca in High Performance Computing, Big Data e Quantum Computing (ICSC) finanziato attraverso il PNRR). Le risorse computazionali sono state ottenute sul supercomputer Leonardo, ospitato e gestito da Cineca, il cui accesso è stato garantito tramite un accordo specifico all'interno del progetto ASGARD.

La tesi riporta i calcoli di dinamica molecolare fuori equilibrio eseguiti su celle di simulazione contenenti alcune migliaia di molecole d'acqua, simulando un flusso parallelo a una superficie di grafene. Sebbene ci siano alcuni studi precedenti, la tesi offre un contributo originale proponendo l'introduzione di una "corsia di velocità" per forzare le molecole a mantenere una velocità prefissata lontano dalla superficie. Questo nuovo metodo, chiamato *Fixed-velocity method*, fornisce profili di velocità lineari in accordo con l'idrodinamica classica, consentendo di calcolare, tramite l'interpolazione di quest'ultima, la lunghezza di slittamento (slip length) e la velocità di slittamento (slip velocity). Queste quantità fisiche sono di fondamentale importanza nella descrizione delle proprietà fuori equilibrio all'interfaccia solido-liquido. I risultati incoraggianti ottenuti mostrano come il metodo sembri raggiungere la convergenza con simulazioni di durata relativamente breve rispetto ad altri metodi noti. Attraverso il *Fixed-velocity method* sono stati ottenuti buoni valori di lunghezza di slittamento compresi tra 17.7 e 22.8 nm in buon accordo con i valori noti in letteratura ottenuti con tecniche di dinamica molecolare simili ma con convergenza molto più problematica.

Abstract

In this thesis work we faced the problem of drag calculations for flow water on graphene through atomistic simulations, within the framework of a larger project where a group from the Department of Physics is involved (*Atomistic Simulations of damaGe, Adhesion and dRag reDuction of graphene-based coating* - ASGARD, Innovation Grant of the National Research Center in High Performance Computing, Big Data and Quantum Computing (ICSC) funded through PNRR). Computing resources have been obtained on the Leonardo supercomputer, hosted and managed by Cineca, whose access has been granted by a specific agreement within the ASGARD project.

The thesis reports on non equilibrium molecular dynamics calculations performed on simulations cells containing some thousands of water molecules simulating a flux parallel to a graphene surface. Although there are some previous studies, the thesis offers an original contributions proposing the introduction of a “velocity lane” to force molecules to have a fixed given velocity far from the surface. This new method called *fixed-velocity method* provides velocity profiles with a linear behavior with respect to the distance from the surface, in agreement with classical hydrodynamics, allowing to calculate, through the interpolation of the latter, the slip length and slip velocity. These physical quantities are of fundamental importance in the description of the out-of-equilibrium properties at the solid-liquid interface. The encouraging results obtained show how the method seems to reach convergence with simulations of relatively short length compared to other known methods. Through the *fixed-velocity method* good slip length values, ranging from 17.7 to 22.8 nm were obtained, in good agreement with the values known in literature, obtained with similar molecular dynamics techniques but with difficult convergence.

1 Introduction

Understanding the interactions between fluids and solid surfaces is a fundamental topic in both physics and engineering, with wide-ranging applications in fields such as nanotechnology, material science, and industrial fluid dynamics. One of the most critical phenomena in this context is the fluid-solid friction, often characterized by the slip length and the friction coefficient at the interface. The ability of a fluid to “slip” or “stick” at a surface influences the drag force experienced by a moving fluid, which, in turn, impacts the efficiency of processes ranging from industrial coatings and lubrication systems to nanofluidic devices and biological systems. Over the past few decades, significant progress has been made in the theoretical and experimental understanding of fluid-solid interactions [1, 2], particularly in systems where fluids flow over smooth, structured, or chemically heterogeneous surfaces. Nevertheless, many open questions remain, particularly when examining these interactions at the nanoscale, where conventional continuum models, such as the Navier-Stokes equations, often break down due to the discrete nature of matter. This thesis introduces *a novel simulation method aimed at improving the precision of slip length and friction coefficient calculations, using molecular dynamics simulations* to explore the fundamental mechanics of fluid-solid drag at the atomic scale.

When a fluid flows over a solid surface, the friction force that develops at the interface, known as the drag force, arises due to the interactions between the fluid molecules and the solid surface. In macroscopic systems, the no-slip boundary condition is commonly applied, which assumes that the fluid velocity at the surface is zero. However, at the nanoscale, where fluid molecules interact with solid atoms directly, this assumption no longer holds. Instead, the slip velocity, a measure of how fast the fluid molecules move relative to the solid surface, can be non-zero, leading to significant variations in the drag force.

The study of slip length and friction at fluid-solid interfaces has a rich history, with foundational work dating back to the 19th century. Early investigations were based on the no-slip boundary condition introduced by Stokes, which dominated classical hydrodynamics models for decades. However, with the advent of nanotechnology and the increasing interest in micro and nanoscale fluid dynamics, researchers began to observe deviations from the no-slip condition. [3, 4] These deviations were particularly noticeable in systems where fluid flowed over hydrophobic [5, 6] or atomically smooth surfaces, such as graphene surfaces or graphene nanochannels [7, 8].

In recent years, **molecular dynamics** (MD) simulations have emerged as one of the most powerful tools for studying nanoscale fluid-solid interactions. MD simulations provide atomistic insights into how individual fluid molecules interact with solid surfaces, enabling researchers to compute slip lengths, friction coefficients, and drag forces. A notable advance in this field was the use of equilibrium molecular dynamics (EMD) simulations to calculate transport properties via the Green-Kubo relations [1], which relate macroscopic properties like viscosity and thermal conductivity to microscopic fluctuations in molecular motion. While EMD methods have been successful in many cases, their application to nanofluidics often faces limitations, particularly when the system is far from equilibrium or when complex boundary conditions are involved. **Non-equilibrium molecular dynamics** (NEMD) methods have been developed to address these limitations, *allow-*

ing to simulate flow-driven systems and directly measure fluid velocity profiles near solid surfaces. These simulations have been instrumental in identifying key parameters that influence slip length, such as surface roughness, fluid density, and temperature [9]. In particular, studies on graphene and other carbon-based materials have shown that the chemical and structural properties of the surface can dramatically affect slip behavior [10, 8]. Despite these advances, several challenges remain in the field. One major issue is the high computational cost associated with NEMD simulations, especially for large systems or systems requiring long simulation times to achieve steady-state flow conditions. Moreover, accurately determining the slip length often requires interpolating velocity profiles near the wall, a process that can introduce significant statistical noise, especially in systems with low slip velocities. These challenges motivate the development of new, more efficient methods for investigating slip and friction at the fluid-solid interface.

In this thesis work we faced the problem of drag calculations for a flux of water on graphene through NEMD calculations, within the framework of a larger project where a group from the Department of Physics is involved (*Atomistic Simulations of damaGe, Adhesion and dRag reDuction of graphene-based coating* - ASGARD, Innovation Grant of the National Research Center in High Performance Computing, Big Data and Quantum Computing (ICSC) funded through PNRR). The main focus of the entire project concerns the study of graphene-based coatings for automotive and aerospace components for drag reduction and self-cleaning properties, i.e. low-friction/low-drag and possibly (super-)hydrophobic surfaces in conditions of high speed airflow and/or water drops. In this thesis we focused on the description of a continuous water flux on a surface, starting from available literature to understand how to simulate the process at the atomistic scale. Although the conditions of high speed airflow are different and would require a different approach, since the density of the constituent molecules is much smaller than water, this study is relevant in many aspects; among them, in the perspective of setting up simulation protocols to test new interatomic potentials that are going to be developed by other participants to the project.

The core contribution of this thesis is the development and validation of a new method for calculating slip length and friction coefficients at fluid-solid interfaces using non equilibrium molecular dynamics simulations. This method builds upon the traditional NEMD approach but introduces a **fixed-velocity** setup that allows for more stable and linear velocity profiles. In the fixed-velocity method, an artificial velocity, which drives the flow, is imposed on the fluid away from the graphene surface. By doing so, this setup overcomes the limitations of traditional Couette flow simulations, reducing statistical errors and improves the accuracy of slip length and slip velocity calculations for slow velocity flows. This linearization of the velocity profile enables a more precise interpolation of the slip velocity at the interface, ultimately leading to a more accurate determination of the slip length. The results obtained using this new method have demonstrated both its accuracy and its computational efficiency. Slip length and friction coefficient calculations for water flow over a graphene surface yielded values consistent with those reported in the literature, with slip lengths ranging from 17.7 nm to 22.8 nm, depending on the size of the simulation cell. Importantly, the method showed good convergence across multiple simulation runs, indicating that it is robust to variations in initial conditions. Furthermore, the linear velocity profiles generated by the fixed-velocity method were more stable

than those obtained through traditional methods, reducing the need for long simulation times and allowing for faster convergence of key properties.

In the next Chapter we review the theory of fluid-solid interface phenomena in order to introduce the relevant quantities and relationships, specifying also two typical conditions (Couette and Poiseuille) for the description of a fluid flow. The end of the Chapter is devoted to give a microscopic description of the drag force. In Chapter 3 we briefly present the basics of molecular dynamics simulations, i.e., of the computational approach that we used in this thesis work. We give an essential description, with some attention of specific tools useful for our calculations. We emphasize the use of a non equilibrium molecular dynamics approach. Chapter 4 is devoted to the details of the simulations: the potential chosen to model the interatomic and intermolecular interactions, the specific protocol set to described a flux with a constant velocity far from and parallel to a given surface, how to calculate quantities of interest (namely, velocity profiles) together with some analysis tools. Chapter 5 reports the main results concerning the slip length and slip velocity calculations.

2 Theory of fluid-solid interface phenomena

In this first chapter, we will introduce some of the fundamental theoretical concepts necessary for understanding the physical phenomena that develop at the interface between solids and liquids. This introduction will provide the conceptual basis for understanding the link between the hydrodynamic description of friction and its atomistic physical origin. In the first part, we will see how to describe and define the physical quantities of interest (drag force, drag coefficient, etc.) from a macroscopic and continuous point of view, showing their link with fluidics dynamics. Subsequently, in Section 2.2, we will discuss how and when this continuous description breaks down, and the discrete nature of matter becomes significant, showing how we can describe the phenomena at the interface starting from an atomistic and statistical description.

2.1 Origin of Fluid-Surface Drag Force

A body moving at a certain velocity through a fluid experiences a force that opposes its motion, commonly referred to as **aerodynamic force**¹. The component of this force that acts parallel to the direction of motion is known as **drag force $\mathbf{D}$** , which is responsible for decelerating the body. By adopting a reference frame fixed to the body, we can analyze the system as a stationary object with a fluid flow approaching it. The magnitude of the drag force relative to the total aerodynamic force depends significantly on the body's geometry concerning the fluid flow. However, our primary interest lies in the physical origin of this force at the smallest possible length scale, where concepts like flow remain applicable². At this scale, any surface, when observed closely, can be approximated as flat. Consequently, we can simplify the physical system under investigation as a fluid flow over a flat surface without loss of generality. At this reduced scale, the fluid flow is parallel to the surface, and it is often characterized as laminar and steady. This thin layer of fluid where the interaction between the fluid and the surface alters the velocity profile is known as the **boundary layer**, and is crucial as it is the origin of the drag force. Indeed, *the origin of the drag force is inherently linked to the formation of the boundary layer*. It is the “tugging” action of the surface on the fluid layer in close proximity that gives rise to the drag force. This force is fundamentally due to the **shear stress** distribution over the surface of the body [11]. Understanding this interaction is essential for elucidating the mechanics of drag force at nano-scale levels. In the following sections, we will introduce the basic concepts necessary to describe the drag force from a fluid dynamics perspective. Specifically, we will treat the fluid and the surface as continuous (and ideal) media.

2.1.1 The Operative Definition of Drag Coefficient

As our discussion progresses, it will become clear that we can define a quantity more fundamental than the drag force itself. This dimensionless quantity is called the **drag coefficient**, defined as follows. Let ρ_∞ and U_∞ be the density and velocity, respectively,

¹If the fluid is dense, like a liquid, one can also be referred to the aerodynamic force as hydrodynamic force.

²We discuss this with more details at Sec. 2.2

in the freestream, far away from the body. We can then define a dimensional quantity called the **freestream dynamic pressure** as

$$q_\infty = \frac{1}{2} \rho_\infty U_\infty^2 . \quad (2.1.1)$$

Additionally, let S be the reference area of the body. We can now define the dimensionless drag coefficient as

$$C_D = \frac{D}{q_\infty S} . \quad (2.1.2)$$

Before continuing our discussion on the origin of the drag force, we must first introduce the concept of **shear stress** (τ). Shear stress is a type of stress that occurs when a force is applied parallel or tangential to a surface. It is defined as the force per unit area exerted by a fluid along a plane. Therefore, the integral of the shear stress over the surface (S) gives the total parallel force experienced by the fluid:

$$F_{\parallel} = \int_S \tau(\vec{r}) da . \quad (2.1.3)$$

At the interface between the fluid and the surface of the body, by the conservation of momentum, this force is equal in magnitude to the force applied to the surface. Thus, the shear stress at this boundary, also called **wall shear stress** (τ_w), is essentially the drag force per unit area. The drag force is therefore given by:

$$D = \int_A \tau_w ds = \int_A \tau(\vec{r}_0) ds , \quad (2.1.4)$$

where $\vec{r}_0$ denotes the surface of the body. Knowing this, we can rewrite equation (2.1.2) using equation (2.1.4) as:

$$C_D = \frac{1}{Sq_\infty} \int_A \tau_w ds = \frac{1}{S} \int_A c_f ds , \quad (2.1.5)$$

where c_f , called the **skin friction coefficient**, is defined as

$$c_f = \frac{\tau_w}{q_\infty} . \quad (2.1.6)$$

This is essentially the “local” drag coefficient, which does not require the definition of the entire body surface to be specified. The strength of this definition is that the skin coefficient carries within itself all the physics of the interaction between the fluid and the surface material. In other words, same body, with different physical interaction with fluid, but subject to the exact same flow have different skin (and drag) coefficient.

2.1.2 The Role of Bulk hydrodynamics

It is therefore understood that it is the behavior of the boundary layer with respect to the shear stress induced by the surface that produces the friction force or rather the drag coefficient. Therefore, we want to understand how to describe the flow near the solid-fluid interface and whether it is possible to link the profile of the latter to the drag coefficient. In other words we want to understand how the bulk description of the fluid (into the continuum assumption) is linked with the interface propriety previously discussed.

Navier-Stokes equations The Navier-Stokes (NS) equations are fundamental partial differential equations in fluid mechanics that describe the motion of viscous fluid substances. They express the balance of linear momentum for a fluid element and are derived from the conservation of mass, momentum, and energy. The equations are named after Claude-Louis Navier and George Gabriel Stokes, who made significant contributions to their development in the 19-th century. Mathematically, the Navier-Stokes equations arise from applying Newton's second law to fluid motion, resulting in a set of equations that account for the forces acting on the fluid, including viscous forces and pressure gradients. For an incompressible fluid, which has constant density, the equations can be simplified, so that the incompressible Navier-Stokes equations in three-dimensional Cartesian coordinates are given by:

$$\begin{aligned}\nabla \cdot \mathbf{u} &= 0, \\ \rho \left[\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right] &= -\nabla p + \nabla \cdot \boldsymbol{\sigma} + \mathbf{f},\end{aligned}\tag{2.1.7}$$

where $\mathbf{u}$ is the fluid velocity field³, ρ is the fluid density, p is the pressure, $\boldsymbol{\sigma}$ is the stress tensor of the fluid, and $\mathbf{f}$ represents external forces. Now, for Newtonian fluid the stress tensor can be taken into the form

$$\boldsymbol{\sigma} = \mu \left[\nabla \mathbf{u} + (\nabla \mathbf{u})^T \right],\tag{2.1.8}$$

Where μ is the **dynamic viscosity** of fluid bulk⁴ [11, 12]. So, the divergence of the stress tensor become

$$\nabla \cdot \boldsymbol{\sigma} = \mu \nabla^2 \mathbf{u},\tag{2.1.9}$$

because the incompressibility of fluid ($\nabla \cdot \mathbf{u} = 0$). Then, with no external force, $\mathbf{f} = 0$, we rewrite NS equation (2.1.7) as

$$\rho \left[\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right] = -\nabla p + \mu \nabla^2 \mathbf{u}.\tag{2.1.10}$$

We see from equations (2.1.10), that NS equations are a set of three second order partial differential equations on the velocity field. So, the solution of this sort of equations need some **boundary condition** (BC) in the mathematical sense (at least two for the simpler Couette case). If we suppose to known the pressure gradient that generate the flow, in any case we need the information of the behaviour of the velocity field at some points in space (also infinity). This mathematical condition have a direct physics representation,

³Here and in what follows, we will use the terms “velocity profile” and “velocity field” almost interchangeably. However, for clarity, when we refer to a velocity field, we mean a vector field that assigns a vector to each point in the space occupied by the fluid. On the other hand, ”velocity profile” specifically refers to a situation where the velocity field varies along a single direction and depends on only one spatial coordinate.

⁴In general the viscosity can not be constant, but for a Newtonian fluid, at constant temperature can be taken constant.

that is to say the value of velocity field on the interface between a fluid and a solid. This leads us to define two types of boundary conditions: the **no-slip** and **slip boundary conditions**. The former is the most commonly used in fluid dynamics and states that at the solid-liquid interface, the velocity profile (or the velocity field in general) vanish. Calling the fluid velocity at the interface the **slip velocity** (v_s), this condition implies that $v_s = 0$. On the other hand, the slip condition assumes a different from zero slip velocity. It's important to note that this condition are, from a hydrodynamics point of view, postulated. This means that, *the continuum bulk description of fluid, does not describe the physics of interaction properties of interface*.

In order to better understand how these boundary conditions are related to the properties at the solid-liquid interface, we will provide two simple example of the NS equations solution known as **Couette flow** and **Poiseuille flow**. The former will be very useful later when discussing how to simulate this physical system from an atomistic perspective.

2.1.3 Couette flow

Couette flow refers to the viscous flow of a fluid between two parallel plates, where one plate is stationary and the other moves with a constant velocity. So, consider two infinite, parallel plates separated by a distance d . The lower plate is stationary, and the upper plate moves with a constant velocity U in the x -direction. In this way, we can guess that the flow's velocity field is zero in every component except for x -direction. Moreover, the velocity field depends only on y coordinates, so we can call its velocity profile $u_x(y)$. Now, to find this velocity, we start with the Navier-Stokes equations (2.1.10), for a steady, one-dimensional flow in the x -direction, which simplify as

$$\frac{\partial p}{\partial x} = \mu \frac{\partial^2 u_x(y)}{\partial y^2}, \quad (2.1.11)$$

where $\frac{\partial p}{\partial x}$ is the pressure gradient in the flow direction. In Couette flow, we assume the pressure gradient $\frac{\partial p}{\partial x} = 0$, as there is no external pressure driving the flow⁵. Thus, the equation simplifies again and integrating this equation twice with respect to y gives a linear profile:

$$u_x(y) = my + q \quad (2.1.12)$$

where, m, q are the integration constant of the differential equations. To determine the latter we have to apply the boundary conditions. At $y = 0$, $u(0) = v_s$, that is the velocity at the stationary plate (slip velocity) and at $y = d$, $u(d) = (U - v_s)$ which is the "slip" velocity at the moving plate. Indeed, the BC condition on the surface physically apply on both the stationary and moving surface. Thus, the velocity profile for Couette flow is

$$u_x(y) = \dot{\gamma}y + v_s \quad (2.1.13)$$

⁵Another simple case is the poiseuille flow, where we assume a pressure driven flow, so the gradient of the pressure is constant in the direction of flow.

where γ , usually called **shear rate**⁶, is the value of the derivative of the flow, which in this case is constant and is equal to $(U - v_s)/d$. So, the velocity profile become

$$u_x(y) = \frac{(U - 2v_s)}{d}y + v_s , \quad (2.1.14)$$

of course, in the case of no-slip BC we will have $v_s = 0$, and the profile is just

$$u_x(y) = \frac{U}{d}y . \quad (2.1.15)$$

These two profile are compared in figure 1(a). In the end, it is important to note that the upper wall does not need to be considered the only source of the second boundary condition. In fact, we can assume that at the distance d , the velocity profile remains constant and equals U . This assumption still satisfies the NS equations as a valid solution, until we stay in the domain $[0, d]$

$$u_x(y) = \frac{U - v_s}{d}y + v_s , \quad y \in [0, d] \quad (2.1.16)$$

2.1.4 Poiseuille flow

Another simple flow, in the same geometry of Couette flow, is the so called Poiseuille flow. The latter refers to the viscous flow of a fluid between two parallel plates in the same geometry discussed in Sec. 2.1.3. Now, insted of moving the upper wall, as in Couette flow, we suppose that the flow is produced by a constant pressure gradient long the x direction, and zero in the others. Then the NS equation for the velocity field is the same as Eq. (2.1.11), with $\partial p/\partial x = \text{const}$. Based on the assumption of steady, incompressible, and laminar flows, the one-dimensional momentum balance for the system is

$$\frac{\partial p}{\partial x} = -\rho F_x , \quad (2.1.17)$$

where ρ is the densisty of the fluid and F_x is the force apply on x direction to produce the pressure gradient. At this point, we taking the system of reference with y axis in the centre, between the two walls. In this way the wall have coordinates $\pm d/2$. Then the differential equation (2.1.11) have the generic solution

$$u_x(y) = \frac{\rho F_x}{2\mu} \left[\left(\frac{d}{2} \right)^2 - y^2 \right] + v_s , \quad (2.1.18)$$

where we used the BC conditions at $y = \pm d/2$, to determine the integration constant. Of course we have apply the slip BC where the velocity profile at the walls not vanish, i.e. $u_x(d/2) = v_s$.

⁶It can be also called strain rate.

2.1.5 Couette flow: link with interface properties

We have seen that, to archive a complete hydrodynamic description of the system (equation (2.1.14)) we need some **constitutive equation** involving the interface. Indeed, in the previous paragraph we introduced the slip velocity as some postulated BC condition, but of course, this condition hides within itself the physics of the system and requires a connection with the shear stress. In our mind, indeed, the status of the constitutive equation relative to interface is in every respect comparable to the one of the bulk equations [12]. This means that it *is a material property, involving the chemical nature of the two phases that create the interface*, it should be amenable to the same type of microscopic justifications and statistical mechanical treatments as bulk properties and it can be extracted unambiguously from transport measurements [1].

As for any constitutive equation, the writing of the interface constitutive equation involves a first step of modeling based on considerations of symmetry and linearity. So, starting with the simple possible relation, consistent with the general description for Newtonian fluids, we can write that the wall shear stress is proportional to the slip velocity, i.e.

$$\tau_w = \lambda v_s \quad (2.1.19)$$

where λ is some proportionality constant, which can have a clear physical interpretation as we will see in the next. We notice that this quantity have units of viscosity over length. So, combining equation (2.1.19) with the constitutive equation for the bulk newtonian fluid (eq. (2.1.8)), we arrive to the so called **Navier boundary condition** (NBC) [6, 12, 1, 2]

$$v_s = \frac{\mu}{\lambda} \frac{\partial u_x(y)}{\partial y} = b\gamma, \quad (2.1.20)$$

where we have introduce (in the second equality) the **slip length** $b = \mu/\lambda$. One can note that the slip length can be interpreted as the distance inside the solid to which the velocity profile has to be extrapolated to reach zero, as is shown in figure 1(b). The standard no-slip boundary condition corresponds to $b = 0$, i.e. $\lambda \rightarrow \infty$, so we can portray the λ as a sort of **constitutive friction coefficient**, dependent only on *microscopical interaction between the solid and fluid*. Of course this can be linked to the definition of skin drag coefficient in eq. (2.1.6)

$$c_f = \frac{2v_s}{\rho_\infty U_\infty^2} \lambda = \lambda \frac{v_s}{q_\infty}. \quad (2.1.21)$$

Conventionally a positive slip length is associated with a positive slip velocity, while a (less common) negative length would indicate an apparent change in the sign of the velocity field near the solid.

2.2 Nanofluidics: Microscopic origin of drag force

The term “nanofluidics” has been introduced to define a specific scientific field, implying that unique phenomena occur when a fluid is confined to a nanometer-sized channel. This raises an important question: why is the nanometer scale significant for fluid transport?

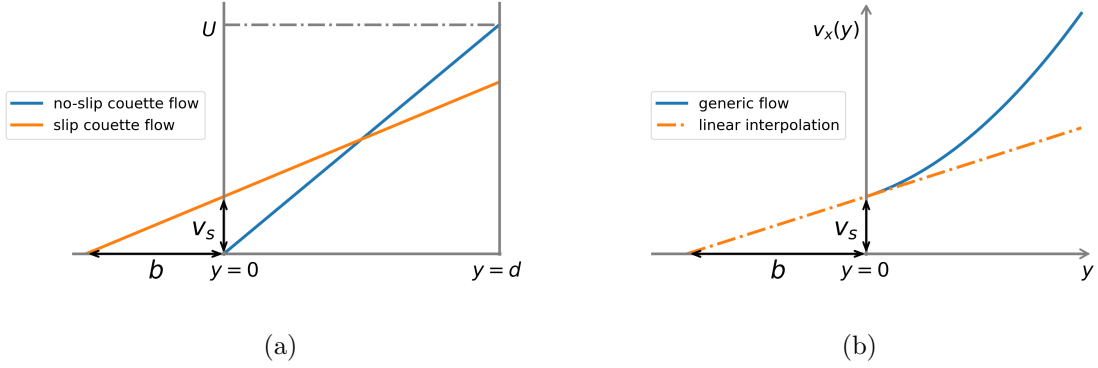


Figure 1: (a) Velocity profiles of couette flow between two walls at distance d long the y axis. U is the velocity of right wall. In blue the profile with the no-slip BC while in orange the ones with slip BC. v_s is the slip velocity while b is the slip length. (b) In blue a generic flow profile (long the x direction) close to the wall surface ($y = 0$). In orange the linear interpolation at the interface, which more generally defines the slip length v_s and slip length b .

Nanofluidics explores the properties of fluids at the nanoscale, prompting us to consider what is specifically being examined in this size range. There are two distinct origins of finite-size effects at the nanometer scale: bulk and surface finite-size effects. Bulk effects are closely related to the applicability of the classical continuum framework, particularly the Navier–Stokes equations of hydrodynamics. We must ask when these traditional descriptions fail and whether we might observe “exotic” fluid behaviors due to the molecular nature of fluids. Conversely, surface effects become increasingly significant as the “surface to volume ratio” rises, meaning as confinement increases [2].

Our goal is, then, understand where and how this finite-size effects originate and if they can explain the phenomenology of interface proprieties.

2.2.1 The role of transport phenomena

Looking at the classical fluid dynamics governed by the NS equations (plus any boundary conditions), one realizes that these equations fall within the larger set of transport phenomena. These phenomena, generally observed in fluids, are those characterized by the non-equilibrium nature of their thermodynamics. Examples of these phenomena are the diffusion of heat, the transport of electric charge in conductors and the diffusion of matter (Fick’s laws). The description of these phenomena is based on the principle of *local, but not global, thermodynamic equilibrium*. This concept (which finds its microscopic counterpart in the concept of linear response regime) allows us to define locally quantities that would be definable only at thermodynamic equilibrium. In general, given the properties $a_i(t)$ of the i -th particle at time t , we define the associated local observable $A(\mathbf{r}, t)$ as

$$A(\mathbf{r}, t) = \sum_i^N a_i(t) \delta(\mathbf{r} - \mathbf{r}(t)) , \quad (2.2.1)$$

where the sum goes over all the particles of the system. Therefore this leads to the formulation of **constitutive equations** that relate flows of these local quantities, with gradients of these local quantities, called thermodynamic forces. These constitutive equations are generalized as

$$\mathbf{J}_A = \gamma_A \mathbf{X}_A , \quad (2.2.2)$$

Where $\mathbf{J}_A$ represents the flux of the local quantity A , $\mathbf{X}_A$ is the thermodynamic force acting on the thermodynamic quantity A , produced by a gradient of another thermodynamic quantity generally different from the first. Finally γ_A is called the **transport coefficient**. An example of this type of constitutive equation is the, well known, Fourier law for heat transfer

$$\mathbf{q}(\mathbf{r}, t) = -\kappa \nabla T(\mathbf{r}, t) , \quad (2.2.3)$$

where the $\mathbf{q}(\mathbf{r}, t)$ is the flow of energy per unit area per unit time, and κ is the transport coefficient. $\nabla T(\mathbf{r}, t)$ is the thermodynamic force which act on energy and how one can see is a gradient of a local temperature. Clearly, the equation (2.2.3), portray the transport of energy, which reflect the nature of non-equilibrium of the system: globally⁷ energy is not conserved and flows from one point in space to another in the system. Now, in our case, the NS equations represent the union between continuity laws (energy, mass and momentum) and the **constitutive law of momentum transport**, already introduced in equation (2.1.8). The latter in component is

$$\sigma_{\alpha\beta}(\mathbf{r}, t) = \mu \left(\frac{\partial}{\partial x_\beta} u_\alpha(\mathbf{r}, t) + \frac{\partial}{\partial x_\alpha} u_\beta(\mathbf{r}, t) \right) , \quad \alpha, \beta = x, y, z , \quad (2.2.4)$$

where we see the similar structure of equation (2.2.3). This analogy is very useful, because allow us to use the linear response theory, through the **Green-Kubo relation** (see Sec. 2.2.3), to obtain from correlation function, the transport coefficient μ . This generic argumentation can be very useful in our goal to understand the microscopic origin of interface phenomena. Indeed, we see in equation (2.1.19) another constitutive equation which link shear stress and the velocity profile. The equation (2.1.19) can also be recast in non local quantity, by integration to the interface surface. So, because neither slip velocity nor λ depends on surface position we have

$$\int_S da \tau_w = D = -S\lambda v_s , \quad (2.2.5)$$

So we have a constitutive equation between the drag force and the velocity field. *The transport coefficient of this equation is exactly the local friction coefficient*, related to the skin drag coefficient (2.1.6). Then one can write a Green-kubo relation for this “interface” transport coefficient [1], how we see in paragraph 2.2.3.

2.2.2 Hydrodynamic limit of validity

We continue our discussion with some short considerations on the validity of bulk hydrodynamics. In practice, this raises the question: when do the Navier–Stokes (NS) equations

⁷Locally anyway the energy density is a conserve quantity in the sense that follows a conservation equation.

break down? As a fact, for simple liquids, the continuum framework of hydrodynamics is apparently valid down to the nanometer scale. In other words, there is no expected deviation to the bulk NS equations for confinement larger than 1 nm. This very surprising result is actually suggested by a number of experimental and molecular simulations studies⁸. Apparently there is no firmly grounded argument for this validity, anyway we propose here a few tentative leads.

Fundamentally the validity of NS equations down to typically 1 nm (for water) is a priori unexpected. Navier-Stokes equations have been developed to account for the fluid dynamics at “large” scales and they rely on an assumption of a local and linear relationship between stress and velocity gradients, as we see in equation (2.1.8). NS equations, like any continuum framework, rely actually on the key assumption of a *separation of length- and time-scales* between the macroscopic fluid motion and the molecular dynamics. To better understand why, we need to introduce the concept of **dynamical regimes**.

Dynamical regimes When studying a liquid from a microscopic point of view, we generally introduce correlation functions that depend on space and time. These correlation functions are nothing but equilibrium thermodynamic averages of continuous quantities (e.g. density) defined as sums of microscopic properties related to the particles as we already introduced in equation (2.2.1). Now the correlation functions between two of this fields, for example A and B , is define as

$$C_{AB}(\mathbf{r} - \mathbf{r}', t) = \langle A(\mathbf{r}, t) B(\mathbf{r}', 0) \rangle , \quad (2.2.6)$$

where we suppose the space and time translation invariance and the $\langle . \rangle$ denotes equilibrium average. This correlation function can give a lot of information about the dynamics of the fluid, and are of profound importance in the study of thermodynamic fluctuation on non equilibrium system [13]. Furthermore, the way in which this correlation function (or its Fourier transform) decay can provide us a powerful method to understand the type of dynamic of the fluid. Generally, one is allow to identify *three different dynamical regimes*: **free**, **kinetic** and **hydrodynamic**. The **free regime** is characterized by a decay of the Fourier transform of the density correlation function, known as *intermediate scattering function* $F(\mathbf{k}, t)$ exponential with a quadratic dependence on time

$$F(\mathbf{k}, t) \sim e^{-\alpha(kt)^2} , \quad (2.2.7)$$

where α is an opportune constant. On the other hand the **hydrodynamic regime**, where the continuous description of the fluid should hold, is characterized by a decay of the intermediate scattering function typical of diffusive phenomena, namely

$$F(\mathbf{k}, t) \sim e^{-\alpha k^2 t} . \quad (2.2.8)$$

Looking at the correlation function of a real fluid, one realizes that both of these behaviors are present. The first on very small time scales, the second on much larger scales. So, defining $t_0 \sim 1$ ps the microscopic time and $\xi_0 \sim 1$ Å the microscopic length, one can differ these regime by their characteristic time and space-scales, as can be seen in table (2).

⁸See [12, 2] for a complete review of experimental and simulation results

regime	time	space	k-space
free	$t \ll t_0$	$r \ll \xi_0$	$ \mathbf{k} \xi_0 \gg 1$
kinetic	$t \sim t_0$	$r \sim \xi_0$	$ \mathbf{k} \xi_0 \sim 1$
hydrodynamic	$t \gg t_0$	$r \gg \xi_0$	$ \mathbf{k} \xi_0 \ll 1$

Table 2: Summary table of length and time scales of dynamical regimes. t , $r = |\mathbf{r}|$ and $\mathbf{k}$ identify the typical decay lengths of the correlation functions (or of their Fourier transforms with respect to space).

Under this scale separation, the microscopic dynamics associated with a huge number of degrees of freedom ($N \approx 10^{23}$) reduces to equations with just a few degrees of freedom (velocity field, pressure, density, temperature, etc.), while all the complexity is hidden in just a few phenomenological coefficients [2]. In other words, until the time an space scale respect the *hydrodynamic limit* in table (2)

Estimate of the characteristic length A easy way to obtain a estimation of the hydrodynamic limit is evaluate the correlation function of some field rule by the NS equation. Because of that we aspect that the dynamical regime of this quantity will be the one in which the continuum framework should hold. So, tho do this we need to define the local particle current

$$j^\alpha(\mathbf{r}, t) = \sum_i^N v_i^\alpha(t) \delta(\mathbf{r} - \mathbf{r}_i(t)) , \quad \alpha = x, y, z \quad (2.2.9)$$

where the sum is over the N particles of the system, and $v_i^\alpha(t)$ is the velocity of i -th particle at time t . Now, using the conservation of particles, energy and momentum one can write the NS equation for the local particle current. Taking the Fourier transform respect the space, one can decouple the complex equation into transverse and longitudinal component [13]. The transverse one is quite simple

$$\frac{\partial}{\partial t} j^\alpha(\mathbf{k}, t) = -\nu k^2 j^\alpha(\mathbf{k}, t) , \quad (2.2.10)$$

where $\nu = \mu/\rho$ is the kinematic (shear) viscosity. One can already see that *this equation have the same structure as the diffusion equation* and the kinematic shear viscosity has the same dimensions as the self-diffusion coefficient. Then if we multiply through (2.2.10) by $j^\alpha(-\mathbf{k}, 0)$ and take the equilibrium average we find that the transverse current auto-correlation function satisfies the equation

$$\frac{\partial}{\partial t} C(k, t) + \nu k^2 C(k, t) = 0 . \quad (2.2.11)$$

This equation is easy solved to give

$$C(k, t) = C(k, 0) \exp(-\nu k^2 t) . \quad (2.2.12)$$

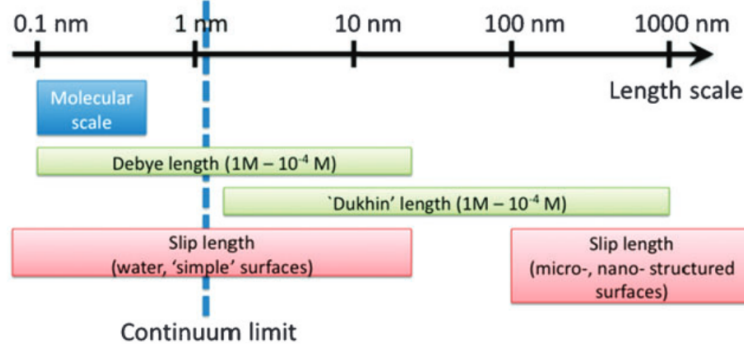


Figure 2: Comparison between different length scale and continuum limit. (Image from [2])

Now, this behaviour is clearly distinctive of hydrodynamic regime, and we expect a validity until $t > t_0$. So the typical time of the auto-correlation function is $\tau = 1/\nu k^2$ therefore we have the implicit condition of validity of hydrodynamic regime

$$\tau > t_0 \implies k < (\nu t_0)^{-2} \quad (2.2.13)$$

and finally, defining the dimension $w \sim 1/k$ we can find the lower limit of validity of bulk hydrodynamics

$$w > l_c = \sqrt{\nu t_0} \quad (2.2.14)$$

Now, putting some numbers, for water at room temperature $\nu \sim 10^{-6} \text{ m}^2 \text{ s}^{-1}$ and then the **characteristic length** l_c is

$$l_c \sim 1 \text{ nm} \quad (2.2.15)$$

A nanometric characteristic length scale thus emerges naturally as a lower boundary for the validity of the notion of viscosity, and thus for the application of standard NS hydrodynamics. This is indeed the experimental value below which strong departure from the continuum framework is observed.

To summarize this section, we have discussed a qualitative argument, based on the microscopic description of fluid systems, that seeks to explain the surprising accuracy of classical hydrodynamics even at very small scales. This is made possible by evaluating the validity of the hydrodynamic regime for the local particle flow dynamics described by the Navier-Stokes equations. Although this argument is simple and not formally rigorous, it provides an estimate of the characteristic length that aligns well with experimental measurements and simulation results. This, in turn, gives us further justification for applying hydrodynamic results within atomistic simulations.

2.2.3 Green-Kubo relation for interface properties

As we saw in Sec. 2.1.5, the local friction coefficient is nothing more than a transport coefficient. So we can use the linear response theory and the hydrodynamic limit to obtain

a microscopical description of λ . We will introduce the linear response theory briefly and in a very general way in the following paragraph, both to clarify the notation and for clarity of exposition. We will, then, specialize the general discussion to our case⁹.

Driven system and linear response theory Consider a classical system, describe by $3N$ generalized coordinates $q_1, q_2, \dots, q_{3N} = q$ and $3N$ generalized momenta $p_1, p_2, \dots, p_{3N} = p$, and an Hamiltonian $\mathcal{H}_0(q, p)$, which, in absence of driving forces, satisfies Hamilton's equations of motion. Now, we would like to include the effect of a weak driving force that is assumed to perturb the system only slightly away from equilibrium. To this end, we introduce the following equation of motions

$$\dot{q}_i = \frac{\partial \mathcal{H}_0}{\partial p_i} + C_i(q, p) F_e(t) \quad (2.2.16)$$

$$\dot{p}_i = -\frac{\partial \mathcal{H}_0}{\partial q_i} + D_i(q, p) F_e(t) , \quad (2.2.17)$$

where, $F_e(t)$ is a time dependent driving force, and C_i and D_i are phase space function, whose form are determined by the particular external perturbation. If we impose that the driving force in study still allow the conservation of the volume of the phase space, i.e. the equations of motion have a zero phase space compressibility. So, denoting $x = (p, q)$, the phase space distribution $f(x, t)$, which describe this equations of motion, satisfies the Liouville equation

$$\frac{\partial}{\partial t} f(x, t) + iL f(x, t) = 0 \quad (2.2.18)$$

where $iL = \dot{x} \cdot \nabla_x$ is the well known Liouville operator. Now, one can use a perturbative approach to solve the Liouville equation, developing the distribution in phase space to the first perturbative order

$$f(x, t) = f_0(\mathcal{H}_0) + \Delta f(x, t) , \quad (2.2.19)$$

where f_0 is the equilibrium phase space distribution. Following this approximation one can prove, that giving some quantity $B(q, p)$, the average on the non equilibrium ensemble $\langle . \rangle_t$ of the quantity can be computed as

$$\langle B \rangle_t = \langle B \rangle - \frac{1}{k_b T} \int_0^t ds F_e(s) \langle B(t-s) j(0) \rangle , \quad (2.2.20)$$

where $\langle . \rangle$ denote the equilibrium average, k_b the Boltzmann constant and $j(t)$ represent the *dissipative flux*, defined as

$$j(t) = j(x(t)) = - \sum_i^{3N} \left[D_i(x) \frac{\partial \mathcal{H}_0}{\partial p_i} + C_i(x) \frac{\partial \mathcal{H}_0}{\partial q_i} \right] \quad (2.2.21)$$

Now, we can specialize the generic discussion of previous paragraph to our case of interest. Because the coefficient that we would like to obtain is independent to the type

⁹For the reader interested in a treatment, see Statistical Mechanics: Theory and Molecular Simulation, Mark.E. Tuckerman

of flow [1], we can reduce ourselves to considering the simpler case. So, suppose to have a fluid with an ideal solid-fluid interface on the plane xz , with a linear velocity profile $u_x(y)$, long the x direction and dependent only by y coordinate perpendicular to xy plane. At the interface we have a slip BC, so the profile goes to zero at some point $-y_0$ under the interface

$$u_x(y) = \dot{\gamma}(y + y_0) , \quad (2.2.22)$$

where $\dot{\gamma}$ is the shear rate. With this profile the velocity at the ideal interface ($y = 0$) is $u_x(0) = y_0\dot{\gamma}$. Now, we need to find the perturbation which create this flow. So, let take $\mathcal{H}_0$ the equilibrium Hamiltonian of the fluid of N particles

$$\mathcal{H}_0 = \sum_i^N \frac{\mathbf{p}_i}{2m_i} + U_f(\mathbf{r}) + U_w(\mathbf{r}) , \quad (2.2.23)$$

where U_f is the interaction potential between the fluid particles and U_w between wall and particles, m_i is the mass of the i -particle and $\mathbf{r} = \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{3N}$. If we perturb the equilibrium Hamiltonian with

$$\Delta\mathcal{H}[\dot{\gamma}, y_0] = \dot{\gamma} \sum_i^N (y_i + y_0) p_{i,x} , \quad (2.2.24)$$

where the sum is over all the N particle of the system, y_i and $p_{i,x}$ are the position and momentum of i -th particle. The equation of motion become then

$$\dot{\mathbf{r}}_l = \frac{\partial\mathcal{H}_0}{\partial\mathbf{p}_l} + \dot{\gamma} (y_l - y_0) \hat{x} \quad (2.2.25)$$

$$\dot{\mathbf{p}}_l = \frac{\partial\mathcal{H}_0}{\partial\mathbf{r}_l} - \dot{\gamma} p_{l,y} \hat{x} \quad (2.2.26)$$

so we see that if we average the (2.2.26), over an equilibrium distribution such as the canonical distribution, the quantity $\langle \partial\mathcal{H}_0 / \partial\mathbf{p}_l \rangle$ vanishes, leaving only an overall component $\dot{\gamma} (\langle y_i \rangle - y_0) \hat{x}$, indicating that, on average, the net flow of the system follows the velocity profile as expected from hydrodynamics. At this point, one can identify

$$\mathbf{C}_i(\mathbf{r}, \mathbf{p}) = \dot{\gamma} (y_i - y_0) \hat{x} = \dot{\gamma} [(\mathbf{r}_i - \mathbf{r}_0) \cdot \hat{y}] \hat{x} \quad (2.2.27)$$

$$\mathbf{D}_i(\mathbf{r}, \mathbf{p}) = -\dot{\gamma} p_{i,y} \hat{x} = -\dot{\gamma} (\mathbf{p}_i \cdot \hat{y}) \hat{x} , \quad (2.2.28)$$

and then, using the definition in equation (2.2.21) and substituting equations (2.2.27) and (2.2.28) we obtain

$$j(\mathbf{r}, \mathbf{p}) = \dot{\gamma} \sum_i^N \left[([\mathbf{r}_i - \mathbf{r}_0] \cdot \hat{y}) (\mathbf{F}_i \cdot \hat{x}) - (\mathbf{p}_i \cdot \hat{y}) \left(\hat{x} \cdot \frac{\mathbf{p}_i}{m_i} \right) \right] \quad (2.2.29)$$

It can be shown that a phase space function can be constructed that represents the microscopic estimator of the stress tensor. For the xy component is

$$\sigma_{xy}(\mathbf{r}, \mathbf{p}) = \sum_i^N \left[(\mathbf{r}_i \cdot \hat{y}) (\mathbf{F}_i \cdot \hat{x}) - (\mathbf{p}_i \cdot \hat{y}) \left(\hat{x} \cdot \frac{\mathbf{p}_i}{m_i} \right) \right] . \quad (2.2.30)$$

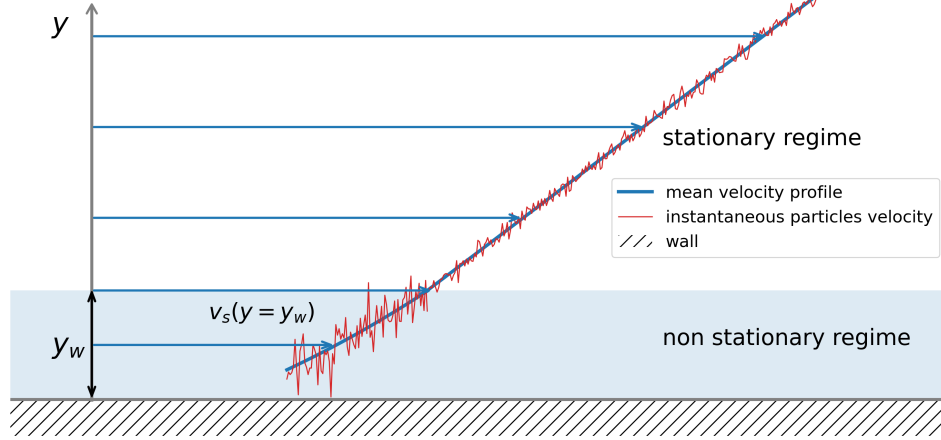


Figure 3: Schematic representation of velocity profile from a microscopic point of view. One can see two regime, the stationary “hydrodynamics” regime, in which the mean of microscopic velocity profile of particles (in red) are linear, and the non-stationary one, where the profile is not linear and the fluctuation are grater. This non-stationary zone start at y_w and is used to define the hydrodynamic slip velocity from molecular dynamics.

This microscopic physical quantity is such that the average in the thermodynamic ensemble gives the hydrodynamic stress tensor of the fluid. Then substituting the equation (2.2.30) into (2.2.29) and specializing the (2.2.20) for $B = F_x^w$ total tangential force that the wall exerts on the fluid molecules, one obtain

$$\langle F_x^w \rangle_t = \langle F_x^w \rangle - \frac{\dot{\gamma}}{k_b T} \int_0^t ds [\langle F_x^w(t-s) \sigma_{xy}(0) \rangle + y_0 \langle F_x^w(t-s) F_x(0) \rangle] \quad (2.2.31)$$

At this point, it is not difficult to convince oneself that $\langle F_x^w \rangle$ is zero, furthermore one can sense that the force that the wall exerts on the fluid $\mathbf{F}^w$ and the force that the fluid exerts on itself $\mathbf{F}^f$ are completely uncorrelated, then $\langle F_x^w(t-s) F_x(0) \rangle = \langle F_x^w(t-s) F_x^w(0) \rangle$ so long as $\mathbf{F} = \mathbf{F}^w + \mathbf{F}^f$. Therefore, we can write

$$\langle F_x^w \rangle_t = -\frac{\dot{\gamma}}{k_b T} (y(t) + y_0) \int_0^t ds \langle F_x^w(t-s) F_x^w(0) \rangle \quad (2.2.32)$$

$$y(t) = \frac{\int_0^t ds \langle F_x^w(t-s) \sigma_{xy}(0) \rangle}{\int_0^t ds \langle F_x^w(t-s) F_x^w(0) \rangle}, \quad (2.2.33)$$

The $y(t)$ have the dimension of length and can be interpreted as a position. Now, if we take the hydrodynamic limit $t \rightarrow \infty$ and we identify $D = \lim_{t \rightarrow \infty} \langle F_x^w \rangle_t$ and $y_w = \lim_{t \rightarrow \infty} y(t)$, we obtain the relation

$$\lambda S v_s = \frac{1}{k_b T} u_x(y = y_w) \int_0^\infty ds \langle F_x^w(s) F_x^w(0) \rangle \quad (2.2.34)$$

finally, if we identify the hydrodynamic slip velocity with the microscopic velocity at point y_w [1] we obtain the Green-Kubo relation for the local friction coefficient

$$\lambda = \frac{1}{k_b T S} \int_0^\infty ds \langle F_x^w(s) F_x^w(0) \rangle \quad (2.2.35)$$

To conclude this section, we note that in the construction of relation (2.2.35) the difference between length scales emerges spontaneously. In fact, from the microscopic point of view, even if we assume to consider an ideal interface, the definition of hydrodynamic slip velocity is to be interpreted differently. In fact, if the hydrodynamic definition on the continuum is nothing other than the velocity at the exact point of the interface, the discrete microscopic nature of the fluid and the minimum possible length for the validity of hydrodynamics, prevent an exact transposition to the microscopic definition. The position y_w is therefore to be interpreted as the minimum distance from the interface at which continuous hydrodynamics still describes the dynamics, and therefore where it still makes sense to be able to define a slip velocity [1]. (Fig. 3)

3 Molecular dynamics: A simulation method

Calculating the partition function and associated thermodynamic and equilibrium properties for a general many-body potential that include non linear interaction becomes an insurmountable task if only analytical techniques are employed. In this case, the only recourses are to introduce simplifying approximation, replace a given system by simpler model system, or employ numerical methods. In this chapter our discussion will focus on such numerical approach, namely, the methodology of **molecular dynamics** (MD), with particular attention to aspects of interest in the simulation of fluids and interface phenomena. Indeed, after a introduction to basic concept of MD we will discuss of **non-equilibrium molecular dynamics** (NEMD) a similar numerical method, useful to simulate transport phenomena.

3.1 Atomistic simulations

Molecular dynamics is a technique that allow a numerical “thought experiment” to be carried out using a model that, to limited extent, approximates the real physical or chemical system. Such a “virtual laboratory” approach has the advantage that many many such “experiments” can be easily set up and carried out in succession bay simply varying the control parameters. Moreover, extreme conditions, such as high temperature or pressure, can be created in a straightforward way than they can in physical laboratory. The obvious downside is that the results are only as good as the numerical model. Therefore MD has become an essential tool in understanding complex physical phenomena, particularly in systems where experimental measurements are challenging or impossible. After the first simulation of liquid water (Stillinger and Rahman 1971-1974), explicit treatment of molecular systems was enabled by introduction of techniques for maintaining specific bounding patterns either by stiff intra-molecular forces or by imposing holonomic constraints into the simulation [14, 15].

This is particularly relevant in the field of fluid dynamics, where atomistic simulations have been used to explore the behavior of flow driven fluids, enabling the calculation of physical quantities, such as viscosity, diffusion coefficients, and interfacial properties, which are difficult to obtain experimentally [2, 12, 6]. For instance, molecular simulations have successfully determined shear viscosity in confined fluids and have been used to study the thermal conductivity of nanofluids. Such capabilities make MD an invaluable method for probing fluid dynamics at a level of detail that complements experimental studies and enhances our ability to model and predict the behavior of real-world systems.

3.2 Basics of Molecular dynamics

We begin our discussion on molecular dynamics by noting a few important proprieties of the microcanonical ensemble. The latter consist of all microscopic states on the constant energy hypersurface $\mathcal{H}(x) = E$. This fact suggest an intimate connection between the microcanonical ensemble and classical Hamiltonian mechanics. So, imagine that we have a system of N particle evolving according to Hamiltonian mechanics, i.e. following the

Newton law of motion, then the force for the i -th particle is

$$\mathbf{F}_i = \nabla_{\mathbf{r}_i} U(\mathbf{r}) = m_i \ddot{\mathbf{r}}_i \quad (3.2.1)$$

where $U(\mathbf{r}) = U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is the interaction potential between the particles. Since the equation of motion conserve the Hamiltonian, a trajectory computed via equations (3.2.1) will generate microscopic configuration belonging to a microcanonical ensemble with energy E . Suppose, further that given an infinite amount of time this system will be able to visit all the configuration on the constant energy hypersurface. This type of system with this property is said **ergodic**, and can be used to generate a microcanonical ensemble. Then, given an ergodic trajectory generated by the Hamiltonian $\mathcal{H}(x)$, microcanonical phase space average can be replaced by time average over a trajectory according to

$$\langle a \rangle = \lim_{\mathcal{T} \rightarrow \infty} \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} dt a(x_t), \quad (3.2.2)$$

where a is some microscopical physical quantity and $a(x_t)$ is the same quantity calculated for the particles configuration at time t . In a molecular dynamics simulation, equations (3.2.1) are solved numerically subject to a given set of initial conditions. Doing so requires the use of a particular **numerical integrator** or solver for equation of motion. An integrator generates phase space vectors at discrete times that are multiples of a fundamental time discretization parameter Δt , called **time step**. Starting with some initial condition x_0 , phase space vectors $x_{n\Delta t}$, where $n = 0, 1, 2, \dots, M$ are generated by applying the integrator iteratively. In this way, the ensemble property a is then related to the discretized time average by

$$\langle a \rangle = \frac{1}{M} \sum_n^M a(x_{n\Delta t}) \equiv \bar{a}. \quad (3.2.3)$$

In equation (3.2.3) it is understood that the quantity $a(x)$ is algebraically averaged over all the particles of the system. Clearly, in a real thermodynamic system the typical number of particles is of the order of Avogadro's number ($N_a \sim 10^{23}$). Therefore it is unthinkable to solve numerically such a high number of equations. The solution to this problem is simple and elegant, and goes under the name of **periodic boundary conditions** (PBC). In a typical MD simulation, a number $N \ll N_a$ of particles is simulated inside a so-called *simulation cell*. The particles obviously feel the vacuum outside the simulation cell and the simulated system, therefore, does not represent a good sample on which to calculate the thermodynamic quantities. These are called boundary effects, and they arise from the limited dimensions of the simulated system. To eliminate these effects, PBCs are implemented in MD simulations. The simulation cell is copied and repeated along all directions, mimicking an infinite system made up of an infinity of volumes where the dynamics of the particles is exactly the same. In this way, the particles in one edge of the simulation cell also interact with those of the next cell, which are nothing more than the same particles of the simulation cell but placed at a distance multiple of the size of the simulation cell. In this way, edge phenomena are contained without the need to simulate an almost infinite number of particles. Depending on the type of simulation cell used, PBC can be implemented in various ways, generally the most flexible is the *minimum image convention* [15].

Before moving on to the discussion of numerical integrators, it is important to note that the molecular dynamics method has the particular advantage of yielding equilibrium average and *dynamical information* simultaneously. For our purposes these dynamic properties, obtainable only through molecular dynamics are of essential importance, and we will discuss them in the section 3.3.

3.2.1 Integrating the equation of motion: finite difference methods

There are three principal aspect to a MD calculation: the model describing the inter-particle interactions; the calculation of energy and forces from the model, which should be done accurately and efficiently and the algorithm used to integrate the equations of motions. So, continuing our discussion on molecular dynamics techniques, we will start by considering the problem of devising a numerical integrator for the equations of motion.

The Verlet algorithm By far the simplest way to obtain a numerical integration scheme is use a Taylor series. In this approach, position of a i -th particle at time $t + \Delta t$ is expressed in terms of its position, velocity and acceleration at time t according to

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \dot{\mathbf{r}}_i(t)\Delta t + \frac{1}{2}\ddot{\mathbf{r}}_i(t)\Delta t^2 + \mathcal{O}(\Delta t^3) \quad (3.2.4)$$

Since $\dot{\mathbf{r}}_i(t) = \mathbf{v}_i(t)$ and $\ddot{\mathbf{r}}_i(t) = \mathbf{F}_i(t)/m_i$ by Newton's second law, we can rewrite the equation (3.2.4) and also write another Taylor series for $t - \Delta t$ point, obtaining

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{\mathbf{F}_i(t)}{2m_i}\Delta t^2 + \mathcal{O}(\Delta t^3) \quad (3.2.5a)$$

$$\mathbf{r}_i(t - \Delta t) = \mathbf{r}_i(t) - \mathbf{v}_i(t)\Delta t + \frac{\mathbf{F}_i(t)}{2m_i}\Delta t^2 - \mathcal{O}(\Delta t^3) \quad (3.2.5b)$$

Adding equations (3.2.5), one obtains, rearranging for $\mathbf{r}_i(t + \Delta t)$

$$\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{\mathbf{F}_i(t)}{m_i}\Delta t^2 + \mathcal{O}(\Delta t^4) \quad (3.2.6)$$

Equation (3.2.6) is a numerical solver known as the **Verlet algorithm** [16], given a set of initial coordinates $\{\mathbf{r}_1(0), \mathbf{r}_2(0), \dots, \mathbf{r}_N(0)\}$ and initial velocities $\{\mathbf{v}_1(0), \mathbf{v}_2(0), \dots, \mathbf{v}_N(0)\}$, equation (3.2.5a) can be used to obtain a set of coordinates $\{\mathbf{r}_1(\Delta t), \mathbf{r}_2(\Delta t), \dots, \mathbf{r}_N(\Delta t)\}$, after which iteratively application of equation (3.2.6) can be used to generate a trajectory of arbitrary length. Note that the Verlet algorithm only generates positions. If needed, the velocity can be constructed at any point in the trajectory via the centered difference formula

$$\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t - \Delta t)}{2\Delta t} + \mathcal{O}(\Delta t^2) \quad (3.2.7)$$

The velocity Verlet algorithm Although appealing in its simplicity, the Verlet algorithm does not explicitly evolve the velocities, and is somewhat inelegant, as phase space is composed of both positions and velocities. Here we will derive a variant of the Verlet integrator, known as the **velocity Verlet algorithm** [17], that explicitly evolve positions

and velocities. Consider, again, the expansion of the coordinates up to second order in Δt (equation (3.2.5a)). Interestingly, we could also start from $\mathbf{r}_i(t + \Delta t)$ and $\mathbf{v}_i(t + \Delta t)$, compute $\mathbf{F}_i(t + \Delta t)$ and evolve backwards in time to $\mathbf{r}_i(t)$, according to

$$\mathbf{r}_i(t) = \mathbf{r}_i(t + \Delta t) - \mathbf{v}_i(t + \Delta t)\Delta t + \frac{\mathbf{F}_i(t + \Delta t)}{m_i}\Delta t^2 - \mathcal{O}(\Delta t^3) \quad (3.2.8)$$

Substituting equation (3.2.5a) into equation (3.2.8) and solving for $\mathbf{v}_i(t + \Delta t)$ yields

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{\Delta t}{2m_i} [\mathbf{F}_i(t) - \mathbf{F}_i(t + \Delta t)] + \mathcal{O}(\Delta t^4) \quad (3.2.9)$$

Thus, velocity Verlet algorithm uses both equations (3.2.5a) and (3.2.9) to evolve the positions and velocities simultaneously.

We end the section pointing out that the Verlet and velocity Verlet algorithms satisfy two properties that are crucial for the long-time stability of numerical solvers. The first one is time-reversibility, which means that if we take as initial conditions $\mathbf{r}_1(t + \Delta t), \dots, \mathbf{r}_N(t + \Delta t), \mathbf{v}_1(t + \Delta t), \dots, \mathbf{v}_N(t + \Delta t) = x(t + \Delta t)$ and step backward in time using a time step $-\Delta t$, we will arrive at the state $x(t)$. Time-reversibility is a fundamental symmetry of Hamilton's equations that should be preserved by a numerical integrator. The second one is the *symplectic property* of classical mechanics. This means that an integrator algorithm maps the initial phase space point x_0 to $x_{n\Delta x}$ without destroying the symplectic property of classical mechanics [15].

3.2.2 Simulate other ensembles

In the previous section, we have seen that the MD methods are based to the fact that a trajectory computed from the Hamiltonian equation (3.2.1) will generate a microscopic configuration belonging to a microcanonical ensemble. Generally speaking, this type of MD simulations are referred as NVE. This naturally rises the question of how molecular dynamics simulations can be performed under condition of other ensembles, like canonical or isobaric.

Let's consider, for example, the canonical ensemble. In the latter, the energy the energy is not conserved but fluctuates so as to generate the Boltzmann distribution $e^{-\beta\mathcal{H}}$ due to exchange of energy between the system and the thermal reservoir to which it is coupled. Although it is known that these energy fluctuations vanish in the thermodynamic limit, most simulation systems are performed far enough from this limit, so the fluctuations can not be neglected. Therefore, the objective is to compute trajectory that sample the Boltzmann distribution, in order to generate these fluctuations in a MD simulation. This type of simulation are called NVT and to perform them we need to mimic the effect of thermal reservoir. Various methods to achieve this have been proposed. From the simpler re-scaling velocities such that the instantaneous kinetic energy corresponds to a desired temperature to more fine methods like extended phase space approach. Of all NVT methods, by far the latter are the most popular. These techniques are based on supplementing the physical phase space with additional variables that serve to mimic the

effect of a heat bath within a continuous deterministic dynamical scheme. The same idea of “extended phase space ” can be used to simulate other ensemble like isobaric (NPT) or isoenthalpic [15].

3.2.3 The holonomic constrain

In this section and in section 3.2.4, we will discuss how to extend the numerical integrators introduced in the section 3.2.1 to the case of a system of points subject to holonomic constraints. These constraints can represent molecules or atomic structures that are to be modeled as rigid. Therefore, this problem is of essential importance, especially for our purposes in modeling the water molecule, as will be seen in section 4.1.

Consider a system of N particles described by the coordinates $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$, with $N_c < N$ constraints imposed on them, which, for instance, define a specific molecular structure. Our goal is to model this structure as a rigid body. Since these constraints are dependent solely on the positions of the particles, they can be classified as holonomic constraints. By definition, holonomic constraints depend only on the positions of the particles and, possibly, time, and can be expressed through a set of conditions in the form:

$$\sigma_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; t) = 0 \quad k = 1, \dots, N_c \quad (3.2.10)$$

For the present discussion, we will only time-independent constraints. So, in this case, the equation of motion can be expressed as [15]

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i + \sum_{k=1}^{N_c} \lambda_k \nabla_i \sigma_k \quad (3.2.11a)$$

$$\frac{d}{dt} \sigma_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = 0 \quad k = 1, \dots, N_c, \quad (3.2.11b)$$

where λ_k is a set of Lagrange multipliers for enforcing the constraints. Although it is possible to obtain an exact expression for Lagrange multipliers using Gauss’s principle of least constraint [15], the numerical integration of the equations of motion obtained by substituting the exact expression for λ_k into equation (3.2.11a) would not exactly preserve the constraint condition due to numerical errors, which would lead to unwanted instabilities and artefacts in a simulation. Moreover, Gauss’s equations of motion are complex non-Hamiltonian equations that can not be treated using simple methods such as the Verlet and velocity Verlet algorithms. These issues can be overcome by implementing a scheme for computing the multipliers “on the fly” in a simulation in such a way that the constraint condition is exactly satisfied within a particular chosen numerical integration scheme. This is the approach we will now describe.

3.2.4 The holonomic constrain: SHAKE algorithm

The constraint problem amounts to integrating the equations (3.2.11a) with constraints (3.2.11b) and $\sigma_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = 0$. We wish to develop a numerical scheme in which the constraint is satisfied exactly as part of the integration algorithm. Starting from the

velocity Verlet approach, for example, we begin with the position update, which when holonomic constraints are imposed reads

$$\mathbf{r}_i(\Delta t) = \mathbf{r}_i(0) + \mathbf{v}_i(0)\Delta t + \left[\mathbf{F}_i(0) + \sum_{k=1}^{N_c} \lambda_k \nabla_i \sigma_k(0) \right] \frac{\Delta t^2}{2m_i}, \quad (3.2.12)$$

where $\sigma_k(0) = \sigma_k(\mathbf{r}_1(0), \dots, \mathbf{r}_N(0))$. In order to ensure that the constraint is satisfied exactly at time Δt , we impose the constraint condition directly on the numerically obtained positions $\nabla_i(\Delta t)$ and determine, on the fly, the multipliers needed to enforce the constraint. Let us define

$$\mathbf{r}_i = \mathbf{r}_i(0) + \mathbf{v}_i(0)\Delta t + \frac{\mathbf{F}_i(0)}{2m_i}\Delta t^2 \quad (3.2.13a)$$

$$\tilde{\lambda}_k = \frac{\Delta t^2}{2} \lambda_k \quad (3.2.13b)$$

so that

$$\mathbf{r}_i(\Delta t) = \mathbf{r}_i + \frac{1}{m_i} \sum_{k=1}^{N_c} \tilde{\lambda}_k \nabla_i \sigma_k(0) \quad (3.2.14)$$

Then, for each constraint condition $\sigma_l(\mathbf{r}_1, \dots, \mathbf{r}_N) = 0$, we impose

$$\sigma_l(\mathbf{r}_1(\Delta t), \dots, \mathbf{r}_N(\Delta t)) = 0, \quad l = 1, \dots, N_c \quad (3.2.15)$$

Then, substituting in for $\mathbf{r}_i(\Delta t)$, we obtain a set of N_c nonlinear equations for the N_c unknown multipliers $\tilde{\lambda}_1, \dots, \tilde{\lambda}_{N_c}$:

$$\sigma_l \left(\mathbf{r}_1 + \frac{1}{m_1} \sum_{k=1}^{N_c} \tilde{\lambda}_k \nabla_1 \sigma_k(0), \dots, \mathbf{r}_N + \frac{1}{m_N} \sum_{k=1}^{N_c} \tilde{\lambda}_k \nabla_N \sigma_k(0) \right) = 0 \quad (3.2.16)$$

Unless the constraints are of particularly simple form, equations (3.2.16) will need to be solved iteratively. A simple procedure for doing this, known as the SHAKE algorithms [14], proceeds as follows. First, if a good initial guess of the solution, say $\{\tilde{\lambda}_k^{(1)}\}$, is available¹⁰, then the coordinates can be updated according to

$$\mathbf{r}_i^{(1)} = \mathbf{r}_i + \frac{1}{m_i} \sum_{k=1}^{N_c} \tilde{\lambda}_k^{(1)} \sigma_k(0). \quad (3.2.17)$$

The exact solution for the multipliers is now written in the form $\tilde{\lambda}_k = \tilde{\lambda}_k^{(1)} + \delta \tilde{\lambda}_k^{(1)}$, and then the equation for $\mathbf{r}_i(\Delta t)$ become $\mathbf{r}_i(\Delta t) = \mathbf{r}_i^{(1)} + (1/m_i) \sum_{k=1}^{N_c} \delta \tilde{\lambda}_k^{(1)} \nabla_i \sigma_k(0)$, so that equations 3.2.16 become

$$\sigma_l \left(\mathbf{r}_1^{(1)} + \frac{1}{m_1} \sum_{k=1}^{N_c} \delta \tilde{\lambda}_k^{(1)} \nabla_1 \sigma_k(0), \dots, \mathbf{r}_N^{(1)} + \frac{1}{m_N} \sum_{k=1}^{N_c} \delta \tilde{\lambda}_k^{(1)} \nabla_N \sigma_k(0) \right) = 0 \quad (3.2.18)$$

¹⁰By this we mean, for example, the multipliers from the previous dynamics time step.

Next, equation (3.2.18) is expanded to first order in a Taylor series about $\delta\tilde{\lambda}_k^{(1)} = 0$:

$$\sigma_l(\mathbf{r}_1^{(1)}, \dots, \mathbf{r}_{N_c}^{(1)}) + \sum_{i=1}^N \sum_{k=1}^{N_c} \left[\nabla_i \sigma_l(\mathbf{r}_1^{(1)}, \dots, \mathbf{r}_{N_c}^{(1)}) \cdot \nabla_i \sigma_k(\mathbf{r}_1(0), \dots, \mathbf{r}_{N_c}(0)) \right] \frac{\tilde{\lambda}_k^{(1)}}{m_i} \approx 0 \quad (3.2.19)$$

Equations (3.2.19) are matrix equations for changes $\tilde{\lambda}_k^{(1)}$ in the multipliers. Indeed, if we define the vectors as

$$\Sigma = \begin{pmatrix} \sigma_1(\mathbf{r}^{(1)}) \\ \vdots \\ \sigma_{N_c}(\mathbf{r}^{(1)}) \end{pmatrix}, \quad \Lambda = \begin{pmatrix} \delta\tilde{\lambda}_1^{(1)} \\ \vdots \\ \delta\tilde{\lambda}_{N_c}^{(1)} \end{pmatrix}, \quad (3.2.20)$$

where $\mathbf{r}^{(1)} = \mathbf{r}_1^{(1)}, \dots, \mathbf{r}_N^{(1)}$, and a $N_c \times N_c$ matrix $\mathcal{C}$ as

$$\mathcal{C}_{lk} = - \sum_{i=1}^N \frac{\nabla_i \sigma_l(\mathbf{r}_1^{(1)}, \dots, \mathbf{r}_{N_c}^{(1)}) \cdot \nabla_i \sigma_k(\mathbf{r}_1(0), \dots, \mathbf{r}_{N_c}(0))}{m_i}, \quad (3.2.21)$$

the equation (3.2.19) become

$$\mathcal{C}\Lambda = \Sigma. \quad (3.2.22)$$

If the dimensionality of this matrix equation is not too large, then it can be inverted directly to yield the full set of $\tilde{\lambda}_k^{(1)}$ simultaneously¹¹. Because equation (3.2.18) was approximated by linearization, however, adding the correction $\sum_{k=1}^{N_c} \delta\tilde{\lambda}_k^{(1)} \nabla_i \sigma_k(0)$ to $\mathbf{r}_i^{(1)}$ does not yield a fully converged $\mathbf{r}_i(\Delta t)$. Therefore, we define a new $\mathbf{r}_i^{(2)}$ as

$$\mathbf{r}_i^{(2)} = \mathbf{r}_i^{(1)} + \frac{1}{m_i} \sum_{k=1}^{N_c} \delta\tilde{\lambda}_k^{(1)} \nabla_i \sigma_k(0) \quad (3.2.23)$$

and write $\mathbf{r}_i(\Delta t) = \mathbf{r}_i^{(2)} + (1/m_i) \sum_{k=1}^{N_c} \delta\tilde{\lambda}_k^{(2)} \nabla_i \sigma_k(0)$ where now $\tilde{\lambda}_k^{(2)} = \tilde{\lambda}_k^{(1)} + \delta\tilde{\lambda}_k^{(1)}$ and $\tilde{\lambda}_k = \tilde{\lambda}_k^{(2)} + \delta\tilde{\lambda}_k^{(2)}$. Then use the linearized equation (3.2.19) with the “(1)” superscript replaced by “(2)” for another iteration. The procedure is repeated until the constraint conditions are satisfied to a given small tolerance.

3.3 NEMD: Non equilibrium molecular dynamics

Although equilibrium time correlation functions are useful in the calculation of transport properties (see Sec. 2.2.3), their connection to the experiments that employ external driving forces is obscured by the fact that the external perturbation is absent in equation (2.2.20). This means we can determine transport coefficient without actually observing the behaviour of the system under action of a driving force. A more intuitive approach would attempt to model the experimental condition via direct solution of equations (2.2.16) and (2.2.17). These equations describe trajectories that are not Hamiltonian, then the total energy is not conserved, and of course, the trajectories don't sample the microcanonical phase space distribution. Therefore, the physical quantities of interest will be local quantities¹² that can be used to monitor the system. These quantities, in the linear regime

¹¹This procedure is known as matrix-SHAKE or M-SHAKE [15]

¹²By local quantities we mean averages over particles in fixed regions of space much smaller than the simulation cell.

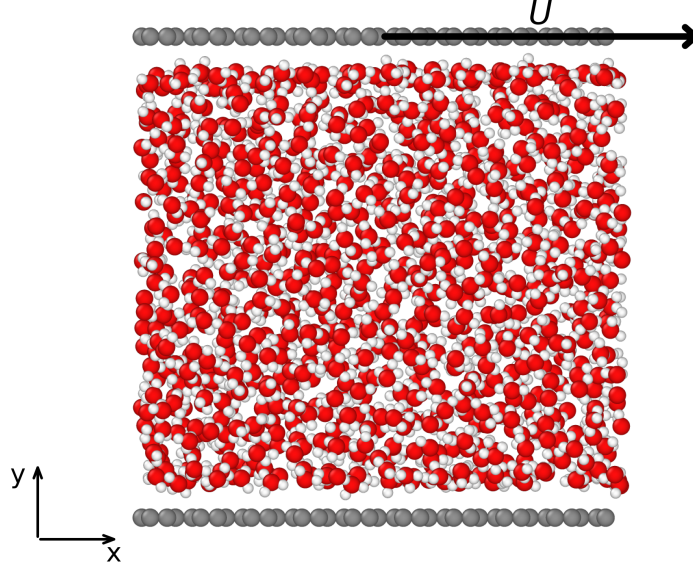


Figure 4: Example of water-graphene couette geometry for NEMD. The image represents the xy plane of a simulation cell. In red and white the H_2O molecules, in gray the carbon atoms of graphene wall. Long the x, z directions are implemented the PBC. The upper wall is moved at some set velocity U , while the lower one is fixed.

limit, are expected to follow the constitutive equations that characterize the perturbation applied to the system. Integrate numerically the equations (2.2.16) and (2.2.17) is anything but trivial. In fact, numerical integration presents two fundamental problems, first of all the a priori knowledge of the instantaneous perturbation to be applied to each particle is not a given. Secondly it is not trivial how to implement the periodic boundary conditions. Depending on the specific transport phenomenon under study these problems can be solved in various ways. This type of methodology is known as **non-equilibrium molecular dynamics** NEMD . Since in this work we are interested in flows deriving from the action of shear forces, we will see in detail how to build simulations of this type in the next sections.

3.3.1 Flow driven simulations: Method and Techniques

Let's consider that we want to produce a flow generated by the presence of a shear force that generates a velocity profile, restricted between two walls¹³. So, let's say we want a slab of fluid, of infinite dimension on plane zx and finite long the y direction, constrain between two walls, on which the flow have the BC. With this geometry, from the NS equation, we can have two simple velocity profile, the **Couette flow** and **Poiseuille flow**. The former, is characterise by *not have pressure gradients and a linear velocity profile*, already seen in Sec. 2.1.3. The latter instead, is distinguished by a *constant gradient pressure long the x direction and a parabolic velocity profile*.

¹³This geometry is often referred to as a *nanochannel*

Clearly, this two solution are given by the classic hydrodynamic assumption, anyway in the already discussed hydrodynamic limit, we aspect that the MD simulation will be in agreement with the NS solutions. Then the strategy for this type of simulations is to simulate a system large enough (larger of the characteristic length l_c , generally on the order of 5 nm) in the way that can be describe by NS solution. In such a way, the simulation are devised to recreate the two, already cite, simple flow. In this way, one can fit and interpolate the velocity profile, and obtain the interested flow interface proprieties, like slip length, slip velocity, and form this calculate the transport coefficient λ using the definition of slip length (Sec. 2.1.3). Depending on which type of flow one want to use, there are different approach to calculate the interest proprieties and different technical difficulties. So, in the next two paragraph we will briefly explain the simulation protocol of the Couette and Poiseuille simulation geometry.

Couette simulation geometry We want to reproduce the linear profile of Couette flow, generated by the presence of a shear force that generates a linear profile. The most used geometry in literature [18, 10, 6] is as follow. A simulation cell is built, with PBC along x and z. Along the y direction, the fluid is confined by simulating solid walls on the upper and lower areas of the cell (Fig. 4). These walls can be modeled in various ways. One can use just a potential that mimics the interaction of the particles with a rigid object with a mass much higher than that of the atoms in the fluid [1, 6, 3]. Or, if one is interested, as in our case, in a more realistic modeling of the solid-liquid interaction, such as a rigid atomic lattice [19, 8, 18] or one that allows oscillations of thermalized atoms around their equilibrium point [10]. In the latter case it is therefore necessary to prevent the motion of the center of mass of the wall, so as to reproduce the interaction with a wall of mass much larger than the mass of the atoms of the fluid. At this point a wall is artificially moved at a fixed speed U , imposing this speed on each atom of the wall for each simulation step. Simulations of this type clearly do not conserve energy and tend to overheat the system. For this reason, generally the velocities perpendicular to the direction of the flow are scaled to maintain the desired (local) temperature [6], or can be apply a thermostat (NVT) only on wall atoms. After a relaxation time necessary to reach a stationary regime, this method produces Couette flows in excellent agreement with the predictions of classical hydrodynamics [19, 8, 18].

Poiseuille simulation geometry In this case, we want to reproduce the parabolic velocity profile of Eq. 2.1.18, produce by a external constant pressure gradient. The simulation procedure typically used is as follow. A simulation cell, the same of the one used for Couette geometry is build. Also the wall are modeled at the same way, but this time both centre of mass of the wall are fixed in position. Then an artificially force field are apply to all the fluid molecules (or atoms) in such a way to reproduce the desired pressure gradient. Typically a constant force or acceleration is add to all the atoms of the fluid for each time step of simulation. Clearly also this procedure do not conserve the energy and need the same attention on thermostating of Couette flow. This technique also produces a parabolic velocity profile, in agreement with the predictions of the NS equations. The fit of this profile with Eq. (2.1.18) can then be used to measure the slip

velocity. Furthermore, using the NBC (Eq. (2.1.20)) it is possible to derive the slip length also from this profile, obtaining

$$v_s = \frac{b\rho d}{2\mu} F_x \implies b = \frac{2\mu}{\rho d} v_s . \quad (3.3.1)$$

where ρ is the density and μ is the kinetic viscosity. The advantage of this type of flow is that can be also apply to CNTs, and not only on flat surfaces as the Couette geometry. On the other hands, the more difficult fit and the not direct measure (from the fit) of the slip length makes the method generally less efficient and less preferable to Couette's method.

3.3.2 Challenges on NEMD nanofluidics simulations

A number of studies have been aimed, in the previous years, at quantifying the slip length and flow rate of water in carbon nanotubes (CNTs) and flat graphene nano-channels both experimentally and in simulations. However, the data are widely scattered: even over orders of magnitude and no consensus has been reached. In experimental study Maali *et al.* found a slip length of 8 ± 2 nm for water on graphite surface. Qin *et al.* found that as the CNT diameter increase to 1.59 nm, its slip length converges to 10 nm, which can be approximated to the slip length of water on planar graphene. On the other hand, Zuh and Granick and Tretheway and Meinhart found a micrometer range slip lengths for water on hydrophobic surfaces.

In simulation Thomas and McGaughey found a slip length for water on graphene surfaces of 30 nm, while Falk *et al.* found 80 nm and Kotsalis found 67 ± 45 nm. Bubu and Sathian found monotonically decreasing slip length as the tube (CNT) diameter is increased from 0.81 to 5.42 nm and in the higher diameter tubes the slip length converges to just about 1 nm, which can be taken as the slip length on a flat graphene surface. Of course some of this variation can be attributed to the difference in water models and carbons model used in simulations. As have shown Shuvo *et al.* [10], in a recent study, the slip length for water-graphite interface calculated with NEMD techniques, like Couette flow, have some great dependence on the interatomic potential used to modeled the carbon-water interaction. Changing the interfacial force field can give a spread of slip length between few nanometers to 60 nm for share rate of orders of $\gamma \sim 10^9 \text{ s}^{-1}$, typical for water at low speed (10 – 100 m/s). Moreover, they have shown that, for all the interface force field used, the slip length exhibit a similar and bimodal response when varying the shear rate of the fluid between $10^9 - 10^{11}$, making the valuation of slip length from simulation even more difficult. Another aspect that can affect the slip length and velocity are the way in which the graphene carbon atoms are modeled. In order to reduce the computational time and thus avoid the complex carbon models a number of study freeze the carbon atoms in their lattice site (Sec. 3.3.1) and thermostat the water directly to maintain the desired temperature. It has been shown that this procedure can lead to unphysical distortion of the fluid stress response and can artificially enhance or reduce the slip, depending on the tye of wall surface. Sokhan *et al.*, indeed, observed an increase of $\sim 20\%$ in slip for methane in flexible graphene/CNTs compared to the rigid counterpart.

All this scattering of result could be caused also by the limitation of the commonly used NEMD method, like Couette and Poiseuille flow. At room temperature water has an average thermal velocity of 340 m/s, and NEMD simulation can only simulate the systems for few nanoseconds at time-step of ~ 1 fs. Due to this computational limitation, NEMD simulation are done with a very high shear rate (or pressure gradients in Poiseuille flow) to obtain a mean fluid velocity comparable to the thermal velocity and thus statistically significant results [18]. At these high field, non linear effects may begin to emerge, as we already mention. Therefore, the extrapolation of NEMD result to experimental field, which have fluid velocity on the order of 0.01 m/s, is not reliable and is likely to lead to deviation from the flow determined under experimental condition where the hydrodynamic proprieties obey to linear relations (Sec. 2.2.1). For high slip system, such water against a hydrophobic surface, the problem becomes even more complicated. A very small change in the measured NEMD velocity profile can result in a very large deviation in the slip length. Indeed, a systematic study of Couette and Poiseuille geometry simulations for a various range of wall velocity and pressure gradients respectively [18], underline some common features on this types of simulations: (i) for both Couette and Poiseuille the NEMD simulation give a reasonably good estimate of slip velocity. (ii) The average velocity difference δv between the two wall, for the Couette, and between the center of cell and the wall for Poiseuille are very small. The statistical error on simulation streaming velocity profile data is generally on the order of m/s, which means that for system with Couette wall velocity in the order of 50 m/s the δv is in the order of statistical error [18]. (iii) The strain rate is very small and the variation is large among different fits. (vi) Some of the fits have negative velocity gradient due to the thermal fluctuations superimposed on very small velocity difference.

From these considerations it emerges that the calculation of interface properties, in particular the slip length, through NEMD simulations is far from trivial. Therefore, in this thesis an alternative method for flow driven NEMD simulation is proposed, inspired by the *fixed-stress method* [19] that we will call **fixed-velocity method**, which will be discussed in detail in the next chapter.

4 Simulation approach and protocols

In this chapter, we will finally introduce and discuss the simulation approach adopted in this thesis work. Our goal is to understand if, a new and different simulation protocol that uses out-of-equilibrium molecular dynamics, could be used to calculate the properties at the solid-liquid interface. To do this, we focused on testing the protocol, verifying the method’s ability to produce results consistent with the various studies present in the literature (Sec. 3.3.2). For this reason we focused on a single model to describe water molecules, graphene and more importantly, the water-graphene interaction. In choosing the model we relied on the most common models and effective potentials currently used for this type of simulations, seeking the best compromise between computational simplicity and physical realism. These models will be discussed on section 4.1. Subsequently, in the section 4.2 we will discuss the molecular dynamics protocol used, the quantities of interest measured and the technical choices of the simulation. Finally, in the section 4.3, we will discuss in detail the validation of the proposed protocol, comparing equilibrium and non-equilibrium simulations in order to verify the non-artificiality of the results obtained and the physical consistency of the proposed method.

4.1 System modeling

As we have discussed in chapter 3, the molecular dynamics techniques are based on a *a priori* modeling of physical system of interest. In this way, the choice of model to use in MD simulation is fundamental for interpretation of results. In order to reduce the computational time and complexity we decide to describe the graphene layer (graphene “sheet”) as a rigid body, freezing the carbon atoms on their lattice positions [18]. For the same reason the water molecule has been modeled as a rigid body knowing as **extended simple point charge** (SPC/E) [20]. In the following, we will discuss the typology of interaction potentials chosen to model both the water-water and graphene-water interactions.

4.1.1 SPC/E Water model

In molecular dynamics simulations, effective pair potentials are commonly employed. These potentials simplify complex many-body interactions by averaging them into interactions between pairs of molecules. For polar molecules, such as water, which has been extensively studied, effective pair potentials can differ significantly from pure pair potentials. The main reason pure pair potentials fail to accurately represent the condensed-state properties of polar molecules is that they overlook the effects of polarizability beyond simple pairwise interactions. In water and other polar liquids, significant average polarization occurs, leading to a cooperative enhancement of intermolecular bonding.

Many effective pair potentials have been used for liquid water, such as the ST2 model, the SPC model, the TIPS potential and its variants (including TIPS2), as well as models based on quantum-mechanical calculations like the MCY model. However, to avoid excessive complexity in the effective potential and due to its established use in literature for NEMD calculations [19, 10, 8], we chose to use the model known as the **extended simple point charge** (SPC/E) [20]. The SPC/E model is based on the simple SPC model,

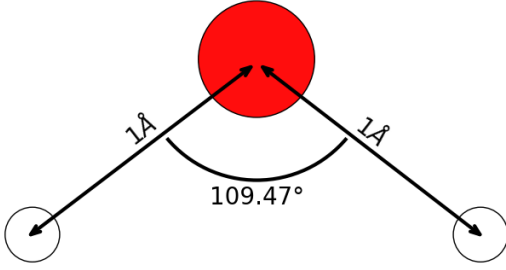


Figure 5: Molecular rigid structure of SPC and SPC/E model. In red the oxygen atom and in white the hydrogen.

	SPC	SPC/E
r_{HO} [Å]	1.0	1.0
θ_{HOH} [deg]	109.47	109.47
r_c [nm]	9	10
ϵ [kcal/mol]	0.1553	0.1553
σ [Å]	3.166	3.166
q_{O} [e]	-0.82	-0.8476
q_{H} [e]	+0.41	+0.4238

Table 3: Comparison of two different water models SPC and SPC/E in terms of bond length, bond angle, Lennard-Jones parameters, and charge distribution [20].

but improved by including a self-energy correction, due to the induced dipole interaction between molecules [20]. The model consists of tetrahedral water with oxygen-hydrogen distance fixed at 0.1 nm and angle between hydrogens of 109.47 (Fig. 5). The molecule is modeled rigid and interacts with other molecules, through a Lennard-Jones (LJ) pair potential centered on oxygen that is canceled for distances greater than a certain cutoff radius r_c . In addition, the model also presents a long-range Coulomb potential centered on each atom. The charges that generate this potential fixed on each atom, incorporate within them the average effect of the dipoles induced by the other molecules, and are therefore different from those of the isolated molecule.

Therefore, the SPCE/E model interacts through an effective pair potential formed by the sum of a contribution of a short-range LJ potential and an effective long-range Coulomb potential. So if we denote the center of mass of i -th molecule as $\mathbf{R}_i$ and $\mathbf{r}_{i\alpha}$ the position of α -th atoms in the i -th molecule respect the center of mass of the molecule. Then the distance between the atom α -th and β -th which belong respectively to i -th and j -th molecule is $r_{ij}(\alpha, \beta) = |\mathbf{R}_i - \mathbf{R}_j + \mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}|$. Now, we can write the pair potential between two molecules as

$$V_{ij} = \sum_{\alpha, \beta} \left[\underbrace{\phi[r_{ij}(\alpha, \beta)]}_{\text{LJ potential}} \delta_{\alpha\text{O}} \delta_{\beta\text{O}} + \underbrace{\frac{1}{4\pi\epsilon_0} \frac{q_{\alpha} q_{\beta}}{r_{ij}(\alpha, \beta)}}_{\text{Coulomb potential}} \right], \quad (4.1.1)$$

where the sum is over all the atoms of i -th and j -th molecules. Finally the LJ potential is

$$\phi[r_{ij}(\alpha, \beta)] = \begin{cases} \epsilon \left[\left(\frac{\sigma}{r_{ij}(\alpha, \beta)} \right)^{12} - \left(\frac{\sigma}{r_{ij}(\alpha, \beta)} \right)^6 \right] & \text{for } r_{ij}(\alpha, \beta) < r_c \\ 0 & \text{for } r_{ij}(\alpha, \beta) \geq r_c \end{cases} \quad (4.1.2)$$

Then the parameter of the model are: $\epsilon, \sigma, r_c, q_{\text{H}}$ and q_{O} . All of them are listed in table 3.

4.1.2 Graphene model

We have just discuss how to model the water molecules, but nothing has been said, yet, about the graphene. For our goal we want to simulate a rigid graphene mono-layer to use as a wall for our simulation. The graphene will be then consider as a rigid structure. This structure is made up of carbon atoms arranged in a perfect hexagonal lattice, also known as “pristine” graphene (Fig. 6).

Then, the only potential that we want to model is the water-carbon potential interaction. A lot of work has been done, in the previous years, to obtain a functional form and parameters value of underling force field which describe the water-carbon interaction. However the models and the respective parameters are still evolving. A number of force field have been proposed (e.g. GROMOS, AMBER96, CHARMM) which have shown to provide accurate description of many molecular systems [21]. Anyway, the simpler and more computationally advantegius effective pair potential are still used in literature to model CNT-water and graphene-water systems. This types of potentials are all based on pairwise additive LJ potential between oxygen atom of water molecule and carbon atoms. Some model also include a carbon-hydrogen LJ interaction or an electrostatic interaction between the partial charges site of water and point quadrupole moment of carbons. Anyway is has been found that the quadrupole moment electrostatic interaction is basically irrelevant, while the hydrogen-carbon LJ interaction has not been sufficiently investigate to be reliable [21, 22]. For these motivations we decide to model the water-graphene interaction as a LJ potential between oxygen and carbon atoms. The parameters choose are the most used in literature to describe the interaction between SPC/E water and CNT or graphene layers.

4.2 Fixed-velocity method

Finally we come to the description of the out-of-equilibrium molecular dynamics method used in this work. Then, how anticipate into chapter 3.3 the proposed method is an alternative at the standard method found in literature to perform this type of simulations. Typically a flow driven NEMD simulation tries to reproduce an analytical known hydrodynamics velocity profile. Knowing that the NS equations remain valid up to the hydrodynamic limit, long-time simulations for confined liquids beyond the characteristic length are expected to reproduce the profile of classical hydrodynamics. One of the simplest case are the reproduction of linear velocity profile, that is to say the Couette flow, in which we aspect that the velocity profile will follow the analytical equation (2.1.14) with some slip condition. The simplicity of the linear Couette profile, and its direct connection with the transport coefficients at the solid-liquid interface (Sec. 2.1.3), makes it one of the most used methods in the simulations, out of equilibrium, at the atomistic level of fluids.

The method proposed here is presented as an alternative simulation protocol that allows the drag coefficient to be calculated in two alternative ways. (a) Fitting the linear velocity profile generated and using the relations of chapter 2 to obtain C_D , and (b) direct calculation of drag coefficient from the equation (2.1.2). The basic idea is to generate, in artificial way, a constant velocity flow parallel to the graphene wall and restricted on a

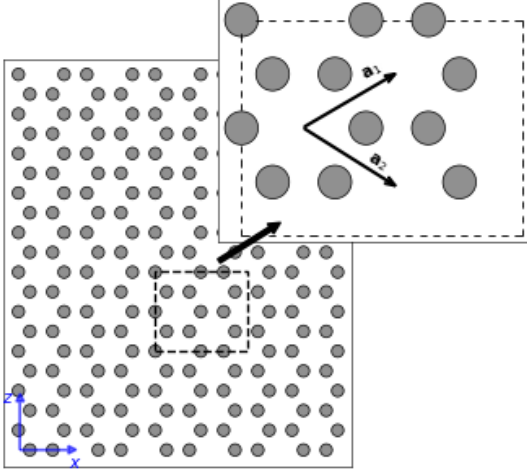


Figure 6: Structure of graphene “pristine” mono-layer used for the simulations. The graphene is organized into the so called “armchair” geometry into xy plane, in which the carbon atom form a zig zag line long the z direction. In the figure the vector of unit cell $\mathbf{a}_1$ and $\mathbf{a}_2$.

	Interactions			
	O-O	H-O	C-O	H-C
ϵ [kcal/mol]	0.1553	-	0.10408	-
σ [Å]	3.166	-	3.22	-
r_c [Å]	10	-	10	-
q [e]	-0.8476	0.4237	0	-

Table 4: Summary table of the parameters used to model water-water and graphene-water interactions. The first three lines refer to the parameters of the effective LJ pair potential, while the last line refers to the point charge given to each atom. In this last line the charge refers to the first atom in the legend (e.g. the charge in the H-O column refers to hydrogen)

well defined zone away from the wall. The goal of this zone is to reproduce the value of velocity profile away from the wall, where we expect it to be unperturbed. We call this zone *velocity lane* (VL) and the remaining space until the graphene wall *bulk zone* (BZ). This configuration allow as to use both method (a) and (b). Indeed, we aspect that for VL not too much away from the wall the velocity profile stay linear, imitating the the profile of Couette configuration in equation (2.1.16). This provides a great advantage over the Couette configuration, since it provides, once stationarity is reached, a velocity profile with a higher share rate for the same target velocity, thus facilitating its interpolation and the subsequent calculation of the slip velocity and slip length. In fact, profiles with small shear rates, typical of low U_T and high slip configurations, are more sensitive to thermal noise, which leads to large statistical errors for least squares fits. Secondly, the method allows the direct calculation of C_D . In fact, considering the artificial flow in the velocity lane as the unperturbed flow, we can write

$$C_D = \frac{\langle F_x \rangle_{NE}}{Sq_\infty} = \frac{2 \langle F_x \rangle_{NE}}{S\rho U_T^2}, \quad (4.2.1)$$

where we use the definition of freestream dynamic pressure and where $\langle F_x \rangle_{NE}$ is the total average force on the graphene wall, defined as

$$\langle F_x \rangle_{NE} = \frac{1}{N\Delta t} \sum_n^N \bar{F}(t_n) \quad (4.2.2)$$

where $\bar{F}(t_n) = \sum_i^{N_c} F_i(t_n)$ is the total force over N_c carbon atoms at time t_n .

4.2.1 Simulation protocol

In the following we discuss how we implemented the fixed-velocity method in practice. First of all we want to specify that all the simulation of this thesis work is done using the computational power of Cineca HPC cluster¹⁴. All the simulation are performed using LAMMPS [23], a software tool for fast parallel molecular dynamic simulations. The basic configuration we decide to study are represented in figure 7(a). A cell of size $L_x \times L_y \times L_z$ with PBC on all the directions. Two graphene walls with the structure describe in section 4.1.2 are place on the zx plane at distance L_b from the center of the cell. This walls defining the box in which are confining the H_2O molecules, that we call “water box”. The remaining volume of the simulation cell, of thikness L_v long the y axis, is keep void and used to remove the LJ and Coulomb interaction of water between the repeated cells long the y direction. In all the simulation the L_v is set to 50 Å, in such a way to have at least 100 Å long the y direction between the repeated water boxes¹⁵. Then are set the VL, of size $\Delta y_L \times L_x \times L_z$ and consequently the bulk zone. We decide to set the Δy_L approximate at 18% of $2L_b$. Into the BZ are then created $N_{\text{H}_2\text{O}}$ water molecules to obtain a density about $\rho_{\text{H}_2\text{O}} \sim 0.97 \text{ g/cm}^3$. We decide to study the latter configuration with two different L_y size. The smaller one of dimension y about half the L_y of bigger one. How is summarise in table 5, for the bigger cell the total volume is $164 \times 264 \times 21 \text{ Å}^3$, with a water box of effective volume of $164 \times 264 \times 21 \text{ Å}^3$ while the small one, the total cell volume is $164 \times 184 \times 21 \text{ Å}^3$, with an effective volume of $164 \times 82 \times 21 \text{ Å}^3$. For both the cells the graphene walls are constituted of 1386 carbon atoms arranged in the hexagonal lattice as describe in Sec. 4.1.2.

Parameters	big cell	small cell
L_x [Å]	164	164
L_y [Å]	264	182
L_z [Å]	21	21
L_b [Å]	82	41
Δy_L [Å]	20	17
L_v [Å]	50	50
$N_{\text{H}_2\text{O}}$	18500	9400
N_C	1386	1386

Table 5: Summarising table of parameters of simulations.

All the simulations are carry out using a velocity Verlet integration algorithm (Sec. 3.2.1) together with the SHAKE algorithm (Sec. 3.2.4) to constrain the water molecules. The used integration time-step Δt is set to 0.05 fs for the motivation in Sec. 4.3.1. The SHAKE algorithm implemented in LAMMPS have two parameters whose can change the way in which the iterative algorithm goes to convergence. The first one, called *tolerance*,

¹⁴In particular using the new pre-exascale Tier-0 EuroHPC supercomputer “Leonardo” <https://www.hpc.cineca.it/systems/hardware/leonardo/>

¹⁵The choice of the dimension of the void is due to the Debye length of pure liquid water, which is about 100 Å

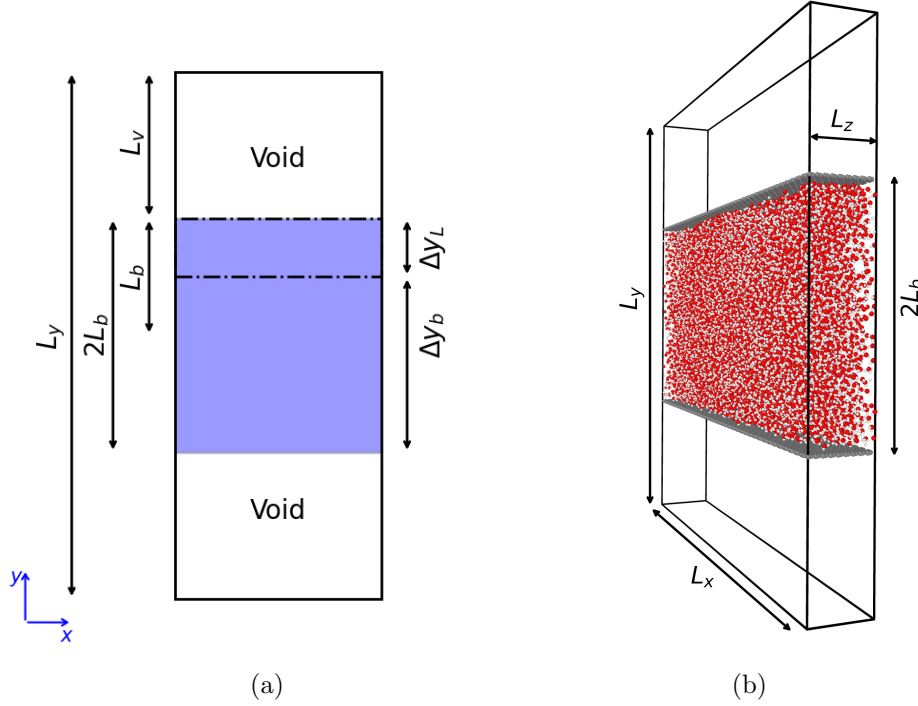


Figure 7: (a) Scheme of cell used for the simulations on the xy plane. In blue the water box delimited by the graphene wall. In dashed line the velocity lane of thickness Δy_L long the y direction. (b) Prospective image of the used cell geometry. In red and white the water molecules, in gray the carbon atoms.

in red and

defining the accuracy tolerance of constrain solution, the second one, called *iteration*, defining the max iteration possible for each constrain solution. In all the simulation the tolerance are set to 10^{-4} and the iteration to 10. Finally, the long-range Coulomb interaction are calculated using the *particle-particle particle-mesh* (PPPM or P3M) algorithm [24] which is a Fourier-based Ewald summation method ¹⁶ [15].

The simulation protocol is divided in two phases, the initialization and the measurements one.

Initialization In this phase the water molecule are randomly created into the water box, and then keeping fixed the graphene walls are perform an NVT equilibrium MD simulation to thermalize the system to the desired temperature $T = 300$ K. This first

¹⁶The Ewald summation is well-known a method for computing long-range interactions (e.g. electrostatic interactions) in periodic systems. This technique is a special case of the Poisson summation formula, replacing the summation of interaction energies in real space with an equivalent summation in Fourier space. In this method, the long-range interaction is divided into two parts: a short-range contribution, and a long-range contribution. The short-range contribution is calculated in real space, whereas the long-range contribution is calculated using a Fourier transform. The PPPM algorithm, to speed up the calculation of the reciprocal (space) potential, maps atom charge to a 3d mesh, uses 3d FFTs to solve Poisson's equation on the mesh, then interpolates electric fields on the mesh points back to the atoms.

simulation run is 2 ps long, after whose the system is freeze and the molecules inside the velocity lane are labelled as “non-physical” ones. On this particles all the forces are set to zero for all the simulation, and then at this particles are given initial velocity equal to the target velocity. All the transverse component of velocity are set to zero, in this way the particle will stay inside the velocity lane for all the simulation. Is important to note that only the force *on* this particles vanish while the force of this “non-physical” particles on the other do not disappear. Then an NVE MD simulation is performed, keeping the lower rigid graphene wall fixed in position. The NVE simulation is carry out for about 1 ns to give the system time to react and reach the steady regime. In all the simulation run, the target velocity U_T is set to 10 m/s, to create a slow boundary level flow into the range of difficult velocity for the Couette geometry.

Measurements In this second phase, the water box are divided into slab parallel to the walls of thickness 2 and 1 Å for big and small cell respectively. These bin are use to measure the dependence on y direction of physical quantities like temperature, x component of velocity and density. For each bin and for each time step these quantities are computed in the following ways. The instantaneous temperature is calculated from the equipartition relation as a mean over the molecules into the bin. Let’s define $t_n = n\Delta t$ with $n \in \mathbb{N}$ the n -th simulation step, and $K(t_n)$ the total kinetic energy of the bin, then

$$T(t_n) = \frac{2}{3k_b}K(t_n) , \quad (4.2.3)$$

where $T(t_n)$ is the temperature on n -th step of one bin. Likewise, the the density is computed for each time step simply as the number of molecules in the bin for the molecular mass, over the bin volume. Finally the velocity is calculated as the x component velocity of center of mass of particle into the bin. All this instantaneous quantity are than average on time to obtain a profile on the y direction. In this way we measure the velocity profile and supervise the temperature and density of the non equilibrium system. Finally, in this phase, we also measure the force on the graphene wall, as already discuss in Sec. 4.2.

4.3 Method validation: free-flow

In contrast to typical non-equilibrium molecular dynamics methods discussed above, the proposed method allows to construct a free flow. That is, by constructing a cell without graphene walls, with $L_v = 0$, therefore without vacuum. In this configuration, since there are no boundary conditions on the walls, the system is expected to converge to a free flow after a relaxation time, with velocity at every point equal to the target velocity. Therefore, this configuration can be used to verify the properties of the fluid, far from the velocity lane, so as to monitor the fluid and verify that no artefacts due to the velocity lane constraint are produced. Several equilibrium MD simulations of the SPC/E water system have been performed to characterize the equilibrium properties of the studied system and to compare them with the same ones out of equilibrium, in free flow regime. In particular, attention has been paid to the distribution of the fluid velocities and to the radial density function.

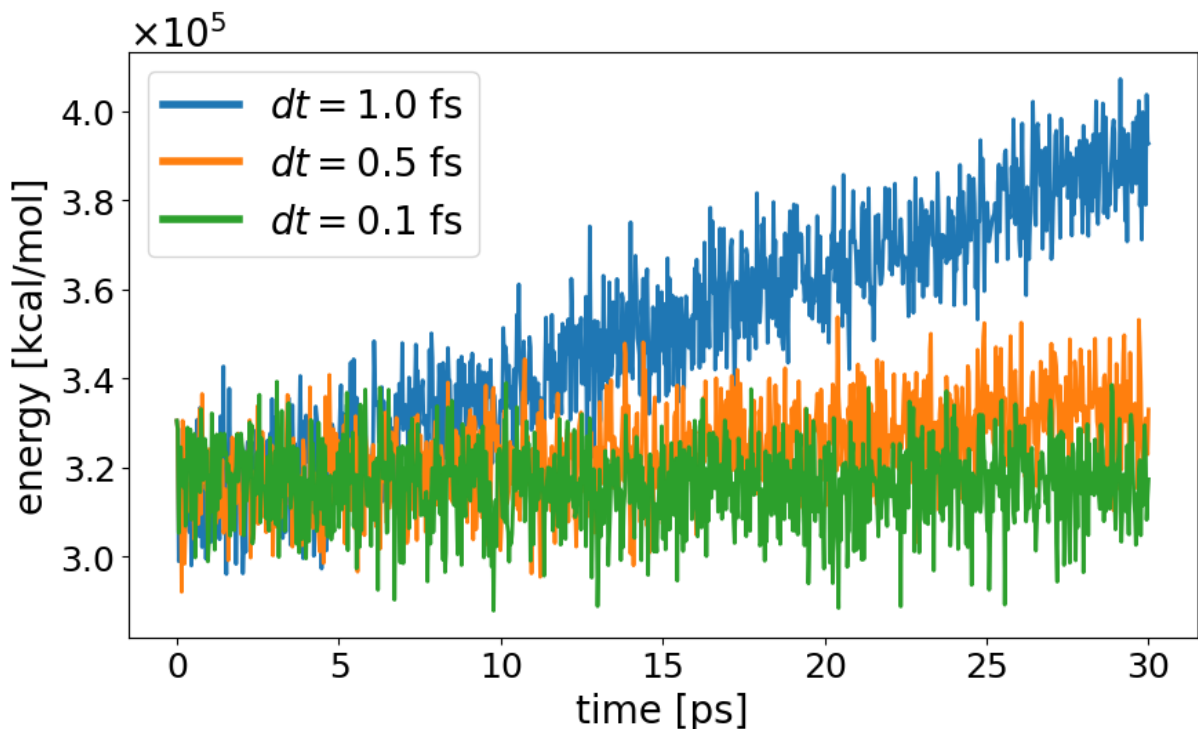


Figure 8: Total energy in function of time of 3 different equilibrium MD simulation of SPC/E water (NVE). Each simulation is performed with a initial velocity distribution of water molecules relative to $T = 300$ K, for different time-step dimension. Is evident the energy drift for $\Delta t = 1$ and $\Delta t = 0.5$ fs.

Furthermore, these equilibrium simulations have proved to be essential in understanding the necessary attention to be given to MD simulations that require the conservation of holonomic constraints, as in our case. Simulations with an implementation of the SHAKE algorithm have, in fact, proven to be very sensitive to the time-step, which if too large can lead to an incorrect conservation of energy. Finally, equilibrium simulations have been used to estimate the correlation time between time-steps, essential to obtain a coherent statistical analysis of the results.

4.3.1 EMD: Conservation of energy and correlation time

First of all, we decide to test the SPC/E water system on equilibrium MD simulations. So, using the big cell geometry with $L_v = 0$ and PBC, we perform various NVE simulations of water on liquid density, varying the time-step and monitoring the total energy conservation. Indeed, in a NVE simulation one would expect that the total energy stay constant. Nevertheless, the SHAKE algorithm implemented into the simulation, not perform a perfect Hamiltonian dynamics due to the iterative method used to find the additional force needed to preserve the constraints (Sec. 3.2.4). Then, a poor convergence on the iterative method can lead to a drift of energy during the simulation. Our tests show that the algorithm gets worse as the time step and the number of molecules in the simulation increase. As a matter of fact, the time-step dimension are the parameter which more contribute to

the good convergence of constrain force. As can be seen in Fig. 8, the energy drift is very evident for simulation with $\Delta t = 1.0$ fs, in which the drift is on the order of $\sim 450\%$ of the energy fluctuations. Decreasing the Δt , we improve the conservation of energy, that we archive for a time-step of 0.1 fs. Of course, the energy conservation is not the only indicator of a good SHAKE convergence. Indeed, the LAMMPS algorithm implementation provide an estimate of error in force convergence for each simulations step. In truth, for each time-step the algorithm obtain the new atoms position through the iteration procedure (as discuss in Sec. 3.2.4), then compute the constrain σ_l (Eq.(3.2.15)) for all the molecules. If the atoms position are perfect we will have that for each l -th constrains the $\sigma_l = 0$. However, since the convergence is not perfect the relation (3.2.15), will not be precisely zero, and can be use to monitoring the convergence of SHAKE algorithm. So, a typical SHAKE output is like the following ¹⁷

```
SHAKE stats (type/ave/delta/count) on step 10000
Bond:   1   1           2.59766e-10   37000
Angle:  1  109.47      2.79062e-08   18500
```

where the third column (delta) is the worst among all the constrain relations. We observed a worsening of this error with increasing time-step, consistent with the behavior of the energy. We observed a worsening of typically 3 orders of magnitude going from a Δt of 0.1 to one of 1 fs. For the NEMD we observed a worse performance of SHAKE algorithm which force us to decrease more the time-step, until 0.05 fs, value which we use for all the successive simulations.

After these tests, we focused on determining the correlation time of the SPC/E water system. Molecular dynamics simulations, in fact, produce configurations in phase space for each simulation step. These configurations, coming from the integration of the equations of motion, are clearly correlated. This correlation, although physically correct (we assume, in fact, that the positions and velocities of the atoms depend on those at the previous instant), provides correlated data. This means that all the physical quantity obtained by time average, derive from correlated data. To avoid this, the most common method is to estimate the **correlation time** of the system τ . That is, the time needed for two configurations in phase space to be uncorrelated. The most commonly used way to do this is to calculate the (normalize) **velocity autocorrelation function** (VACF). The latter is defined as

$$Z(t) = \frac{\langle \mathbf{v}(s+t) \cdot \mathbf{v}(s) \rangle}{\langle \mathbf{v}(s) \cdot \mathbf{v}(s) \rangle}, \quad (4.3.1)$$

where the $\langle . \rangle$ is an equilibrium statistical average and $\mathbf{v}(t)$ is the average velocity of atoms in the system at time t . It can be shown that the decay time of this function estimates the correlation between configurations in phase space [13]. Therefore, with the same SPC/E water system discussed above, an equilibrium NVT simulation are performed at a temperature of 300 K. From this simulation, the VACF was calculated as follows. We define an partial VACF as

$$C^\alpha(t_n) = \frac{1}{N-n} \sum_{j=1}^{N-n} \left[\frac{1}{N_{\text{H}_{20}}} \sum_{i=1}^{N_{\text{H}_{20}}} v_i^\alpha(t_j) v_i^\alpha(t_j + t_n) \right] \quad \alpha = x, y, z, \quad (4.3.2)$$

¹⁷The reported output refers to the run with the smallest time-step

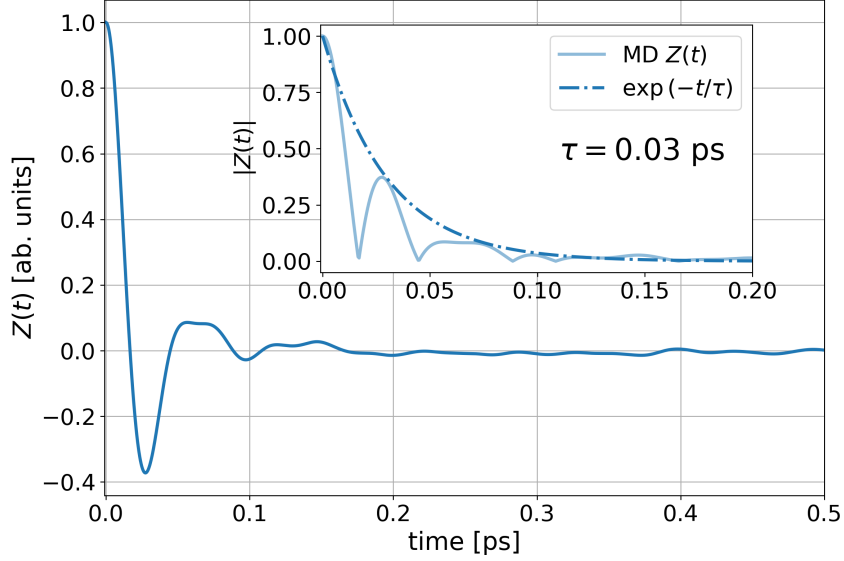


Figure 9: Velocity autocorrelation function for SPC/E water, calculated on equilibrium NVT simulation at $T = 300$ si. In the smaller graph one can see the absolute value confined by the exponential decay.

where N is the total number of time-steps of the simulation, t_n is the n -th step, $N_{\text{H}_2\text{O}}$ is then number of water molecules and $v_i^\alpha(t_j)$ is the velocity α -th component of i -th particle velocity at the time-step t_n . Then the VACF is of course

$$Z(t_n) = \frac{\sum_{\alpha} C^{\alpha}(t_n)}{\sum_{\alpha} C^{\alpha}(0)} . \quad (4.3.3)$$

Is known that, the upper limit of the absolute value fluctuation of VACF, for a liquid system is exponentially decreasing [13], like $\exp(-t/\tau)$, where τ is the correlation time that we are looking for. From the Fig. 9, we can see that the our water system have a $\tau = 0.03$ ps. Then we aspect that after this time the velocity of the molecules will be uncorrelated. This corresponds to about 600 time-steps. For this reason all the data used in the work are then taken at least 1000 time-steps away to guarantee that they are not correlated.

4.3.2 NEMD and EMD comparison: Radial density function and velocity distribution

At this point one could ask itself if the fixed velocity method produce some artefact on simulation. Indeed, we constrain a part of molecules to have some fixed velocity, and we don't know *a priori* if this constrain is physically acceptable. What we would like to obtain is a system that remains homogeneous in the measurement zone, i.e. far from the graphene walls and the velocity lane, whose spatial distribution of water molecules remains the same as that at equilibrium. Furthermore, we want the velocity distribution of the particles to be analogous to that at equilibrium but shifted by the contribution of the flow velocity. To verify that the desired behavior is actually that of the simulated

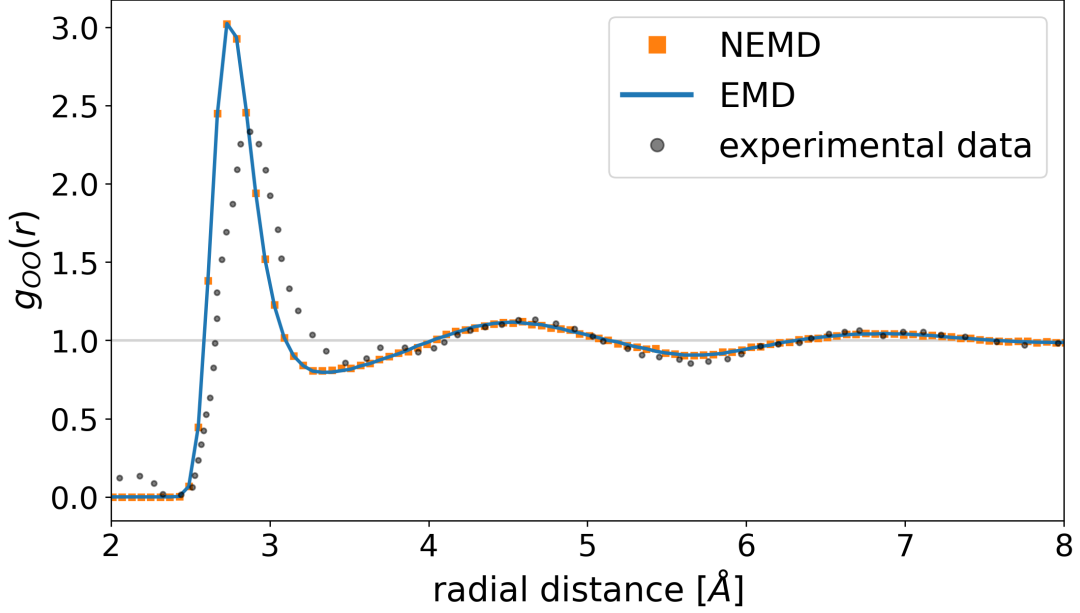


Figure 10: Comparison between the oxygen-oxygen RDF ($g_{OO}(r)$) calculated from NEMD (orange) and EMD (blue) of SPCE/E water. In black the data from real water at $T = 298$ K for reference. (experimental data from [20])

water molecules, the radial density functions and the velocity distributions, obtained from equilibrium simulations and “free-flow” non-equilibrium simulations, are performed with our method, were compared. Both types of simulations, are performed at the same temperature (300 K) and density.

The radial density functions $g(r)$ (RDF) describes how density varies as a function of distance from a reference particle, it is the most useful measure of the “structure” of a fluid at molecular length scales. $g(r)$ provides a statistical description of the local packing and particle density of the system, by describing the average distribution of particles around a central reference particle. So, for different atoms types we can define the partial density functions $g_{\alpha\beta}(r)$ between the atoms species α and β , as

$$g_{\alpha\beta}(r) = \frac{\langle \rho_{\beta}(r) \rangle}{\langle \rho_{\beta} \rangle} = \frac{1}{\langle \rho_{\beta} \rangle N_{\alpha}} \sum_{j \in \alpha} \sum_{i \in \beta}^{N_{\beta}} \frac{\delta(r_{ij} - r)}{4\pi r^2}, \quad (4.3.4)$$

where $\langle \rho_{\beta}(r) \rangle$ is the density of atoms β at distance r from an atom of type α , while $\langle \rho_{\beta} \rangle$ is the total density of β type atoms. Now, for our case, because the hydrogen-oxygen bond is fixed, we are interested on the oxygen-oxygen RDF, which give us the real information about the packing of water molecules. The comparison of oxygen-oxygen RDF between the NEMD and EMD simulations highlights that the fixed-velocity method does not change the water local packing and its local density. Indeed, as can be seen from Fig.10, the NEMD $g_{OO}(r)$ is in perfect agreement with the equilibrium one.

Let’s now move on to comparing the velocity distribution. As previously discuss, we want to inspect the velocity distribution of water molecules into the measurement

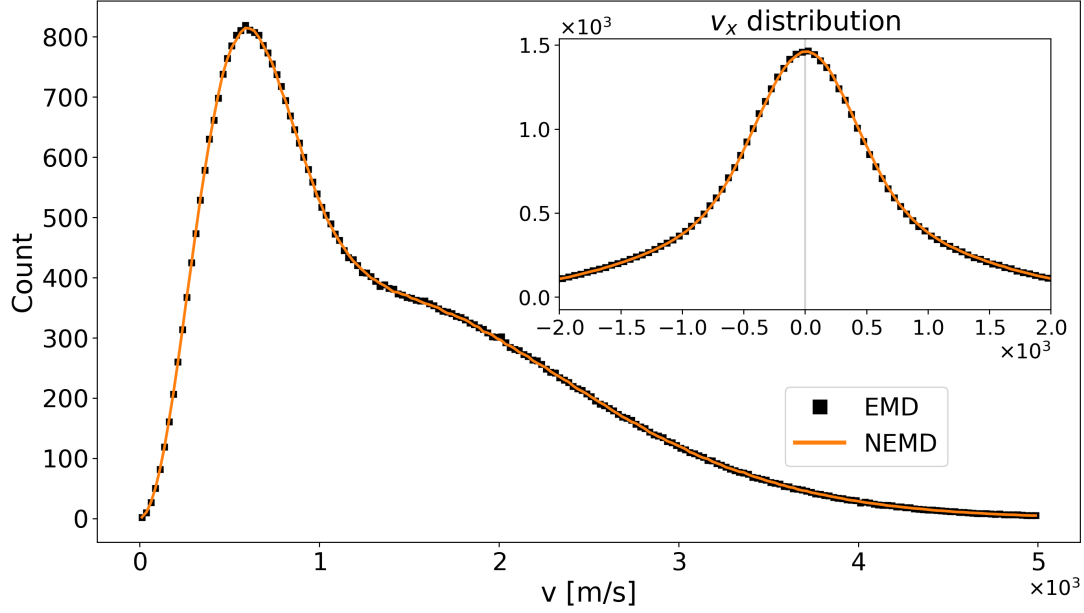


Figure 11: magnitude velocity distribution and v_x distribution comparison between EMD (orange) and NEMD (black). In light gray the zero for reference. One can see that the non equilibrium velocity distributions of water molecules are in very good agreement with the equilibrium one.

zone, to find out if the fixed velocity in the velocity lane produce some artefact on the distribution, i.e. the molecules are strongly perturbed from their equilibrium. So, we compare the distribution obtain from the velocity of particle on the measurement zone (then we excluded the particle into the velocity lane) of NEMD and EMD simulations. As we can see from Fig. 11, the two obtained distribution are in perfect agreement. Of course, one would aspect that the average of x component velocity distribution will be shifted from zero (the value at equilibrium) to the target velocity of the flow. Anyway, the thermal velocity of water molecules is so great, also to liquid water at room temperature, that the drift is basically invisible.

So, finishing this section we can confirm that our method not create artificial bias to the water away from the velocity lane, and than we can be quite sure that the physical quantities of interest are physically relevant and not affected by some artificial constraint.

4.3.3 Profile measurements

We conclude this chapter discussing about the more relevant measured quantity, the velocity profile. As previously mentioned, the bulk zone are divided into slabs long the y direction, in the way to form a series of bin into the y direction. For each of these bin at each time steps, let's say m -th one, we calculate the average x component velocity $v_x(y_m)$, as

$$v_x(y_n, t_m) = \frac{1}{N(t_m)} \sum_i^{N(t_m)} v_x(t_m, i) , \quad (4.3.5)$$

where $v_x(t_m, i)$ is the x component of particle i velocity at the time steps t_m . Of course, the sum runs over the $N(t_m)$ particle into the slab at the t_m time-steps. In this way, we can obtain the velocity profile of the flow in function of the y direction (orthogonal to the graphene walls). This is a instantaneous value, and then is needs to be time average over the trajectory length. As we have said in Sec. 4.3.1, the correlation time of the SPC/E liquid water forces us to use only $v_x(t_m, i)$ that are at least $N_{every} = 1000$ time step away. So, all the profile measurements are collected in the following way. Profile data at a distance of N_{every} steps are temporary save, then every N_{freq} the previously N_{freq}/N_{every} save data are average, saving permanent time average data. We decide to save $M = 10$ profile at nanosecond, so for our $\Delta t = 0.05$ fs we save profile data every 2×10^6 steps (100 ps), produced with the average of $2 \times 10^6/1000 = 2000$ different profiles. Then, the 10 velocity value obtain in a 1 ns of simulations, on one bin are to be considered completed uncorrelated. This allow us to calculate the error associated with the global average of these profile as $\sigma/\sqrt{M}$, where the σ is the standard deviation of the sample.

5 Results

In this chapter, we present the data and result obtained using the fixed-velocity method simulation, with graphene walls. We first describe how we calculate the slip length and the slip velocity from the velocity profile presenting the obtained results, then we discuss about the convergence of the calculated quantities and the difficulties encountered.

To make the reader more comfortable with the subsequent analysis of the data obtained, first of all let's pause to describe how the simulations were divided and organized. Considering the flux along the armchair direction of graphene (Fig. 6), we perform a total of 5 different run for each cell. Each run is performed with different initial condition (position and velocity), and labelled with a seed¹⁸ (Table 6). With the first 3 seeds we perform the longest runs, about 6.7 ns. As we already said, initial ~ 1 ns is discarded. The total useful velocity profile data originate from about 5.7 ns of simulations. The saved velocity profile for a simulation of 1 ns is visible in figure 12. The light blue lines depicts the average profiles on 100 ps of simulation, as discuss in Sec. 4.3.3. The blue line, instead, is the average of all profiles, thus the global time average over the simulation (1 ns).

For the last two seeds, the runs are shorter, about 2 ns. This is due to the computational effort needed to run the simulations. Indeed, for the bigger cell, a nanosecond of simulation takes about 20 hours, with about 1280 of CPU hours. So, to simulate trajec-

¹⁸A seed is numerical code which is use to initialize the random number generator used to produce the initial position of atoms and their initial velocity distribution.

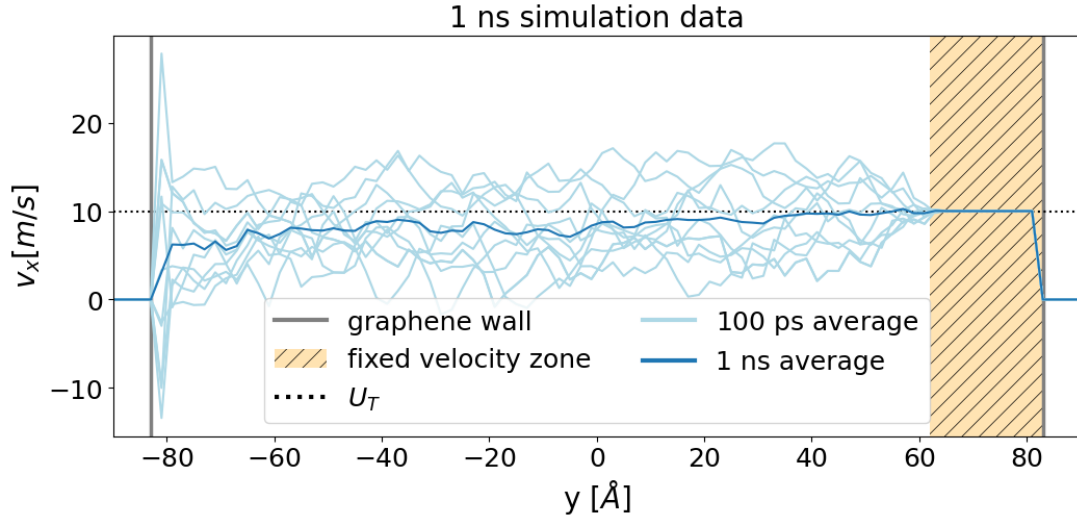


Figure 12: Velocity profiles of 1 ns of simulation for the seed Σ_5 . In the x axis the the orthogonal direction between the two graphene walls . In yellow the velocity lane where the velocity is fixed to $U_T = 10$ m/s, which is represented with a dotted black line. We see in light blue the time average profiles on 10 times interval of 100 ps each ones, as discuss in Sec. 4.3.3. The dark blue velocity profile is the global average over all the 10 profile. In gray the graphene walls.

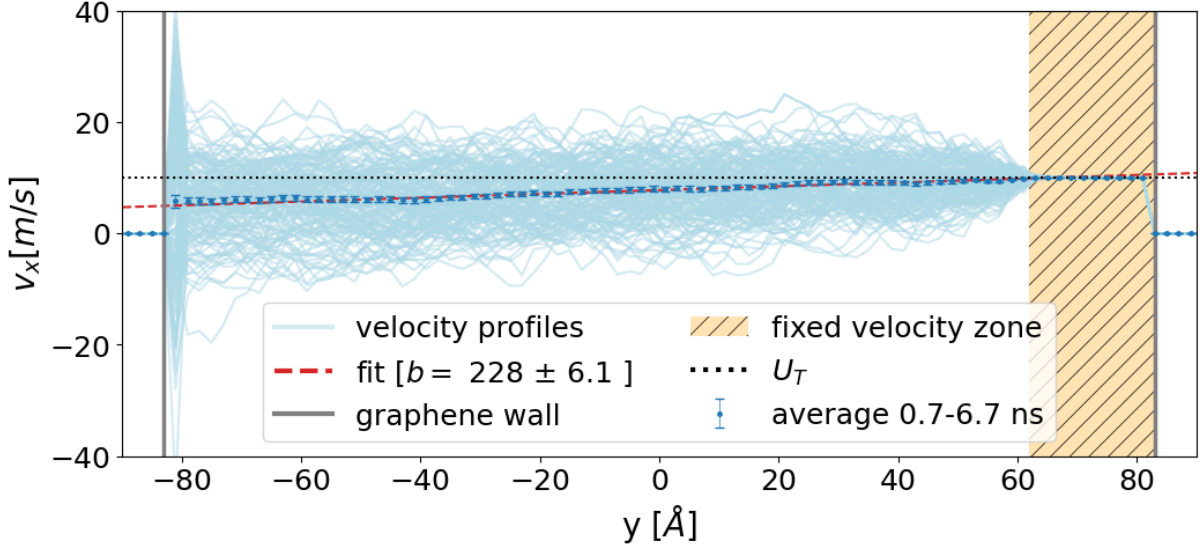


Figure 13: Total set of profiles calculated, each 100 ps, for the big cell (light blue), with the total time average (dark blue). In red the liner fit on profile data, which gives $b = 22.7 \pm 0.5$ nm and $\dot{\gamma} = 0.342 \pm 0.008 \times 10^9$ s⁻¹.

tories of 6.7 ns for 3 different seeds we use something like 25700 CPU hours. However, we were able to produce short trajectories also for two other seeds. In this way, we were also able to compare the convergence of the results as a function of the seed, to verify the possible dependence on the initial conditions (seed) and to compare whether it is more advantageous to average on many profiles obtained from simulations from different seeds or on one longer run. Then, the 3 long simulations with different seed have been averaged together to obtain the average velocity profile used to fit the data in Sec. 5.1. Details will be discussed in the next section.

Before reporting of the calculation of the slip length, we want to draw attention on the behaviour of velocity profiles. From this preliminary data observation we can see a few important things, first of all is evident the dispersion of profiles, due to the thermal noise of the water molecules. Anyway, the time average of the velocity profile (dark blue) is as expected in agreement with a linear profile and we can state that the average profiles respect the boundary conditions of slip. Secondly, it is evident, as we see in figure 12, that the profiles in the proximity of graphene wall change their behaviour from a profile with thermal noise, but still linear, to some more “irregular” behaviour. This is, evidently, a non stationary regime zone, delimited by the y_w as discussed in Sec. 2.2.3. From our simulations then, y_w seems to be about 3.5 Å; taking as water radius $r_{\text{H}_2\text{O}} = 2.75$ Å, we have $y_w \sim 1.3r_{\text{H}_2\text{O}}$, which is reasonable.

5.1 Slip length and slip velocity calculations

As we see in Sec. 2.1.3, the slip length and the strain rate can be obtained from the linear velocity profile. Then, a simple linear regression on velocity profile give us all the wanted information. Of course we need to use only the part of the profile in the bulk

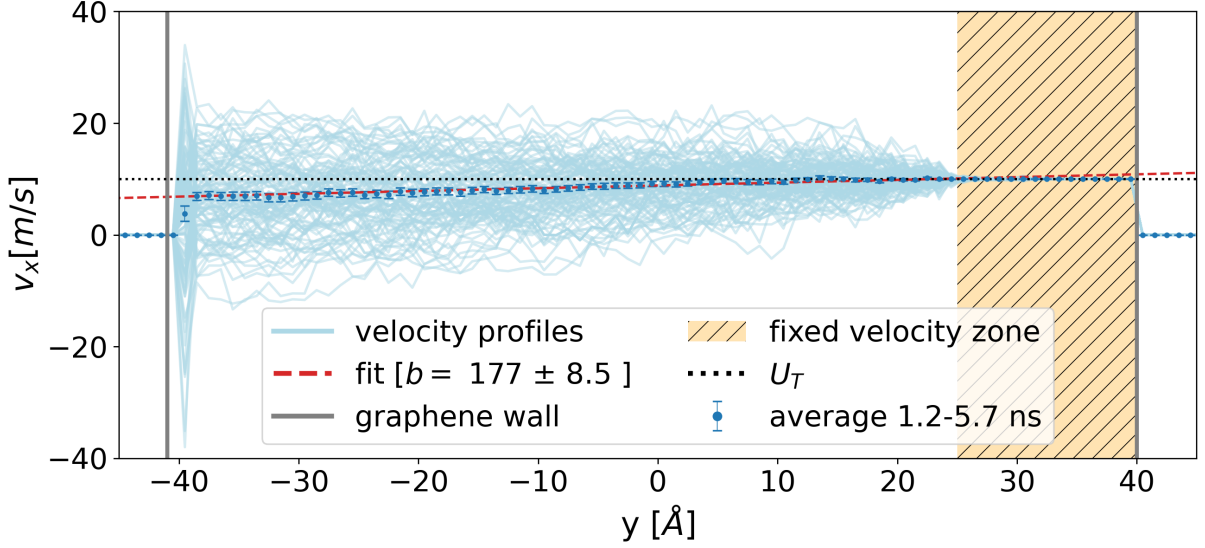


Figure 14: Total set of profiles calculated, each 100 ps, for the small cell (light blue), with the total time average (dark blue). In red the liner fit on profile data, which gives $b = 17.7 \pm 0.9$ nm and $\dot{\gamma} = 0.499 \pm 0.026 \times 10^9 \text{ s}^{-1}$

zone, neglecting the profile into the velocity lane and also in the proximity of the graphene wall. Indeed, one can clearly see from figure 12 and 13 that the profile is not longer linear between y_w and the graphene wall. Then the data used for the fit are included between y_w and the beginning of velocity lane. The linear regression algorithm provides us the two parameters of the linear function $v(y) = my + q$, that is m and q , with the respective statistical error. Clearly, the strain rate $\dot{\gamma}$ will be the m parameter while the slip length b (in absolute value) will be q/m , where the relative error is obtained simply by error propagation.

The results so obtained seem to be in good agreement with the value found in literature for a similar potential¹⁹, which gives a slip length of about 20 nm. We found a slip length of $b = 22.8 \pm 0.6$ nm, with a strain rate of about $0.342 \pm 0.008 \times 10^9 \text{ s}^{-1}$, for the big cell with a simulation 6 ns long. The small cell seems to perform a bit worst with a final slip length of 17.7 ± 0.9 nm and a strain rate of $0.499 \pm 0.026 \times 10^9 \text{ s}^{-1}$ for a simulations run of 4.5 ns. We remember that the velocity profiles used here are the “global” one, averaged also on 3 different seeds. At this point it is worth to discuss the behaviour of these profile as a function of time. Are these profiles stationary profiles of hydrodynamic description? Maybe longer simulations could give different velocity profiles. These global averages hide the dynamic behaviour of the velocity profiles. In order to shed light onto this question partial time averages of profile, every 1 ns are shown in figure 15.

For each nanosecond we plotted the velocity profile averaged on the first 3 seeds in table 6 and on the previous nanosecond, for the bigger cell. As we can see the profiles are quite scattered. Also for the last nanosecond of simulation (brown one), we see a great variation from the previous profile (purple one). This variation is more visible in

¹⁹See [10] Fig. 5, yellow data, for $\dot{\gamma} \sim 10^9 \text{ s}^{-1}$.

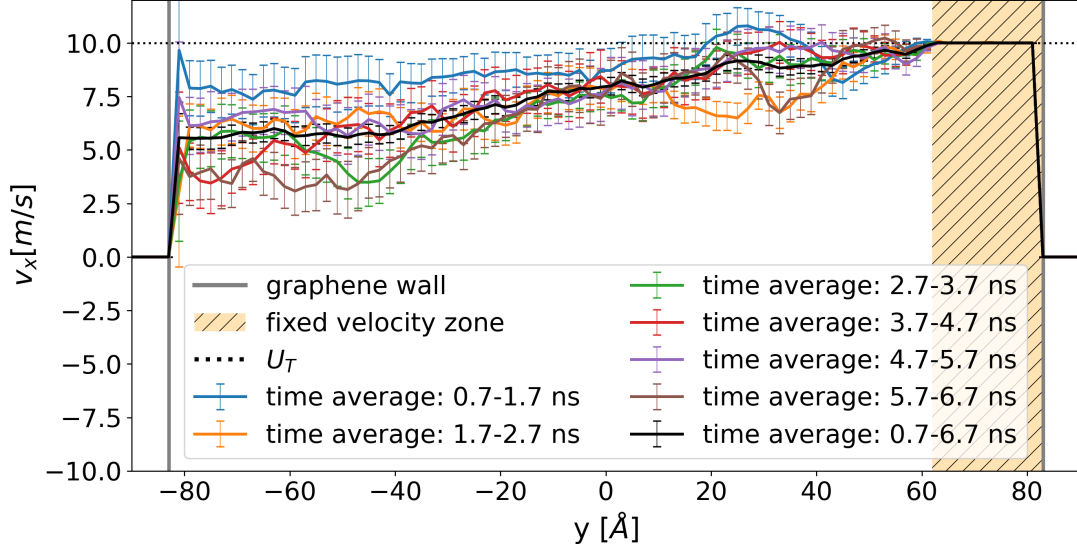


Figure 15: Velocity profiles for the big cell averaged on time intervals of 1 ns of simulation, of big cell from 0.7 to 6.7 ns. In black the total time average.

the proximity of graphene wall, which makes us speculate that moving away from the velocity lane it is increasingly difficult to obtain a stable profile. This is also supported by the increasing scatter of profiles towards graphene in figure 13. Watching, indeed, the same graph for the small cell (Fig. 16), we see a similar behaviour, with the difference that the scattering of the profile is more contained. So, it seems that longer distances from the velocity lane create more profile fluctuations and less stable velocity profile.

In this case, indeed, we see that the velocity profiles are less dispersed, and the local fluctuations follow more closely a gaussian distribution. This can make us think that profiles in the small cell are in a more steady state than the big one. We can also observe

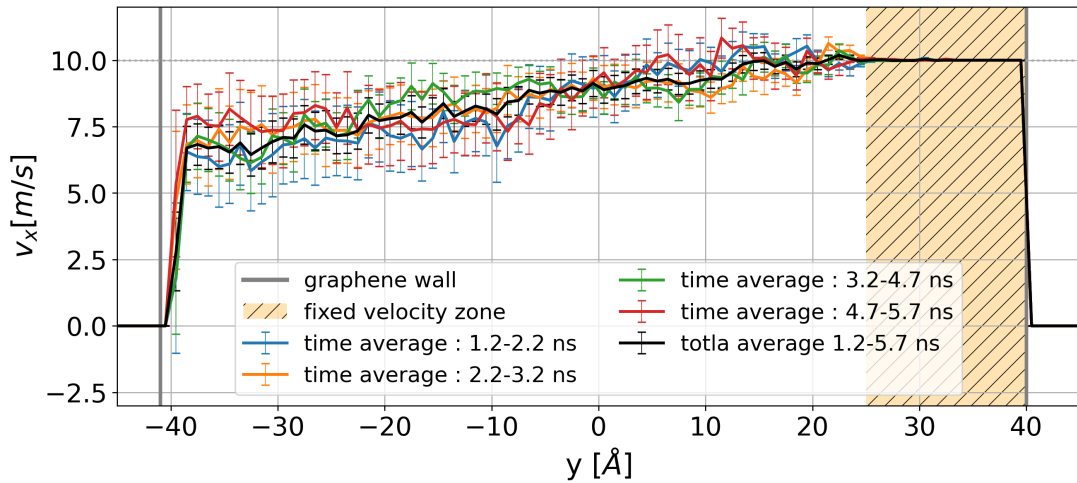


Figure 16: Velocity profiles for the big cell averaged on time intervals of 1 ns of simulation, of small cell from 1.2 to 5.7 ns. In black the total time average.

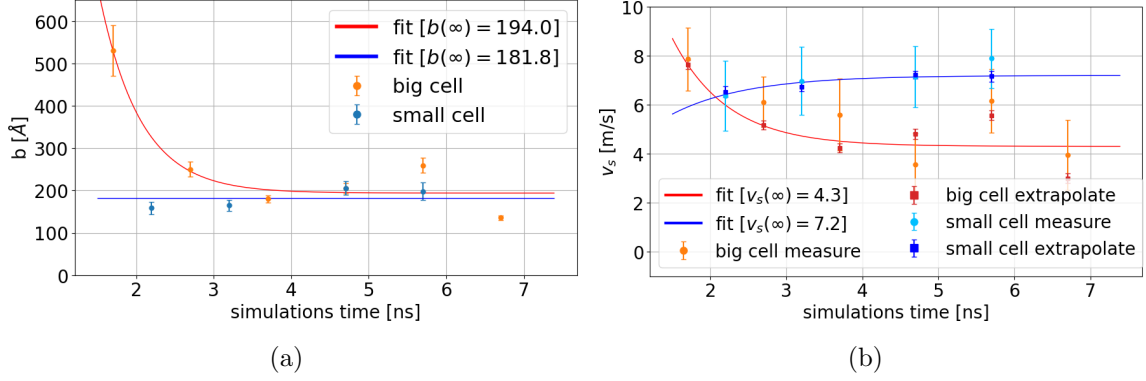


Figure 17: (a) Calculated slip length in subsequent time windows of the simulations. Each point is the result of average over time since the previous point. For example the point at time 5.7 ns is obtained from the fit over the average of 1 ns from 4.7 to 5.7 ns. The solid lines are exponential fit. $b(\infty)$ are the values of hypothetical convergence of results (b) Same graph with the slip velocity, both measured at y_w (lighter colors) or extrapolated at the graphene wall by the fit of the velocity profiles (darker colors). The solid line are exponential fits on extrapolated values, The $v_s(\infty)$ are the values of hypothetical convergence of results. The v_s shows to have a greater difference between the two cell than the b .

that in the big cell (Fig. 15) the first profile (in blue), averaged between 0.7 and 1.7 ns, of simulation seems to have a different behaviour as compared to the others. In fact, the profile seems to maintain a higher speed than the others, showing smaller presence of friction (which translates into a greater slip length and slip velocity). This suggests that the system is not yet on a steady state, and needs more time to reach it. In other words, we can suppose that the time needed to reach a stationary regime is different for different cell lengths (L_b), so the larger is the distance between the graphene wall and the velocity lane, the larger will be the relaxation time needed to reach a stationary regime.

To better understand this, we can study the convergence of the slip velocity and the slip length. For each profile in figures 15 and 14 we can fit the data and obtain the slip velocity and the slip length. In this way, since the values are always obtained from averages over a nanosecond, the fluctuations are not suppressed as the simulation time increases. However, in this way the “dynamic” behavior of the flow as a function of time is more evident (Fig. 17). In figure 17(a) we see the slip length values obtained, for the big and small cell. We can assume an exponential convergence for both cells and fit the data (solid lines in the figure). One can see that, for the small cell, b has a good convergence, with values that seem stable around 20 nm. Also the value for the big cell seems to converge around the same value, despite the presence of more fluctuation. As one could expect, the the slip length value relative to the first velocity profile is the value with the worst error and the one most distant from the convergence value. This could be interpreted as another indication of the longer relaxation time needed for the big cell. Then, knowing this, we exclude also another nanosecond from the collection of useful data, to average only on profiles with a good convergence. In this way we obtain

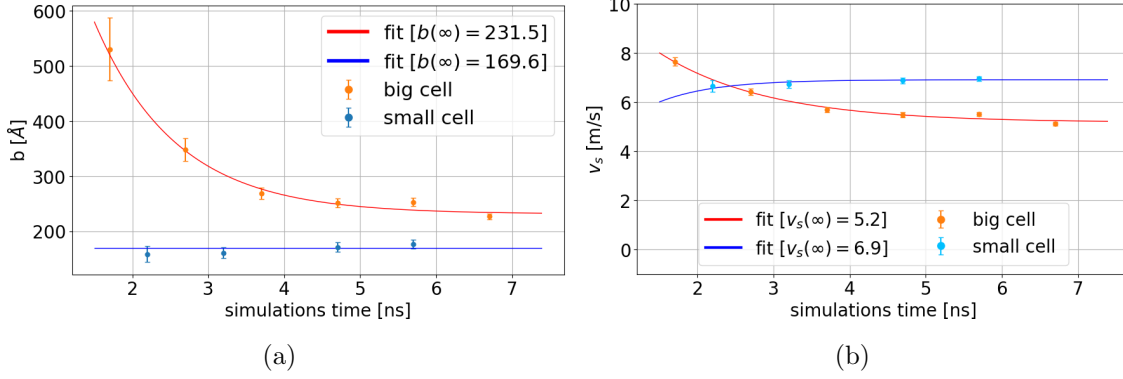


Figure 18: Slip and length and slip velocity as function of time. The difference with respect to Fig. 17 is that now each value is averaged over all the obtained profiles, not only over the last nanosecond. For example, the point at 4.7 ns of the large cell is obtained median over the velocity profiles ranging from 0.7 ns to 4.7 ns. (a) Slip length values obtained by fitting the average velocity profile as a function of time, for the large (orange) and small (blue) cells. The solid lines are the exponential fits. $b(\infty)$ represents the hypothetical convergence value. (b) Same graph but with the slip velocity.

results for the big and small cell in very good agreement and moreover in best agreement with the literature result for similar systems [10].

These fit give us a slip length value, for the big cell of $b = 19.9 \pm 0.4$ nm and a strain rate value of $\dot{\gamma} = 0.378 \pm 0.009 \times 10^9 \text{ s}^{-1}$, while for the small cell we obtain a value of $b = 19.2 \pm 0.1$ nm and a strain rate value of $\dot{\gamma} = 0.46 \pm 0.026 \times 10^9 \text{ s}^{-1}$ (Fig. 19). Of course we don't expect that the strain rate will be the same, because of the difference size of the cell.

From the figure 17(b), instead, we notice that the slip velocity has a more complex behaviour. The light color points are the v_s values obtained from the last bin where the profile is still linear, in other words at the y_w , while in the darker colors are the extrapolated values of the fits at the graphene wall. As we can see, the slip velocities seem to have a larger difference between large and small cells, compared to the slip length results. We can assume, also for the slip velocity, an exponential behavior towards convergence. Therefore, fits (solid lines in the figure 17(b)) show a rather different convergence values between large and small cells. In fact, the large cell seems to converge, with more difficulty, towards a slip velocity value of about 4.3 m/s, while the small cell to a value of 7.2 m/s. This difference, however, is understandable from a geometric point of view: being b unequal between cells of different sizes, we expect a different intercept with the graphene wall. This would suggest to think that the drag coefficient depends on the cell size due to slip velocity.

To smooth out the fluctuations and make the convergence clearer, we have make a “cumulative” time average of profiles from which we have calculated the slip length and velocity. In figure 18, we plotted the same quantities as in Fig. 17, but now with slip velocity and slip length obtained from velocity profiles average over all the previous times. In this case the exponential convergence is even more evident for both quantities of interest

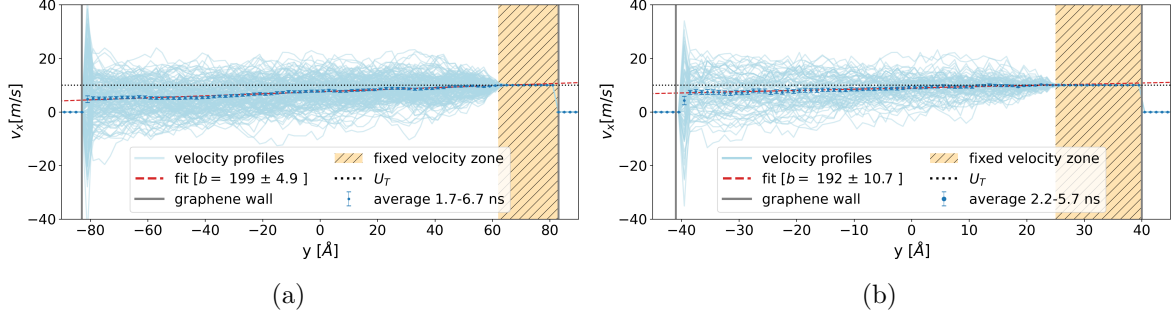


Figure 19: Velocity profiles for the two cell without the second nanosecond of simulations. (a) Big cell profiles, from 1.7 to 6.7 ns of simulation for all the 3 seeds, with the time average (darker blue), fit with a linear function (red). (b) Small cell profiles, from 2.2 to 5.7 ns of simulation for all the 3 seeds with the average (darker blue), fit with a linear function (red).

(Figs. 18(a) and 18(b)).

Seed role The last issue we want to discuss in this section concerns the role of the seed in these simulations. The initial conditions in out-of-equilibrium molecular dynamics simulations can be, in fact, quite important. Variations of the initial conditions, for this type of flow simulations, can lead to different velocity profiles. This fact is known for Couette flow so that to obtain reliable results one has to average even on dozens and dozens of different seeds [18]. In our case, the variation of the profiles is not so drastic, but it is still present, even after a few nanoseconds.

In figure 20 are represented 5 velocity profiles obtained averaged over a nanosecond of simulation, for different seeds. The average on these seeds is represented in black. It is clearly noticeable that two seeds, Σ_1 and Σ_2 respectively, seem to correspond to average higher and lower velocities than the other seeds. However, as the simulations length increased, the difference between the results corresponding to the two seeds, while still remaining, was damped and reduced to the order of the thermal fluctuations of the profiles.

5.1.1 Temperature drift

As we see in the Sec. 4.2, our NEMD simulation method don't simulate an Hamiltonian system. Indeed, even if we integrate an NVE system (so with energy conservation), the constraint we give to the particles in the velocity lane is such that the momentum of the

	Seeds				
Codes	424242	170905	210899	130924	010101
Names	Σ_1	Σ_2	Σ_3	Σ_4	Σ_5

Table 6: Seed names, for a clearer explanation, associated with the numeric codes used in the simulations

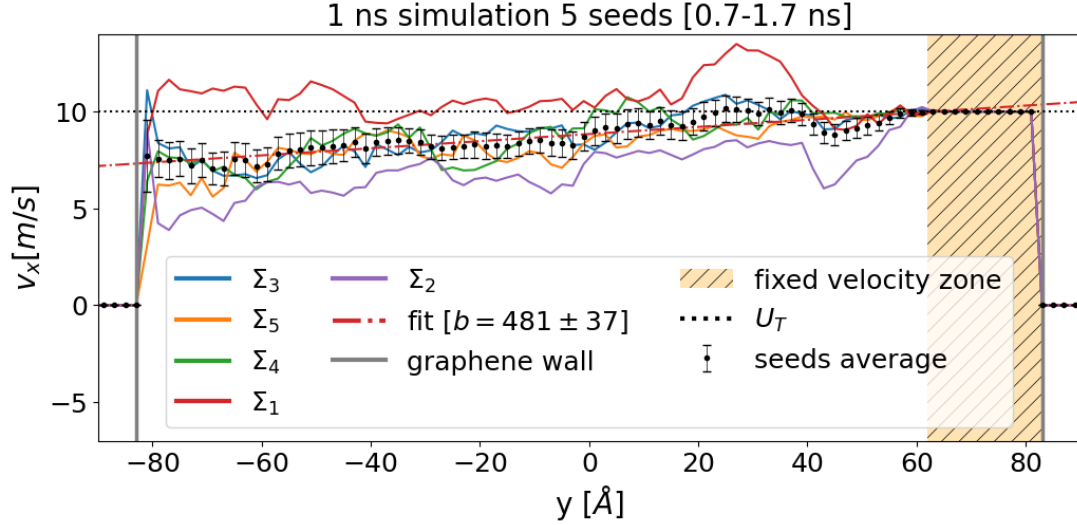


Figure 20: Time average velocity profile of 1 ns of simulation for 5 seeds. In black the average over the different profile. In table 6 the correspondance between seeds code and the seeds name in figure.

particles is not conserved. This is typical of all flow driven simulations, and is the main problem of Couette flow geometry, as we already discussed (Sec. 3.3.2). Therefore, it is not strange to expect that the temperature of the system does not remain constant. The increase in temperature, due to the flow, is therefore an inevitable drawback for this type of simulations. In our case, it was decided not to thermalize either the water or the graphene, leading to an evident but not worrying increase in temperature. In our simulation protocol, the system equilibrates (without flow) for 2 ps at 300 K for the big cell and 350 K for small cell. At this point the forces are canceled and the target velocity is set on the “non-physical molecules”, so the water loses part of its kinetic energy, cooling down. Therefore, in our case the temperature decreases before increasing due to the flow. To monitor this change of temperature, we take the temperature profile of the flow, as discussed in Sec. 4.2.1, using the same procedure used for the velocity profile, that is, saving a profile every 100 ps. We recall that this temperature profile is calculated not considering the flow velocity, in other words considering the kinetic energy of the particles without the net velocity along the x direction, due to the flow. In this way we obtain the real temperature of water without the bias due to the flow velocity.

In figure 21(a) we plotted the value of these profiles for a $y = 0$ coordinate as a function of the simulation time. We can see the drift in temperature for the big cell (blue) and small cell (orange) for tree different seeds. One can clearly see that the for the big cell all the seed have a similar temperature, which extend from 260 K to 330 K. For the small cell we can see a similar behaviour for two seeds (the ones in the upper part) while one seed has a quite different temperature, about 50 K smaller than the others two. This is due to a different initialization temperature of the simulation. Indeed this run has an initialization temperature of 300 K instead of 350 K. This apparent problem anyway, as we can see from the velocity profiles, has not created different water density (Fig. 21(b)).

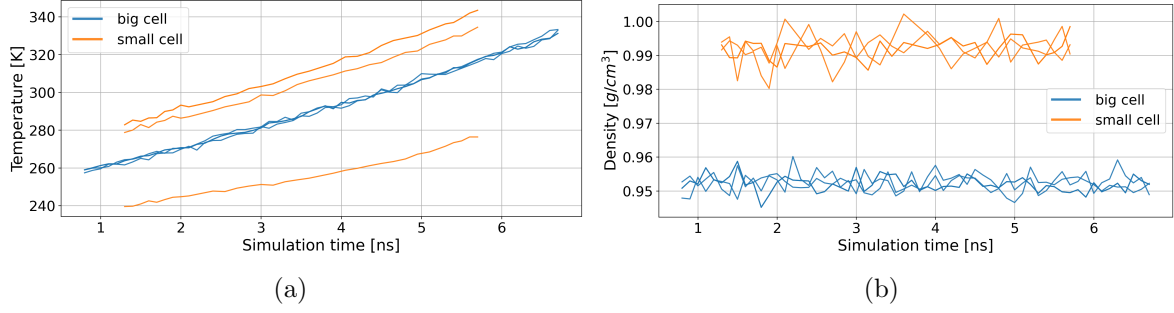


Figure 21: (a) Temperature of water at the center of the cells in function of time. (b) Density of water at the center of the cell in function of time.

As a matter of fact, in general this temperature drift has not created particularly different behaviour of velocity profile, and also if in a total of 6 ns of simulation we observe a change of about 60 K we don't observe a strong dependence of temperature of hydrodynamics properties. We want to note that the water model used (SPC/E) have a phase diagram different from the "real" water. The SPC/E water, indeed, does not freeze at 273.15 K but at about 225/230 K [25]. In this way we are sure that we remain in the liquid phase of water.

6 Conclusions

The focus of this study was to develop and validate a novel method for calculating slip length and slip velocity in a condition of continuous water flux on a surface, using non equilibrium molecular dynamics simulations. The novelty concerns on the specific method used to simulate a flux with a given constant velocity far from the surface. The results obtained through this new approach were compared to the values typically reported in literature and verified through extensive computational simulations. The method, which allows for the direct calculation of slip properties, demonstrated robustness consistency in its predictions, offering enhanced precision and reliability in scenarios that are challenging for traditional simulation techniques.

The results are in good agreement with the established values for water-graphene interactions. Specifically, the calculated slip length for a water flux over a graphene surface was approximately 22.7 nm for larger simulation cell and 17.7 nm for smaller cell. These values are consistent with literature estimates, where the slip length for water under similar conditions is typically around 20 nm.

A key contribution of this work is the application of an artificial velocity lane (VL) to simulate flow away from the graphene wall. This setup allowed for a more stable and linear velocity profile compared to conventional methods such as Couette flow simulations. The benefit of this is twofold: it improves the accuracy of the velocity profile interpolation and reduces the statistical errors in calculating the slip velocity and slip length.

One of the main challenges addressed in this study was the computational cost associated with running long, atomistic molecular dynamics simulations. The simulations, particularly those for larger cells, required significant computational time — up to 25,700 CPU hours for a 6.7 ns trajectory on the LEONARDO Cineca supercomputer. Despite this, the results showed good convergence across different seeds (initial conditions for velocity and position), indicating that the method is robust against variations in initial conditions.

The analysis of velocity profiles over time further supports the stability of the results. For both large and small cells, velocity profiles remained relatively consistent over long simulation times. However, the larger cell exhibited more fluctuation near the graphene wall, especially towards the end of the simulation. This suggests that larger simulation boxes may require even longer runs to fully stabilize the velocity profiles near the wall. By contrast, the small cell exhibited more stable and Gaussian-distributed velocity profiles, indicating that the smaller cell configuration may provide a more reliable estimate of slip properties in shorter simulations. Compared to traditional approaches, the new fixed-velocity method offers several distinct advantages.

- (a) *Higher Precision of results*, indeed the linear velocity profile generated in the velocity lane allows for a more accurate determination of the slip length and slip velocity. Traditional methods often struggle with high levels of thermal noise, especially in systems with high slip velocities and low shear rates. The fixed-velocity method mitigates these issues by producing a profile with a greater shear rate, leading to more reliable interpolation of the slip properties.
- (b) *The computational effort*, although the simulations required a significant amount of

computational resources, the method’s ability to produce stable velocity profiles over time suggests that it may be more efficient than traditional methods in terms of the required simulation length. The improved profile stability, especially in the small cell configuration, reduces the need for overly long simulations to achieve accurate results.

- (c) *Robustness Across Different Initial Conditions.* The results showed minimal dependence on the initial velocity and position conditions, further validating the robustness of the method. This contrasts with some other simulation techniques, where variations in initial conditions can significantly affect the outcome.

The successful validation of the new method opens several avenues for future research. One potential application is the investigation of more complex fluid-solid interactions, such as those involving non-water liquids or structured surfaces. Additionally, the method could be applied to other nanofluidic systems, including those involving non-planar or heterogeneous surfaces, to explore how surface roughness or chemical heterogeneity affects slip properties.

A critical future development would be conducting a detailed finite size analysis to assess the method’s dependence on the simulation cell size. In the current study, two different cell sizes were tested, and it was observed that larger cells introduced fluctuations near the wall towards the end of the simulations. While smaller cells demonstrated more stable velocity profiles, a systematic investigation of how cell dimensions influence the results is essential. This analysis could help optimize cell size to balance computational cost and result accuracy, ensuring that boundary effects or artifacts are minimized. Understanding the finite size dependence is particularly important when simulating systems that require long-range interactions, such as hydrodynamic correlations, which may behave differently as the size of the simulated box increases.

Additionally, an intriguing avenue would be to apply the method to different lattice orientation of the graphene surface such as the zig-zag geometry rather than arm-chair. In the present simulations, we primarily examined a flux parallel to the arm-chair direction. Testing the method on a zig-zag direction could reveal new insights into how the atomic structure of the solid surface influences the drag force and slip behavior at the interface. Graphene’s anisotropy in different configurations may lead to varying degrees of interaction with the fluid, possibly affecting the velocity profile and slip length. This would not only provide a more comprehensive understanding of fluid flow over graphene but also enhance the method’s applicability to a wider range of materials with different surface structures.

Another direction for future research could be to explore the applicability of the method by modifying the interaction potential between carbon atoms and water molecules. In particular, by implementing a more accurate interatomic potential, which contains quantum effects of the interaction. One possibility is to use potentials built through machine learning techniques through ab initio calculations of electronic structure. These potentials are indeed very efficient in the use of computational resources, allowing simulations of thousands of atoms, while conveying an accurate description of the atomic interaction.

In summary, this thesis has demonstrated the effectiveness of a new method for calculating slip properties in molecular dynamics simulations. The method offers enhanced precision, computational efficiency, and robustness, making it a valuable tool for investigating fluid dynamics at the nanoscale. The results align well with established values in the literature, providing confidence in the method's validity and potential for broader application.

Acknowledgments

Thanks to Antimo Marrazzo (SISSA) for the support and help in the work in this thesis project. Finally, thanks also to HPC cineca for the hours of computing granted and to the ASGARD group.

A Additional tables

Cells	Seeds	Runs time						
		01	02	03	04	05	06	07
Big	424242	0-700	700-1700	1700-2700	2700-3700	3700-4700	4700-5700	5700-6700
	210899	0-700	700-1700	1700-2700	2700-3700	3700-4700	4700-5700	5700-6700
	170905	0-700	700-1700	1700-2700	2700-3700	3700-4700	4700-5700	5700-6700
	010101	0-1000	1000-2000	-	-	-	-	-
	130522	0-1000	1000-2000	-	-	-	-	-
Small	424242	0-1200	1200-2200	2200-3200	3200-4700	4700-5700	-	-
	210899	0-1200	1200-2200	2200-3200	3200-4700	4700-5700	-	-
	170905	0-1200	1200-2200	2200-3200	3200-4700	4700-5700	-	-
	010101	0-1000	1000-2000	-	-	-	-	-
	130522	0-1000	1000-2000	-	-	-	-	-

Table 7: Summary of total simulation done, organize for type of cell, seeds and time duration.

Time	b	Error
1700	530	$\pm 60.$
2700	250	$\pm 17.$
3700	180	± 8.5
4700	205	$\pm 12.$
5700	259	$\pm 17.$
6700	135	± 5.6

Table 8: Time, b values, and corresponding errors for the big cell. Data of the figure 17(a)

Time	b	Error
2200	158	± 14
3200	164	± 12
4700	205	± 16
5700	198	± 20

Table 9: Time, b values, and corresponding errors for the small cell. Data of the figure 17(a)

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