Prediction of Fluid Slip at Graphene and Carbon Nanotube Interfaces

by

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Submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

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2013
Abstract

The hydrodynamic boundary condition is now a subject of greater interest than ever before, even though the problem of formulating the correct boundary condition has existed from the beginning of the 19th century. Since then, many researchers have attempted to formulate a general boundary condition for fluid-solid interfaces. The 21st century has seen revolutionary advancement in nanoscale science and technology, which in turn, poses many fundamental questions about the nature of fluid flow in nanometric pores such as carbon nanotubes (CNTs) and aquaporins. Among them, one of the most important is the boundary condition.

In this work, based on a statistical mechanics approach, we present a method to calculate the intrinsic interfacial friction coefficient between a fluid and solid at a planar and cylindrical interface, which determines the slip and boundary condition. We apply the method in conjunction with equilibrium molecular dynamics (EMD) simulation technique to fluids such as argon, methane and water flowing in planar graphene nanoslit pores and CNTs.

We compare our model predictions against direct non-equilibrium molecular dynamics (NEMD) simulations and find excellent agreement. We identify several limitations of generally used NEMD methods to predict the slip and boundary condition and show that great care needs to be taken in analyzing the results of NEMD slip data for high-slip systems. We suggest some procedures to increase the reliability of the slip estimates. We also study the shear rate and external field dependent behavior of slip in Couette and Hagen-Poiseuille type flows. The slip length remains
constant (indicating a linear response of the fluid to the external perturbation) only for low shear rates/external fields and as the field increases, the slip length increases rapidly. At these high fields the Navier-slip model breaks down.

We attempt to resolve the highly debated issue of flow rates of water in carbon nanotubes, the values of which are scattered over 1 to 5 orders of magnitude in literature. We accurately predict these flow rates using both the CNT diameter dependent interfacial friction coefficient between water-CNTs and NEMD simulations streaming velocity profiles. Very narrow tubes show higher flow rate enhancements and as the tube diameter increases, the flow rates approach classical Navier-Stokes predictions with the no slip boundary condition. As the diameter of the tube increases, the slip length decreases monotonically and asymptotically approaches a constant value, which is equal to the slip length on a planar graphene surface.

Our model gives the linear regime slip length which corresponds to experimental condition flow rates, which is otherwise cumbersome to find using NEMD simulation techniques. The proposed method is robust, general and can be used to find the slip and boundary condition accurately at any fluid-solid interface.
Acknowledgement

The time has come to reflect on a wonderful journey called PhD. My first and deepest gratitude is to my supervisor Prof. Billy D Todd and to my co-supervisors Prof. Peter J Daivis and A/Prof. Jesper S Hansen. They are excellent researchers, teachers, supervisors and above all great humanitarians. I am most fortunate to have them as my supervisors and by far I had a very pleasant PhD experience than it is in general. I remember those encouraging words from Prof. Billy that “I am least bothered about you” for his trust and unconditional freedom given to me. I thank Swinburne University for the scholarship and travel grants to Europe and USA.

My special thanks to Dr. Stefano Bernardi for his support and the discussions in the early stage of my work. After Stefano left for a postdoctoral fellowship, Remco Hartkamp filled that space. Some other friends Sai, Abhi, Igor, Tesfaye, etc and Melbourne made my stay memorable here. My research began at MCS lab, University of Hyderabad and a special thanks to all the members of that lab. Many friends from India made my life beautiful and joyful, Anil, Suri, Sagar, Subbi, Anji, Ramana are only a very few to mention.

I am very much indebted to my family, Amma, Nanna, Thammudu, and grand parents. I can never thank them enough for their love and support through out my life.

My spiritual and philosophical friends Jiddu Krishnamurti, Alan Watts, Osho, Swami Vivekananda, Sadguru, and a few others. Your wisdom and insight is invaluable.
A special thanks to awesome Linux (everything you need is just at the terminal), Octave, C, Latex, and the developers of all other free tools I have used, hopefully I will contribute to some open source projects in the future.

Many other people in the journey of 28 years of life who helped me, inspired me, made my life joyful, shared laughter, love and life.........
Declaration

I hereby declare that the thesis entitled “Prediction of Fluid Slip at Graphene and Carbon Nanotube Interfaces”, is submitted in fulfillment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Engineering and Industrial Science of Swinburne University of Technology, and is my own work. It contains no material which has been accepted for the award of any other candidate for any other degree or diploma, except where due reference is made in the text of the thesis. To best of my knowledge and belief, it contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Sridhar Kumar Kannam

June 2013
“A hundred times every day I remind myself that my inner and outer life depend on the labors of other men, living and dead, and that I must exert myself in order to give in the same measure as I have received and am still receiving” - Albert Einstein
“Where the mind is without fear and the head is held high, Where knowledge is free, Where the world has not been broken up into fragments by narrow domestic walls, Where words come out from the depth of truth, Where tireless striving stretches its arms towards perfection, Where the clear stream of reason has not lost its way into the dreary desert sand of dead habit, Where the mind is led forward by thee into ever-widening thought and action, Into that heaven of freedom, my Father, let my country awake”- Rabindranath Tagore
Publications from this thesis

S. K. Kannam, B. D. Todd, J. S. Hansen, and P. J. Daivis
Slip flow in graphene nanochannels

S. K. Kannam, B. D. Todd, J. S. Hansen, and P. J. Daivis
Slip length of water on graphene: Limitations of non-equilibrium molecular dynamics simulations

S. K. Kannam, B. D. Todd, J. S. Hansen, and P. J. Daivis
Interfacial slip friction at a fluid-solid cylindrical boundary

S. K. Kannam, B. D. Todd, J. S. Hansen, and P. J. Daivis
How fast does water flow in carbon nanotubes?

Publication not from this Thesis

R. Hartkamp, S. K. Kannam, B. D. Todd, S. Bernardi, D. Searles, and P. J. Daivis
Transient-time correlation function calculations of the shear, elongational and mixed flow rheology of linear chain molecular fluids
(in preparation)
Thesis outline

In chapter 1, we give a brief introduction to the hydrodynamics, nanofluidics, statistical mechanics, and molecular dynamics simulation techniques relevant to this thesis.

In chapter 2, we present the method to calculate the interfacial friction at a fluid-solid planar interface and derive an explicit expression for the slip length for a planar Poiseuille and planar Couette flow. We then extend the method (both friction coefficient and slip length) to a cylindrical boundary. We also review other methods in the literature on predicting the interfacial friction coefficient at a fluid-solid interface.

In chapters 3 and 4, we apply the planar interface method to argon, methane and water flow in planar graphene nanoslit pores. We compare our friction method predictions with direct NEMD simulations. We study the rate dependent (external field in a Hagen-Poiseuille flow and shear rate in a Couette flow) slip behaviour. We show some limitations of NEMD techniques to predict high slip and suggest some procedures to increase the reliability of the NEMD slip estimates.

In chapters 5 and 6, we verify the cylindrical interface method by applying it to methane flow in CNTs. We compare our extended model curvature dependent surface friction predictions with direct NEMD simulations. We then accurately predict the flow rates/enhancement of water in CNTs. We comment on several issues concerning the prediction of nanofluidic flow rates, with a focus on water flow.
in CNTs.

In chapter 7, we draw some conclusions and suggest some future research directions.
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<table>
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<tr>
<td>EMD</td>
<td>Equilibrium Molecular Dynamics</td>
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<td>Reactive Empirical Bond-Order</td>
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Notation

Frequently used symbols

\( \eta_0 \) Shear viscosity
\( \xi_0 \) Friction coefficient
\( \sigma_{xy} \) Shear stress of the fluid
\( \dot{\gamma} \) Strain rate of the fluid
\( \frac{\partial u}{\partial y} \) Velocity gradient of the fluid in confining direction in a planar channel
\( \frac{\partial u}{\partial r} \) Velocity gradient of the fluid in radial direction in a cylindrical tube
\( L_s \) Slip length
\( u_s \) Slip velocity
\( U \) Upper wall velocity in a Couette flow
\( u_{x}(y) \) Streaming velocity in \( x \) direction in a planar channel
\( u_{z}(r) \) Streaming velocity in \( z \) direction in a cylindrical tube
\( \Delta \) Slab width
\( F'(t) \) Wall-slab shearing force
\( u_{\text{slab}}(t) \) CM velocity of the slab
\( C_{uu}(t) \) Slab velocity auto correlation function
\( C_{uF}(t) \) Slab velocity-force correlation function
\( \tilde{C}_{uu}(s) \) Slab velocity auto correlation function in Laplace space
\( \tilde{C}_{uF}(s) \) Slab velocity-force correlation function in Laplace space
\( h \) Planar channel width
\( R \) Radius of the tube
\( D \) Diameter of the tube
\( \sigma \) van der Waals radius
\( \rho \) Density of the fluid
\( F_e \) External field applied to the fluid
\( \Delta t \) Time step
\( A \) Surface area of the solid
\( Q_{\text{no-slip}} \) Flow rate with no-slip boundary condition
\( Q_{\text{slip}} \) Flow rate with no-slip boundary condition
\( E \) Enhancement
Chapter 1

Introduction

In this chapter we give a brief introduction to hydrodynamics, nanofluidics, statistical mechanics, and molecular dynamics simulation techniques relevant to this thesis.
1.1 Hydrodynamics

Understanding the behaviour of fluids, gases and liquids in confinement and at the interface with solids is of both fundamental and practical interest. Any fluid is composed of finite size molecules with a structure, which move continuously through space in random directions, collide with each other, and with the walls of the container when they are confined. The study of fluids and forces acting on them is largely based on the continuum hypothesis, which treats the fluids as a continuum, i.e., any fluid properties such as density, velocity, temperature, and pressure are taken to be well defined at infinitely small points and they vary continuously from one point to another [1, 2].

In most applications of fluid mechanics, the physical dimensions of the flow are extremely large compared to the size of molecules and the molecular mean free path. For example, in our daily life we feel air and water as being continuous. When measured with any devices that continuum hypothesis would seem natural because the measuring instruments are sensitive enough for the measurements to be local relative to the macroscopic scale and at the same time quite large enough to contain an enormous number of molecules [1]. A small volume such as $10^{-3}$ cm$^3$ contains about $3 \times 10^{16}$ molecules, so we can safely ignore the atomic details of the fluid. Based on these assumptions, changes in flow parameters are regarded as continuous.

In Fig. 1.1, the continuum assumption for a fluid is illustrated by a thought experiment that consists in measuring the density of a fluid sample of arbitrary volume. The continuum assumption holds when the sample volume contains a sufficiently large number of atoms, and at the same time is much smaller than the size of the system, (any point on the density plateau in Fig. 1.1). At any given point, let $\delta V$ be an arbitrary volume around the point and $\delta m$ be the mass of fluid in the volume $\delta V$. The density is then defined as

$$\rho = \lim_{\delta V \to \delta V_m} \left( \frac{\delta m}{\delta V} \right)$$  \hspace{1cm} (1.1)
where $\delta V_m$ is the smallest volume around the point for which statistical averages can be obtained. The local fluid properties are considered as point values which vary continuously in space. Hence, the flow parameters are spatially continuous and the expression ‘continuum’ is used to describe the concept.

These continuum assumptions work well from macro scale down to micro scale because the associated system length scales are many orders of magnitude higher than the interatomic distances between fluid atoms, characteristic physical scaling lengths of the fluid (e.g. Debye length, hydrodynamic radius), and any spatial correlation lengths. In other words, when the mean free path of the molecules $\lambda$ is smaller than the smallest characteristic dimension of the system $L$, i.e., the Knudsen number $K_n = \frac{\lambda}{L} \ll 1$. 

Figure 1.1: Illustration of the continuum hypothesis. This image is taken from Introduction to Fluid Dynamics by Batchelor [1].
1.1.1 Navier-Stokes equations

Classical hydrodynamics is governed by a differential equations referred to as the Navier-Stokes equations [1, 2]. The equations are based on the continuum hypothesis and are derived by applying Newton's second law of motion to the fluid together with the conservation of mass, momentum and energy. For momentum transport we assume that the fluid is incompressible, which for water and aqueous solutions is a good approximation (e.g., when the pressure increases from 1 to 2 atm the density of water changes by only 0.01%). The principle of mass conservation with the incompressibility criterion is expressed as

\[ \nabla \cdot \mathbf{u} = 0 \]  \hspace{1cm} (1.2)

where \( \mathbf{u} \) is the (streaming) velocity field of the fluid flow.

The Navier-Stokes equation for momentum transport is derived by applying Newton's second law of motion to a small volume of fluid. This law describes the velocity field in a Newtonian liquid as

\[ \rho \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = \mathbf{F} - \nabla P + \eta \nabla^2 \mathbf{u} \]  \hspace{1cm} (1.3)

where \( \rho, \eta, \) and \( P \) are the density, shear viscosity, and the pressure of the fluid. The terms on the right hand side represents the total force per unit volume acting on the volume of fluid, in which \( \mathbf{F} \) is the total body force per unit volume (for e.g., gravitational force \( F = \rho g \)), and the term \( -\nabla P + \eta \nabla^2 \mathbf{u} \) expresses the surface stress force per unit volume. Using Newton's second law of motion, this total force is equal to the mass times the acceleration per unit volume. We obtain the left hand terms by expressing the acceleration in terms of the velocity field.

To apply these equations to any hydrodynamic problem, the boundary conditions should be specified. At a solid-fluid interface the normal component of the fluid velocity vanishes and the tangential component is assumed to be equal to the velocity of the surface, which is referred to as the no-slip boundary condition.
1.1.2 Hydrodynamic boundary condition

To describe a hydrodynamic problem, the boundary condition should be specified \textit{a priori}. This boundary condition along with the fluid transport coefficients is used in the Navier-Stokes equations to solve for the relevant flow properties. The fluid transport coefficients are intrinsic to the fluid and there are several methods of finding them accurately. As the boundary condition cannot be derived from Navier-Stokes hydrodynamics, one often assumes the no-slip boundary condition, according to which the tangential velocity of the fluid relative to the adjacent solid is zero irrespective of the nature of both fluid and solid as stated above [1, 2]. Here we emphasise that this no-slip boundary condition has no theoretical foundation.

In this work we study three general problems of interest, which have exact analytical solutions when we assume the no-slip boundary condition.

Planar Poiseuille flow

Planar Poiseuille flow is generated by a pressure gradient or a uniform external field on the fluid confined between two parallel plates. The streaming velocity profile across the channel can be solved by using the Navier-Stokes equations along with the no-slip boundary condition.

Let us consider a fluid confined between two parallel plates positioned at \( y = -h/2 \) and \( y = +h/2 \) along the \( y \) direction, see Fig. 1.2. Let the fluid be acted on by a uniform external field \( F_e \) in the \( x \) direction. As the plates are stationary, and according to the no-slip boundary condition, the fluid velocity at both walls \((y = -h/2 \text{ and } y = +h/2)\) is zero. For this case the Navier-Stokes equation reduces to a Stokes (or in general mathematical terminology Poisson) equation

\[
\frac{\partial^2 u}{\partial y^2} = -\frac{\rho F_e}{\eta_0} .
\tag{1.4}
\]

With the boundary condition \( u_x(y) = 0 \) at \( y = +h/2 \) and \( y = -h/2 \), we get the
solution

\[ u_x(y) = \frac{\rho F_0}{2\eta_0} \left[ \left( \frac{h}{2} \right)^2 - y^2 \right] . \] (1.5)

Hence the velocity profile across the channel is parabolic with no-slip at the walls. The streaming velocity of the fluid is maximum at the centre of the channel \( y = 0 \).

In the case of slip flow the fluid has a finite slip velocity \( u_s \) at the walls and the slip modified velocity profile is given by

\[ u_x(y) = \frac{\rho F_0}{2\eta_0} \left[ \left( \frac{h}{2} \right)^2 - y^2 \right] + u_s . \] (1.6)

**Planar Couette flow**

Planar Couette flow is shear driven and it is generated by moving one of the confining plates relative to the other. Here the flow is caused by the shear force between moving plate and the fluid.

Let us consider a fluid confined between two parallel plates positioned at \( y = 0 \) and \( y = h \) along the \( y \) direction, see Fig. 1.2. Let the upper plate move with a constant velocity \( U \) in the \( x \) direction and the lower plate remain stationary. Again, assuming the no-slip boundary condition, the fluid velocity at the upper wall is equal to the wall velocity and zero at the lower wall as it is held stationary. For this case Navier-Stokes equation reduces to a simple Laplace equation

\[ \frac{\partial^2 u}{\partial y^2} = 0 . \] (1.7)

With the boundary condition \( u_x(y) = 0 \) at \( y = 0 \) and \( u_x(y) = U \) at \( y = h \), the solution is

\[ u_x(y) = \frac{U y}{h} . \] (1.8)

Hence the velocity profile across the channel is linear with no slip at the walls, i.e.,
1 Introduction

Figure 1.2: The slip and no-slip velocity profiles for Poiseuille and Couette flows.

zero at the lower wall $y = 0$ as it is stationary and equal to wall velocity $U$ at the upper wall $y = h$.

Again in the case of slip flow the fluid has a finite velocity $u_s$ at the lower wall and $U - u_s$ at the upper wall, and the slip modified velocity profile is given by

$$u_x(y) = \left( \frac{U - 2u_s}{h} \right) y + u_s.$$ (1.9)

Hagen-Poiseuille flow in a circular tube

In this case the fluid is confined in a cylindrical tube and acted on by an external field or a pressure gradient.

Let us consider a fluid confined in a circular tube of radius $R$ and let the fluid be acted on by a uniform external field $F_e$ in the $z$ direction. It is convenient to use cylindrical coordinates $(r, \theta, z)$ to solve this problem. According to the no-slip
boundary condition, the fluid velocity at the wall \((r = R)\) is zero. For this case the
Navier-Stokes equation also reduces to the Stokes (or Poisson) equation which in
cylindrical coordinates reads

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u_z(r)}{\partial r} \right) = -\frac{\rho F_e}{\eta_0}.
\] (1.10)

With the boundary condition \(u_z(r) = 0\) at \(r = +R\), the solution is

\[
u_z(r) = \left(\frac{\rho F_e}{4\eta_0}\right) (R^2 - r^2),
\] (1.11)

where it is used that \(u_z(r)\) must be finite at \(r = 0\). Hence the velocity profile across
the tube is parabolic with no slip at the walls. The streaming velocity of the fluid
is maximum at the centre of the tube \(r = 0\) and zero at the wall surface \(r = R\).

Note that in all the above classical hydrodynamics equations, the friction and slip
derivations in Chapter 2 assume a bulk-like fluid of uniform density and viscosity
across the nanopore. This assumption is not valid for very narrowly confined fluids
due to the layering effects and heterogeneity of the fluid near the wall surface. These
issues are explained in more detail in chapters 5 and 6.

For very dilute gaseous or rarefied systems, Maxwell described the flow using
tangential momentum accommodation coefficients (TMAC) based on kinetic theory
[3, 4]. In this thesis we concentrate on liquid densities where the Maxwell TMAC
model breaks and the fluid transport can be partially described by the slip length.

## 1.2 Nanofluidics

Nanoscience and nanotechnology offer many fundamental challenges for scientists
and engineers in research and the possibility of a new industrial revolution. The
world market for Nanotechnology products is estimated to be worth one trillion dol-
ars in 2015, which signifies its research possibilities and importance. Nanofluidics
is an integral part of nanotechnology and it is interdisciplinary to many branches
of science including physics, chemistry, biology and geology [3, 4]. Conventionally nanofluidics is defined as the scientific investigation and technical application of fluid flow in and around nanosized materials with at least one dimension below a few hundred nm characteristic dimensions. A variety of rich phenomena (e.g. new phase transitions) occur in such fluidic systems due to the confinement effects. The growth in this research field has been enormous in the past decade due to our new understanding of nanoconfined fluids, which is enabled by technical advancement and driven by practical interest. Transport of fluid at the nanoscale is very important for the design and fabrication of nanofluidic devices such as nanopumps, micro/nano electro mechanical systems (MEMS/NEMS), nanobiosensors, nanoreactors, nanoactuators, nanoengines, lab-on-a-chip, etc [3]. These devices have many potential applications such as water desalination, molecular computing, lubrication, drug delivery, fuel storage, mixing and separation, lubrication, in reduction of viscous friction to reduce energy dissipation and to amplify flow rates by inducing slip, just to mention a few. Apart from these applications, the study of nanofluidics elucidates our understanding of the fluid behaviour in biological channels such as proteins and aquaporins, water flow in plants, soil science, and geology, all of which involves flow in nanometric pores.

In order for these applications to become a commercial reality, we need to understand the fundamental behaviour of fluids confined to the nanoscale from a theoretical point of view. This will then enable one to precisely control and manipulate fluids in applications. When fluids are confined to channel widths of only a few molecular diameters, the well established classical hydrodynamic theories based on the Navier-Stokes equations may fail, and the no-slip boundary condition may no longer be valid. Experimentally we still have to overcome certain limitations on probing and controlling molecules at the nanoscale. This is a very complex problem. Fluids confined to the nanoscale exhibit new physical and chemical behaviour (new phase transitions and anomalous behaviour [5, 6] are observed along with the change in many other properties) not observed in larger structures (e.g. one dimensional water chain in carbon nanotubes) such as those of micrometer dimensions and above for the following reasons [3, 4, 7-10].
In nanofluidic systems, the solid surface area to fluid volume ratio becomes very high, so the interfacial effects at the fluid-solid interface become very important. The characteristic physical scaling lengths of the fluid very closely coincide with the nanostructure itself (Knudsen number is comparable to 1), and as a result new physical constraints are imposed on the fluid and they alter the behaviour of the fluid. The confining walls induce strong density oscillations of the fluid across the channel so the fluid becomes highly inhomogeneous and as a result transport properties of the fluid such as diffusion and viscosity become non-local in nature and will vary over very small length scales. The influence of finite size effects of the molecules on fluid transport needs to be taken into account, while such effects may be largely neglected for liquid flows in macroscopic channels. The depletion layer near the solid surface affects the thermodynamic properties and may also alter the chemical reactivity of the species at the fluid-solid interface. The fluid-solid interaction such as hydrophilic or hydrophobic interactions can have a profound influence on the flow characteristics. Our understanding of the boundary condition at the fluid-solid interface is not yet clear at the nanoscale. Most importantly, the well established Navier-Stokes equations based on continuum theories may not be valid for fluids confined to a few molecular diameter channel widths.

Computer simulations where we can model molecules explicitly, can be considered as a bridge between the experiments and theory, and are playing an increasing role in our understanding of the nanofluidic behaviour and exploring new possibilities.

### 1.2.1 Water, graphene, and carbon nanotubes

Carbon is the most important element of the nanorevolution. CNTs are the smallest cylindrical nanopores we can make (10,000 times smaller than a human hair) and graphene is the 2-dimensional ultra-thin atomic layer. Both CNTs and graphene have unusually high mechanical strength, elastic, thermal and electric properties, ultra smooth hydrophobic surface, high aspect ratio, etc. In fluidic applications, both graphene and CNTs have shown superlubricity, ultra fast mass transport of
Water is one of the most vital elements of life. Even though it is the most studied material on earth, its anomalous bulk properties are still surprising and properties of confined water are mysterious. Understanding the transport properties of water in nanopores, such as biological aquaporins and CNTs, is of both fundamental and practical interest. In this work we study the transport of water in both graphene slit pores and CNTs of various diameters which has been a subject of intense research over the last decade.

1.3 Statistical Mechanics

Matter is composed of a very large number of atoms and its observable properties are an average result of the microscopic properties of the individual atoms. Statistical mechanics is the framework that connects the microscopic properties of the individual atoms of the system to the macroscopic observable bulk properties such as pressure and temperature. Statistical mechanics is a fusion of classical mechanics with statistics and is based on probabilistic concepts. It provides us the mathematical tools to derive the useful information about the system [19].

To get the average value of a macroscopic quantity using simulations we take the time average. An ensemble is a collection of all possible microstates that result in the same macroscopic thermodynamic state. In an isolated system, the volume $V$ and the number of atoms $N$ do not change. If Newton’s equations of motion are integrated for an isolated system then the total energy $E$ is also a constant of motion. Simulations in which $N$, $V$ and $E$ are fixed are said to be in a microcanonical ($NVE$) ensemble. While a microcanonical ensemble is the most natural ensemble for simulations, in experiments and other realistic systems it is often the temperature $T$ or the pressure $P$ which is constant. A collection of all possible systems (each with its own different microscopic state) with a fixed number of atoms, a fixed volume and a fixed specified temperature is called a canonical ($NVT$) ensemble. This ensemble can be generated with a suitable heat bath, and thus corresponds to
a closed system, where exchange of energy is permitted.

The average value of a macroscopic property $A$ in the canonical ensemble is calculated as an ensemble average $\bar{A}$

$$\bar{A} = \frac{\int A e^{-\beta H(r_1, r_2, \ldots, r_N, p_1, p_2, \ldots, p_N)} d\Gamma}{\int e^{-\beta H(r_1, r_2, \ldots, r_N, p_1, p_2, \ldots, p_N)} d\Gamma},$$

(1.12)

where $k_B$ is the Boltzmann constant, $T$ is the temperature, $\beta = \frac{1}{k_B T}$, $H$ is the Hamiltonian of the system in terms of its constituent coordinates $r_i$ and momenta $p_i$, $N$ is the total number of atoms in the system, and $\Gamma \equiv (r_1, r_2, \ldots, r_N, p_1, p_2, \ldots, p_N)$ is the phase space vector. According to the Ergodic hypothesis the above ensemble average is equal to a sufficiently long time average of a single system in the steady state.

1.4 Molecular Dynamics Simulations

Computer simulations are a powerful modern technique to study the scientific problems as a numerical virtual experiment. Molecular dynamics is a computer simulation technique that is used to study the dynamics of atoms and molecules of a given system in space and time [20-24]. The atoms in the system interact via the forces acting between them which are often modelled through a potential energy function. The trajectories of atoms are solved numerically according to Newton’s equations of motion. We use statistical mechanics as a bridge to convert the microscopic atomic information (e.g. positions and velocities) to macroscopic thermodynamic observables of the system such as pressure and temperature.

1.4.1 Empirical potentials

The reliability of any simulation results depends on the empirical potential energy functions and their parameters chosen to model the system [20-24]. The level of complexity of a potential describes the level of precision in the interactions between
particles. It is often desirable to use simple models with minimum parameters in simulations because they are easy to implement and they reduce the computational time.

The Lennard-Jones potential is very simple yet it captures the important interactions between neutral atoms or molecules. The interaction potential between two atoms \( i \) and \( j \) located at sites \( \mathbf{r}_i \) and \( \mathbf{r}_j \) takes the form

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

(1.13)

where \( \epsilon \) is the interaction strength (depth of the potential well) and it is a measure of how strongly the atoms interact with each other, \( \sigma \) is the length scale, the distance at which the inter-atomic potential is zero and it is a measure of how close two nonbonded atoms can get and is thus referred to as the van der Waals radius, and \( r_{ij} = |\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j| \).

The Lennard-Jones potential is attractive as two atoms approach one another from a distance, but strongly repulsive when they are close. The last term \( \left( \frac{\sigma}{r_{ij}} \right)^6 \) describes the attractive interaction and it is a result of the induced dipole-dipole moment interaction of the atoms and van der Waals forces and electrostatic effects due to electronic correlations at long distances. The first term \( \left( \frac{\sigma}{r_{ij}} \right)^{12} \) describes the repulsive interaction which is due to the hard core repulsion and overlapping of electronic clouds at close distances.

Similar to the Lennard-Jones potential the electrostatic interaction between charges ions \( i \) and \( j \) with charges \( q_i \) and \( q_j \) is described by Coulomb’s law

\[
U(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}},
\]

(1.14)

where \( \epsilon_0 \) is permittivity of free space. As this potential is long ranged, the above form can not be implemented directly in a simulation and a few techniques are proposed to handle this, see Appendix A.1.

In addition to the above interatomic interactions, we may have intra-molecular
interactions within a molecule. Two such interactions are bond stretching and bond bending. For example in a water molecule, we need to capture the bond length between hydrogen and oxygen atoms and bond angle between hydrogen-oxygen-hydrogen atoms. These interactions are often described using the Hookean type potentials. For bond length we have

\[ U(r_{ij}) = \frac{1}{2} K_l (r_{ij} - l_0)^2 \]  

and for bond angle

\[ U(\theta_{ijk}) = \frac{1}{2} K_a (\theta_{ijk} - \theta_0)^2 \]  

where \( l_0 \) is the equilibrium bond length, \( K_l \) bond length interaction strength and \( \theta_{ijk} \) is the equilibrium bond angle, and \( K_a \) bond angle interaction strength.

To model the covalent bonds in solid-state materials such as graphene and CNTs more complicated potentials such Tersoff-Brenner are used, see Appendix A.2.

### 1.4.2 Newton’s equations of motion

As mentioned before, in molecular dynamics simulations the classical equations of motion are integrated to determine the positions and momenta of atoms in time [20-24]. Once we calculate the force acting on atoms due to the above mentioned potential interactions, we use Newton’s equations of motion to solve for their velocities and positions. According to Newton’s second equation of motion

\[ \mathbf{F}_i = m_i \ddot{\mathbf{r}}_i \]  

where \( \mathbf{F}_i \) is the force acting on atom \( i \), \( m_i \) is its mass, and \( \ddot{\mathbf{r}}_i \) is the second derivative of its position vector with respect to time. The above second order differential equation can be written as two first order differential equations in a more convenient form as
follows

\[ \dot{r}_i = \frac{\dot{p}_i}{m_i}, \quad (1.18) \]

\[ \dot{p}_i = F_i = -\nabla U_i, \quad (1.19) \]

where \( p_i \) is the momentum of atom \( i \) and \( \dot{r}_i \) is its first derivative of the position vector, which is the velocity. Using the forces calculated from the potential, we calculate the momentum of the atoms and then their new positions in time.

### 1.4.3 Integration algorithm

It is very important that the integration algorithms conserve energy and momentum [20-24]. Furthermore, time-reversible integrators are preferable for theoretical analysis. Also, the algorithm should allow for a large time step without too much loss of accuracy. The error of an integration algorithm is a combination of the order \( p \) of the algorithm and the step size \( h \), the global error is then \( O(h^p) \). Since we are often interested in averages rather than individual trajectories, a large step size is often preferred over higher order algorithms. In this work we use the leapfrog integrator, which is a second order method, very simple to code, fast, time reversible, and energy conserving to a good approximation.

\[ r_i(t + \Delta t) = r_i(t) + v_i(t + \frac{1}{2} \Delta t) \Delta t, \quad (1.20) \]

\[ v_i(t + \frac{1}{2} \Delta t) = v_i(t - \frac{1}{2} \Delta t) + a_i(t) \Delta t, \quad (1.21) \]

where \( v_i \) and \( a_i \) are the velocity and acceleration vectors of atom \( i \). The velocity at time \( t \) is given by

\[ v_i(t) = \frac{1}{2} \left( v_i(t - \frac{1}{2} \Delta t) + v_i(t + \frac{1}{2} \Delta t) \right). \quad (1.22) \]
1.4.4 Nosé-Hoover thermostat

Newton’s equations of motion conserve energy and the resulting ensemble is microcanonical \((N, V, E)\) provided the volume and the number of atoms in the system are constant. We are often required to study systems in the canonical ensemble, where the temperature is fixed \((N, V, T)\). To maintain a desired temperature, the natural way is to keep the system in contact with a thermal reservoir with a large enough heat capacity not to be influenced by heat exchange with the system in contact. As simulating an external heat bath in addition to the system is not practical, we directly modify the equations of motion of the system by extending its Hamiltonian. This type of mechanism is called an extended system method. Many variants of thermostats have been developed over the years and in this work we have used the Nosé-Hoover thermostat \([20-24]\).

In this method we add an additional degree of freedom to the system which is associated with the heat bath with a mass \(Q > 0\), i.e., we consider the bath as an integral part of the system. The magnitude of \(Q\) can be viewed as the strength of the thermostat and it determines the coupling between the reservoir and the system and so influences the temperature fluctuations. Wrong values of \(Q\) result in a incorrect velocity distribution and too slow heat transport. Small values of \(Q\) imply loose coupling and may cause a poor temperature control with the simulations taking a very long time to reach the canonical distribution. Too high values of \(Q\) mean a tight coupling between heat bath and the system and may cause high-frequency temperature oscillations. As \(Q \to \infty\) the Nose-Hoover thermostat generates a microcanonical ensemble. The heat bath can also be viewed as a friction factor to control the particle velocities.

The modified equations of motion with a bath included are

\[
\begin{align*}
\dot{\mathbf{r}}_i &= \mathbf{p}_i/m_i, \\
\dot{\mathbf{p}}_i &= \mathbf{F}_i^\phi - \zeta \mathbf{p}_i, \\
\dot{\zeta} &= \frac{1}{Q} \left[ N \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - N_f k_B T \right].
\end{align*}
\]
where \( N_f \) is the total number of degrees of freedom. The additional degree of freedom, \( \zeta \), is Gaussian variable, with zero mean and a variance of \( \langle \zeta^2 \rangle = k_B T / M \). In this work we have thermostated only the wall atoms [25] and the reasons are explained in the results chapters 3 to 6.

1.4.5 Reduced units

As the characteristic scales of the molecular dynamics simulations are very small in conventional SI units, reduced units are often used as units for the physical variables [20-23]. These reduced units make it possible to avoid working in the vicinity of the numerical precision of the computer. The length scale \( \sigma \), energy scale \( \epsilon \), and the atomic mass \( m \) are taken as the basic units and are set to unity, \( \sigma = \epsilon = m = 1 \), and hence other quantities are scaled by appropriate factors.

The basic parameters for argon are given in Table 1.1 and a few derived quantities in reduced units are expressed in Table 1.2.

<table>
<thead>
<tr>
<th>Basic Units</th>
<th>Symbol</th>
<th>Argon parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>( \sigma )</td>
<td>( 3.405 \times 10^{-10} ) m</td>
</tr>
<tr>
<td>Energy</td>
<td>( \epsilon )</td>
<td>( 1.67 \times 10^{-21} ) J</td>
</tr>
<tr>
<td>Mass</td>
<td>( m )</td>
<td>( 6.626 \times 10^{-26} ) kg</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Variable</th>
<th>Reduced units</th>
<th>In SI units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>( \rho^* = \rho \sigma^3 )</td>
<td>1680 kg/m(^3)</td>
</tr>
<tr>
<td>Temperature</td>
<td>( T^* = k_B T / \epsilon )</td>
<td>121 K</td>
</tr>
<tr>
<td>Viscosity</td>
<td>( \eta^* = \eta \sigma t / m )</td>
<td>( 9.076 \times 10^{-4} ) pa.s</td>
</tr>
<tr>
<td>Pressure</td>
<td>( p^* = p \sigma^3 / \epsilon )</td>
<td>41.9 MPa</td>
</tr>
<tr>
<td>Time</td>
<td>( t^* = \sqrt{m \sigma^2 t / \epsilon} )</td>
<td>( 2.14 \times 10^{-12} ) s</td>
</tr>
<tr>
<td>Force</td>
<td>( f^* = f \sigma / \epsilon )</td>
<td>( 4.9 \times 10^{-16} ) N</td>
</tr>
</tbody>
</table>
1.4.6 Periodic boundary conditions

Any physical system consists of a number of atoms many orders of magnitude larger than what is feasible to simulate in molecular dynamics simulations due to the computational constraints. To remove the surface effects resulting from this unreliably small system size and to make the system virtually infinite in size, periodic boundary conditions (PBCs) are often implemented where necessary [20-23]. This way we can the study the bulk properties of a system by simulating only a small number of atoms.

Let the shaded box in Fig. 1.3 represent the system we are simulating, and the surrounding boxes are its exact replica. Using PBCs an atom in the original simulation box can interact with the atoms in the neighboring cell if they are within the cutoff distance. Here the cutoff distance should always be less than half the width of the cell to avoid duplicate interactions with other atoms. This criterion is called the minimum image convention. If an atom leaves the simulation box from one side it enters from the opposite side when updating the position. The total number of atoms in the box is conserved.

When we have confined systems such as fluid flow in slit/cylindrical pores the PBCs are not applied in the confining directions to account for the confinement and surface effects.

1.4.7 Density and streaming velocity profiles

In this work, as we have studied the behaviour of fluids confined in a nanochannel, here we provide the mathematical formula to compute the properties such as density and streaming velocity across the channel.

The microscopic density and the momentum density at a position $r$ enclosing a volume $v$ are given by

$$
\rho_v(r, t) = \frac{1}{v} \int_v \sum_{i \in v} m_i \delta(r - r_i(t)) dv ,
$$

(1.26)
Figure 1.3: Illustration of periodic boundary conditions. Image source [26].
where $v \to 0$, $\mathbf{u}(r, t)$ is the streaming velocity and $\delta(r)$ is the Dirac delta function. In a simulation, the channel is divided into bins of carefully chosen width across the channel. Too wide bins result in poor resolution while too narrow bins result in poor statistics.

Any quantity value $A(y_{bin})$ at a position $y_{bin}$ centered between $y_{bin} + \Delta/2$ and $y_{bin} - \Delta/2$ is defined as

$$A(y_{bin}, t) = \frac{1}{\Delta} \int dx \int dz \int_{y_{bin} - \Delta/2}^{y_{bin} + \Delta/2} dy A(y, t) \delta(y - y_i(t)) .$$  \hspace{1cm} (1.28)
Chapter 2

The fluid-solid interfacial friction coefficient and slip length

In this chapter, we present the method developed to calculate the interfacial friction at a fluid-solid planar interface and derive an explicit expression for the slip length for a planar Poiseuille and planar Couette flow. We then extend the method to a cylindrical geometry. We also review other methods in the literature on predicting the interfacial friction coefficient at a fluid-solid interface.
Over the last two centuries, many scientists including for example Bernoulli, Coulomb, Navier, Couette, Poisson, Stokes, Poiseuille, Hagen, Helmholtz and Maxwell have worked on formulating appropriate hydrodynamic boundary conditions at a fluid-solid interface [4]. Despite this, the hydrodynamic interfacial friction between a fluid and solid is not understood as much as the friction between two solid surfaces in contact with each other. Navier formulated the slip boundary condition using the fluid-solid interfacial friction coefficient [27]. Slip has more recently been studied extensively over the years using experiments and NEMD simulations. However, it still remains to develop a satisfactory method to evaluate the intrinsic fluid-solid interfacial friction. A few attempts have been made to quantify this friction coefficient using EMD simulations, each having its own limitations [28-34].

Here, we present a new method to calculate this friction coefficient based on a statistical mechanics approach. First, we derive the expression for the friction coefficient and slip length at a planar boundary and then extend the method to a cylindrical boundary. The planar boundary method was originally derived by Hansen \textit{et al.} [35].

### 2.1 The Navier boundary condition

Consider a fluid confined in the $y$ direction and flowing in the $x$ direction. Let $u_s$ be the slip velocity which is the relative velocity in the tangential direction at the fluid-solid interface. In the steady state, the fluid shear stress $\sigma_{xy}$ must be continuous across the channel. Navier [27] proposed the slip boundary condition by relating this shear stress to the fluid slip velocity at the wall via the fluid-solid interfacial friction coefficient $\xi_0$,

$$\sigma_{xy} = \xi_0 u_s , \quad (2.1)$$

Using the above relation with Newton’s law of viscosity, which relates the shear stress to the strain rate $\dot{\gamma}$ (at the wall, $y_w$) via the fluid shear viscosity $\eta_0$,

$$\sigma_{xy} = \eta_0 \dot{\gamma} , \quad (2.2)$$
Navier derived

\[ u_s = \frac{\eta_0}{\xi_0} \dot{\gamma} . \]  

(2.3)

Here \( \frac{\eta_0}{\xi_0} \) has the unit of length and is identified as the slip length \( L_s \). Therefore the Navier slip length is defined as

\[ L_s = \frac{\eta_0}{\xi_0} . \]  

(2.4)

We refer to the above expression as the EMD slip length as we use EMD simulations to predict the interfacial friction for a given fluid-solid interface. The conventional slip length is defined as,

\[ L_s = u_s \left[ \frac{\partial u}{\partial y} \right]_{y=w}^{-1} . \]  

(2.5)

We refer to the above expression as the NEMD slip length as it is calculated using NEMD simulations streaming velocity profiles.

### 2.2 Literature review

#### 2.2.1 Bocquet and Barrat model

Bocquet and Barrat presented the first derivation to quantify the interfacial friction coefficient at a fluid-solid interface [30, 31]. Their method uses a Green-Kubo type integral of the autocorrelation function of the shear stress (force) on the solid due to the fluid

\[ \xi_0 = \frac{1}{A k_B T} \int_0^\infty dt \langle F_x(t)F_x(0) \rangle , \]  

(2.6)

where \( A \) is the surface area of the solid and \( F_x(t) \) is the total shear force on the solid from the fluid in the streaming direction. For a given fluid-solid interface, the shear force can then be computed directly using EMD simulations. Bocquet and Barrat
noted that the above integral becomes zero as $t \to \infty$ if the volume of liquid is not infinite. They attribute this to constraints such as thermodynamic and long time limits in molecular dynamics simulations [31]. They compute the time integral after it had reached some roughly constant value in time $t'$,

$$\xi_0 = \frac{1}{S k_B T} \int_0^{t'} dt \langle F_x(t')F_x(0) \rangle .$$

(2.7)

The slip length is then calculated from Navier’s slip definition, Eq. (2.4).

### 2.2.2 Sokhan and Quirke model

Sokhan and Quirke approached the problem in a different way [32, 33]. They consider the confined fluid as a single Brownian particle described using the Langevin equation. The collective velocity of the fluid blob is given by,

$$u_x(t) = \frac{1}{N} \sum_i v_{xi}(t).$$

(2.8)

From the fluctuation-dissipation theorem, they define the velocity autocorrelation function of the fluid blob,

$$C_{xx}(t) = \langle u_x(t)u_x(0) \rangle = \frac{1}{N^2} \sum_{i,j} \langle v_{xi}(t)v_{xj}(0) \rangle .$$

(2.9)

The above autocorrelation function is shown to decay exponentially with a relaxation time $\tau$ [33],

$$C_{xx}(t) = m^{-1}k_B T\exp(-t/\tau) ,$$

(2.10)

where $m$ is the total mass of the fluid. By connecting the shear stress on the wall due to the fluid as a result of an external driving force acting on the fluid with the Stokesian drag force per unit area exerted on the wall by the moving fluid, they
derive the following expression for the slip length [32, 33],

\[ L_s = \frac{\tau \eta_0}{\rho h} - \frac{h}{3}. \] (2.11)

Using EMD simulations they compute the velocity auto-correlation function (ACF) of the fluid blob and then fit it to Eq. (2.10) to find the relaxation time \( \tau \). The slip length is then calculated using the above Eq. (2.11).

### 2.2.3 Petravic and Harrowell model

Petravic and Harrowell developed a boundary fluctuation theory for transport coefficients of confined fluids [28, 29]. They claimed that the friction coefficient computed using the Bocquet and Barrat model is actually not the intrinsic interfacial fluid-solid friction coefficient, but the total effective friction, which is the sum of slip friction at both walls and the viscous friction within the fluid. They consider a case of fluid confined between two different walls \( w_1 \) and \( w_2 \) to show this. In mechanical equilibrium, the shear stress must be uniform and equal across the system. Hence, the integral of the surface force autocorrelation function, Eq. (2.6), is the same for both walls, which says the slip is also same at both the walls. As we know, the slip and friction are intrinsic properties of the fluid-solid combination, so they should be different for difference walls. Thus the integral evaluated using Eq. (2.6) does not reflect the fluid-solid intrinsic friction of the wall on which the stress autocorrelation integral is computed.

Further, Petravic and Harrowell gave a mathematical proof of their argument by considering a planar shear flow of a fluid confined between two walls. If the walls are moving in opposite shear directions with a relative velocity \( \Delta u \), this velocity is equal to the sum of slip velocities at both walls \( \Delta u_1 \) and \( \Delta u_2 \) and the velocity difference of the fluid across the channel \( \Delta u_L \), i.e.,

\[ \Delta u = \Delta u_1 + \Delta u_L + \Delta u_2. \] (2.12)

As mentioned before, in mechanical equilibrium, the shear stress is constant across
2 The fluid-solid interfacial friction coefficient and slip length

the whole system. At the walls (1 and 2), and in the fluid the shear stress takes the form

\[ P_{yx} = -\xi_1 \Delta u_1 \quad \text{and} \quad P_{yx} = -\xi_2 \Delta u_2 \quad \text{and} \quad P_{yx} = -\eta_0 \Delta u_L / L_y \, . \]  

(2.13)

The total effective friction in the system is also related to the shear stress via,

\[ P_{yx} = -\xi_0 \Delta u \, . \]  

(2.14)

Substituting the above constitutive shear stress equations into Eq. (2.12), we get

\[ \frac{1}{\xi_0} = \frac{1}{\xi_1} + \frac{1}{\xi_2} + \frac{L_y}{\eta_0} \, . \]  

(2.15)

The above equation is analogous to the effective resistance of resistors in parallel. Petravic and Harrowell examined the constitutive equation used by Bocquet and Barrat to derive the friction coefficient, and they claimed that the constitutive equation gives the effective friction coefficient rather than the fluid-solid intrinsic interfacial friction coefficient. Hence, by dividing the fluid shear viscosity with the effective friction coefficient, one will obtain the sum of the slip lengths at both the walls and the channel width, rather than the slip length at the wall of which the shear stress autocorrelation integral is computed [28],

\[ L_{s1} + L_{s2} + L_y = \frac{\eta_0}{\xi_0} \, . \]  

(2.16)

The above mentioned methods have uncertainty due to contradictory claims (system size dependent effective friction rather than intrinsic friction). We still need to have a direct method to compute the fluid-solid intrinsic interfacial friction coefficient, to determine the hydrodynamic boundary condition and precisely quantify the flow rates of fluids in nanopores. In this work, based on a Statistical Mechanics approach, we utilised and developed new methods to compute this friction coefficient at planar and cylindrical interfaces. The method is based upon forming equilibrium time correlation functions of relevant measurable fluid properties, based upon rel-
The fluid-solid interfacial friction coefficient and slip length

Evant constitutive equations for solid-fluid friction and fluid viscous forces. These correlation functions are formed for fine-grained slabs of fluid adjacent to the walls. By computing the various correlation functions we are able to extract the slab friction coefficient adjacent to the wall for a limiting slab width, and hence the slip velocity for the fluid, to very high accuracy. We derive explicit expressions for the slip length using the integral boundary condition and verify that this slip length approaches the Navier slip length in the limit of zero slab width.

2.3 Planar interface

2.3.1 The fluid-solid interfacial friction coefficient

As mentioned before this planar boundary method was derived by Hansen et al. [35]. Assume that a fluid is confined between two parallel walls in y direction, with positions \( y_w = 0 \) (wall 1) and \( y_w = L_y \) (wall 2), respectively. We consider a fluid element with constant mass \( m \), and average volume \( V = L_x \Delta L_z \), that is, a fluid slab adjacent to wall 1 and of average width roughly one molecular diameter \( \Delta \), see Fig. 2.1. In the case of slip flow this fluid layer slips over the solid surface, hence a method is proposed to calculate the interfacial friction between this fluid layer and the adjacent solid surface. The planar interface method is taken as it is from Ref. [35] by Hansen et al.

The fluid slab may be subjected to an external constant force per unit mass \( F_e \) in the \( x \) direction. The acceleration of the slab in this direction is governed by Newton’s second law, i.e.,

\[
m \frac{du_{slab}}{dt} = F'_x(t) + F''_x(t) + m F_e ,
\]

where \( u_{slab} \) is the center of mass velocity of the slab, say, adjacent to wall 1, in the \( x \) direction, \( F'_x \) is the force due to wall-slab interactions and \( F''_x \) is the force due to fluid-slab interactions. Note that \( F''_x \) includes a kinetic contribution due to the momentum of fluid particles entering and leaving the slab. Furthermore, it should
The fluid-solid interfacial friction coefficient and slip length

Figure 2.1: Schematic illustration of the system. The arrows inside the box indicate the velocity field forming the profile. $L_s$ is the slip length and $\Delta$ is the slab width, typically, one molecular diameter. This image is taken from Hansen et al. [35]
be mentioned that the fluid-fluid forces between particles inside the slab cancel out due to Newton’s third law and do not contribute to the slab acceleration.

The wall-slab force term, $F'_x$, can be viewed as a frictional shear force that depends on the relative velocity between the wall and the fluid. For sufficiently small relative velocities we may propose the following linear constitutive equation relating the wall-slab shear force to the velocity difference, $\Delta u' = u_{slab} - u_w$,

$$F'_x(t) = -\int_0^t \zeta(t - \tau) \Delta u'(\tau) \, d\tau + F'_r(t) ,$$

(2.18)

where $\zeta$ is a friction kernel. $F'_r$ is a random force term with zero mean that is assumed to be uncorrelated with $u_{slab}$, that is,

$$\langle F'_r(t) \rangle = 0 \text{ and } \langle u_{slab}(0) F'_r(t) \rangle = 0 .$$

(2.19)

For steady flows the time average of Eq. (2.18) is given by

$$\langle F'_x \rangle = -\zeta_0 \langle \Delta u' \rangle ,$$

(2.20)

where $\zeta_0$ is the zero frequency friction coefficient. It is worth noting that Eq. (2.18) is a local relation, i.e. the kernel $\zeta$ only depends on the force between the slab and the wall.

In order to account for the fluid-slab shear force, $F''_x$, one can apply Newton’s law of viscosity. Thus, for steady flows we have

$$\langle F''_x \rangle = A \eta_0 \langle \dot{\gamma} \rangle = A \eta_0 \frac{\partial u}{\partial y} \bigg|_{y=\Delta} ,$$

(2.21)

where $A = L_x L_z$ is the surface area. For $u_w = 0$, Eq. (2.18) is written as

$$F'_x(t) = -\int_0^t \zeta(t - \tau) u_{slab}(\tau) \, d\tau + F'_r(t) .$$

(2.22)

Multiplying both sides with $u_{slab}(0)$ and taking the ensemble average it is possible to form the corresponding relation between the slab velocity-force correlation function
$C_{uF'_x}$ and the slab velocity autocorrelation function $C_{uu}$,

\[ C_{uF'_x}(t) = - \int_0^t \zeta(t-\tau)C_{uu}(\tau) \, d\tau , \tag{2.23} \]

such that

\[ C_{uF'_x}(t) = \langle u_{\text{slab}}(0)F'_x(t) \rangle \quad \text{and} \quad C_{uu}(t) = \langle u_{\text{slab}}(0)u_{\text{slab}}(t) \rangle . \tag{2.24} \]

In Eq. (2.24) we have used the properties of $F'_r$ as given in Eq. (2.19). We can transform Eq. (2.23) into a more convenient algebraic form by a Laplace transform yielding

\[ \tilde{C}_{uF'_x}(s) = -\tilde{\zeta}(s) \tilde{C}_{uu}(s) , \tag{2.25} \]

where the Laplace transformation is defined as

\[ \mathcal{L}[f(t)] = \int_0^\infty f(t) e^{-st} \, dt = \tilde{f}(s) . \tag{2.26} \]

We will assume that the friction kernel can be written as an $n$-term Maxwellian memory function

\[ \zeta(t) = \sum_{i=1}^n B_i e^{-\lambda_i t} , \tag{2.27} \]

which means that

\[ \tilde{\zeta}(s) = \sum_{i=1}^n \frac{B_i}{s + \lambda_i} . \tag{2.28} \]

Substituting this into Eq. (2.25) we trivially get

\[ \tilde{C}_{uF'_x}(s) = -\sum_{i=1}^n \frac{B_i \tilde{C}_{uu}(s)}{s + \lambda_i} . \tag{2.29} \]

We here focus on steady flows, as we are primarily interested in $\zeta_0$. From Eq. (2.27)
we have,

\[ \zeta_0 = \int_0^\infty \sum_{i=1}^n B e^{-\lambda_i t} \, dt = \sum_{i=1}^n B_i / \lambda_i , \]  

(2.30)

It is found that a one-term \( n=1 \) Maxwellian memory function is sufficient for the above fitting. The Navier interfacial friction coefficient is

\[ \xi_0 = \zeta_0 / A. \]  

(2.31)

It is important to point out that the friction can be evaluated directly from Eq. (2.25), that is, without suggesting a functional form of the kernel. However, we find that this gives rather large statistical errors, especially for large \( s \). Using EMD simulations it is possible to evaluate \( C_{uF'_y} \) and \( C_{uu} \) and therefore also the Laplace transforms. From this, one can fit the right hand side of Eq. (2.29) to the \( \tilde{C}_{uF'_y} \) data using \( B_i \) and \( \lambda_i \) as fitting parameters.

### 2.3.2 The fluid-solid slip length

For steady flows, using integral boundary conditions (IBCs), it is possible to solve the Navier-Stokes equation in terms of the slab center of mass velocity, \( u_{\text{slab}} \). In this way we also obtain an equation for the strain rate at \( y = \Delta \). From Eq. (2.17) we can then express \( u_{\text{slab}} \) as a function of the friction coefficient \( \zeta_0 \) using Eqs. (2.20) and (2.21). This finally leads to an explicit equation for the slip length [35] using Eq. (2.5).

In general, the IBCs read,

\[ \overline{u}_{(1)} = \frac{1}{\Delta} \int_0^\Delta u(y) \, dy \quad \text{and} \quad \overline{u}_{(2)} = \frac{1}{\Delta} \int_{L_y-\Delta}^{L_y} u(y) \, dy , \]  

(2.32)

thus, it is the same as the center of mass velocity of a slab under the assumption
2 The fluid-solid interfacial friction coefficient and slip length

that the fluid density is constant. For example, for the lower boundary we have,

$$u_{cm} = \frac{1}{m} \int_V \rho u(y) dV = \frac{L_x L_z \rho}{m} \int_0^\Delta u(y) dy = \frac{1}{\Delta} \int_0^\Delta u(y) dy,$$

(2.33)

where we recall that $V = L_x \Delta L_z$ and $\rho = m/V$. Thus, if wall 1 is at rest the average center of mass velocity of the slab, $\langle u_{slab} \rangle$, can be approximated with $\pi^{(1)}$.

The definitions of slip length and slip velocity for planar Couette flow and planar Poiseuille flow are illustrated in Fig. 1.2.

Planar Couette flow

For Couette flow with identical walls and where wall 2 has velocity $u_w$ the Navier-Stokes equation reduces to a simple Laplace equation [35]

$$\frac{\partial^2 u}{\partial y^2} = 0.$$

(2.34)

The IBCs are

$$\bar{\pi}^{(1)} = \langle u_{slab} \rangle = \frac{1}{\Delta} \int_0^\Delta u(y) dy \quad \text{and} \quad \bar{\pi}^{(2)} = u_w - \langle u_{slab} \rangle = \frac{1}{\Delta} \int_{Ly-\Delta}^{Ly} u(y) dy$$

(2.35)

yield the solution

$$u_x(y) = \frac{u_w - 2\langle u_{slab} \rangle}{Ly - \Delta} \left( y - \frac{\Delta}{2} \right) + \langle u_{slab} \rangle.$$

(2.36)

The strain rate at $y = \Delta$ is then,

$$\dot{\gamma} = \frac{u_w - 2\langle u_{slab} \rangle}{Ly - \Delta}.$$

(2.37)

For Couette flow, Eq. (2.17) reads $\langle F'_x \rangle + \langle F''_x \rangle = 0$, that is, from Eqs. (2.20), (2.21) and (2.37),

$$-\zeta_0 \langle u_{slab} \rangle + A\eta_0 \frac{u_w - 2\langle u_{slab} \rangle}{Ly - \Delta} = 0,$$

(2.38)
which is rearranged to give an expression for the average slab center of mass velocity at wall 1, namely,

\[ \langle u_{\text{slab}} \rangle = \frac{\eta_0 u_w}{\xi_0 (L_y - \Delta) + 2\eta_0}, \tag{2.39} \]

where \( \xi_0 = \zeta_0 / A \). The slip length now follows from Eqs. (2.5), (2.36) and (2.39), thus, for wall 1 we have

\[ L_s = -u(0) \frac{\partial u}{\partial y} \bigg|_{y=0}^{-1} = \frac{\Delta}{2} \frac{\eta_0}{\xi_0}. \tag{2.40} \]

Note that \( L_s < 0 \) due to the geometry we considered. In the limit of zero slab width, \( \Delta \to 0 \), we obtain

\[ |L_s| = \frac{\eta_0}{\xi_0} \tag{2.41} \]

in accordance with the Navier slip length, Eq. (2.4).

**Planar Poiseuille flow**

If an external force per unit mass, \( F_e \), is applied to the fluid and both walls are at rest the Navier-Stokes equation is reduced to the Stokes (or Poisson) equation \([35]\),

\[ \frac{\partial^2 u}{\partial y^2} = -\frac{\rho F_e}{\eta_0}. \tag{2.42} \]

Subjected to the IBCs

\[ \langle u_{\text{slab}} \rangle^{(1)} = \frac{1}{\Delta} \int_0^\Delta u(y) \, dy \quad \text{and} \quad \langle u_{\text{slab}} \rangle^{(2)} = \frac{1}{\Delta} \int_{L_y - \Delta}^{L_y} u(y) \, dy. \tag{2.43} \]

the solution to this boundary value problem is,

\[ u_x(y) = \frac{\rho F_e}{12\eta_0} \left[ 6y(L_y - y) + \Delta(2\Delta - 3L_y) \right] + \langle u_{\text{slab}} \rangle, \tag{2.44} \]
which resembles a planar Hagen-Poiseuille flow. For this steady flow Newton’s second law is \( \langle F'_x \rangle + \langle F''_x \rangle + mF_e = 0 \). By assuming constant density and applying the constitutive equations Eqs. (2.20) and (2.21) we obtain,

\[
-\zeta_0 \langle u_{slab} \rangle + \frac{A\rho L_y}{2} (L_y - 2\Delta) + mF_e = 0 ,
\]

(2.45)
giving

\[
\langle u_{slab} \rangle = \frac{\rho F_e L_y}{2\zeta_0} .
\]

(2.46)

Note that since \( \langle u_{slab} \rangle \) increases with increasing slab width, it can be seen from Eq. (2.46) that \( \zeta_0 \) must be a decreasing function of \( \Delta \), that is, if the density is constant. The slip length follows as,

\[
L_s = \Delta \left( \frac{1}{2} - \frac{\Delta}{3L_y} \right) - \frac{\eta_0}{\zeta_0} ,
\]

(2.47)

which means that \( |L_s| = \eta_0/\zeta_0 \) as \( \Delta \to 0 \) as expected.

It is important to note here that the slip length given in Eq. (2.47) is different from Eq. (2.40) with the term \( -\Delta^2/3L_y \), that is, the slip length depends on the flow type for nonzero slab width. The effect from the term cannot be measured using NEMD simulations within statistical errors. In chapters 3 and 4 we have shown that the slip length from Poseuille and Couette flow simulations is equal within statistical errors.

### 2.4 Cylindrical interface

Here, we extend the above planar boundary interfacial friction method to a cylindrical geometry. We again derive an explicit expression for the slip length of a fluid flowing in a cylindrical tube using the slab CM velocity integral boundary condition and verify that this slip length is equal to the Navier slip length in the limit as the slab width goes to zero, \( \Delta \to 0 \), [36].
Figure 2.2: Schematic illustration of the cylindrical system.

2.4.1 The fluid-solid interfacial friction coefficient

Assume that a fluid is confined in a cylindrical tube of radius $R$ and length $L$. Let $z$ be the fluid streaming direction (axial direction). We consider a cylindrical fluid annulus (or slab) with a constant mass $m$, and average width of one molecular diameter $\Delta$ close to the solid surface, see Fig. 2.2. Even though the above friction method was developed for planar interfaces, the determination of the friction coefficient is found to be similar for cylindrical interfaces. The only difference is that we consider a cylindrical fluid annulus, whereas for a planar boundary we consider a planar fluid slab near the solid boundary [36].
2.4.2 The fluid-solid slip length

Again, we derive an explicit expression for the slip length using the slab centre of mass (CM) velocity integral boundary condition and verify that our slip length is equal to the Navier slip length in the limit as the slab width $\Delta \to 0$ goes to zero.

The Navier-Stokes equation for fluid flow in a cylindrical tube when acted upon by an external force per unit mass, $F_e$, is [1, 2]

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u_z(r)}{\partial r} \right) = -\frac{\rho F_e}{\eta_0} , \quad (2.48)$$

with general solution

$$u_z(r) = -\left( \frac{\rho F_e}{4\eta_0} \right) r^2 + C_1 \ln(r) + C_2 . \quad (2.49)$$

Since $u_z$ is finite at $r = 0$, $C_1$ must always be zero. The general IBC is expressed as [35]

$$\langle u_{\text{slab}} \rangle = \frac{1}{\Delta} \int_{R-\Delta}^{R} u(r) \, dr . \quad (2.50)$$

Applying this IBC, the solution to the above boundary value problem is

$$u_z(r) = \left( \frac{\rho F_e}{12\eta_0} \right) (3R^2 - 3r^2 + \Delta^2 - 3R\Delta) + u_{\text{slab}} . \quad (2.51)$$

One can obtain the classical solution of a no-slip Hagen-Poiseuille flow in a cylindrical tube by setting $u_{\text{slab}} = 0$ i.e, the slip velocity to be zero.

Let $F'_z$ be the shearing frictional force on the fluid slab due to the wall and $F''_z$ is the shearing force between fluid slab and the rest of the fluid adjacent to it, then in the steady state we have (as for the planar geometry)

$$\langle F'_z \rangle + \langle F''_z \rangle + mF_e = 0 . \quad (2.52)$$

The wall-slab shear force is proportional to the relative velocity between the wall
and slab for sufficiently small velocities (i.e. \( u_{\text{slab}} \)). We write this as
\[
\langle F'_z \rangle = -\zeta_0 \langle u_{\text{slab}} \rangle ,
\] (2.53)
where \( \zeta_0 \) is the zero-frequency friction term and the slab-fluid shearing force is given by Newton’s law of viscosity
\[
\langle F''_z \rangle = A\eta_0 \langle \dot{\gamma} \rangle = A\eta_0 \frac{\partial u}{\partial r} \bigg|_{r=R-\Delta} ,
\] (2.54)
where \( A = 2\pi(R - \Delta)L_z \) is the surface area of the contact, and the strain rate at \((R - \Delta)\) is
\[
\dot{\gamma} = \frac{\partial u_z(r)}{\partial r} \bigg|_{r=R-\Delta} = -\frac{\rho F_e}{2\eta_0} (R - \Delta) .
\] (2.55)
By substituting the constitutive Eqs. (2.53) and (2.54) in Eq. (2.52) we can solve for \( u_{\text{slab}} \),
\[
-\zeta_0 u_{\text{slab}} - A\eta_0 \dot{\gamma} + mF_e = 0
\] (2.56)
giving
\[
u_{\text{slab}} = \frac{\rho F_e}{2\xi_0} R .
\] (2.57)
\[
u_s = u(R) = L_s \left| \left( \frac{\partial u(r)}{\partial r} \right)_{r=R} \right|
\] (2.58)
Finally, by using the slip length definition for this geometry,
\[
L_s = -u_s \left/ \left| \left( \frac{\partial u(r)}{\partial r} \right)_{r=R} \right| \right.
\] (2.59)
we can derive
\[
L_s = \frac{\eta_0}{\xi_0} + \Delta \left[ \frac{\Delta}{6R} - \frac{1}{2} \right]
\] (2.60)
which means that $|L_s| = \eta_0/\xi_0$ as $\Delta \to 0$ in agreement with the Navier slip length definition. The $\Delta$ term can be neglected for sufficiently wide pores, but when it is comparable to the pore diameter its effect becomes important. For high slip systems, such as those studied in this thesis, the effect of the $\Delta$ terms can be neglected even for small diameter CNTs. Here we note that for $R \approx \Delta$ non-local effects can become important and the friction coefficient includes viscous contributions as well. [11, 12, 29]

Also, note that as for the planar wall $u_{slab}$ is equal to the CM velocity of the slab $u_{cm}$ under the assumption that the fluid density of the slab is constant.

$$u_{cm} = \frac{1}{m} \int_V \rho u(r) \, dV = \frac{\pi L(2R-\Delta)\rho}{m} \int_{R-\Delta}^R u(r) \, dr = \frac{1}{\Delta} \int_{R-\Delta}^R u(r) \, dr , \quad (2.61)$$

where the volume of the slab is, $V = \pi L\Delta(2R-\Delta)$. 
Chapter 3

Slip flow in graphene nanochannels

In this chapter, we apply the planar interface method to argon and methane flow in planar graphene nanoslit pores. We compare our friction method predictions with direct NEMD simulations. We study the shear rate dependent behaviour of slip due to an externally applied field and shear.
We investigate the hydrodynamic boundary condition for simple nanofluidic systems such as argon and methane flowing in graphene nanochannels using EMD simulations in conjunction with the planar boundary interfacial friction method. We first calculate the fluid-graphene interfacial friction coefficient, from which we can predict the slip length and the average velocity of the first fluid layer close to the wall (referred to as the slip velocity). Using direct NEMD simulations we then calculate the slip length and slip velocity from the streaming velocity profiles in Poiseuille and Couette flows. The slip lengths and slip velocities from the NEMD simulations are found to be in excellent agreement with our EMD predictions. Our EMD method therefore enables one to directly calculate this intrinsic friction coefficient between fluid and solid and the slip length for a given fluid and solid, which is otherwise tedious to calculate using direct NEMD simulations at low pressure gradients or shear rates. The advantages of the EMD method over the NEMD method to calculate the slip lengths/flow rates for nanofluidic systems are discussed, and we finally examine the dynamic behaviour of slip due to an externally applied field and shear rate.

The assumption of a no-slip boundary condition has no theoretical foundation, and although slippage may be present at macroscopic scale, it usually has negligible effect on the flow characteristics. At the nanoscale, however, we deal with nanolitre volumes of fluids in applications such as drug delivery and nanofiltration, etc. Under these small flows slip can have a significant effect on the flow rate, so precise quantification and control of the fluid is required and hence the effect of slip becomes very important. When the slip length is comparable to the channel size, the permeability of the channel increases by a significant amount, which can have many potential advantages. The slip length is used to determine flow enhancement, defined as the ratio of the observed flow rate (in simulation or experiment) to that predicted from classical hydrodynamics with the no slip boundary condition. For example, a slip length of about 60 nm (water on graphene) in a 10 micrometer channel has no measurable effect on the flux, but in a 10 nm channel, the flux is enhanced by 37 times. The Navier slip length is assumed to be constant, i.e., independent of the applied field or shear rate, however we note that it has been shown to increase rapidly at high shear rates [37, 38].
For a considerable time slip has been a controversial subject [4, 39], but now it is well established that a liquid can slip on a solid surface in contact with it, i.e., the no-slip boundary condition is indeed violated. However, the data for the slip length is scattered both in experiments and simulations and the precise quantification of the slip length is a subject of great interest. The boundary condition is a property of the combined fluid-solid system and many other factors. Slip has been studied extensively using simulations, theory and experiments, but still the fundamental mechanism underlying slip is not clear and there are many open questions as it depends on various parameters in a very complex way. Refer to the reviews on slip and the references therein [4, 39-41]. In simulations, slip can be quantified in two different ways. The widely used method is direct NEMD simulations. For example in a Poiseuille flow, the tangent to the fluid velocity at the wall is extrapolated from the wall to the position where it is equal to zero. In Couette flow, the simple linear velocity profile is extrapolated to match that of the wall velocity. Both of these NEMD methods use Eq. (2.5) to calculate the slip length. Due to the few nanoseconds of limited simulation times, NEMD simulations are generally done at high shear rates in Couette flow (or equivalently, field strengths in the case of Poiseuille flow) to generate reliable velocity profiles, i.e., to have satisfactory signal to noise ratio within the available computational time. This is possible only if the mean streaming velocities are at least comparable with the thermal velocity of the fluid due to the temperature. The NEMD shear rates are therefore orders of magnitude higher than the shear rates we use in experimental studies and applications [4]. As mentioned above, slip is found to be constant at low shear rates, but increases rapidly and diverges at high shear rates. One should therefore be careful when interpreting the NEMD slip lengths, which are computed at a particular shear rate. Hence, to find out the limiting or minimum slip length for a given fluid-solid interface, one must perform NEMD simulations at various shear rates and extrapolate the results to experimental shear rates, which may also result in large statistical errors in the case of high slip systems. This is a cumbersome process and clearly necessitates an alternative method to quantify the slip, which should be tested for a variety of fluid and solid materials.
Another less commonly used method is EMD, where one calculates the friction coefficient between solid and fluid, and then uses the simple ratio of viscosity to the friction coefficient to give the slip length using Eq. (2.4). This method overcomes the limitations of NEMD methods and different methods have been applied to quantify the friction from EMD simulations [28, 30, 32, 35].

Slip depends on various parameters, such as the nature of the wall and fluid, interaction strength between them, structure and pattern of the wall, density of fluid and surface density of wall, wetting properties, contact angle of the fluid on the surface, temperature, viscosity of the fluid, etc. Reviews on slip dependence on various parameters can be found in Refs. [4, 39-41]. Decoupling these factors from one another is not a feasible way to study their individual effects. Moreover, counter to intuition some of these studies found increasing slip with increasing surface roughness, decreasing slip with increasing contact angle on hydrophobic surfaces, and constant slip length at high shear rates, etc., making slip a very complex phenomenon requiring greater study.

We now briefly discuss the special properties of graphene surfaces which affect slip. In general, as the interaction strength between fluid and wall is decreased, slip increases [37]. Slip also increases with increasing fluid contact angle on the wall surface (non-wetting) [4], and as surface density (incommensurate) of the wall increases, slip also increases [37]. Atomically smooth walls are also shown to produce larger slip due to the small corrugations of the wall potential along the channel [42]. Graphene possesses all these characteristics. (i) The interaction strength between fluid atoms is stronger than that between fluid and carbon atoms, which makes the fluid recede from the wall and induces a high contact angle. (ii) The surface density of graphene in reduced units is 5.54, which is much higher than the fluid density and usual molecular walls (0.8 - 1.2) studied in simulations. (iii) The very strong covalent bonds between the carbon atoms in the graphene layer makes it very smooth. Therefore fluids in graphene nanochannels are expected to show high slip. Currently there is a lot of interest in the research community and industry to devise nanoengineered channels for various fluids to exhibit large and controlled slip [43].
Due to the high surface density of carbon walls and the complexity of carbon potential models, most of the simulations of fluid flows in carbon nanochannels have used rigid walls (carbon atoms are fixed to their lattice sites) to decrease the simulation times, and to maintain a desired temperature the fluid is thermostated. Sokhan et al. [44] performed NEMD simulations of methane in flexible graphene nanochannels and found a 20 percent increase in the flux compared to using rigid walls. In a very recent study, Bernardi et al. [25] found that fixing the wall atoms and thermostating the fluid can induce severe artifacts for nanoflows. Furthermore, Martini et al. [45] found that the transport of momentum between fluid and wall is very important in determining the nanofluidic properties, thus rigid and non-rigid walls are expected to result in different fluidic behaviour.

3.1 Simulation details

The molecular dynamics simulations are carried out using standard techniques described in chapter 1. The reliability of any simulation depends among other things on the accuracy of the potentials applied. As mentioned before, in nanofluidic systems the wall-fluid interactions become as important as the fluid-fluid interactions, whereas at the macroscale the wall has no effect on the hydrodynamic properties of the fluid, other than just confining the fluid and providing the boundary condition for the velocity. Here we model graphene using the second generation reactive empirical bond order Tersoff-Brenner potential (REBO), which is widely used for graphene/CNT structures [46]. It is parameterised using quantum mechanical calculations and it describes the mechanical properties, elastic properties and dynamics of covalently bonded carbon atoms accurately [18]. The atomic structure of carbon layers is taken into account explicitly. The bond strength between two carbon atoms also depends on the neighbouring atoms and the bond environment and can be written as
\[ E_b = \sum_i \sum_{j(>i)} \left[ V^R(r_{ij}) - b_{ij} V^A(r_{ij}) \right], \]  

(3.1)

where \( r_{ij} \) is the distance between particles \( i \) and \( j \). The terms \( V^R(r_{ij}) \) and \( V^A(r_{ij}) \) are pair additive interactions that represent interatomic repulsions and attraction, respectively. The term \( b_{ij} \) is called the bond order term and it incorporates the bond environment, coordination number, bond angle and dihedral angle with its covalently bonded neighbouring carbon atoms.

The interactions between the fluid-fluid and fluid-wall atoms are modelled using the standard Lennard-Jones potential

\[ \phi = \sum_i \sum_{j(>i)} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right], \]  

(3.2)

where \( \epsilon \) and \( \sigma \) are the interaction strength and the length scale, respectively. The interaction cutoff is set to 1 nm. To maintain the stability of the system we have used two layers of graphene at each wall. The separation of the two layers is kept at 0.34 nm using the Lennard-Jones potential acting between carbon atoms belonging to different layers, and the centre of mass of each graphene layer is then kept fixed to avoid drift.

The simulated state points and the interaction parameters are listed in Table 3.1. The fluid-carbon interaction parameters are derived using the Lorentz-Berthelot rule. A Nosé-Hoover thermostat [47, 48] is applied to the wall atoms to maintain a desired temperature, so the viscous heating generated by the flow is transmitted to the walls as is done in a real experimental system. The equations of motion for all particles were integrated forward in time using a leap-frog integration scheme with time step \( \Delta t = 1 \) fs. The very strong covalently bonded interactions between carbon atoms demand a relatively small time step for the integration scheme. The system’s dimensions along the \( x \) and \( z \) directions are \( L_x = 3.44 \) nm and \( L_z = 3.4 \) nm.
and the distance between the two innermost graphene layers along the confinement direction is \( L_y = 5.1 \) nm so the full system size in the \( y \) direction is 5.78 nm. Periodic boundary conditions are imposed along the \( x \) and \( z \) directions. All simulation results are averaged over 20 independent simulations which run from 10 to 30 million time steps depending on the shear rate and external field. For fluids in very smooth channels such as graphene, simulations require a long time [44].

### 3.2 Results and discussion

First we begin with the EMD simulations, where the confined fluid is at equilibrium. The friction between solids can be viewed as the shearing force between two surfaces in contact with each other. Similarly the hydrodynamic friction can also be viewed as the shearing force between the solid surface and the first fluid layer in contact with the solid surface. Niavarani et al. [42] quantified the slip length using the structure and density of the first fluid layer close to the wall. Hansen et al. [35] found that for slab widths 0.75 to 1.25 molecular diameters the friction coefficient is constant and the results are in agreement with NEMD data. In this thesis we choose a fluid slab of average slab width about one molecular diameter and constant mass adjacent to the wall [35]. After equilibration, the total wall-slab shearing force is evaluated directly via

\[
F'_x(t) = \sum_{i \in \text{slab}} \sum_{j \in \text{wall}} F_{ij,x}(t),
\]

(3.3)

where \( F_{ij,x} \) is the force in the \( x \) direction on slab particle \( i \) due to wall particle \( j \) at time \( t \). Similarly the \( x \) component of the center of mass velocity of the slab is calculated via

\[
u_{\text{slab}}(t) = \frac{1}{m} \sum_{i \in \text{slab}} m_i v_{i,x}(t),
\]

(3.4)

where \( v_{i,x} \) is the velocity of slab particle \( i \) and \( m = \sum_{i \in \text{slab}} m_i \). From these two quantities, we evaluate the correlation functions \( C_{uF'_x}(t) \) and \( C_{uu}(t) \). In Fig. 3.1
Table 3.1: Interaction parameters, fluids state point under study, and results. For density and temperature the values inside the parentheses are corresponding standard reduced molecular dynamics units. For carbon $\sigma = 0.34$ nm and $\epsilon/k_B = 28$ K.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$\sigma_{ff}$ [nm]</th>
<th>$\epsilon_{ff}/k_B$ [K]</th>
<th>$\sigma_{fw}/k_B$ [nm]</th>
<th>$\epsilon_{fw}/k_B$ [K]</th>
<th>$\rho$ [kg m$^{-3}$]</th>
<th>$T$ [K]</th>
<th>$\eta/10^{-6}$ [Ref. 49]</th>
<th>$\xi_0/10^4$ [kg m$^{-2}$ s$^{-1}$]</th>
<th>$L_s$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.34</td>
<td>120.0</td>
<td>0.34</td>
<td>57.96</td>
<td>1361.8(0.8)</td>
<td>120.0(1)</td>
<td>17.7 ± 1.7</td>
<td>1.62 ± 0.04</td>
<td>11 ± 1</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.38</td>
<td>148.1</td>
<td>0.36</td>
<td>64.39</td>
<td>387.6(0.8)</td>
<td>148.1(1)</td>
<td>9.9 ± 0.9</td>
<td>1.67 ± 0.04</td>
<td>5.9 ± 0.6</td>
</tr>
</tbody>
</table>
Figure 3.1: Section of the normalized correlation functions a) $C_{uu}$ and b) $C_{uF'x}$ versus time for CH$_4$.

we show an example of normalized slab velocity ACF $C_{uu}(t)$ and slab velocity-force correlation function $C_{uF'_x}(t)$ for CH$_4$. The slab velocity and force are anti-correlated to each other, since the shearing force on the fluid slab due to the adjacent wall acts in the direction opposite to the flow. The correlation function data are then Laplace transformed, and an example is given in Fig. 3.2. Note, Fig. 3.2(b) also includes the Maxwellian fit ($n=1$) to the transformed correlation functions, Eq. (2.29). The friction coefficient is then evaluated by using the fitting parameters and the surface area of graphene using Eqs. (2.30) and (2.31).

The slip length is directly calculated using this friction coefficient and the shear viscosity of the fluid, Eq. (2.4). Our EMD simulations thus predict slip lengths for argon and methane of $11 \pm 1$ nm and $5.9 \pm 0.6$ nm respectively, with the corresponding friction coefficients $(1.62 \pm 0.04) \times 10^4$ kg m$^{-2}$ s$^{-1}$ and $(1.67 \pm 0.04) \times$
Figure 3.2: Normalized Laplace transform of the correlation functions a) $C_{uu}$ and b) $C_{uF_x}$ shown in Fig. 3.1. The square symbols in b) are Maxwellian fit, Eq. (2.29). For clarity we have removed some of the fitting data points.
$10^4 \text{ kg m}^{-2} \text{ s}^{-1}$. Here note that the fluids are at different state points and the size and interaction strength of methane is slightly higher than that of argon, see Table 1.

To compare our EMD model predictions with standard NEMD simulations, we carried out both Poiseuille and Couette flow simulations. In Poiseuille flow, each fluid atom is acted upon by an external body force and in Couette flow the upper graphene wall is moved at a constant velocity while the lower wall is held fixed. We have carried out these simulations for a wide range of external fields and shear rates to capture both the constant and diverging behaviour of the slip length. In Poiseuille flow, the smallest field we used results in a mean fluid velocity around 2 m/sec and in Couette flow we move the upper graphene layer with velocity as small as 5 m/sec. Below these fields and shear rates the velocity profiles are too noisy to extract useful data. Note that these low field and shear rate are an order of magnitude smaller than typical values used in NEMD simulations [4]. During NEMD simulations, fluid velocity, density and temperature profiles are evaluated by dividing the channel into bins of 0.1 nm width.

The Poiseuille flow velocity profiles are fitted to a quadratic fit, i.e., $u_x(y) = ay^2 + b$ whereas the Couette flow profiles are fit to a linear function, i.e., $u_x(y) = ay + b$. From these fits we can calculate the slip velocity and velocity gradient at the wall, and hence the NEMD slip lengths from Eq. (2.5).

In Figs. 3.3 and 3.4 we plot the Poiseuille flow velocity profiles of argon and the Couette flow velocity profiles of methane along with their corresponding fits. As can be seen, the fluid has a significant velocity at the wall compared to its mean velocity in Poiseuille flow. In Couette flow one can see the finite velocity difference between the fluid velocity at the wall and the wall velocity. These indicate significant slip is occurring in both systems.

In Figs. 3.5 and 3.6 we plot the slip length of argon and methane as a function of the external field along with our EMD predicted $L_s$, which is a constant. As can be seen from the figures at low fields, the slip length is constant and is in excellent agreement with our EMD prediction before it diverges at high fields. In Figs. 3.7
Figure 3.3: Poiseuille flow streaming velocity profiles of argon. Points are NEMD data and continuous lines are corresponding fits. The external fields are $0.1 \times 10^{11}$ to $1.0 \times 10^{11}$ m/s$^2$ with an increment of $0.1 \times 10^{11}$ (bottom to top).
Figure 3.4: Couette flow streaming velocity profiles of methane. Points are NEMD data and continuous lines are corresponding fits. The upper wall velocities are 5 to 60 m/s with an increment of 5 (bottom to top).
Figure 3.5: Slip length as a function of external field in Poiseuille flow of argon. The straight line is prediction from EMD (Eq. (2.4)) and the shaded region is the standard error in EMD. The continuous line is drawn to guide the eye.

and 3.8 the slip length of argon and methane is shown as a function of the upper wall velocity (shear rate can be found by dividing the wall velocity with the channel width) along with our EMD predicted slip length $L_s$. Again, as can be seen from the figures, at low shear rates the slip length is constant and is in excellent agreement with our EMD prediction before it diverges at high shear rates. The continuous line in slip length as a function of external field or shear rate in all the figures of this thesis is drawn to guide the eye.

Both the Poiseuille and Couette flow NEMD slip lengths are found to be equal and are in excellent agreement with our EMD based friction model. Our results convincingly demonstrate that one can avoid the cumbersome NEMD methods to calculate the limiting slip length for a given fluid-solid combination by using our
Figure 3.6: Slip length as a function of external field in Poiseuille flow of methane. The straight line is prediction from EMD (Eq. (2.4)) and the shaded region is the standard error in EMD.
Figure 3.7: Slip length as a function of shear rate in Couette flow of argon. The straight line is prediction from EMD (Eq. (2.4)) and the shaded region is the standard error in EMD.

In the literature, various researchers have found constant, increasing, decreasing, and nonlinear slip behaviour for different systems as the shear rate is increased. Thompson et al. [37] found a constant slip length below a critical shear rate and diverging slip length above the critical shear rate. Priezjev et al. [50] found linearly increasing slip length with shear rate, while Niavarani et al. [42] found non-linear variation of the slip length with shear rate. Martini et al. [45] found a constant slip length at high shear rates, and using atomic force microscopy Zhu et al. [16] found a non-linear behaviour of slip for different fluids. We refer to the original
Figure 3.8: Slip length as a function of shear rate in Couette flow of methane. The straight line is prediction from EMD (Eq. (2.4)) and the shaded region is the standard error in EMD.
papers, reviews [4, 39, 41, 51] and the references therein for more details. These results suggest that the behaviour of slip due to the changes in applied shear rate is nontrivial. A shear rate $\dot{\gamma}_l$ which corresponds to limiting slip length for one fluid-solid system may not result in limiting slip length for other systems. The maximum shear rates which correspond to the limiting slip length in this study are smaller than the shear rates which resulted in limiting slip length in a previous study of the same fluid with molecular Lennard-Jones walls, where the slip length is an order of magnitude smaller than the slip length found here [35]. Water on the same graphene surface is expected to show even higher slip (Chapter-4), hence even smaller shear rates should be used to find the limiting slip length using NEMD simulations. For CH$_4$ and H$_2$O confined in molecular crystal walls (LJ) and graphene surfaces (C), we have $\dot{\gamma}_l$(CH$_4$−LJ) > $\dot{\gamma}_l$(CH$_4$−C) > $\dot{\gamma}_l$(H$_2$O−C). Thus if one has to predict the limiting slip length from NEMD simulations, several shear rates should be used and the dynamical behaviour of slip has to be examined to quantify the limiting slip length as one does not know the shear rate which corresponds to the limiting slip length a priori. On the other hand, EMD methods such as ours can predict the limiting low velocity slip from a single simulation, making it a far more appealing and reliable method.

We further predict the slip velocities from our model using Eq. (2.39) and Eq. (2.46) and compare them with the direct NEMD data. In Figs. 3.9 and 3.10 we plot the slip velocity of argon and methane as a function of the external field, along with our model prediction for Poiseuille flow. As can be seen from the figures in the linear regime the predicted slip velocities are in excellent agreement with the direct NEMD slip velocities.

In Figs. 3.11 and 3.12 we plot the slip velocity of argon and methane as a function of the shear rate, along with our model prediction for Couette flow. Again as can be seen from the figures in the linear regime the predicted slip velocities are in excellent agreement with the direct NEMD slip velocities.

All the NEMD streaming velocity profiles in Figs. 3.3 and 3.4 result in constant slip length and the slip velocities are in agreement with their corresponding EMD
Figure 3.9: Comparison of slip velocity predicted from EMD (Eq. (2.46)) (straight line) and direct NEMD (points) as a function of external field in Poiseuille flow of argon. The shaded region is the standard error in EMD and the standard error in NEMD data is smaller than the symbol size.
Figure 3.10: Comparison of slip velocity predicted from EMD (Eq. (2.46)) (straight line) and direct NEMD (points) as a function of external field in Poiseuille flow of methane. The shaded region is the standard error in EMD and the standard error in NEMD data is smaller than the symbol size.
Figure 3.11: Comparison of slip velocity predicted from EMD (Eq. (2.39)) (straight line) and direct NEMD (points) as a function of wall velocity in Couette flow of argon. The shaded region is the standard error in EMD and the standard error in NEMD data is smaller than the symbol size.
Figure 3.12: Comparison of slip velocity predicted from EMD (Eq. (2.39)) (straight line) and direct NEMD (points) as a function of wall velocity in Couette flow of methane. The shaded region is the standard error in EMD and the standard error in NEMD data is smaller than the symbol size.
predictions. Above these shear rates non-linear effects begin and the results show deviations from our model predictions, as expected.

As explained earlier, several properties of graphene contribute to the observed slip and the slip lengths are higher than the channel’s width which significantly influences the nanofluidic behaviour. To our knowledge this is the first time that the EMD predicted slip length is compared in both Poiseuille and Couette flow NEMD simulations for a wide range of external fields and shear rates respectively.

3.3 Conclusion

Using extensive molecular dynamics simulations of methane and argon flowing in graphene nanochannels we examined the boundary condition. The no-slip boundary condition is shown to be violated for fluids confined by graphene surfaces owing to their atomic smoothness and lyophobicity. The friction coefficient between the fluids studied here and graphene is found to be an order of magnitude smaller than the friction between the same fluids and the molecular Lennard-Jones crystal walls generally employed in computer simulations. In nanoscale fluidic systems the boundary condition is a combined property of both fluid-fluid and fluid-solid interactions. Slip is shown to be independent of the flow type, confirming its intrinsic nature. Our EMD method is shown to be both computationally highly efficient and superior in predicting the slip compared to the conventional NEMD methods of estimating slip. Our EMD method computes the limiting or minimum slip length for a given fluid and solid surface without the need to do cumbersome NEMD simulations for various shear rates or external fields and their extrapolation to experimental conditions. We note that care should be taken when interpreting the NEMD slip length as it may not correspond to the limiting slip length. Using our method one can also predict the slip velocity of the fluid near the solid surface. Flow rates are found to be an order of magnitude higher compared to classical hydrodynamic no-slip boundary condition predictions, which is very important in reducing the friction in lubrication applications and enhancing the flow rates to design novel nanofluidic devices.
Chapter 4

Slip length of water on graphene: Limitations of non-equilibrium molecular dynamics simulations

In this chapter we study the slip behaviour of water confined in a planar graphene slit pore. We precisely quantify the slip length of water on a planar graphene surface, which serves as one extreme slip length value of water in CNTs. We show some limitations of the NEMD technique when applied to high slip systems and we suggest some procedures to increase the reliability of the NEMD slip estimates.
Data for the flow rate of water in carbon nanopores is widely scattered, both in experiments and simulations. In this chapter, we aim to precisely quantify the characteristic large slip length and flow rate of water flowing in a planar graphene nanochannel. First, we quantify the slip length using the intrinsic interfacial friction coefficient between water and graphene found from EMD simulations. We then calculate the flow rate and the slip length from the streaming velocity profiles obtained using NEMD simulations and compare these with the predictions from the EMD method. The slip length calculated from NEMD simulations is found to be extremely sensitive to the curvature of the velocity profile and it possesses large statistical errors. We therefore pose the question: Can a micrometer range slip length be reliably determined using velocity profiles obtained from NEMD simulations? Our answer is “not practical, if not impossible”. We therefore conclude that in the case of high slip systems, such as water in carbon nanochannels, the EMD method results are more reliable, accurate and computationally more efficient compared to the direct NEMD method for predicting the nanofluidic flow rate and the slip length.

Starting from the last decade, water confined in carbon nanostructures has received significant attention due to the importance of water and the unique properties of carbon [52-82]. A number of studies have aimed to quantify the slip length and flow rate of water in CNTs and flat graphene nanochannels, both experimentally [53-60] and in simulations [61-77]. However, the data is widely scattered, and differs in orders of magnitude and no consensus has been reached. Water has been shown to have an almost plug like velocity profile, resulting in 1 to 5 orders of magnitude flow enhancement compared to classical Navier-Stokes prediction assuming a no-slip boundary condition. Some studies have found a very high slip length in very small diameter CNTs and as the tube diameter increases, the slip length approaches a constant value which is equal to the slip length on a flat graphene surface [69, 72, 73, 82]. Contrary to this, some researchers have found the opposite behavior and attribute this to the increase in surface friction as the tube diameter is decreased [63-65]. In a very recent field effect transistor (FET) experimental study, Qin et al. [59] found non-monotonic behavior of slip, which has also been reported by Sokhan et al. [83] for slip of methane in CNTs. Hence, even qualitatively we have reports of
contradictory slip behavior in CNTs.

In experimental studies, Maali et al. [58] found a slip length of 8 ± 2 nm for water on a graphite surface. Qin et al. [59] found a decreasing slip length as the CNT diameter is increased from 0.81 to 1.59 nm with a non-monotonic behavior at 1.08 nm diameter tube. As the tube diameter increases to 1.59 nm, their slip length converges to 10 nm, which can be approximated to the slip length of water on planar graphene. Zhu et al. [38] and Tretheway et al. [84] found micrometer range slip lengths for water on hydrophobic surfaces. In simulations, Thomas et al. [69] found 30 nm, Falk et al. [72] found 80 nm and Kotsalis et al. [74] found 67 ± 45 nm slip lengths for water on graphene surfaces. Babu et al. [73] found monotonically decreasing slip length as the tube 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. Some of this variation can be attributed to the difference in water models and carbon models used in simulations.

Theoretically, Myers [82] predicted 39 nm slip length in the limit of high diameter CNTs. As explained by Kotsalis et al. [74] the large uncertainties (67 ± 45 nm) are due to the large variation in the velocity gradient of water at the graphene surface. Thomas et al. [69] calculated the viscosity of confined water in EMD simulations by using the Einstein self-diffusion coefficient and they used this viscosity to constrain the fit to the NEMD streaming velocity profiles. They found that unconstrained fits result in almost 100% variation in the predicted slip length and the viscosity of water.

Experimentally, fabricating a perfect defect-free individual carbon nanotube is extremely difficult. Moreover measuring the tube diameter, controlling the pressure difference to drive the fluid, and finally performing the nanoliter volume experiment is a cumbersome procedure, which could be one reason for the scattered data in experiments [53-60]. In simulations, the commonly used NEMD methods also have their limitations. At room temperature water has an average thermal velocity of 340 m/s and the fluid velocities in experiments are on the order of 0.01 m/s. NEMD simulations can only be run for a few nanoseconds with a time step of ~ 1 fs. Due to this computational limitation, NEMD simulations are done with very high
pressure gradients (or shear rates in Couette flow) to obtain a mean fluid velocity comparable to the thermal velocity and thus statistically significant results. At these high fields non-linear effects may begin to emerge and the slip length diverges [85]. Therefore, the extrapolation of NEMD results to experimental fields is not reliable and is likely to lead to deviation from the flux determined under experimental conditions, where the hydrodynamic properties obey linear relations [80]. Moreover, to do the extrapolation these NEMD simulations have to be performed for a range of pressure gradients or shear rates. In order to reduce the computational time and thus avoid the complex carbon models, a number of studies freeze the carbon atoms to their lattice sites and thermostat the water directly to maintain the desired temperature. It has been shown that the molecular momentum transfer at the fluid-solid interface plays a key role in nanofluidic behavior as the fluid transport properties are dominated by the interface [25, 45, 83], and freezing the wall atoms is likely to affect the momentum transfer.

For high slip systems such as water against a hydrophobic surface, the problem becomes even more complicated. As mentioned above, and as we will show in the results section, a very small change in the measured NEMD velocity profile can result in a very large deviation in the slip length. This suggests the need for developing new theoretical methods for the prediction of such a highly sensitive phenomena. In the previous chapter we have shown that our method has successfully predicted the slip length for atomic fluids and methane confined between Lennard-Jones solid walls [35] and inside graphene nanochannels [85]. Our results for methane flow in CNTs (next chapter) show that the minimum slip length for any diameter CNT is greater than or at least equal to the slip length on a flat graphene surface [36]. Understanding the behavior of water on a flat graphene surface and documenting its slip length is crucial before we completely understand the behavior in CNTs which are a cylindrical form of graphene, where the curvature of the tube affects the friction. This is the motivation of the present study. In this work using EMD simulations (with no pressure gradient or shear rate), thus bypassing limitations of NEMD methods, we calculate the interfacial friction coefficient between water and graphene. Using this friction coefficient we determine the slip length and flow rate.
We also perform NEMD simulations of Poiseuille and Couette flows for a wide range of external fields and shear rates to understand the slip phenomena further and compare these results to our EMD method predictions.

### 4.1 Simulation details

We use the recently parameterized flexible SPC/Fw model for water, which reproduces the dynamical properties of water close to experimental values [86-89]. Graphene is modeled using the second generation reactive empirical bond order Tersoff-Brenner potential, which is widely used for carbon allotropes [46]. Electrostatic interactions between water molecules are modeled using the Wolf method [87, 90, 91], which enables us to simulate for longer times and conduct 20 simulations at each state point. The interaction between water molecules and carbon atoms of the graphene is modeled using the Lennard-Jones potential with parameters of Werder et al. [81]. We have used two layers of graphene at two walls to produce a stable system and better heat conduction between fluid and solid. A weak Lennard-Jones potential is applied between carbon atoms belonging to the different graphene layers to hold them together at 0.34 nm distance. All Lennard-Jones interactions are truncated at a distance of 1 nm. The channel width, i.e., the distance between the two innermost graphene layers is set to 3.9 nm (roughly 12 molecular diameters) in the $y$ direction and periodic boundary conditions are applied along the $x$ and $z$ directions. The van der Waals size of the carbon atoms (0.34 nm) is subtracted from 3.9 nm to define the available channel width. Room temperature (300 K) is maintained by applying the Nosé-Hoover thermostat to the carbon atoms, so that the heat produced by the slip and viscous friction in the water is conducted away through the graphene as is done in a real experiment. The water density in the channel is kept at 1000 kg/m$^3$. Simulation time spans are from 5 to 10 ns with a time step of $\sim$ 1 fs using the leap-frog integration algorithm. The SPC/Fw water model parameters are given in Table 4.1.
Table 4.1: SPC/Fw water model parameters.

<table>
<thead>
<tr>
<th>$k_b$ (kcal mol$^{-1}$ Å$^{-2}$)</th>
<th>$r_{OH}$ (Å)</th>
<th>$k_a$ (kcal mol$^{-1}$ rad$^{-2}$)</th>
<th>$\theta_{HOH}$ (deg)</th>
<th>$\epsilon_{OO}$ (kcal mol$^{-1}$)</th>
<th>$\sigma_{OO}$ (Å)</th>
<th>$q_O$ (e)</th>
<th>$q_H$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1059.162</td>
<td>1.012</td>
<td>75.90</td>
<td>113.24</td>
<td>0.1554253</td>
<td>3.165492</td>
<td>-0.82</td>
<td>0.41</td>
</tr>
</tbody>
</table>

4.2 Results and discussion

As described in the previous chapter, in equilibrium simulations we define a water slab of width one molecular diameter close to the graphene surface. We evaluate the relevant correlation functions and find the friction coefficient of water on a graphene surface to be $(1.25 \pm 0.10) \times 10^4$ kg m$^{-2}$ s$^{-1}$. Using the Navier slip length definition, along with the bulk SPC/Fw water shear viscosity $\eta_0=(7.5 \pm 0.5) \times 10^{-4}$ kg m$^{-1}$ s$^{-1}$, the slip length of water on a planar graphene surface is thus estimated as 60 ± 6 nm.

We perform both Poiseuille and Couette flow NEMD simulations for a wide range of external fields and shear rates starting from the lowest possible values. Poiseuille flow is generated by applying a constant external field to all the atoms of the water molecules and Couette flow is generated by moving the upper graphene wall with a constant velocity while keeping the lower graphene wall fixed. We fit the Poiseuille flow velocity profiles to a quadratic equation $u_x(y) = ay^2 + b$ and Couette flow velocity profiles to a linear equation $u_x(y) = ay + b$. Using these fits one can determine the slip velocity and the fluid velocity gradient at the wall, see Fig. 1.2.

In the analysis of the velocity profiles we have neglected the data in the wing regions (around 0.3 nm near the graphene surface) where the statistical noise is very high. For the case of small slip systems, the velocity in these wing regions can vary significantly compared to the central region of the channel. But for the case of high slip systems, even though the data in the wing regions are statistically noisy, their values do not deviate much from the value in the central region. We have make sure that including the data in the wing region does not effect the results within statistical errors.
**Couette flow**

To our knowledge Couette flow type simulations have not previously been carried out on the water-graphene system in order to determine the slip length. We move the upper wall with a constant velocity in the range 5 to 1000 m/s. Within this range, linearity is expected to hold over a small range of low fluid velocities, above which the slip length is no longer a constant. Even the lowest applied shear rate (wall velocity divided by channel width) is 3 to 4 orders of magnitude higher than the highest experimental shear rate [4]. When we have a small slip system, we can use low wall velocities as the wall can induce a measurable fluid flow in the shearing direction. For high slip systems, the difference in wall to fluid velocity increases, so the momentum transfer between wall and fluid decreases, i.e. higher wall velocity is required to induce a measurable fluid flow.

In Fig. 4.1 we plot the fits to 20 independent simulations, after symmetrizing [92] the streaming velocity data at wall velocity 50 m/s, which is 10 times higher than the smallest velocity we have used. As mentioned earlier, with increasing wall velocity we obtain statistically better NEMD data. We notice four things from the graph. (i) We have a reasonably good estimate of the average slip velocity ($u_s = 24.3 \pm 0.7$ m/s). (ii) The average velocity difference of the fluid from upper to lower wall is very small ($\delta v \simeq 1.4$ m/s, with the no-slip boundary condition it is 50 m/s). (iii) The fluid strain rate (velocity gradient or slope of the line) is very small and the variation is large. (iv) Some of the fits have a negative velocity gradient due to the thermal fluctuations superimposed on the very small velocity difference (very weak effective strain rate) which is a result of very strong slip. The standard error in the NEMD simulation streaming velocity data is generally of the order of a few m/s, which means that for the current system, $\delta v$ is comparable with the standard error in the velocity data. The number of simulation steps for each independent simulation is 5 million ($t=5$ ns, $dt=1$ fs) which is higher than most previous simulation studies of water in carbon nanopores. Each simulation took about 325 hours of CPU time, i.e. we should expect that from a simulation point of view the velocities are reasonable. We calculate the slip length from the NEMD data in different ways using Eq. (2.5)
Figure 4.1: Linear fits to Couette flow velocity profiles at upper wall velocity 50 m/s for the 20 independent simulations. The 4 dotted velocity profiles cannot be used to calculate the slip length (see method-C1). For the other 16 profiles, the slip length varies between 11 to 369 nm.

C1. The general way is to calculate the slip length for all the 20 profiles and then perform the error analysis on this set of 20 independent slip lengths. As mentioned above, some of the velocity fits have negative slope (fluid velocity at the lower wall is greater than at upper wall). For these negative slope profiles the slip length cannot be defined. Using this procedure we cannot estimate the average slip length. If we disregard these data and only use positive slope velocities to calculate the slip length, it varies from 11 to 369 nm due to the large variation in the velocity gradient.

C2. In this second method, we average the 20 NEMD velocity profiles, and use this averaged data for fitting. In Fig. 4.2 we plot the averaged NEMD data with
error bars and weighted errors method for the fit. The standard error in the NEMD data is approximately equal to the average velocity difference at the walls. Using the method of weighted errors for the fitting, the calculated slip length is $65 \pm 2$ nm. Without including the NEMD data errors in the fit (unweighted), the slip length is also $65 \pm 2$ nm. However, this method underestimates the standard error in the slip length. We have a good estimate of the slip velocity $(24.3 \pm 0.7 \text{ m/s})$ but not the slope even though the slope is calculated from the velocity, since the slope is very small. The fluid velocity at lower and upper walls is $24.3 \pm 0.7 \text{ m/s}$ and $25.7 \pm 0.7 \text{ m/s}$ respectively. From this, the maximum to minimum slope (strain rate) varies between $(26.4-23.6)/(3.56 \times 10^{-9}) = 0.4 \times 10^9 \text{ s}^{-1}$ to $(25.0-25.0)/(3.56 \times 10^{-9}) = 0 \text{ s}^{-1}$ ($h=3.56 \text{ nm}$ being the available channel width). With the slip velocity $24.3 \pm 0.7 \text{ m/s}$ and strain rate $(0.4 \pm 0.4) \times 10^9 \text{ s}^{-1}$, the calculated slip length is thus $61 \pm 55$ nm.

In Fig. 4.3 we plot the average NEMD data and the corresponding fits for wall velocities of 5 to 60 m/s as in Fig. 4.2. For sufficiently small velocities, the slip length is expected to be constant and around $60 \text{ nm}$ (our EMD prediction). Due to statistical variations, some anomalous results occurred. For example, at wall velocity 20 m/s, due to the very weak effective strain rates, the average velocity profile across the channel becomes flat resulting in a slip length in the order of microns. The computed slip length is also inconsistent with the shear rate. So this method is also not reliable in estimating the slip length. At higher wall velocities 70, 80, 90, 100, 125, 150, 200, 250, 300, 500, 750 and 1000 m/s the slip length is 78, 74, 75, 65, 89, 93, 106, 97, 113, 110, 115 nm respectively.

C3. The classical solution for the velocity profile in Couette flow with the no-slip boundary condition is given in Eq. (1.8). The fluid velocity at the lower wall ($y = 0$) is zero as it is stationary and at the upper wall ($y = h$) it is equal to the wall velocity $U$ (see Fig. 1.2). In the case of slip flow, the fluid has a finite velocity $u_s$ at the lower wall and $U - u_s$ at the upper wall. The Couette flow solution with these boundary conditions is given in Eq. (1.9). Using the slip length definition we can derive

$$u_s = \left( \frac{L_s}{h + 2L_s} \right) U \quad \text{and} \quad u_s = \left( \frac{\eta_0}{\xi_0 h + 2 \eta_0} \right) U ,$$

(4.1)
Figure 4.2: Average velocity of 20 independent Couette flow simulations at upper wall velocity 50 m/s with error bars and linear fit. With slip velocity $24.3 \pm 0.7$ m/s and shear rate $(0.4 \pm 0.4) \times 10^9$ s$^{-1}$, the predicted slip length using Eq. (2.5) is 61 ± 55 nm (method-C2).
Figure 4.3: Same as in Fig. 4.2 for wall velocity range 5 to 60 m/s with an increment of 5. At the wall velocity 20 m/s, the velocity profile is flat across the channel due to statistical fluctuations and very weak effective strain rate, resulting in a slip length of approximately 2 µm (method-C2).
which means, in the linear regime, where the slip length (friction coefficient) remains constant, the slip velocity is proportional to wall velocity. By plotting slip velocity against wall velocity for low wall velocities we can then find a slope $m$ that enables us to find the slip length. If the no slip boundary condition holds the slope is zero as the slip velocity is zero irrespective of the wall velocity. As the slip for different wall-fluid systems increases, this slope also increases. The maximum slope value can be close to 0.5 and it should always be less than 0.5. From this slope value, the slip length or friction coefficient can be calculated directly

$$L_s = \left( \frac{mh}{1-2m} \right) \quad \text{and} \quad \xi_0 = \frac{n_0}{\hbar} \left( \frac{1}{m} - 2 \right).$$

(4.2)

As $m$ goes to 0.5, the friction coefficient goes to zero and the slip length goes to infinity. In Fig. 4.4 we plot slip velocity as a function of wall velocity for wall velocities below 60 m/s. The slip velocity is calculated using the method-C2 described above. The slope of the line is $0.485 \pm 0.002$, which is close to 0.5 as the slip is very strong and the slip velocity is close to half of the wall velocity. Using this slope (with zero intercept), the slip length is $58 \pm 8$ nm. To extract this, we have used $10 \times 20 = 200$ simulations each with 325 hours of CPU time. The estimated slip length is in agreement with our EMD prediction. Notice, even a 1% increase in the slope leads to a very high slip length as the slip length approaches infinity quickly as $m$ goes to 0.5.

**Poiseuille flow**

For Poiseuille flow we increase the length of the simulations from 5 to 10 million time steps (10 ns). The external fields range from $0.25 \times 10^{11}$ to $20.0 \times 10^{11}$ m/s$^2$. For the lowest field we used results $\simeq 3.5$ m/s mean velocity, which is well below the molecular thermal velocity and smaller than the previous simulations mean velocities. The slip length here is expected to be a constant for low field ranges (low slip velocities).

In Fig. 4.5 we plot the fits of data to a quadratic equation for all 20 simula-
Figure 4.4: Slip velocity as a function of wall velocity for low slip velocities where the slip length is expected to be constant. The slip length calculated using Eqs. (4.1) and (4.2) is $58 \pm 8$ nm, with the slope $0.485 \pm 0.002$ (method-C3).
tions, using symmetrized streaming velocity data at field $1.00 \times 10^{11}$ m/s$^2$. This corresponds to a pressure gradient of $1 \times 10^{14}$ Pa/m, which is equal to the pressure gradient used by Thomas et al. [69] and the average streaming velocity is also comparable with their Fig. 5. Note that their figure shows the streaming velocity of water in a CNT. Again we note the following observations. (i) We have a reasonable estimate of the average slip velocity ($14.7 \pm 0.4$ m/s). (ii) The velocity difference from the centre to the wall is very small ($<0.25$ m/s). (iii) The fluid strain rate at the wall is very small and the variation is large among different fits. (iv) Some fits are an inverted parabola, which again is the result of statistical fluctuations. The latter point is due to the very small velocity difference from the centre of the channel to the wall (very weak effective strain rate). In Poiseuille flow, as we increase the external field, the fluid velocity difference from the centre to the wall increases (see Eqs. (1.5) and (1.6)). Even though these fields are 3 to 4 orders of magnitude higher than typical experimental fields, they are still very small for NEMD simulations. At high fields, we can see clear quadratic velocity profiles. In addition to the above mentioned three methods for Couette flow analysis, we use two more methods to calculate the slip length from this NEMD data.

P1. Again compute the slip length for each simulation run separately and then average the slip lengths. For the weak velocity profiles (inverted parabola) the slip length cannot be defined, so this method cannot be used to calculate the average slip length. For the other profiles, the slip length varies from 10 to 268 nm.

P2. We now average the NEMD data over the 20 simulations, and fit the average data. See reference [93] for the streaming velocity profiles in the literature. In Fig. 4.6 we plot the average data with error bars and weighted errors method for fits at fields $1.00 \times 10^{11}$, $1.25 \times 10^{11}$ and $1.50 \times 10^{11}$ m/s$^2$ (note this figure also includes an additional constrained fit which we will explain in method-P4). The estimated slip lengths for the three external fields using weighted errors for the fitting are $60 \pm 9$, $46 \pm 3$ and $130 \pm 21$ nm. Without including the NEMD data errors in the fit (unweighted), the slip lengths are the same as that obtained using weighted errors, which means the standard error in the slip length is underestimated. The calculated shear viscosities from the fitting parameters at three fields are $(7.2 \pm 1.0) \times 10^{-4}$,
Figure 4.5: Quadratic fits to the Poiseuille flow velocity profiles at external field $1.00 \times 10^{11}$ m/s$^2$ for the 20 independent simulations. Inverted parabola fits cannot be used to determine the slip length. For the other profiles slip length vary from 10 to 268 nm (method-P1).
(5.6 ± 0.4) × 10^{-4}, and (15.7 ± 2.5) × 10^{-4} kg m^{-1} s^{-1} respectively. The shear viscosity of bulk water is (7.5 ± 0.5) × 10^{-4} kg m^{-1} s^{-1}.

As the available channel width is 11 molecular diameters (3.56 nm) and the external fields are small, the shear viscosity of water is not expected to change. Non-local effects occur for channel widths of only a few molecular diameters [11] and non-linear effects occur at high fields [85]. At field 1.00 × 10^{11} m/s^2 the NEMD viscosity is in excellent agreement with the bulk water shear viscosity and the slip length is also in excellent agreement with our EMD prediction. At field 1.25 × 10^{11} m/s^2 the viscosity is underestimated and at field 1.50 × 10^{11} m/s^2 the viscosity is overestimated. At field 1.25 × 10^{11} m/s^2 the slip length is underestimated since the viscosity is underestimated (strain rate is overestimated) (See Eq. (2.5)). At field 1.50 × 10^{11} m/s^2 we have the opposite behavior, i.e. the viscosity is overestimated resulting in overestimation of the slip length. For the three fields, the slip velocities are 14.7, 18.3 and 21.9 m/s which are small and hence the shear viscosity and slip length are expected to be constant. This is further explained in method-P3 below.

P3. The Poiseuille flow solution with no slip boundary condition is given in Eq. (1.5). The velocity profile is quadratic across the channel, with zero velocity at the walls \( y = ±h/2 \) and maximum at the centre \( y = 0 \) (see Fig. 1.2). The slip modified solution is given in Eq. (1.6). Thus the effect of slip is only an upward shift in the velocity profile. Using the slip length definition we can derive

\[
    u_s = \left( \frac{L_s \rho h}{2 \eta_0} \right) F_e \quad \text{and} \quad u_s = \left( \frac{\rho h}{2 \xi_0} \right) F_e ,
\]

which means, in the linear regime, where the slip length (friction coefficient) remains constant, the slip velocity is proportional to the external field. By plotting slip velocity as a function of external field for low fields we can determine the slope \( m \). Using this slope, the slip length can be directly calculated

\[
    L_s = \frac{2m \eta_0}{\rho h} \quad \text{and} \quad \xi_0 = \frac{2m}{\rho h} .
\]

Unlike Couette flow, these relations do not suffer from any singularity. In Fig. 4.7 we plot the slip velocity as a function of external field for low fields (slip velocities). The
Figure 4.6: Average velocity of 20 Poiseuille flow simulations at external fields $1.00 \times 10^{11}$, $1.25 \times 10^{11}$, and $1.50 \times 10^{11}$ m/s$^2$ (from top to bottom) with error bars and both unconstrained fit (red line and method-P2) and constrained fit (blue line and method-P4) with shear viscosity.
Figure 4.7: Slip velocity as a function of external field for low slip velocities for which the slip length is expected to be constant. The predicted slip length calculated using Eqs. (4.3) and (4.4) is 63 ± 4 nm, with slope $(14.9 \pm 0.2) \times 10^{11}$ s$^{-1}$ (method-P3).

linear increase in slip velocity with the external field suggests that these external fields are small enough and do not produce non-linear effects, so the results are applicable to experimental fields also. From the slope the estimated slip length is 63 ± 4 nm which is in agreement with our EMD method prediction.

P4. Unlike the Couette flow solution, the Poiseuille flow solution includes a fluid property (shear viscosity). Thomas et al. [69] found that the unconstrained fit to the velocity profiles resulted in almost 100% deviation in the slip length and shear viscosity from the expected values. In Fig. 4.6 we plot the constrained fits using the bulk water shear viscosity for the average data of 20 simulations at three external fields $1.00 \times 10^{11}$, $1.25 \times 10^{11}$ and $1.50 \times 10^{11}$ m/s$^2$. The calculated slip length for all the three fields is 62 ± 5 nm. These constrained fit results are also in very
good agreement with our EMD prediction. At high fields we notice an increase in temperature of the fluid which also affects the shear viscosity. We have used the shear viscosity at a temperature of 300 $K$ for the constraining fit. As mentioned before, our goal is to determine the limiting slip length corresponding to experimental fields. If we used a temperature dependent shear viscosity the qualitative behaviour of slip would still remain the same at high fields [85].

P5. The flow enhancement $\epsilon$ is defined as the ratio of observed flow rate $Q_{\text{slip}}$ in experiments or simulations to that predicted from the classical no-slip boundary condition $Q_{\text{no-slip}}$. For a planar Poiseuille flow it is related to slip length via

$$E = \frac{Q_{\text{slip}}}{Q_{\text{no-slip}}} = 1 + \frac{6L_s}{h} ,$$

(4.5)

During the NEMD simulations we have counted the number of water molecules crossing a fixed plane in the streaming direction, i.e., we measure the flow rate directly. By dividing this observed flow rate with the Navier-Stokes predicted flow rate, we can directly calculate the flow enhancement at each field. Using this $\epsilon$ we calculate the slip length from the above Eq. (4.5). As this method does not require any fitting to the velocity profiles, it does not suffer from the sensitivity of streaming velocity profiles. In Fig. 4.8 we have summarized our results and plotted the slip length calculated using methods-P4 and P5 along with the constant slip length from method-P3, method-C3 and our EMD prediction.

From all the above analysis a good estimate of the slip length is $L_s = 60 \pm 6$ nm. So for the channel width of 3.56 nm used here, the flow enhancement is $102 \pm 10$ (valid for experimental pressure gradients also).

In the literature, experimental studies have found up to 400 $\mu m$ slip length at a planar fluid-solid interface [94], whereas the slip lengths reported in simulations are in the nm range [4]. We now return to the question: Can a micrometer range slip length be reliably determined using NEMD simulations? On the basis of the analysis above, our answer is “not practical, if not impossible”. The reason again is the computational limitations discussed above. NEMD simulations are generally done with a channel width of around 5 nm (15 molecular diameters). For high slip
4 Slip length of water on graphene: Limitations of non-equilibrium molecular dynamics simulations

Figure 4.8: Slip length as a function of external field using method-P4 and method-P5. The constant slip length predicted from method-P3 (63 ± 4 nm), method-C3 (58 ± 8 nm) and our EMD prediction (60 ± 6 nm) is also indicated on the graph. The shaded region is the standard error in EMD slip length.
systems, the constant slip length external field/shear rate range shifts to lower values [85]. In a typical shear flow simulation, the upper wall velocity is around 20 m/s and lower wall velocity is zero. For the slip length to be 1 $\mu$m, the fluid velocity at lower and upper walls should be 9.975 and 10.025 m/s respectively, which means the fluid velocity at the upper wall is just 0.5% higher than the fluid velocity at the lower wall. Using simulations one cannot resolve such a small difference in velocity (0.05 m/s) as the error in the velocity is of the order of m/s. In a channel width of 1 $\mu$m, the fluid velocity at the lower and upper walls of 6.66 and 13.33 m/s gives the same 1 $\mu$m slip length, but we cannot simulate such a wide channel. In a Poiseuille flow simulation, the slip length remains constant for a very small range of slip velocities. At these small slip velocities, for the slip length to be on the order of a micrometer the fluid velocity gradient has to be too small to determine from NEMD simulations.

We also note that the slab CM velocity derived using Navier-Stokes equations by applying IBCs for Poiseuille flow in Eq. (2.46) is identical to the slip velocity in Eq. (4.3) and for Couette flow in Eq. (2.39) it is identical to the slip velocity in Eq. (4.1) in the limit of the slab width $\Delta \to 0$.

There is a small uncertainty in defining both the slip velocity and the channel width. Slip velocity is defined as the fluid velocity at the wall as well as the average velocity of the first fluid layer close to the wall. These two definitions are not exactly the same as the fluid remains some distance away from the wall due to the hard core repulsive interactions depending on the type of wall and fluid. There is also uncertainty in defining the channel width. Sometimes it is taken as the distance between the CM of the solid atoms of the innermost solid layers, sometimes the van der Waals size of the solid atoms ($\sigma$) is subtracted from it and at other times the location of the first minimum of the fluid density profile near the wall is considered as the effective wall position. In this work we have substracted the van der Waals size of the carbon atoms from the distance between innermost graphene layers in defining the available channel width.

The matching of the IBC slab velocity using the friction coefficient with the slip modified Navier-Stokes solutions is another confirmation of the validity of our
EMD based friction coefficient method. We note that our method has successfully predicted the slip for a variety of systems such as simple fluids (Ar and CH₄) confined between molecular crystal walls [35], in graphene nanochannels [85], and for water on a graphene surface, where the slip is low (\(~\sim\) 1 nm), moderate (\(~\sim\) 8 nm) and high (\(~\sim\) 60 nm) respectively. Our method can be applied to any complex fluid-solid system to predict the slip and boundary condition accurately.

The computational time required to calculate the friction coefficient from the EMD method is equal to the time required to generate just one NEMD data point at low fields on Fig. 4.8 which is $20 \times 650 = 13000$ hours of CPU time. For determination of the friction coefficient by NEMD methods, this time is repeated for each data point, e.g. in Fig. 4.8 this amounts to roughly an order of magnitude increase in CPU time.

4.3 Conclusion

Using flexible models for both water and graphene, we have conducted molecular dynamics simulations to precisely quantify the slip length of water on graphene and formulate a boundary condition for water-graphene nanofluidic systems. The calculation of slip is found to be extremely sensitive to the NEMD velocity profiles, and the NEMD results suffer from large statistical errors. As demonstrated, the generally used NEMD methods are found to be inaccurate and therefore unreliable in the case of high slip systems unless extreme care is taken, which could be a reason for the disagreement in previous simulation results. On the other hand, one can predict such a highly sensitive non-equilibrium phenomenon with our equilibrium simulation method, accurately and computationally efficiently. With a single set of EMD simulations, one can determine the interfacial friction coefficient and the slip length between the fluid and solid, and overcome the limitations of NEMD methods. The observed high slip can have many potential implications for nanofluidic devices. Water can be a good lubricant for graphene in shearing experiments and graphene nanochannels can act as an efficient water transport device either for enhanced flow or energy saving flow.
Chapter 5

Hydrodynamic boundary condition for carbon nanotubes

In this chapter we investigate the boundary condition for CNTs. We apply our cylindrical interface method to predict the interfacial surface friction between methane and CNTs of various diameters. We then verify the curvature dependent friction coefficient with direct NEMD simulations.
As mentioned before, the boundary condition is a property of the fluid-fluid and fluid-solid interactions, but the no-slip boundary condition is widely accepted mainly for two reasons. The first is, even if some slip is present its effect is negligible at the macroscale [95]. The second is the experimental difficulties in probing and measuring the fluid velocity within sub-nanometer length scales from the solid surface, which is needed for correct formulation of the boundary condition [39].

Recent developments have enabled the fabrication of nanofluidic devices and measurement of nanolitre flow rates of fluid [96]. CNTs are ideal for nanofluidic transport and to understand nanofluidic phenomenon. Over the last decade many experimental and simulation studies have found volumetric flow rates enhanced by orders of magnitude compared to the classical hydrodynamics prediction with the no-slip boundary condition in CNTs. The observed flow enhancement is believed to be due to the non-zero fluid velocity (velocity slip) at the solid, and hence the no-slip boundary condition is no longer valid. However, the enhancement data is widely scattered, [53-56, 59, 63, 65, 69, 71-73, 83] hence, the formulation of a precise boundary condition is a subject of great interest and significant challenge in nanofluidic research [28, 30, 32, 34, 35, 37, 42, 50, 97], in particular to find out the flow rates of fluids in CNTs.

5.1 Simulation details

We model the CNTs using the Tersoff-Brenner (REBO) [46] potential and the interactions between fluid-fluid and fluid-solid atoms are modeled using the Lennard-Jones potential with a 1 nm cutoff distance. The bulk liquid state point is \((\rho, T) = (387.6 \text{ kg m}^{-3}, 148.1 \text{ K})\). A Nosé-Hoover thermostat is applied to the wall atoms so that the intrinsic dynamics of the fluid atoms is not affected (compared to being thermostated directly) [25]. Simulations are carried out for 10 to 40 ns depending on the tube size and external field, using the leap-frog integration algorithm with a time step of 1 fs. We have simulated eleven armchair CNTs of diameter ranging from 1.62 to 9.76 nm. For the higher diameter CNTs the curvature effects are expected to be small and both the fluid-tube slip friction coefficient force and fluid-
planar surface (graphene) slip friction coefficient are equal and indeed the results show this.

5.2 Results and discussion

In equilibrium simulations, for each tube we define a cylindrical fluid annulus (slab) of average width one molecular diameter adjacent to the CNT surface, $\Delta = 0.38$ nm. After equilibration, we evaluate the slab CM velocity $u_{\text{slab}}(t) = \frac{1}{m \Delta} \sum_{i \in \text{slab}} m_i v_{i,z}(t)$ and tangential force on the slab due to the wall atoms $F'_z(t) = \sum_{i \in \text{slab}} \sum_{j \in \text{wall}} F_{ij,z}(t)$ in the axial direction. From the above two quantities, we evaluate the slab CM velocity ACF $C_{uu}(t)$, and slab velocity-force correlation function $C_{uF'}(t)$. In Fig. 5.1 we plot the slab CM velocity ACF for a short time with the chirality vector [98] of each CNT indicated on the graph. As the tube diameter is decreased, the slab velocity correlations are found to persist for a longer time, indicating that the fluid dynamics become more correlated. The two correlation functions are then Laplace transformed and the friction coefficient is found using the parameters of the Maxwellian fit and the surface area of the slab, as explained in chapter 2. We find the slip length for each CNT by dividing the shear viscosity of bulk methane by the corresponding friction coefficient of the tube [72]. We shall comment on this later.

In the non-equilibrium simulations, Poiseuille flow is generated by applying a range of external fields. We fit the streaming velocities to a quadratic equation $u_z(r) = ar^2 + b$. We constrain the fit such that the parameters satisfy the shear viscosity of bulk methane. Due to the high slip and small external fields, constraining the fit is necessary as shown in chapter 4. From these fits we find the slip length using Eq. (2.59). In Fig. 5.2 we plot the slip length as a function of external field for all the CNTs simulated. The plot also includes the slip length on a planar graphene surface [85]. As expected, the slip length remains constant for low external fields and increases at high fields [37, 85]. The increase in slip length with field is small in smaller diameter CNTs, which already have a high slip length in the linear regime, whereas in the larger diameter CNTs, the slip length increased rapidly with the external field as compared to smaller diameter CNTs. Hence, the same external
Figure 5.1: Slab CM velocity ACF for a short time. The chirality vector [98] and the radius of each CNT in nm is indicated on the plot.
field may not result in the linear regime slip length for the same fluid and solid in two different diameter CNTs. In the previous chapters we have shown that for the same fluid, the same external field may not give the limiting slip length confined in two different solid material walls [35, 85]. Therefore, care should be taken when interpreting the NEMD results for the slip length of a fluid in different diameter CNTs, which are computed only at a single external field as these NEMD fields are orders of magnitude higher than the experimental fields and hence the slip length may not correspond to the limiting experimental slip length [4]. The slip length is maximum in the smallest diameter CNT where the curvature effects are large, and as the tube size increases, the slip length decreases and approaches a constant value which is equal to the slip length on a planar graphene surface, as anticipated. This result is in qualitative agreement with Refs. [69, 72, 73], but disagree with the findings in Refs. [63, 65, 83]. For tubes of diameter 1.36 to 2.72 nm Sokhan et al. [83] found a non-monotonic slip length of below 10 nm whereas for 1.62 to 2.72 nm diameter tubes we found a monotonically decreasing slip length of around 110 to 20 nm. Here we note the fluid state points are different in two studies. Some discrepancy in the results is due to the fitting method. We have constrained the velocity profiles with the bulk methane shear viscosity due to the very small difference in the fluid velocity from the centre to the wall of the tube, whereas Sokhan et al. used a constrained fit which might have underestimated the shear viscosity. We still need to develop new methods for predicting the confined fluid shear viscosity which takes into account non-local effects [99, 100].

Both the EMD predicted slip length and the limiting NEMD slip length are plotted as a function of CNT diameter in Fig. 5.3. As can be seen, our friction method slip length predictions are in good agreement with the direct NEMD data in the linear regime, where the slip length is constant and fluid mean velocity increases linearly with the applied pressure gradient. This slip length is valid at experimentally accessible pressure gradients, where the fluid velocity is of the order of 0.01 m/s. For tube diameters greater than 2 nm, our EMD slip length predictions are within 5% of the direct NEMD estimates. For a discussion on the superiority of the EMD method over NEMD methods in predicting the slip, refer to chapters 3 and 4.
Figure 5.2: The slip length as a function of external field for the 11 CNTs studied using NEMD simulations. Also, included the slip length on a planar graphene surface (gra) [85].
Figure 5.3: The slip length as a function of CNT diameter using both EMD and NEMD methods. The dashed line is the slip length on a planar graphene surface [85].
We now comment on the issue of tube diameter dependent effective shear viscosity. When fluids are very highly confined (below 3-4 nm or approximately 10 molecular diameters), the shear viscosity is not well defined. The shear viscosity is defined for a homogeneous fluid based on a continuum hypothesis [1, 2]. Surprisingly even down to roughly 3-4 nm channel widths confinement, the fluid shear viscosity does not show significant variation [100]. But below these channel widths, the fluid becomes highly inhomogeneous and fluid density oscillations exist across the whole channel leaving the uniform density hypothesis and hence the classical definition of the viscosity invalid. In Fig. 5.4 we plot the density of the fluid along the radial direction, for the 3 smallest and 3 widest diameter CNTs we have simulated. In the wider diameter CNTs, the density oscillations can be seen near the wall and in the middle of the channel bulk homogeneous fluid can be seen. In the small diameter tubes, we can see inhomogeneity and density oscillations throughout the tube, for which the hypothesis of a uniform density is clearly invalid. In simulation studies of water confined in CNTs researchers have found a large variation (increasing, decreasing, non-monotonic) in the behaviour of the effective shear viscosity with the tube diameter [69, 72, 73, 78, 79, 101, 102]. In experimental studies with slit pores of few molecular widths also, the shear behavior of water is not yet clearly resolved [16, 51, 103-105] The discrepancy could be due to the breakdown of existing methods of defining and measuring viscosity for such tightly confined fluids, where non-local effects occur and a viscosity kernel must be considered [11, 99], which is beyond the scope of this thesis. Both the EMD and NEMD slip lengths are proportional to the shear viscosity of the fluid. So the effect of a change in the viscosity is the same for both methods, hence, with a tube diameter dependent effective viscosity also, our friction method results will agree with direct NEMD simulation results.

The slip length definition assumes a quadratic streaming velocity profile for the fluid across the channel which is also based on the constant density continuum hypothesis [1, 2, 106]. As this hypothesis is not valid for such narrowly confined fluids the velocity profile may not be quadratic, as has been shown in the literature [17, 107]. Therefore the slip length definition may not be valid at this confinement level. Due to the high slip and very small velocity difference of the fluid from centre
Figure 5.4: Density of the fluid in the radial direction for the 3 smallest and 3 widest CNTs simulated. Bulk fluid reduced number density is 0.8.
to the wall we are unable to resolve such a non-quadratic velocity profile even if it exists [106].

As mentioned before, it is generally stated that both the friction coefficient and the slip length of a fluid-solid interface are intrinsic properties and independent of channel width for a planar boundary [28, 30, 32, 35, 108]. This is true for fluids confined at the macroscale down to a few (3-4) nanometers channel width. Below these channel widths, they may depend on the channel width due to various molecular level confinement effects.

### 5.3 Conclusion

In summary, we have investigated the hydrodynamic boundary condition for liquid methane in CNTs using the fluid-solid intrinsic interfacial friction coefficient proposed by Navier. We have applied our extended cylindrical interface method to predict the interfacial surface friction between methane and CNTs of various diameters. We have found good agreement between our curvature dependent friction predictions and direct NEMD simulations. The method predicts the non-equilibrium slip phenomenon from EMD calculations. The slip length is found to decrease monotonically as the tube diameter increases and approaches a constant value, which is equal to the slip length on a planar graphene surface. Hence, the flow enhancement increases as the diameter of the tube is decreased. Smaller diameter CNTs can be both highly selective and highly permeable and could be used in potential membrane science applications such as nanofiltration. The cylindrical interfacial method is robust, general and can be used to predict the slip for cylindrical nanofluidic systems.
Chapter 6

How fast does water flow in carbon nanotubes?

In this chapter, first, we review the existing literature on flow rates of water in carbon nanotubes. Data for the slip length which characterizes the flow rate is scattered over 5 orders of magnitude for nanotubes of diameter 0.81 nm to 10 nm. Secondly, we precisely compute the slip length using EMD simulations, from which the interfacial friction between water and carbon nanotubes can be found, and also via external field driven NEMD simulations. We discuss some of the issues in simulation studies which may be reasons for the large disagreements reported. Finally, we comment on several issues concerning water flow rates in carbon nanotubes which may lead to some future research directions in this area.
The transport properties of water in nanopores are of both fundamental and practical interest. Water flow in CNTs has received significant attention over the last decade due to the importance of water and the unique properties of CNTs. Even though water is the most studied material on earth, its anomalous bulk properties are still surprising and properties of highly confined water are fascinating. On the other hand, CNTs possess unique properties such as having nanoscale diameters, ultra-smooth hydrophobic surfaces, and high aspect ratio. Hence, water flow in CNTs is a subject of intense research (see Refs. [52, 55, 109-115] and the references therein).

The flow rates of water in CNTs depend strongly on the slip length. Numerous experimental and simulation studies have been carried out in order to find the transport properties of water through CNTs [53-82, 116-125]. The flow enhancement results differ by 1 to 5 orders of magnitude compared to the classical no-slip flow predictions (see Fig. 6.1 and Table 6.1). For a cylindrical tube the flow enhancement is related to the slip length via

\[
E = \frac{Q_{\text{slip}}}{Q_{\text{no-slip}}} = \left( 1 + \frac{8L_s}{D} \right),
\]

where \( D \) is the diameter of the tube, (see Appendix A.3).

In 2005, Majumder et al. [53] reported a slip length of 39-68 \( \mu \)m for a 7 nm diameter CNT membrane in their experimental studies, which results in a flow enhancement of \((44-77) \times 10^3\). The following year, Holt et al. [54] studied even smaller nanotube membranes and found 0.14-1.4 \( \mu \)m slip length for diameters 1.3-2.0 nm. These two studies, along with a simulation study by Hummer et al. [61] in 2001, showing that water can be transported through a 0.81 nm diameter hydrophobic CNT, generated immense interest in the research community and hence numerous experimental and simulation studies have been undertaken, many with a special focus on the slip length. Most of the subsequent studies have found smaller slip lengths and some have found just around \(~10\) nm slip length for the same diameter range tubes. In experimental studies, Whitby et al. [56] found 113 to 177 nm slip length for a 44 nm diameter nanopipe. Sinha et al. [57] found no significant
Figure 6.1: Literature on the slip length of water in CNTs of diameter 0.81 to 10 nm. Our predictions are in red square symbols with a connected line. Notice the logarithmic scale on the y axis.

deviation from classical behaviour for 200-300 nm diameter tubes. As the diameter of the tube increases, the curvature effects on the fluid transport diminish. Using a 10 nm diameter CNT membrane Du et al. [121] found a slip length of 485 µm. Qin et al. [59] found just 53-8 nm non-monotonic slip length for 0.81-1.59 nm diameter tubes (for diameters 0.81, 0.87, 0.89, 1.10, 1.42, 1.52, 1.59 nm the corresponding slip lengths are 53, 44.6, 29.3, 56.6, 13.5, 8.4, 7.9 nm respectively). In 2011, in their extended studies, Majumder et al. [60, 117] confirmed their earlier results from 2005. Thus far in experimental studies slip lengths varying over 5 orders of magnitude for tubes of diameters 0.81 to 10 nm have been reported.

During this time many molecular dynamics simulation studies have also been carried out due the feasibility of conducting simulations compared to the difficulty
Table 6.1: Literature on the slip length of water in CNTs and on a planar graphene surface. E, S, and T stands for experiment, simulation, and theory respectively. The reader is suggested to refer the original papers for details.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Journal</th>
<th>Year</th>
<th>Diameter (nm)</th>
<th>Slip length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Kotsalis et al. [63]</td>
<td>2004</td>
<td>2.71, 4.07, 5.42</td>
<td>11, 13, 15</td>
</tr>
<tr>
<td>2</td>
<td>Majumder et al. [53]</td>
<td>2005</td>
<td>7</td>
<td>(39-68) $\times 10^3$</td>
</tr>
<tr>
<td>3</td>
<td>Holt et al. [54]</td>
<td>2006</td>
<td>1.3-2.0</td>
<td>140-1,400</td>
</tr>
<tr>
<td>4</td>
<td>Thomas et al. [69]</td>
<td>2008</td>
<td>1.66-4.99</td>
<td>110-30</td>
</tr>
<tr>
<td>5</td>
<td>Joseph et al. [68]</td>
<td>2008</td>
<td>2.22</td>
<td>556</td>
</tr>
<tr>
<td>6</td>
<td>Whitby et al. [56]</td>
<td>2008</td>
<td>44</td>
<td>113±9-177±15</td>
</tr>
<tr>
<td>7</td>
<td>Sinha et al. [57]</td>
<td>2009</td>
<td>200-300</td>
<td>negligible</td>
</tr>
<tr>
<td>8</td>
<td>Falk et al. [72]</td>
<td>2010</td>
<td>1-10</td>
<td>500-120</td>
</tr>
<tr>
<td>9</td>
<td>Thomas et al. [118]</td>
<td>2010</td>
<td>1.66-4.99</td>
<td>110-30</td>
</tr>
<tr>
<td>10</td>
<td>Qin et al. [59]</td>
<td>2011</td>
<td>0.81-1.59</td>
<td>53-8</td>
</tr>
<tr>
<td>11</td>
<td>Myers [82]</td>
<td>2011</td>
<td>1.4, 40</td>
<td>8.5, 35</td>
</tr>
<tr>
<td>12</td>
<td>Du et al. [121]</td>
<td>2011</td>
<td>4</td>
<td>260</td>
</tr>
<tr>
<td>13</td>
<td>Du et al. [121]</td>
<td>2011</td>
<td>10</td>
<td>$485 \times 10^3$</td>
</tr>
<tr>
<td>14</td>
<td>Babu et al. [73]</td>
<td>2011</td>
<td>0.81-5.42</td>
<td>6.5-1</td>
</tr>
<tr>
<td>15</td>
<td>Majumder et al. [60]</td>
<td>2011</td>
<td>7</td>
<td>(40±18-53±14) $\times 10^3$</td>
</tr>
<tr>
<td>16</td>
<td>Majumder et al. [117]</td>
<td>2011</td>
<td>7</td>
<td>(39-68) $\times 10^3$</td>
</tr>
<tr>
<td>17</td>
<td>Ma et al. [75]</td>
<td>2011</td>
<td>2.71</td>
<td>200-1100</td>
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<tr>
<td>18</td>
<td>Nicholls et al. [122]</td>
<td>2012</td>
<td>0.96</td>
<td>100</td>
</tr>
<tr>
<td>19</td>
<td>present work</td>
<td>2012</td>
<td>1.62-6.5</td>
<td>180-75</td>
</tr>
</tbody>
</table>

of performing nanoscale fluidic experiments. Kotsalis et al. [63] found just 11, 13, 15 nm slip lengths for 2.71, 4.07, 5.42 nm diameter tubes respectively. For 1.66-4.99 nm diameter tubes, Thomas et al. [69] found monotonically decreasing slip length from 105 to 30 nm. This slip length approached 30 nm for larger diameter tubes.

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and on a planar graphene surface. Later they found non-continuum (fluid structure dependent) and non-monotonic transport in the diameter range 0.83-1.66 nm with a slip length below 1000 nm [70]. They attribute the non-monotonic behaviour to the changing fluid structure. In an attempt to understand the mechanism of fast transport, Joseph et al. [68] found a slip length of 556 nm in a 2.17 nm diameter tube. Du et al. [121] found 260 nm slip length for a 4 nm diameter tube. Recently, Falk et al. [72] and Babu et al. [73] found monotonically decreasing slip length as the tube diameter increases, but with a different magnitude. Falk et al. [72] found 2.6 µm to 120 nm slip length for tubes of diameter 0.81 to 7 nm, whereas Babu et al. [73] found just 3 to 0.3 nm for 0.83 to 5.42 nm diameter tubes. For a 2.72 nm diameter tube, Ma et al. [75] found 200 to 1100 nm slip length depending on the contact angle by varying the water-carbon interaction strength. While studying the effects of defects on the nanotube, Nicholls et al. [122] found a slip length of 100 nm for a 0.96 nm diameter defect free nanotube. Theoretically, using a reduced viscosity in the depletion layer near the nanotube surface, Myers [82] found a monotonically decreasing flow enhancement (not the slip length) as the tube diameter increases. For a 40 nm diameter tube they predicted a 35 nm slip length. The maximum limit to the enhancement predicted by the model is 50 for a 1.4 nm diameter tube with a slip length of 8.57 nm. In a recent simulation study with tube diameter range 1.09 to 1.62 nm, Wang et al. [126] found just 10 to 15 flow enhancement which is equivalent to a slip length of just a few nm. Some simulation studies have immersed the CNT in a water bath or connected the CNT to two water reservoirs and then applied a pressure gradient. For a given tube diameter, these studies have found CNT length affecting flow enhancement and attribute this to the entrance and exit effects at the ends of the CNT [120, 122, 123]. In summary, simulation studies show slip lengths between ~1 to 1100 nm for the tube diameter range 0.81 to 7 nm.

Understanding the slip behaviour of water on a planar graphene surface is also an important problem. As mentioned before, as the diameter of the tube increases, the curvature effects diminish and the fluid confined in it behaves as it would confined in a planar graphene slit pore [36, 69, 72, 85]. Therefore, the slip length of water on a planar graphene surface serves as one extreme value of the slip length for CNTs. It is
found that the minimum slip length we can expect for any diameter carbon nanotube is equal to or larger than the slip length of water on a graphene surface [36, 69, 72], although a few studies have found increasing friction (slip is inversely proportional to the friction) as the tube diameter decreases [63-65]. They have attributed this to the increasing confinement leading to a high surface to volume ratio. In Table 6.1, we have also included the slip length of water on a planar graphene surface. As can be seen the data span the range $\sim 1$ to $80$ nm.

In this chapter, we address some of the issues which may be a reason for the disagreement in simulation results. We use EMD simulations to predict the interfacial friction between water and CNTs of various diameters. This friction coefficient is then used to determine the slip length. By taking this approach, we overcome the limitations of NEMD simulations. In NEMD simulations, for each tube we apply a range of external fields to determine the linear response of the fluid to the field and reliably extrapolate the results for the slip length to experimentally accessible pressure gradients.

### 6.1 Simulation details

We use flexible models for both water and CNTs. For water, we use the SPC/Fw model [86] which has been shown to produce the values of transport properties such as diffusion and shear viscosity of liquid water close to experimental values [89]. CNTs are modelled using the Tersoff-Brenner second generation reactive empirical bond order potential [46]. The interactions between the oxygen atoms of the water molecules and carbon atoms of the CNTs are modeled using the Lennard-Jones potential with the parameters of Werder et al. [81] All Lennard-Jones interactions are truncated at a distance of 1 nm. Electrostatic interactions are handled using the Wolf method [90, 91]. The temperature is maintained at 300K by applying the Nosé-Hoover thermostat to the CNT atoms, so that the heat produced by the viscous dissipation is conducted away through the wall. The overall water density in the tube is kept at $1000$ kg/m$^3$. At each state point, up to 20 independent simulations are carried out for up to 20 ns depending on the tube size and external field, using
6. How fast does water flow in carbon nanotubes?

the leap-frog integration algorithm with a time step of $\sim 1$ fs. We have simulated nine single walled water filled CNTs of diameter 1.62 to 6.5 nm with vacuum outside.

6.2 Results

Here we use the cylindrical geometry interfacial friction method to find the friction coefficient between water and CNTs of various diameters using equilibrium simulations. In brief, for each tube we choose a cylindrical fluid slab (annulus) of average width $\Delta$ of one molecular diameter adjacent to the CNT surface, i.e. $\Delta = 0.316$ nm. After equilibration, we evaluate the the CM velocity of the slab $u_{\text{slab}}(t)$ and wall-slab shearing force $F_z(t)$ in the axial direction, here the $z$ direction. Using these two quantities, we evaluate the slab CM velocity autocorrelation function $C_{uu}(t) = \langle u_{\text{slab}}(0)u_{\text{slab}}(t) \rangle$ and the slab velocity-force cross correlation function $C_{uF_z}(t) = \langle u_{\text{slab}}(0)F_z(t) \rangle$. The friction coefficient is then found via the relation $\tilde{C}_{uF_z}(s) = -\tilde{\zeta}(s)\tilde{C}_{uu}(s)$ in Laplace space. We then find the slip length for each CNT by dividing the shear viscosity of bulk water by the corresponding friction coefficient of the tube [36, 72] (see the discussion section on shear viscosity).

In non-equilibrium Poiseuille flow simulations, we drive the fluid by applying a range of constant external fields to all the atoms of water molecules. We fit the streaming velocities to a quadratic equation $u_z(r) = ar^2 + b$ by constraining the fit such that the parameters satisfy the shear viscosity of bulk water. Due to the high slip and small velocity difference from the centre to the solid surface, constraining the fit is necessary [69, 106]. Using the fitting parameters the slip length is found from its definition in Eq. (2.59).

In Fig. 6.2, we plot the slip velocity for each tube from the NEMD data as a function of external field at the low fields we have used. For each tube, we fit the data to a straight line with zero $y$-axis intercept (slip velocity). Even though these fields are equivalent to pressure gradients 2-3 orders of magnitude higher than those experimentally accessible, the linear increase in the fluid slip velocity with external field suggests that the results can be reliably extrapolated down to fields...
corresponding to experimentally accessible pressure gradients. As the difference in fluid velocity from the centre to the wall is very small, this slip velocity can be approximated to the fluid average velocity in the tube.

![Image](image_url)

Figure 6.2: The slip velocity against the external field in the low field range for different diameter CNTs. The continuous lines are linear fits to the data, with zero intercept on the $y$-axis.

In Fig. 6.3, we plot the slip length for each tube from NEMD data as a function of external field. At low fields, where the fluid mean velocity is much smaller than the fluid thermal velocity, the slip length shows large uncertainties as expected. As we increase the field, the uncertainties in the fluid streaming velocity data decrease, as do the uncertainties in the slip length. In the low field range, the slip length is constant for each tube within statistical uncertainty. At a given low field, smaller diameter tubes show high slip length compared to the wider diameter tubes and the linear regime (where the slip length is constant) extends over a larger range of external field for smaller diameter tubes compared to the wider diameter tubes.
With increasing field, wider diameter tubes begin to show the non-linear behaviour for relatively small fields compared to the smaller diameter tubes. In Fig. 6.3, we also have included the slip length of water on a planar graphene surface [106]. As can be clearly seen, with increasing tube diameter, the water slip behaviour approaches what it would if confined in a planar graphene slit pore (tube of infinite diameter). Thus, with increasing tube diameter, both the confinement and curvature effects become negligible, as one expects.

Figure 6.3: The slip length against external field for different diameter CNTs. The plot also includes the slip length of water on a planar graphene surface [106].

In Fig. 6.4 we plot the same slip length data as a function of tube diameter at different external fields. The plot also includes open red circles with a connected line, which we explain in the following paragraph.

Using the slip modified Poiseuille flow Navier-Stokes solution (see Eq. (6.3) below) one can derive the following expression for slip length and interfacial friction between
Figure 6.4: The slip length against the diameter of CNTs at different external fields. The open red circles with a connected line are slip lengths measured using the fitting procedure described in the text. The black line at 60 (± 6) is the slip length of water on a planar graphene surface [106].

water and CNT [106]

\[ L_s = \frac{4m\eta_0}{\rho D} \quad \text{and} \quad \xi_0 = \frac{4m}{\rho D}, \]  

(6.2)

where \( \rho \) is the fluid density and \( m \) is the slope obtained by plotting the slip velocity against the external field, in the low field range (linear regime). As extrapolating the slip length to linear regime fields from data in Fig. 6.3 becomes unreliable, we have used the following method to determine the slip length for each tube. For a given tube, we combine the slip velocity data at different external fields to get a reliable slip length. The slope \( m \) is determined from the linear fits to the slip velocity data in Fig. 6.2. The open red circles with a connected line in Fig. 6.4 represent the slip
length determined by this method, and as can been seen it overlaps with the slip length data at low external fields within the statistical errors [106].

Slip lengths and flow rate enhancements predicted from EMD and NEMD are plotted as a function of CNT diameter in Fig. 6.5. Good agreement between both of the methods can be seen in the plot. The NEMD method required an order of magnitude higher computational time, as the simulations needed to be done at different external fields to check the linearity and to predict the slip length reliably by combining the data at different external fields.

Figure 6.5: The slip length predicted using the EMD and NEMD methods and flow enhancement (E) against the diameter of CNTs. The black line at 60 (± 6) is the slip length of water on a planar graphene surface [106].
The slip length is high in smaller diameter tubes and as the tube diameter increases, the slip length decreases monotonically and asymptotically approaches a constant value, which is equal to the slip length on a planar graphene surface [106]. This trend is in qualitative agreement with the findings in Refs. [36, 69, 72]. Equivalently, the flow enhancement is very high in narrow diameter tubes and as the tube diameter increases, the flow enhancement decreases monotonically and the flow rates approach the Navier-Stokes prediction with the no-slip boundary condition for micrometer diameter tubes. For wider tubes of diameter in the micrometer range, the effect of slip on flow enhancement is negligible. Notice, the slip length still remains around 60 nm, but its effect on enhancement becomes negligible, see Eq. (6.1).

For a long time slip has been a controversial subject. Tubes in the micrometer diameter range were used in earlier experiments [4]. For such relatively wide tubes the effect of nanometer scale slip length on flow rates is negligible, and hence the results have supported the no-slip boundary condition, even if slip is present. These effects only become significant in nanometer diameter range pores.

We now compare our predictions with experimental results, see Fig. 6.1 and Table 6.1. For tubes of diameter 1.63 to 2.17 nm, our predicted slip length is in the range of 180 to 145 nm, which is in agreement with the lower end of results by Holt et al. [54], who predict 140 to 1400 nm slip length for tubes of diameter 1.3 to 2.0 nm. For similar diameter tubes, the results of Qin et al. [59] are just below 10 nm. We are unable to study tubes of larger diameter than those used here due to computational limitations. Our results suggest only around 60 nm slip length for tubes of diameter 7 nm and 10 nm and above, for which Majumder et al. [53, 60, 117] measure slip lengths four orders of magnitude higher (3.9 to 6.8 \( \mu \)m) and Du et al. [121] measured similar (485 \( \mu \)m) slip lengths. For a 44 nm diameter carbon nanopipe Whitby et al. [56] measured 113 to 117 nm slip length. For tubes of diameter 200-300 nm, our results suggest a flow enhancement of 2.6 to 3.4, which is close to a factor of 2 found by Sinha et al. [57].

Comparing our predictions with other simulation results, the variation of slip length with CNT diameter is in qualitative agreement with the predictions by Falk
et al. [72] and Thomas et al. [69] but quantitatively differ by a factor of 2. For tubes of diameter 1 to 7 nm Falk et al. predicted 500 to 120 nm slip length, and Thomas et al. predicted 125 to 30 nm slip length for tubes of diameter 1.66 nm to 4.99 nm, whereas we predict 180 to 75 nm slip length for tubes of diameter 1.66 to 6.5 nm. Other simulation results are scattered with around an order of magnitude deviation from our predictions. Again we refer to Fig. 6.1 and Table 6.1. Some variation in simulation results is accounted for by the differences in the molecular models used to simulate the system and the simulation details.

6.3 Discussion

We now briefly comment on several important issues in relation to the computation of flow rates of water in CNTs (and in general fluid flow rates in nanopores). We hope this will point to future research directions in this area.

The two key concepts in predicting nanofluidic flow rates are (i) the fluid effective shear viscosity and (ii) the fluid-solid slip length (boundary condition). Both of these concepts are usually defined using the uniform fluid density hypothesis, which breaks down at the nanoscale. From the macroscale down to around 4 nm channel width (around 10 fluid molecular diameters), the fluid shear viscosity and the predicted quadratic velocity profiles across the channel do not show any significant variation [17, 107]. Below this level of confinement the breakdown of the constant density assumption becomes significant. At what scale the classical hypothesis of constant density and constant viscosity breaks down is a general question and the transition is very weak and depends on the nature of both the fluid and solid.

For the effective shear viscosity of water, different studies have found increasing, decreasing and non-monotonic variation with respect to the CNT diameter [59, 69, 71, 73, 78, 79, 101, 102]. Some publications report less than a factor of 2 variation [59, 69] and others report variation of 1 to 2 orders of magnitude [71, 73]. At this high level of confinement, the fluid becomes highly inhomogeneous, showing density oscillations across the whole channel, which is likely to result in
position dependent transport properties and non-local response functions. Hence, the transport coefficients such as shear viscosity become position dependent across the channel and for a complete description a non-local viscosity kernel in space is needed [11, 99, 100]. The discrepancy in the shear viscosity of water confined in CNTs could be due to the breakdown of existing methods of defining and measuring viscosity for such tightly confined fluids, which are in general devised for bulk fluids.

The slip length of water has been reported even for 0.81 nm diameter tubes, which can accommodate only a single water molecule across the tube diameter. In such a 1D pore, water forms a single file molecular chain, and the fluid velocity profile is no longer well defined [17, 107]. The relation between the slip length and flow enhancement (Eq. (6.1)) is valid only when the classical Navier-Stokes quadratic velocity profile shifts upwards by the slip velocity (see Eq. (6.3)). Eq. (6.1) and the definition of slip length itself breaks down when the inhomogeneity is strong. In this case, it is more useful to discuss transport through the pore in terms of permeability [127] rather than slip flow.

Molecular dynamics simulations use empirical potentials to model the system and hence the reliability of any simulation results largely depends on the potential model and the parameters. Even though the water molecule is relatively simple, the collective properties are very complex and hence several models have been proposed for water (e.g. Guillot [128] listed 46 models), each one predicting certain properties correctly under certain conditions only. Most of these models are parameterized using the bulk water experimental properties of interest. Therefore, the validity of these models at the nanoscale is questionable, which may be another reason for the large gap between experimental and simulation flow rates.

The interaction strength between water and wall carbon atoms is also very important. Hummer et al. [61], found that even a small change in the water oxygen-carbon interaction strength results in drying-to-wetting transitions of water in CNTs of diameter 0.83 nm. Recently, Melillo et al. [125] also found that a 0.075 kcal/mol change in the interaction strength can effect the flux by a large amount. Werder et al. [81] studied the contact angle of water on a graphite surface with varying inter-
action strength. Most of the subsequent simulation studies use the parameters from their study, which reproduce the experimental contact angle of water on a graphite surface. How well these parameters can capture the interaction between water and CNTs of varying diameter is yet to be studied.

Modelling the electrostatic interactions is also an important issue. The Ewald summation method was developed for systems that are periodic in 3 directions [129] and later it was extended for systems that are periodic in 2 directions (e.g. fluids confined in slit pores) [130]. In systems such as water confined in CNTs, the system is periodic only in 1 direction. For very narrow tubes, the applicability of the Ewald technique to handle electrostatics has yet to be examined in detail. Other methods such as the Wolf [69, 90] and smooth cut-off [63, 74, 81, 131] are also often used for water confined in CNTs. In the literature, some spurious effects resulting from mishandling of the electrostatic interactions for water-CNT systems have also been shown [132-134].

Thermostating the system is another important issue [25]. When a fluid is confined in a pore within a solid pore, the natural way to maintain the desired temperature for the fluid is to thermostat the solid at that temperature and keep the fluid unthermostated, so that the heat generated by viscous flow of the fluid is conducted away through the fluid-solid interface. In this way the intrinsic dynamics of fluid atoms are unaffected. Thermostating the fluid directly to maintain the desired temperature can affect the results depending on the property of interest (e.g. as mentioned before, the slip length is very sensitive to the fluid velocity gradient (strain rate) at the wall) [69, 106]. For graphene and CNTs, the Tersoff-Brenner potential is widely used when predicting their structural, elastic, and mechanical properties. This is a non-additive pair potential and takes the nature of chemical bonding and environment into account in a complex way. In nanofluidic simulation studies, allowing flexibility of the tube by using the REBO potential increases the computational time by an order of magnitude [135]. To avoid this, and for simplicity, most simulation studies keep the carbon atoms of the nanotube fixed and thermostat the water directly to maintain the desired temperature. As mentioned above, this may have an undesired artificial effect on the streaming velocity profiles.
Sokhan et al. [83] found a 20% increase in the flux/flow rates for methane with flexible CNTs compared to rigid nanotubes. Care must be taken in applying the thermostat depending on the sensitivity of the property of interest. Proposing a simplified potential (and parameters) for CNTs by comparing against the REBO potential, where the properties of interest are of fluids, would overcome this problem.

Some limitations of NEMD simulations also contribute to the discrepancy in simulation results. The thermal velocity of water at room temperature is approximately 340 m/s. As NEMD simulations can generally be done only for a few nanoseconds with a time step of around a femtosecond, the pressure gradients or external fields used are 4-5 orders of magnitude higher than the experimental values in order to have the fluid mean velocity comparable to the thermal velocity i.e., to have a reasonable signal to noise ratio [4]. The typical mean fluid velocities in experiments are smaller than 0.01 m/s. At such high fields generally used in simulations, the linearity of Eq. (2.59) may not hold and the flux/slip length determined may not correspond to the value found under experimental conditions. As shown previously the slip length remains constant [36] (flux increases linearly with pressure gradient) [80] in the low field/shear rate range, above which it increases rapidly with the field [85]. As one does not have any prior knowledge about the extent of the linear regime, a few test simulations should be done to check for a linear response to the field. The field should be low enough to ensure a linear response and high enough to get a reasonable velocity signal. Moreover, an external field, which gives the limiting slip for a tube, may not give the limiting slip length for a different diameter tube for the same fluid and solid [36]. For very large slippage, NEMD simulations cannot resolve the small difference in velocity between the centre of the channel and the wall [106].

As shown before, the slip length is very sensitive to the fluid strain rate at the wall, and using NEMD one can not predict the slip length reliably when the slip length is high.

To elaborate on this point, we note that water flow in carbon nanotubes is often described as a plug flow, meaning a flat velocity (Euler flow) profile across the tube.
On the other hand, the slip modified Poiseuille flow solution is

\[ u_z(r) = \left( \frac{\rho F_e}{4\eta_0} \right) (R^2 - r^2) + u_s. \]  

Therefore, the only difference compared to the no-slip solution is the slip velocity added to the no-slip boundary solution, i.e., the effect of slip is only an upward shift in the velocity profile. The velocity difference from centre to the wall (proportional to the external field) still remains the same and hence so too does the curvature of the flow profile. Compared to the fields used to drive the fluid confined between Lennard-Jones walls (which are normally attractive and highly corrugated resulting in a small or zero slip) [4] for water in nanotubes we use 1 to 2 orders of magnitude smaller fields as the slip is high which results in high mean velocities. This small field decreases the velocity difference of the fluid from the centre to the wall proportionately. As mentioned above, one can not resolve the velocity difference below \( \sim \) a few m/s using NEMD. These two reasons make the velocity profiles apparently look flat cross the channel (plug like). Therefore describing the velocity profile as plug-like can be misleading sometimes for very high slip systems as water in CNTs.

The effect of a change in the shear viscosity on flow enhancement is not clear. A decrease in effective shear viscosity due to the confinement may or may not increase the average flow rate. A decrease in effective shear viscosity increases the fluid velocity gradient at the wall, to which the slip length is inversely proportional. So, a decrease in effective shear viscosity does not necessarily mean increase in flow enhancement when the pressure gradient is kept constant.

The uncertainty in defining the actual tube diameter (available volume) becomes comparable to the tube diameter itself for very narrow tubes. The one atomic diameter uncertainty (0.34 nm van der Waals size of the carbon atoms) in the tube diameter makes a significant difference in the measured flow enhancement for small diameter tubes. For example, if the distance between the centre of mass of the opposite carbon atoms (\( D \)) on a CNT is 0.81 nm, defining the tube diameter as 0.81 nm has a 0.34 nm uncertainty, which is 42%. Different variants in defining the tube diameter are \( D \), \( D-0.34 \), \( D-(0.34+\sigma_O)/2 \), where \( \sigma_O \) is the van der Waals diameter of
the oxygen atom in a given water model and sometimes the wall positions are taken from where the density of fluid has a finite value.

The issue of entrance and exit effects which resulted in a tube length dependent flow enhancement also has to be examined in detail [120, 123, 122].

Finally, as defined sometimes, the slip length is not the additional length at which the no-slip boundary condition holds, neither is it the length from the wall at which the extrapolated velocity profile reaches zero. The slip length is the additional length from the wall at which the tangent to the fluid velocity at the wall is extrapolated to reach zero relative tangential velocity between fluid and solid. As the slip length is very sensitive, specifying the boundary condition and quantifying the flow enhancement using the slip length should be done carefully.

6.4 Conclusion

To conclude, we have predicted the slip length of water in CNTs using equilibrium simulations to compute the interfacial friction of water in CNTs and extensive field driven nonequilibrium simulations. Due to the high sensitivity of the computed slip length to the streaming velocity profiles, computing the slip using the NEMD methods is unreliable if it is not done with sufficient care and it is computationally intensive. We found a monotonically decreasing 180 to 75 nm slip length for tubes of diameter 1.66 to 6.5 nm. The slip length is high in small diameter tubes where the curvature and confinement effects are large. As the diameter of the tube increases, the slip length decreases monotonically and it asymptotically approaches a constant value (60 ± 6 nm) around the slip length of water on a planar graphene surface. In other words, the flow enhancement is very high in narrow tubes and as the diameter of the tube increases, the flow rate slowly approaches the classical Navier-Stokes prediction with the no slip boundary condition (and no significant enhancement). For tubes of diameter 1.66 to 6.5 nm our results suggest a flow enhancement of around 870 to 90. For a 1.0 μm diameter tube, the slip length of 60 nm results in only an enhancement of 1.5. The effects of both confinement and curvature on slip
become negligible at around $\sim$10 nm, and the slip length becomes independent of the tube diameter around and above $\sim$10 nm, which is still in the nanoscale regime. We have briefly reviewed the literature on flow rates of water in CNTs highlighting the many pitfalls related to this problem, and suggested some future research directions that will lead to a better understanding of water transport in CNTs.
Chapter 7

Conclusion and outlook

In this chapter we draw some conclusions and suggest some future research directions.
7.1 Conclusion

In the past two decades the hydrodynamic boundary condition has become an important research problem in the field of nanofluidics due to the revolutionary advancement in nanoscale science and technology. This interest is driven by both the desire to understand the nature of fluid flow in nanopores such as synthetic CNTs and biological aquaporin membranes and in order to have a precise access and control in nanofluidic devices which are an integral part of nanotechnological devices.

In this thesis we have used a new method to calculate the intrinsic interfacial hydrodynamic friction coefficient between a fluid and solid based on a statistical mechanics approach. This friction coefficient is then used to determine the slip and boundary condition at a fluid-solid interface as proposed by Navier. The slip length is in turn used to calculate the flow rates and flow enhancement of fluids in nanopores.

In chapter 2 we presented the method to calculate the interfacial friction at a fluid-solid planar interface. The derivation is based upon relevant constitutive equations for solid-fluid friction and fluid viscous forces. These forces are evaluated by forming equilibrium time correlation functions for a fine-grained fluid slab adjacent to the walls. The friction coefficient is then extracted from these correlation functions, and hence the slip length (also the slip velocity) for the fluid to a very high accuracy. Using the same constitutive equation in conjunction with integral boundary condition we derive the slip length for Poiseuille and Couette flow and verified that this slip length approaches the Navier slip length in the limit of zero slab width. We then extended the model for both the friction coefficient and the slip length to a cylindrical fluid-solid boundary.

In chapter 3 we applied the method to argon and methane flow in planar graphene slit pores. The no-slip boundary condition is found to be clearly violated owing to the ultra-smoothness and lyophobicity of the graphene surface. The friction coefficient between these fluids and graphene is found to be an order of magnitude smaller than the friction between the same fluids and the molecular Lennard-Jones crystal walls.
Conclusion and outlook

generally employed in computer simulations. As a result of the slip the flow rates are an order of magnitude higher compared to classical hydrodynamic no-slip boundary condition predictions. As the interaction strength between methane and graphene is higher than the argon-graphene interaction strength, the slip length is found to be higher for argon than methane. So at the nanoscale the boundary condition is a combined property of both fluid-fluid and fluid-solid interactions. Slip is found to be independent of the flow type, confirming its intrinsic nature. The slip length remained constant, i.e. independent of the external field and shear rate for low to moderate values, after which the slip length is found to diverge as the field or shear rate is increased. At such high fields the Navier linear slip model breaks down. The EMD method predictions are in excellent agreement with NEMD simulation results in the linear regime. The EMD method is shown to compute the limiting or minimum slip length for a given fluid and solid surface without the need to do cumbersome NEMD simulations for various shear rates or external fields and their extrapolation to experimental conditions. The EMD method is shown to be both computationally highly efficient and superior in predicting the slip compared to the conventional NEMD methods of estimating the slip.

In chapter 4 we aimed at accurately quantifying the slip length of water on a planar graphene surface, the knowledge of which would be useful in understanding the unusual higher flow rates of water in CNTs (Chapter 6). Slip is found to be extremely sensitive to the NEMD velocity profiles, and the NEMD results are shown to suffer from large statistical errors. As a result of high slip, the water velocity from the center of the channel to the graphene walls is too small to be measured using NEMD simulations within statistical errors. This could even result in inverted parabola streaming velocity profiles in the case of Poiseuille flow and negative velocity gradient profiles in the case of Couette flow for which the slip length can not be defined. So for high slip systems, the generally used NEMD methods are found to be inaccurate and therefore unreliable. On the other hand, one can predict such a highly sensitive non-equilibrium phenomenon with our equilibrium simulation method accurately and computationally efficiently. We have therefore shown that great care needs to be taken in analyzing the results of NEMD slip data for high-slip systems. We
suggest some procedures to increase the reliability of the slip estimates. We found that the linear regime of the slip length shifts to lower fields/shear rates as the slip between the fluids and solids is increased for different systems.

In chapter 5 we have studied the curvature dependent friction coefficient by applying the EMD method to methane flow CNTs. The friction coefficient (or the slip length) is found to increase (or decrease) monotonically as the tube diameter increases and approaches a constant value, which is equal to the friction coefficient (or the slip length) on a planar graphene surface. Hence, the flow enhancement increases as the diameter of the tube is decreased. We found good agreement between our curvature dependent friction predictions and direct NEMD simulations.

In chapter 6 we have attempted to resolve the highly debated issue of flow rates of water in CNTs, the results of which are scattered over 1 to 5 orders of magnitude in literature. We have studied tubes of diameter 1.66 to 6.5 nm for which the slip length is monotonically decreased from 180 to 75 nm. As the diameter of the tube decreases the hydrogen bonding in the tube axial direction, and the fluid structure along the radial direction, becomes stronger. This resulted in the high slip length in small diameter CNTs. As the diameter of the tube increases, the confinement and curvature effects decreases which results in a monotonically decreasing slip length. This slip length approaches a constant value (60 ± 6 nm) around the slip length of water on a planar graphene surface. The flow rate is 3 orders of magnitude higher than the Navier-Stokes no-slip boundary prediction for the smallest tube (1.66 nm diameter) we have studied. The effect of slip on flow enhancement decreases as the diameter of the tube is increased, and for a 1.0 µm diameter tube the slip length of 60 nm results in only an enhancement of 1.5. Due to the high sensitivity of the slip length to the streaming velocity profiles, computing the slip using NEMD methods is unreliable if it is not done with sufficient care. Moreover it is computationally intensive. We have highlighted the many pitfalls related to this problem, and suggested some future research directions that will lead to a better understanding of water transport in CNTs.

From our findings in this thesis, the proposed EMD method gives the linear
regime slip length which corresponds to experimental condition flow rates, which is otherwise cumbersome to find using NEMD simulation techniques. With a single set of EMD simulations, one can determine the interfacial friction coefficient between the fluid and solid, and from that the slip length, and overcome the limitations of NEMD methods. The method predicts the non-equilibrium slip phenomenon from equilibrium simulation calculations. The proposed method is robust, general and can be used to find the slip and boundary condition accurately at any fluid-solid interface.

The friction coefficient and the slip length methods used in this thesis are valid only when the channel width/pore diameter is at least 4 to 5 molecular diameters. The model breaks down for pores of diameter around just 1 nm, where the fluid is only 2 to 3 layers inside the pore without any bulk region and leaving the slip length and viscosity definitions completely invalid. Also, when the fluid inside the pore is in a very dilute gaseous phase, the density oscillations near the pore can be profound and thus further invalidate the model.

7.2 Outlook

There are still several gaps in our understanding of the behaviour of fluid transport in nanopores. Theoretically and computationally some models and techniques need to be improved or rebuilt if necessary.

As discussed in the thesis, the two important parameters in determining the nanofluidic flow rates are fluid (effective) shear viscosity and the boundary condition, i.e. the slip at fluid-solid interface. In this work we shed light on the second issue and our models have shown to predict the interfacial friction and slip accurately. The effective shear viscosity for a confined fluid is still an open question. Theoretically accounting for non-local effects on shear viscosity is very challenging, before any computational models can be used to quantify it.

The flow enhancement expressions used in this thesis assume a quadratic velocity
profile which may not be true for very narrowly confined fluids. Therefore new models have to be derived to account for the effect of non-quadratic velocity behaviour on flow enhancement. Ewald summation based calculations of electrostatic interactions for highly confined fluids have to be reexamined. The effect of thermostating the fluid directly needs to be quantified accurately. The water models which have been parameterised based on the bulk water properties need to be re-estimated, which we believe is also a reason for the gap between experimental and simulation findings of flow rates. The interaction parameters between fluids and solids should also be improved as a small change in them has been shown to result in a large effect on the transport of water in CNTs. Our knowledge of entrance and exit effects at nanopores is still at a preliminary stage. The small uncertainties such as defining the channel width or tube diameter, which we ignored at the macro-scale become important and need to be considered for nanopores.

It is very difficult to develop theoretical methods that can predict slip without any input from simulations. Many parameters which can be safely neglected at the macroscale can play an important role at the nanoscale, including the structure and even the orientation of the wall. Such parameters can affect the slip and fluid flow properties in nanopores in a profound manner.

There is, therefore, plenty of room for future research in understanding very narrowly confined fluid behaviour.
Appendix A

Appendix

A.1 Wolf Method

Wolf et al. [90] found that the cutoff artifacts in dealing with the electrostatic interactions are a result of the net charges within the cutoff sphere caused by a finite numbers of charged molecules (within the sphere). They proposed an expression for the damped Coulomb potential which overcomes the two problems encountered in truncating the interactions at a cutoff distance $r_c$ that involves (i) local charge neutrality within the sphere of radius cutoff distance $r_c$ and (ii) shifting the force, so that both the potential and force go to zero smoothly at the cutoff distance $r_c$ [90].

The Wolf method is computationally more efficient, conceptually more transparent and easier to implement in practice, compared to the traditional Ewald sum method [87, 91]. For simulations which are computationally demanding the Wolf method is desirable. We note that the Wolf method also has its own limitations, for example, in simulating liquid-vapor co-existence [131, 136].

The potential energy and the magnitude of force are expressed as follows in the
Wolf method,

\[
U(r_{ij}) = \begin{cases} 
q_i q_j \left[ \frac{\text{erfc}(\alpha r_{ij})}{r_{ij}} - \frac{\text{erfc}(\alpha r_c)}{r_c} \right] + \left( \frac{\text{erfc}(\alpha r_c)}{r_c^2} + \frac{2\alpha}{\pi^{1/2}} \exp(-\alpha^2 r_c^2) \right) (r_{ij} - r_c) & r_{ij} < r_c \\
0 & \text{otherwise}
\end{cases} \tag{A.1}
\]

\[
F(r_{ij}) = \begin{cases} 
q_i q_j \left[ \frac{\text{erfc}(\alpha r_{ij})}{r_{ij}^2} + \frac{2\alpha}{\pi^{1/2}} \text{erf}(-\alpha^2 r_{ij}^2) \right] + \left( \frac{\text{erfc}(\alpha r_c)}{r_c^2} + \frac{2\alpha}{\pi^{1/2}} \exp(-\alpha^2 r_c^2) \right) & r_{ij} < r_c \\
0 & \text{otherwise}
\end{cases} \tag{A.2}
\]

In this work we have used the parameters \( \alpha = 0.018 \text{ nm}^{-1} \) and the cutoff \( r_c = 1.0 \text{ nm} \) [87, 91, 136].

A.2 Tersoff-Brenner potential

In materials physics, the covalent bonds between molecules cannot be described by a simple two body pair potential. For example, in hydrocarbons, the difference between single and double bonds often is important. Also, in some phenomena the chemical bonds may break. This means that the interatomic potential model has to be able to handle bond breaking and making. These models which can handle chemical reactions are called “reactive interatomic potentials”. Furthermore, to be fully transferable the models should be able to also describe all the phases of the material in a single parametrization [18].

Abell derived the first of this kind of potential based on chemical pseudopotential theory. Later Tersoff [137] and Brenner et al. [46] developed the Reactive Empirical Bond Order (REBO) potential, which is quite different from other classical potentials in that it is explicitly a four-body potential with implicit many body interactions. It was designed to be highly transferable and has proven to be reasonably accurate in describing structural, elastic, mechanical and dynamical properties of hydrocarbons, graphite, diamond, and CNTs.
The total chemical binding energy $E_b$ in a system is given by,

$$E_b = \sum_i \sum_{j(i)} [(V^R(r_{ij}) - b_{ij} V^A(r_{ij}))], \quad (A.3)$$

where $r_{ij}$ is separation distance between bonded atoms $i$ and $j$. The pair additive interaction functions, $V^A(r)$ represent the attraction between valence electrons of bonded atoms and $V^R(r)$ represent all interatomic repulsions (core-core, etc),

$$V^R(r) = f^c(r) \left(1 + \frac{Q}{r}\right) A \exp(-\alpha r), \quad (A.4)$$

$$V^A(r) = f^c(r) \sum_{n=1}^3 B_n \exp(-\beta_n r). \quad (A.5)$$

The repulsive energy goes to infinity as the interatomic distance approaches zero. The function $f^c(r)$ takes the values between zero and one, and ensure that the interactions include nearest neighbors only

$$f^c_{ij}(r) = \begin{cases} 
1 & \text{for } r < D_{ij}^{\min} \\
1 + \cos \left(\frac{r - D_{ij}^{\min}}{D_{ij}^{\max} - D_{ij}^{\min}}\right) & \text{for } D_{ij}^{\min} < r < D_{ij}^{\max} \\
0 & \text{for } x > D_{ij}^{\max}
\end{cases}, \quad (A.6)$$

where $D_{ij}^{\max} - D_{ij}^{\min}$ defines the distance over which the function goes from one to zero.

The main feature of the potential is the bond order term $b_{ij}$, which describes the instantaneous hybridization of the atomic bonding orbitals and has the following form [46],

$$b_{ij} = \frac{1}{2} \left[ b^\sigma_{ij} - b^\pi_{ji} + b^\pi_{ij} \right] + b^\pi_{ij}. \quad (A.7)$$

The functions $b^\sigma_{ji}$ and $b^\pi_{ji}$ describe the local coordination and bond angles of
atoms $i$ and $j$. The function $b_{ij}^\pi$ is sum of a further two functions,

$$b_{ij}^\pi = \pi_{ij}^{RC} + b_{ij}^{DH} .$$  \hspace{1cm} (A.8)

The function $\pi_{ij}^{RC}$ depends on whether a bond has a radical character and is part of a conjugated system. The second function $b_{ij}^{DH}$ describes the dihedral angle between double bonded carbon atoms.

The analytic forms the of the above functions are given below

$$b_{ij}^\pi = \left[ 1 + \sum_{k(\neq i,j)} f_{ik}(r_{ik})G(\cos(\theta_{ijk})) \exp^{\lambda_{ijk}} + P_{ij}(N_i^C, N_j^H) \right]^{-1/2} ,$$  \hspace{1cm} (A.9)

where $P$ represents a bi-cubic spline and the quantities $N_i^C$ and $N_i^H$ represents the number of carbon and hydrogen atoms, respectively, that are neighbors of atoms $i$

$$N_i^C = \sum_{k(\neq i,j)} f_{ik}^C(r_{ik}) ,$$  \hspace{1cm} (A.10)

$$N_i^H = \sum_{l(\neq i,j)} f_{il}^H(r_{il}) .$$  \hspace{1cm} (A.11)

The function $G(\cos(\theta_{ijk}))$ modulates each nearest neighbor (bonds between atoms $i$ and $j$ and between $i$ and $k$) to the bond-order strength.

The function $\pi_{ij}^{RC}$ describes the influence of radical energetics and $\pi$-bond conjugation on the bond energies,

$$\pi_{ij}^{RC} = F_{ij}(N_i^t, N_j^t, N_{ij}^{conj}) ,$$  \hspace{1cm} (A.12)

$$N_i^t = N_i^C + N_i^H ,$$  \hspace{1cm} (A.13)
\[ N_{ij}^{\text{conj}} = 1 + \left[ \sum_{k(\neq i, j)} \text{carbon} f_{ik}^c(r_{ik}) F(X_{ik}) \right]^2 + \left[ \sum_{l(\neq i, j)} \text{carbon} f_{jl}^c(r_{jl}) F(X_{jl}) \right]^2, \quad (A.14) \]

\[ F(x_{ik}) = \begin{cases} 
1 & x_{ik} < 2 \\
[1 + \cos(2\pi(x_{ik} - 2))] / 2 & 2 < x_{ik} < 3 \\
0 & x_{ik} > 3 
\end{cases} \quad (A.15) \]

\[ x_{ik} = N_k^t - f_{ik}^c(r_{ik}) \cdot (A.16) \]

Finally, the dihedral term is given by

\[ b_{ij}^{DH} = T_{ij}(N_i^t, N_j^t, N_{ij}^{\text{conj}}) \left[ \sum_{k(\neq i, j)} \sum_{l(\neq i, j)} (1 - \cos^2(\theta_{ijkl})) f_{ik}^c(r_{ik}) f_{jl}^c(r_{jl}) \right] \quad (A.17) \]

\[ \theta_{ijkl} = e_{jik} e_{ijl} \quad (A.18) \]

\( T_{ij}(N_i^t, N_j^t, N_{ij}^{\text{conj}}) \) is a tricubic spline, \( e_{jik} \) and \( e_{ijl} \) are unit vectors in the direction of the cross products \( R_{ji} \times R_{ik} \) and \( R_{ij} \times R_{jl} \) where the \( R \) vectors connect the subscripted atoms.

**Table A.1: Parameters for the carbon-carbon pair terms in REBO potential.**

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<tr>
<td>( B_1 )</td>
<td>12 388.791 977 98 eV</td>
<td>( \beta_1 )</td>
<td>4.720 452 3127 \text{Å}^4</td>
<td>( Q )</td>
<td>0.313 460 296 0833 \text{Å}^4</td>
<td>( D_{\text{min}} )</td>
<td>1.7</td>
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<tr>
<td>( B_2 )</td>
<td>17.567 406 465 09 eV</td>
<td>( \beta_2 )</td>
<td>1.433 213 2499 \text{Å}^4</td>
<td>( A )</td>
<td>10 953.544 162 170 eV</td>
<td>( D_{\text{max}} )</td>
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</tr>
<tr>
<td>( B_3 )</td>
<td>30.714 932 080 65 eV</td>
<td>( \beta_3 )</td>
<td>1.382 691 2506 \text{Å}^4</td>
<td>( \alpha )</td>
<td>4.746 539 060 6595 \text{Å}^4</td>
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</table>
Table A.2: Parameters for the angular contribution to the carbon bond order.

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<th>$\theta$ (rad)</th>
<th>$G(\cos(\theta))$</th>
<th>$\frac{dG}{d(\cos(\theta))}$</th>
<th>$\frac{d^2G}{d(\cos(\theta))^2}$</th>
<th>$\gamma(\theta)$</th>
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<tr>
<td>0</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>$\pi/3$</td>
<td>2.0014</td>
<td>-</td>
<td>-</td>
<td>0.416335</td>
</tr>
<tr>
<td>$\pi/2$</td>
<td>0.37545</td>
<td>-</td>
<td>-</td>
<td>0.271856</td>
</tr>
<tr>
<td>$0.6082\pi$</td>
<td>0.09733</td>
<td>0.40000</td>
<td>1.98000</td>
<td>-</td>
</tr>
<tr>
<td>$2\pi/3$</td>
<td>0.05280</td>
<td>0.17000</td>
<td>0.37000</td>
<td>-</td>
</tr>
<tr>
<td>$\pi$</td>
<td>-0.001</td>
<td>0.10400</td>
<td>0.00000</td>
<td>-</td>
</tr>
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</table>
A Appendix

A.3 Flow enhancement

Here we derive the relation between slip length and flow enhancement for a cylindrical pore and state the result for a slit pore. As assumed before, consider a fluid flowing in a cylindrical pore of radius $R$. Solving the Navier-Stokes equations with no-slip boundary condition in cylindrical coordinates gives the result,

$$u_z(r) = \left( \frac{\rho F_e}{4\eta_0} \right) (R^2 - r^2) . \quad (A.19)$$

The total volumetric flow is found by integrating the above velocity profile over the tube cross section area,

$$Q_{\text{no-slip}} = \int_0^R 2\pi ru_z(r)dr = \frac{\pi R^4 \rho F_e}{8\eta} . \quad (A.20)$$

Now, the slip modified Navier-Stokes solution to the above problem is,

$$u_z(r) = \left( \frac{\rho F_e}{4\eta_0} \right) (R^2 - r^2) + u_s . \quad (A.21)$$

It is worth noting that this solution does not account for any variation in tube diameter dependent effective shear viscosity and the effect of slip is only an upward shift in the velocity profile by the slip velocity. One can obtain the slip velocity $u_s$, by using the slip length definition along with the fluid strain rate at the wall,

$$u_s = L_s \left( \frac{\rho F_e}{4\eta_0} \right) (-2R) , \quad (A.22)$$

where

$$L_s = u(R) \left. \frac{\partial u}{\partial r} \right|_{r=R}^{-1} . \quad (A.23)$$
Integrating this slip modified velocity profile over the tube cross section area as above, one can obtain the slip modified volumetric flow rate,

\[ Q_{\text{slip}} = \frac{\pi R^4 \rho F_e}{8 \eta_0} + \frac{\pi R^4 \rho F_e}{2 \eta_0} \frac{L_s}{R} + \frac{\pi R^4 \rho F_e}{8 \eta_0} \frac{L_s}{R} = Q_{\text{no-slip}} \left(1 + \frac{4L_s}{R}\right). \] (A.24)

The flow enhancement, which is the ratio of observed flow rate (either in experiment or simulation) to the expected flow rate is,

\[ E = \frac{Q_{\text{slip}}}{Q_{\text{no-slip}}} = \left(1 + \frac{4L_s}{R}\right). \] (A.25)

Hence the flow enhancement is directly proportional to the ratio of slip length to the tube diameter. If one rederives the above flow enhancement expression by taking into account the tube radius dependent effective shear viscosity \( \eta(R) \), the enhancement would be [69],

\[ E = \frac{Q_{\text{slip}}}{Q_{\text{no-slip}}} = \left(1 + \frac{4L_s}{R}\right) \frac{\eta_0}{\eta(R)}. \] (A.26)

For a planar slit pore of width \( 2h \), the flow enhancement is related to the slip length via [106],

\[ E = \frac{Q_{\text{slip}}}{Q_{\text{no-slip}}} = \left(1 + \frac{3L_s}{h}\right). \] (A.27)
Bibliography


[26] This image source is Wikipedia.


[59] X. Qin, Q. Yuan, Y. Zhao, S. Xie, and Z. Liu, Nano Lett. 11, 2173 (2011).


[92] In Couette flow, if the fluid velocity at a plane is \( u \) then the velocity opposite to the centre is \( u_w - u \). (see Eqs. (1.8) and (1.9) ). To highlight the negative velocity gradient we use this fact to symmetrize the velocity profile across the channel. This in another words is equivalent to constraining the velocity fit to give \( u_w/2 \) velocity at the centre of the channel.

[93] The Poiseuille flow velocity profiles of water in CNTs can be seen in figures 2, 4-5, 1, 5, 1 and 4 in references [63, 65, 68, 69, 71] and [72]-supporting information respectively. Also see figure 5 in reference [83].


For a given (m, n) chirality CNT, the radius is equal to $0.142 \times \sqrt{3} \times \sqrt{m^2 + n^2 + mn} / (2 \times \pi)$ nm, where 0.142 nm is the bond length between two carbon atoms.


M. Whitby and N. Quirke, Handbook of Nanophysics Chapter-11 (CRC Press, 2010).


[129] P. P. Ewald, Ann. Phys. 64 253 (1921)

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