Abstract

In this dissertation, using systematic coarse-graining, we develop multiscale models to study structural and dynamical properties of confined fluids. With the advent of nanofluidics and nanobiotechnology, fluids confined inside nanometer scale geometries have become a subject of both fundamental investigation and applied research. An understanding of the structural and dynamical properties of fluids at nanoscale is essential for designing novel engineering applications such as nanofiltration, carbon-dioxide sequestration, single-file transport, nanomedicine and many others. Our structural model is based on an empirical potential based quasi-continuum theory (EQT). EQT is a multiscale theory that seamlessly integrates the interatomic potentials describing various atomic interactions into a continuum framework to obtain the equilibrium density and potential profiles of confined fluids in a self-consistent manner. The density and potential profiles obtained from it are comparable in accuracy with those obtained from particle-based methods such as molecular dynamics (MD) simulations. Also, being a continuum approach, EQT is very simple to implement and is computationally several orders of magnitude faster than MD simulations. The central task in EQT is the development of quasi-continuum potential models that accurately describe the wall-fluid and fluid-fluid interactions in confined fluids. Using systematic coarse-graining, we discuss the development of coarse-grained single-site (CGSS) pair-potentials and quasi-continuum potential models for poly-atomic fluids. Proposed potential models systematically incorporate the effect of size, geometric shape and orientation of poly-atomic fluids to predict the correct microstructure in confined environments. We take carbon-dioxide as an example fluid and demonstrate the applicability of the potentials models in EQT as well as coarse-grained MD (CG-MD) simulations to predict the center-of-mass (COM) density and potential profiles of carbon-dioxide inside slit-shape graphite nanochannels at several high and low pressure confinements. The results obtained from EQT and CG-MD simulations are found in good agreement with those obtained from all-atom MD (AA-MD) simulations.

To develop dynamical models, one fundamental question is to understand the role of thermal noise in nanofluidic dynamics and transport. We discuss a combined memory function equation (MFE) and generalized Langevin equation (GLE) based approach (referred to as MFE/GLE formulation) to characterize
thermal noise in molecular fluids. Using MFE/GLE formulation in conjunction with MD simulation, we extract and analyze the statistical properties of thermal noise in confined fluids. We find that the thermal noise correlation time of the confined fluid does not vary significantly across the confinement and is quite similar to that of the corresponding reference bulk state fluid. We show that it is the cross-correlation of the mean force with the molecular velocity that gives rise to the spatial anisotropy in the velocity-autocorrelation function of the confined fluids. Further, we demonstrate that using the noise characteristics of reference bulk state fluid, and the structural information obtained from EQT, GLE can be used to simulate the single-particle dynamical properties of confined fluids. As an application, we use the GLE formulation to compute the interfacial friction coefficient at solid-liquid interface. Interfacial friction coefficient is an important macroscopic modeling parameter that provides the atomistic to continuum bridge by incorporating the effect of the wall-lattice structure and the nature of wall-fluid interactions on the fluid transport. The attractive feature of the GLE approach is that all the inputs to the GLE are obtained from EQT and simulation data of the reference bulk state fluid, thereby eliminating the need to perform computationally expensive equilibrium molecular dynamics (EMD) simulation of the confined system to estimate the interfacial friction. We also use the GLE formulation to understand the memory effects in the dynamics and transport of nanoparticles such as fullerenes immersed in host fluid environment. Finally, we discuss a GLE based approach to simulate the dynamics of interacting-particles.
To my family.
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Chapter 1

Introduction

1.1 Motivation

With the advent of nanofluidics and nanobiotechnology, fluids confined inside nanometer scale geometries have become a subject of both fundamental investigation and applied research. An understanding of the structural and dynamical properties of fluids at nanoscale is essential for designing novel engineering applications such as nanofiltration [3–5], carbon-dioxide sequestration [6, 7], single-file transport [4, 8–12], nanomedicine [13] and many others. Computational analysis plays a very important role in the design and optimization of these nanofluidic devices. Also, computational analysis can provide fundamental insights into nanoscale flow physics, which could be hard to characterize in experiments. Inside nanoscale confinements, due to the strong interaction of the surface with the fluid, the fluid becomes inhomogeneous and exhibits behavior that is quite different from the corresponding bulk state [14]. Also, at such smaller scales, thermal fluctuations influence the flow characteristics [15–18] at the solid-fluid interface. Continuum or classical theories, which assume a homogeneous variation of state variables and ignore the discrete atomic structure of the fluid and the confining wall molecules, fail to predict the correct behavior at nanoscale confinement. Also, most continuum based classical theories ignore thermal fluctuations. Hence, it is imperative to develop computational models/strategies that incorporate the missing atomic-scale physics into the classical theories to study the fluid behavior in nanoscale confinements.

1.2 Survey of computational approaches for confined fluids

In the past four decades, a great deal of progress has been made towards developing both theoretical and computer simulation based tools to study confined fluids. Statistical physics based models, which explicitly include the finite-size and discrete atomic structure of the fluid and the confining wall molecules, are used to study fluid confined inside nanometer scale geometries. From a theoretical standpoint, several approaches based on the modified kinetic theory (modified Enskog theory, local average density model) [19, 20], density functional theory (DFT) [21, 22] and integral equation theory (IET) [23] are proposed that can predict the
static and dynamical properties of confined fluids. Though most of these theories have a firm statistical foundation, from an engineering viewpoint, they are very difficult to implement and computationally expensive to study general nanoscale flow problems. Extension and application of these approaches beyond structureless hard-sphere and simple Lennard-Jones (LJ) type fluids is rather complicated and is still an active area of research [20, 24].

From a simulation standpoint, with the dramatic increase in computational power during the last two decades, atomistic molecular dynamics (MD) [25] has emerged as a powerful simulation tool to study confined fluids. While MD simulation can accurately predict the structural and dynamical properties, and has greatly enhanced our understanding of the behavior of confined fluids, it requires enormous computing resources that practically inhibits its usage to study systems at length and time scales of practical interest (experimental time scales). This practical limitation of MD arises from the usage of very stiff inter-atomic potentials, which are physically needed to incorporate the finite-size and excluded volume effect, but computationally limit the largest time step that can be used to perform a stable simulation. To overcome this limitation, the concept of coarse-graining is used. In coarse-graining, softer interaction potentials are constructed from the stiff atomistic potentials either by (a) averaging the molecular field over the rapidly fluctuating short time scale motions that are lesser relevant to the macroscale phenomena of interest [26], or by (b) constructing a reduced order representation of the actual system and designing effective or coarse-grained (CG) potentials that reproduce the desired macroscopic quantity of interest [27–29]. Further, CG potentials are used to develop multiscale models that attempt to combine the atomic-scale and continuum-scale methods and provide a unified framework to study fluid behavior across a broader spectrum of length and time scales. Although CG potentials allow the simulation of systems closer to experimental scales, they have some limitations. By definition, there is a loss of structural and dynamical information in coarse-graining. During coarse-graining, the structural and chemical details of the system at scales smaller than the coarse-grained scale are completely lost. Also, most CG potentials only perform well in the thermodynamic conditions of the reference atomistic system used to parameterize them and suffer from the loss of transferability [30–32].

In recent years, a lot of effort is devoted in developing systematic approaches to coarse-graining. There exist several systematic techniques such as iterative Boltzmann inversion (IBI) [33], inverse Monte Carlo (IMC) [34], potential of mean force (PMF) matching [35], relative entropy minimization [36, 37], and force-matching (FM) [27, 38] that can be used to construct CG potentials for confined fluids. These CG potentials yield an accurate description of the static properties of the underlying reference system. However, they fail to reproduce the correct dynamical properties such as diffusivity and viscosity. This discrepancy in the dynamical quantities occurs because these techniques completely ignore the instantaneous force fluctuations that the coarse-grained or eliminated degrees of freedom exert on the retained degrees of freedom. These
instantaneous force fluctuations must be explicitly incorporated into CG description to correctly reproduce
the dynamical behavior. Dissipative particle dynamics (DPD) [14, 39, 40] is one such simulation method,
which has been extensively used to study the dynamics of complex fluids such as colloidal suspensions,
polymer melts, etc., at length and time scales far beyond the reach of MD simulations. In DPD model, CG
particles interact by three forces: a softer conservative force, a dissipative force and a random force. Softer
conservative force characterizes the structure and dissipative and random forces together provide the force
fluctuations that the eliminated degrees of freedom exert on the retained degrees of freedom. Although DPD
is very simple to implement and conserves both mass and momentum, it fails to reproduce the structural
and dynamical properties of both bulk and confined fluids. This limitation of DPD stems from the fact
that in high density bulk and confined fluids, the time scales of fluid motion and thermal fluctuations are
not separable and the Markovian approximation on which DPD model is based, is not valid. Also, the
softer conservative force used in DPD, which allows the use of a time step significantly larger than MD
simulations, does not preserve the atomic structure (radial distribution function) of the fluid. Moreover, the
functional form of the softer conservative force used in DPD model is an ansatz, and it is not clear how
such softer conservative potentials can be developed using systematic coarse-graining. The development of
a non-Markovian DPD framework, which retains all the nice features of Markovian-DPD, and reproduces
both the structural and dynamical properties of confined fluid is an open problem [41].

There also exist hybrid combined atomistic-continuum approaches [42–46], in which continuum model
is solved in one part of the domain while MD is solved in another part, usually around the boundary. An
overlapping region is used between these two domains in which the two descriptions are forced to match
each other by either constrained MD or Schwartz iteration [45, 46]. The Schwartz iteration method is used
to ensure that the two descriptions are consistent in an overlapping region at the steady state. Although
the idea is quite natural and promising, these methods have had limited success, especially in predicting
dynamical properties, due to coupling of the time scales and complexity of the algorithms.

1.3 Research objectives

In this research work, using systematic coarse-graining, we develop multiscale models to study structural
and dynamical properties of confined fluid. The first objective of this research is based on an empirical
potential based quasi-continuum theory (EQT), proposed by Raghunathan, Park and Aluru [47], to predict
the equilibrium structure (inhomogeneous density and potential profiles) of confined fluids. EQT is a multi-

scale theory that seamlessly integrates the interatomic potentials describing various atomic interactions into
a continuum framework to obtain the equilibrium density and potential profiles in a self-consistent manner.
As EQT incorporates the finite-size and excluded volume effects through interatomic potentials, the density and potential profiles obtained from it are comparable in accuracy with those obtained from particle-based methods such as MD simulations. Also, being a continuum approach, EQT is very simple to implement and is computationally several orders of magnitude faster than MD simulations. The central task in EQT is the development of CG quasi-continuum potential models that accurately describe the wall-fluid and fluid-fluid interactions in confined fluids. The original work by Raghunathan et al. [47] discussed the development and parameterization of quasi-continuum potentials for spherical LJ-type fluids using the PMF matching technique. Although these quasi-continuum potentials include the finite-size and excluded volume effects, they suffer from the usual limitations associated with coarse-graining. In these models, the fluid and the wall structure is described in terms of density and all the structural and chemical details are lost. Also, these potential models are thermodynamic state dependent. The issue of thermodynamic transferability was considered in a subsequent work by Sanghi and Aluru [48], and two thermodynamic state dependent scaling relations were obtained (normalized by LJ energy and distance parameters) to parameterize the quasi-continuum potentials for different LJ type fluids across a wide range of thermodynamic states. Such scaling relations allow one to parameterize the quasi-continuum potentials without using computationally expensive MD simulation. With the successful application of EQT to simple LJ type fluids, the first specific objective of my research is to extend it to study poly-atomic fluids. We discuss the development of quasi-continuum potential models that incorporate the effect of size, geometric shape and orientation of poly-atomic fluids. The developed potentials are used in both coarse-gained MD (CG-MD) and EQT to predict the center-of-mass (COM) density and potential profiles of carbon-dioxide confined inside graphite slit nanochannels.

The second objective of my research is to utilize the structural information obtained from EQT and develop computational approaches to study the dynamical properties of confined fluids. The conceptual idea is that once the equilibrium structure is known, it can be combined with dynamical equations such as Langevin equation, time dependent Nerst-Planck equation, etc., to simulate the dynamics of confined fluids. To develop dynamical approaches, one fundamental question is to understand the role of thermal noise in nanofluidic dynamics and transport. We discuss a combined memory function equation (MFE) and generalized Langevin equation (GLE) based approach (referred to as MFE/GLE formulation) to characterize thermal noise in molecular fluids. Using MFE/GLE formulation in conjunction with MD simulation, we extract and analyze the statistical properties of thermal noise in confined fluids. We find that the thermal noise correlation time of the confined fluid does not vary significantly across the confinement and is quite similar to that of the corresponding reference bulk state fluid. We show that it is the correlation of the mean force with the molecular velocity that gives rise to the spatial anisotropy in the velocity-autocorrelation
function of the confined fluids. Further, we demonstrate that using the noise characteristics of reference bulk state fluid, and structural information obtained from EQT, GLE can be used to simulate the single-particle dynamical properties of confined fluids. As an application, we use the GLE formulation to compute the interfacial friction coefficient at solid-liquid interface. The interfacial friction coefficient characterizes the influence of solid-fluid interactions on the fluid transport, and is used to estimate the slip velocity and design slip boundary conditions for nanoscale transport. We also use the GLE formulation to understand the memory effects in the dynamics and transport of nanoparticles such as fullerenes immersed in host fluid environment. Finally, we discuss a GLE based approach to simulate the dynamics of interacting-particles.

1.4 Thesis layout

This thesis is organized as follows: In Chapter 2, we review the EQT formulation and discuss its extension to study the structure of poly-atomic fluids. We take carbon-dioxide as an example, and using the systematic coarse-graining technique of PMF matching, develop coarse-grained single-site (CGSS) pair-potentials and quasi-continuum potential models to study the structure of carbon-dioxide in confined environments. In Chapter 3 we discuss the MFE/GLE formulation to characterize thermal noise in molecular fluids. Using MFE/GLE formulation in conjunction with MD simulation, we extract and analyze the statistical properties of thermal noise in confined fluids. We also demonstrate that using the noise characteristics of reference bulk state fluid, and structural information obtained from EQT, GLE can be used to simulate the single-particle dynamical properties of confined fluids. The application of the GLE formulation to compute the interfacial friction coefficient at solid-liquid interface is discussed in Chapter 4. In Chapter 5, we use the GLE formulation to characterize and understand the memory effects in nanoparticle dynamics and transport. Chapter 6 discusses a GLE based approach to simulate the dynamics of interacting-particles. Finally, accomplishments of this research work are summarized in Chapter 7.
Chapter 2

EQT for poly-atomic fluids

2.1 Introduction: EQT formulation

We first discuss the empirical potential based quasi-continuum theory (EQT) [A. V. Raghunathan, J. H. Park, and N. R. Aluru, J. Chem. Phys. 127, 174701 (2007)]. In EQT, steady-state Nernst-Planck (NP) equation [49] is solved to obtain self-consistent density and potential profiles of the confined fluid. To discuss the formulation, we consider fluid confined inside a semi-infinite slit-shape nanochannel of width $H$ as shown in Fig. 2.1. The nanochannel walls are assumed to be infinite in $x$ and $y$ directions, and one-dimensional (1-D) variation of the fluid density along the $z$ direction is considered. To capture the density variation along the $z$ direction, 1-D steady-state NP equation can be written as

$$
\frac{d}{dz} \left[ \frac{d\rho}{dz} + \frac{\rho}{RT} \frac{dU}{dz} \right] = 0.
$$

(2.1)

Here, $\rho$ is unknown fluid density, $U$ is the total interaction potential, $R$ is the gas constant and $T$ is the temperature of the confined fluid. Dirichlet boundary conditions are applied on both the channel wall boundaries, i.e., on $(z = 0)$ and $(z = H)$, (see Figure 2.1(b)) as

$$
\rho(z = 0) = 0, \\
\rho(z = H) = 0.
$$

(2.2a)

(2.2b)

Because both the boundary conditions are zero at the channel walls, an additional constraint on the fluid density is needed to obtain the non-trivial density profile inside the channel. It is assumed that the average density, $\rho_{avg}$, of the fluid inside the channel is known, and an integral constraint on the density profile is imposed to maintain the average density as $\rho_{avg}$, i.e.,

$$
\frac{1}{H} \int_{0}^{H} \rho(z) dz = \rho_{avg}.
$$

(2.3)
Figure 2.1: Atomistic (a) and Continuum (b) representation of fluid confined inside a slit shape nanochannel. $H$ is channel width, $\rho_{wall}$ is wall density and $\rho(z)$ is fluid density.
The primary task in EQT is the development of quasi-continuum potential models to compute the total interaction potential $U(z)$ of the confined fluid. Once $U(z)$ and $\rho_{\text{avg}}$ in the channel are known, Eq. (2.1) with boundary conditions and integral constraint given by Eqs. (2.2) and (2.3), is solved iteratively to obtain self-consistent density and potential profiles of the confined fluid. For confined fluids, the total interaction potential is obtained as a summation of the wall-fluid interaction energy, $U_{wf}$, and the fluid-fluid interaction energy, $U_{ff}$. In quasi-continuum formulation, the total potential energy $U(r)$ at a position $r$ is computed by applying the continuum approximation locally to the discrete summation expression for the interaction energy in the molecular representation [47, 48], i.e.,

$$U(r) = U_{wf}(r) + U_{ff}(r),$$

$$U(r) = \sum_{i=1}^{N_w} u_{w_i}^{AA}(|r - r_i|) + \sum_{i=1}^{N_f} u_{f_i}^{AA}(|r - r_i|),$$

$$\approx \int_V u_{w_{M}}^{AA}(|r - r'|) \rho_{\text{wall}}(r') \, dV + \int_V u_{f_{M}}^{AA}(|r - r'|) \rho(r') \, dV. \quad (2.6)$$

Here, $u_{w_i}^{AA}$ and $u_{f_i}^{AA}$ are the inter-atomic separation dependent pair potentials that describe the wall-fluid and the fluid-fluid interactions, respectively. $N_w$ and $N_f$ are, respectively, the number of wall and fluid atoms that lie within the cutoff sphere around the position $r$, $r_i$ is the location of atom $i$, $\rho_{\text{wall}}(r')$ and $\rho(r')$ are, respectively, the wall and the fluid density in the volume element $dV$ and $V$ is the volume circumscribed by the cutoff sphere. For spherical, non-polar LJ type spherical molecules, $u_{w_i}^{AA}$ and $u_{f_i}^{AA}$ are the 12-6 Lennard-Jones (LJ) pair-potentials used in the MD simulation. In the quasi-continuum formulation, the wall-fluid and the fluid-fluid interaction energy is computed in terms of a density weighted integration of the inter-atomic pair potentials as shown in Figs. 2.2(a) and 2.2(b), respectively. Using the structural information of the wall, the integral representing the wall-fluid interaction energy $U_{wf}$ can be evaluated easily. Such density based wall-fluid interaction models were originally discussed by Steele [50, 51] and are widely used in the simulation of gas physisorption phenomena. Two well-known examples of such potentials for planar walls are the LJ 9-3 wall and LJ 10-4 potentials. The development of the quasi-continuum wall-fluid potential models for cylindrical and spherical shape confinement and many industrially important heterogeneous/patterned walls are discussed in Refs. [50–56]. For LJ type confined fluids, $U_{wf}$ is independent of the fluid density and depends only on the wall structure and the wall-fluid interaction parameters. Also, as the structure of the wall does not change, $U_{wf}$ is computed just once in the EQT formulation.

We now discuss the evaluation of integral representing the fluid-fluid interaction energy

$$U_{ff}(r) = \int_V u_{f_{M}}^{AA}(|r - r'|) \rho(r') \, dV. \quad (2.7)$$
Figure 2.2: Computation of the wall-fluid and fluid-fluid interaction energy in the quasi-continuum formulation. (Figure courtesy of Mohammad Hossein Motevaselian).
Unlike wall-fluid potential integral, the computation of the fluid-fluid interaction energy integral is complicated and needs to be performed carefully. As fluid-fluid interaction energy is a function of the unknown fluid density \( \rho(r) \), integral given by Eq. (2.7) is computed iteratively in the EQT formulation, until a self-consistent density and potential profiles are obtained. Due to the highly inhomogeneous nature of the fluid density near the interface and the singular nature of the inter-molecular potential \( u^{AA}_{ff}(r) \) as \( r \to 0 \), the evaluation of this integral leads to numerical singularity. This numerical singularity is a classic example of the length and time scale mismatch complexity that can arise while developing multiscale models. The physical origin of this singularity is the implicit use to the mean-field approximation (MFA) in writing the quasi-continuum expression for the fluid-fluid interaction energy (Eq. (2.7)). In MFA, two-particle correlation, \( g(|r - r'|) \), which specifies the relative probability of finding two particles at a distance \( |r - r'| \) is assumed to be 1. At very small distances \( (|r - r'| \to 0) \), due to finite size and excluded volume effects this probability is zero.

One possible approach to avoid this problem is to develop models for \( g(|r - r'|) \), which is the approach taken in integral equation theories (IET) [23]. Although, a great deal of progress has been made in developing pair-correlations for real fluids, the IET framework is mathematically quite complex to implement and suffers from the “closure” problem. In a very recent extension of EQT for studying thermodynamic properties of confined fluids [24], pair-correlation models based on hard-sphere radial distribution function are used to compute this integral. In this work, we use an alternative strategy of replacing the singular \( u^{AA}_{ff} \) by a truncated soft-core potential \( u^{t}_{ff} \) and compute the \( U_{ff} \) as

\[
U_{ff}(r) = \int_{V} u^{t}_{ff}(|r - r'|) \rho(r') \, dV, \tag{2.8}
\]

where \( u^{t}_{ff}(r) \) is defined as

\[
u^{t}_{ff}(r) = \begin{cases} 
0 & r \leq R_{crit} \\
 b_0 + b_1 r + b_2 r^2 & R_{crit} < r \leq R_{min} \\
u^{AA}_{ff}(r) & r > R_{min}
\end{cases} \tag{2.9}
\]

A schematic comparison of \( u^{AA}_{ff} \) and \( u^{t}_{ff} \) is shown in Fig. 2.3. It can be observed that \( u^{t}_{ff} \) is exactly same as \( u^{AA}_{ff} \) until \( r = R_{min} \), has a softer second-order polynomial repulsive form between \( R_{crit} \) and \( R_{min} \) and becomes zero for \( r \leq R_{crit} \). \( R_{min} \) and \( R_{crit} \) are two coarse-graining parameters which define the softer repulsive region and the zero potential core, respectively. The coefficients \( b_0 \), \( b_1 \) and \( b_2 \) of the softer polynomial repulsive potential are calculated by enforcing the continuity of the potential and its first and second derivative at \( R_{min} \). The functional form of the softer repulsive potential is an ansatz and lacks any
fundamental derivation. The parameters $R_{min}$ and $R_{crit}$ are obtained using the PMF matching technique that matches the total interaction energy $U(r)$ of the confined fluid as obtained from the quasi-continuum potentials with that obtained from all-atom MD (AA-MD) simulation. For a given thermodynamic state, PMF matching requires one AA-MD simulation to parameterize the quasi-continuum potentials. We discuss the PMF matching algorithm in detail in Sec. 2.2.4. Once the quasi-continuum potentials are parameterized, they can be used in EQT to predict the density and potential profiles of fluids confined inside different width channels which are loaded at the same thermodynamic state. Figure 2.4 shows the comparison of the density profile of the LJ oxygen atoms confined inside different width slit-shape channels as obtained from EQT (solid line) and MD simulations (open circle). It can be observed that the results obtained from EQT capture both the interfacial (non-continuum inhomogeneous behavior) and the bulk (continuum behavior) structure of the confined LJ oxygen. Further, as EQT is a continuum-based approach, it is several orders of magnitude faster than MD simulation. The development of transferable quasi-continuum potential models for confined LJ type fluids is discussed in detail in Ref. [48].

We wish to mention that though the EQT formulation is discussed for fluids confined inside slit-shape nanochannels, it can be straightforwardly applied to other geometries such as a carbon nanotube (CNT). In addition, for confinements where the total potential varies in two or three dimensions, the EQT framework can be extended by considering a multi-dimensional form of Eq. (2.1). With the successful application of EQT for spherical, non-polar LJ type fluids, we now address the first research objective of extending the EQT framework to study the structure of poly-atomic molecules in confined environments.
2.2 EQT for poly-atomic fluids

For poly-atomic molecules, the molecular interactions in MD are typically described through the interaction potentials that define the interactions between the constituent atoms and depend on the internal coordinates of each molecule. To develop the quasi-continuum potentials, we first develop coarse-grained single-site (CGSS) pair-potentials that describe an effective interaction between the two molecules (averaging out the internal degrees of freedom) and then use them in the continuum approximation (Eq. (2.6)) to compute the total interaction potential of the confined poly-atomic fluid. We take 3-site carbon-dioxide (CO$_2$) molecule as an example, which is a linear molecule with both LJ and electrostatic interactions present, and discuss the development of CGSS pair-potentials and quasi-continuum potential models that predict the correct microstructure of CO$_2$ in confined environments. We coarse-grain CO$_2$ as a single-site point particle placed at its center-of-mass (COM) position. Over the years, several potential models have been proposed to represent carbon dioxide [2, 57–59]. Most of these models can be categorized into two sub-groups: 1) All atom (AA) site-site potentials in which carbon dioxide is modeled as a rigid two/three site Lennard-Jones (LJ) molecule with quadrupole moment either stated explicitly or decomposed into partial charges. These models are computationally quite expensive, but provide a fairly accurate description of the structural properties of carbon dioxide, both in the bulk state and under nanoscale confinement. 2) Single-site LJ
Figure 2.5: COM density of confined CO$_2$ from a bulk CGSS potential model [1] (broken line) and a 3-site AA potential model [2] (solid line).

Type potentials which ignore the microscopic structural information related to the shape of the molecule and model CO$_2$ as a spherical and isotropic single-site molecule. There exist several COM position based single-site potential models that provide a fairly accurate description for CO$_2$ in the bulk state [1, 59]. We first show that CGSS bulk potentials cannot be used to predict the correct microstructure of CO$_2$ in confined environments. Figure 2.5 shows the comparison of the 1-D COM density, $\rho(z)$, for CO$_2$ confined inside a 2.232 nm wide graphite slit nanochannel, as obtained by using a bulk CGSS potential [1] and a AA 3-site potential model [2] in a MD simulation. It can be observed that the density profile obtained from the bulk CGSS model over-predicts the density layering and completely fails to predict the splitting of the first peak into a second sub-layer (shoulder peak) near the confining surface. This confinement induced splitting of the first density layer is a consequence of the shape and the orientation of the CO$_2$ molecules which is absent in the CGSS models developed for the bulk state. To develop CGSS pair potentials for nanoconfined poly-atomic fluids, the geometric shape and the orientation information must be considered. We now discuss the development of the CGSS pair-potentials to describe wall-fluid and fluid-fluid interactions for CO$_2$ in confined environments.

### 2.2.1 CGSS Potentials: Functional Form

The specification of the functional form of the interaction potential is one of the most important and challenging tasks in the process of coarse-graining [28, 29]. Typically, the specification of the functional form
is guided by the understanding of the physics of the problem. To propose the functional form for CGSS wall-CO$_2$ and CO$_2$-CO$_2$ interaction potentials, we first discuss the microstructure of CO$_2$ molecules under nanoscale confinement. Figures 2.6(a) and 2.6(b) show the COM density profile, $\rho(z)$, and the molecular orientation profile, $S_\theta$, respectively, for CO$_2$ confined inside a 2.232 nm wide graphite slit nanochannel. The molecular orientation is computed using the order parameter $S_\theta$ defined as

$$S_\theta = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \quad (2.10)$$

Here, $\theta$ is the angle between the molecular axis and a normal vector through the walls and angular brackets denote ensemble averaging. The order parameter takes a value of $-0.5$ if molecules are aligned parallel to the wall, a value of $1$ if the molecules are aligned perpendicular to the wall, and a value of $0$ if they are randomly oriented. Further, to understand the effect of the wall-fluid and the fluid-fluid interactions separately, we divide the confining geometry into two regions. The region up to 0.5 nm from the walls ($z \leq 0.5$ nm and $z \geq 1.732$ nm), where the wall-fluid interactions are the dominant interactions, is defined as the interfacial region and the remaining region is defined as the central region of the nanochannel. It can be observed from Figs. 2.6(a) and 2.6(b) that the two sub-layers in the first peak have a different preferred molecular orientation. In the first sub-layer, the order parameter is less than zero ($S_\theta \approx -0.4$) and molecules are aligned parallel to the wall, while in the second sub-layer the order parameter is greater than zero ($S_\theta \approx 0.2$) indicating that the molecules are rotated with respect to the wall. Under high pressure (or high density) nanoscale confinement, the molecules arrange themselves into layers which are rotated relative to each other. This type of arrangement occurs because of the linear shape of the carbon dioxide molecule and results in the most efficient packing under confinement. To capture this orientation dependent arrangement of molecules in the interfacial region, we use piecewise interaction functions and define the wall-CO$_2$ interaction potential as

$$u_{CGSS \text{wall-CO}_2}(r) = \begin{cases} 
  u_{LJ}(r, \sigma_1, \epsilon_1) & r \leq R_{trans} \\
  a_0 + a_1 r + a_2 r^2 + a_3 r^3 & R_{trans} < r \leq R_{trans} + \Delta \\
  c_1 u_{LJ}(r, \sigma_1, \epsilon_1) + c_2 u_{LJ}(r, \sigma_2, \epsilon_2) & r > R_{trans} + \Delta 
\end{cases} \quad (2.11)$$

where $u_{LJ}(r, \sigma_i, \epsilon_i)$ is defined as

$$u_{LJ}(r, \sigma_i, \epsilon_i) = 4\epsilon_i \left( \frac{\sigma_i}{r} \right)^{12} - \left( \frac{\sigma_i}{r} \right)^{6}, \quad i = 1, 2. \quad (2.12)$$

Here, $r$ is the distance between the wall atom and the CG CO$_2$ molecule. $\sigma_i$ and $\epsilon_i$ are the distance and the energy parameters, respectively. The first region is a 12-6 LJ potential up to $R_{trans}$ to model the interaction
Figure 2.6: (a) COM density profile, $\rho(z)$, (b) Molecular orientation profile, $S_\theta$, (c) Functional form of $u_{\text{wall-CO}_2}(r)$ and $u_{\text{CO}_2-\text{CO}_2}(r)$, and (d) Relative orientation profile of CO$_2$ confined inside a 2.232 nm wide graphite slit nanochannel. Inset: COM coordinate system used to define relative orientation.
of the wall atoms with the CO$_2$ molecules in the first sub-layer. The second region is a linear superposition of two 12-6 LJ potentials, and operates at separation distances greater than $R_{trans} + \Delta$ to model the interaction of the wall atoms with the CO$_2$ molecules in the second sub-layer. $c_1$ and $c_2$ are two constants that control the contribution of the two 12-6 LJ potentials in the second region. The two regions are connected by a polynomial bridge function of width $\Delta$. The coefficients $a_0$, $a_1$, $a_2$ and $a_3$ of the bridge function are computed to ensure smooth transition of the potential (continuity of the potential and its first derivative) at $R_{trans}$ and $R_{trans} + \Delta$. A sketch of the functional form is given in Fig. 2.6(c).

To define the fluid-fluid interactions, we plan to use the same functional form as proposed for the wall-CO$_2$ interactions. Although this molecular orientation analysis guides us to define the functional form, it does not provide any information on the relative orientation of the two fluid molecules, which could be different in the interfacial and the central region. This information on the relative orientation is required to understand if one uniform fluid-fluid potential could be used across the entire length of the confinement. If the relative orientation profile is different in the two regions, then one would have to define a separate fluid-fluid interaction potential for each region. Figure 2.6(d) shows the relative orientation profile of CO$_2$ molecules in the interfacial (solid line) and the central (broken line) region of the confinement. The relative orientation is defined in the COM coordinates $r_{COM}$, $\theta_1$, $\theta_2$ and $\phi$ (see inset of Fig. 2.6(d)). $r_{COM}$ is the separation between the COM of the two molecules, $\theta$ is the angle made by the molecular axis of each molecule with the $r_{COM}$ and $\phi$ is the dihedral angle between the two planes defined by the $r_{COM}$ and the molecular axis for each molecule. It can be observed that the relative orientation profile in the interfacial region is not significantly different from that in the central region ($\Delta \theta_1 \approx 7^\circ$, $\Delta \theta_2 \approx 7^\circ$, $\Delta \phi \approx 3^\circ$; $\Delta \theta_1$, $\Delta \theta_2$ and $\Delta \phi$ are the difference between the values of $\theta_1$, $\theta_2$ and $\phi$ in the interfacial and the central region, respectively). Thus, we specify one uniform interaction potential and define the CO$_2$-CO$_2$ interaction potential as

$$u_{CGSS}^{CO_2-CO_2}(r) = \begin{cases} u_{LJ}(r, \sigma_1, \epsilon_1) & r \leq R_{trans} \\ a_0 + a_1 r + a_2 r^2 + a_3 r^3 & R_{trans} < r \leq R_{trans} + \Delta \\ c_1 u_{LJ}(r, \sigma_1, \epsilon_1) + c_2 u_{LJ}(r, \sigma_2, \epsilon_2) & r > R_{trans} + \Delta \end{cases} \quad (2.13)$$

Here, $r$ is the distance between the two CG CO$_2$ molecules. All other functions and parameters have the same meaning as defined above for $u_{CGSS}^{wall-CO_2}$.

### 2.2.2 CGSS Potentials: Parameterization

Once the functional form is specified, the next step is the parameterization of the potential to reproduce the property of interest, commonly referred to as the target function in the coarse-graining literature. We
parameterize $u_{CGSS}^{wall-CO_2}$ and $u_{CGSS}^{CO_2-CO_2}$ to reproduce the potential of mean force (PMF) of the confined fluid. The PMF variation, $U_i(r)$, of a particle $i$ at position $r$ is computed as [60]

$$U_i(r) = U_i(r_o) - \int_{r_o}^{r} \langle F_i(r') \rangle \, dr'$$

(2.14)

Here, $\langle F_i(r) \rangle$ is the mean force that acts on particle $i$ (at position $r$) due to its interaction with all other particles. $U_i(r_o)$ is the value of the potential at a reference position $r_o$. For semi-infinite slit nanochannels considered in this work, the reference position $r_o$ is taken to be the center of the nanochannel, i.e., $r_o(x, y, z) = (x, y, H/2)$; $H$ is the slit width. Also, since the slit is infinite in $x$ and $y$ directions, only the variation in the $z$ direction is relevant. To parameterize the potentials for a given thermodynamic state, we first run an AA-MD simulation and compute the wall-fluid PMF (PMF profile due to the wall-fluid interactions), $U_{AA}^{wall-CO_2}(z)$, and the fluid-fluid PMF (PMF profile due to the fluid-fluid interactions), $U_{AA}^{CO_2-CO_2}(z)$, of the confined fluid. The wall-fluid and the fluid-fluid PMF are computed by decomposing the total force that acts on a molecule as contributions from the wall-fluid and the fluid-fluid interactions, respectively. To find the contribution from the wall-fluid (or fluid-fluid) interactions, we take AA-MD equilibrium trajectories as input and recompute the total force on each molecule due to the wall-fluid (or fluid-fluid) interactions alone. This can be performed using the rerun option in the mdrun program of the simulation package GROMACS. [61] $U_{AA}^{wall-CO_2}(z)$ and $U_{AA}^{CO_2-CO_2}(z)$ are computed as

$$U_{AA}^{wall-CO_2}(z) = U_{AA}^{wall-CO_2}(z_o) - \int_{z_o}^{z} \langle F_{AA}^{wall-CO_2}(z') \rangle \, dz'$$

(2.15)

$$U_{AA}^{CO_2-CO_2}(z) = U_{AA}^{CO_2-CO_2}(z_o) - \int_{z_o}^{z} \langle F_{AA}^{CO_2-CO_2}(z') \rangle \, dz'$$

(2.16)

Here, $\langle F_{AA}^{wall-CO_2}(z) \rangle$ and $\langle F_{AA}^{CO_2-CO_2}(z) \rangle$ are the mean force experienced by the molecules at position $z$ (molecules whose COM lie in the bin $[z, (z + \Delta z)]$) due to the wall-fluid and the fluid-fluid interactions, respectively. $U_{AA}^{wall-CO_2}(z_o)$ and $U_{AA}^{CO_2-CO_2}(z_o)$ are the reference wall-fluid and fluid-fluid potentials at position $z_o = H/2$. $U_{AA}^{wall-CO_2}(z)$ and $U_{AA}^{CO_2-CO_2}(z)$ are the target wall-fluid and fluid-fluid PMF profiles, which we want to reproduce with $u_{CGSS}^{wall-CO_2}$ and $u_{CGSS}^{CO_2-CO_2}$, respectively. The CG wall-fluid and fluid-fluid PMF profiles are computed following the same procedure as discussed above for the computation of the target PMF profiles. First, the total force experienced by each CG CO$_2$ molecule ($CO_2$ is coarse-grained as a spherical bead placed at its COM position) due to the CG wall-fluid and fluid-fluid interactions (defined by
Here, \( u_{\text{CGSS}}^{\text{wall-CO}_2}(r) \) and \( u_{\text{CO}_2-\text{CO}_2}^{\text{CGSS}}(r) \) is computed, i.e.,

\[
F_{\text{wall-CO}_2}(r_{i}^{\text{AA}}) = \sum_{j=1}^{N_i} -\frac{d}{dr} u_{\text{wall-CO}_2}^{\text{CGSS}}(|r_{i}^{\text{AA}} - r_{j}|)
\]  
(2.17)

\[
F_{\text{CO}_2-\text{CO}_2}(r_{i}^{\text{AA}}) = \sum_{j=1}^{N_j} -\frac{d}{dr} u_{\text{CO}_2-\text{CO}_2}^{\text{CGSS}}(|r_{i}^{\text{AA}} - r_{j}|)
\]  
(2.18)

Here, \( r_{i}^{\text{AA}} \) and \( r_{j}^{\text{AA}} \) are the COM position of the molecules \( i \) and \( j \), as obtained from AA-MD trajectories and \( N_j \) is the number of molecules within the cutoff sphere around the molecule \( i \). \( F_{\text{wall-CO}_2}(r_{i}^{\text{AA}}) \) and \( F_{\text{CO}_2-\text{CO}_2}(r_{i}^{\text{AA}}) \) are the total force that acts on the molecule \( i \) (at position \( r_{i}^{\text{AA}} \)) due to the wall-fluid and the fluid-fluid interactions, respectively. This step can be performed using the table [62] and rerun option in the mdrun program of the simulation package GROMACS. Then, the CG wall-fluid PMF, \( U_{\text{wall-CO}_2}^{\text{CG}}(z) \), and the CG fluid-fluid PMF, \( U_{\text{CO}_2-\text{CO}_2}^{\text{CG}}(z) \), are computed as

\[
U_{\text{wall-CO}_2}^{\text{CG}}(z) = U_{\text{wall-CO}_2}^{\text{AA}}(z_0) - \int_{z_0}^{z} \langle F_{\text{wall-CO}_2}(z') \rangle \, dz'
\]  
(2.19)

\[
U_{\text{CO}_2-\text{CO}_2}^{\text{CG}}(z) = U_{\text{CO}_2-\text{CO}_2}^{\text{CGSS}}(z_0) - \int_{z_0}^{z} \langle F_{\text{CO}_2-\text{CO}_2}(z') \rangle \, dz'
\]  
(2.20)

Here, \( \langle F_{\text{wall-CO}_2}(z) \rangle \) and \( \langle F_{\text{CO}_2-\text{CO}_2}(z) \rangle \) are the mean force experienced by the molecules at position \( z \) due to the CG wall-fluid and fluid-fluid interactions, respectively. \( U_{\text{wall-CO}_2}^{\text{CG}}(z_0) \) and \( U_{\text{CO}_2-\text{CO}_2}^{\text{CG}}(z_0) \) are the reference wall-fluid and fluid-fluid potentials at position \( z_0 = H/2 \). This process (Eqs. (2.17) to (2.20)) is repeated by varying the parameters of the CGSS potentials, \( u_{\text{wall-CO}_2}^{\text{CGSS}} \) and \( u_{\text{CO}_2-\text{CO}_2}^{\text{CGSS}} \), until a good match between the CG and the target PMF profiles is obtained. The parameterization procedure is summarized in Algorithm 1. Figures 2.7(a) and 2.7(b) show the comparison of the CG wall-fluid and fluid-fluid PMF profiles (solid line)

**Algorithm 1** Parametrization of CGSS wall-fluid and fluid-fluid interaction potential.

1: Perform an all-atom molecular dynamics (AA-MD) simulation and compute \( U_{\text{wall-CO}_2}^{\text{AA}} \) and \( U_{\text{CO}_2-\text{CO}_2}^{\text{AA}} \) using Eqs. (2.15) and (2.16), respectively.
2: Take initial guess for \( [\sigma_1, \epsilon_1, \sigma_2, \epsilon_2, R_{\text{trans}}, \Delta, c_1, c_2] \) for both \( u_{\text{wall-CO}_2}^{\text{CGSS}} \) and \( u_{\text{CO}_2-\text{CO}_2}^{\text{CGSS}} \).
3: Take AA-MD simulation trajectories and use Eqs. (2.17) to (2.20) to compute \( U_{\text{wall-CO}_2}^{\text{CG}} \) and \( U_{\text{CO}_2-\text{CO}_2}^{\text{CG}} \).
4: Obtain \( [\sigma_1, \epsilon_1, \sigma_2, \epsilon_2, R_{\text{trans}}, \Delta, c_1, c_2] \) by solving the non-linear equations
\[
U_{\text{wall-CO}_2}^{\text{CG}} - U_{\text{wall-CO}_2}^{\text{AA}} = 0 \quad \text{and} \quad U_{\text{CO}_2-\text{CO}_2}^{\text{CG}} - U_{\text{CO}_2-\text{CO}_2}^{\text{AA}} = 0
\]

with their respective target PMF profiles (open circle) for supercritical carbon dioxide (\( T = 323 \, \text{K} \) and \( P = 10.1 \, \text{MPa} \)) confined inside a 2.232 nm wide graphite slit nanochannel. The parameters used in the CGSS potentials are reported in Table 2.1. It can be observed that the CG wall-fluid and fluid-fluid PMF profiles match well with their respective target PMF profiles. The proposed functional form for \( u_{\text{wall-CO}_2}^{\text{CGSS}} \)
Figure 2.7: Comparison of (a) CG wall-fluid PMF profile, $U_{\text{wall-CO}_2}^{\text{CG}}$, (solid line) and (b) CG fluid-fluid PMF profile, $U_{\text{CO}_2-\text{CO}_2}^{\text{CG}}$, (solid line) with their respective target AA-MD PMF profiles (open circle) for carbon dioxide confined inside a 2.232 nm wide graphite slit nanochannel at $T = 323$ K and $P = 10.1$ MPa. The reference potential value is subtracted from each PMF profile while plotting.

Table 2.1: Parameters of CGSS wall-fluid and fluid-fluid interaction potentials.

<table>
<thead>
<tr>
<th>Thermodynamic State</th>
<th>Potential</th>
<th>$\sigma_1$</th>
<th>$\epsilon_1$</th>
<th>$\sigma_2$</th>
<th>$\epsilon_2$</th>
<th>$R_{\text{trans}}$</th>
<th>$\Delta$</th>
<th>$c_1$</th>
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<tr>
<td>$T=323$K $P=10.1$MPa</td>
<td>$u_{\text{wall-CO}_2}^{\text{CGSS}}$</td>
<td>0.335</td>
<td>0.45</td>
<td>0.405</td>
<td>0.55</td>
<td>0.345</td>
<td>0.05</td>
<td>0.55</td>
<td>0.45</td>
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<td></td>
<td>$u_{\text{CO}_2-\text{CO}_2}^{\text{CGSS}}$</td>
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<td>0.405</td>
<td>1.75</td>
<td>0.375</td>
<td>0.03</td>
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<tr>
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<td>$u_{\text{wall-CO}_2}^{\text{CGSS}}$</td>
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<td>0.405</td>
<td>0.55</td>
<td>0.345</td>
<td>0.05</td>
<td>0.55</td>
<td>0.45</td>
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<tr>
<td></td>
<td>$u_{\text{CO}_2-\text{CO}_2}^{\text{CGSS}}$</td>
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<td>0.405</td>
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<td>0.405</td>
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<tr>
<td></td>
<td>$u_{\text{CO}_2-\text{CO}_2}^{\text{CGSS}}$</td>
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<td>0.405</td>
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<tr>
<td>$T=323$K $P=1.01$MPa</td>
<td>$u_{\text{wall-CO}_2}^{\text{CGSS}}$</td>
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<td></td>
<td>$u_{\text{CO}_2-\text{CO}_2}^{\text{CGSS}}$</td>
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<td>0.40</td>
<td>0.03</td>
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</tr>
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</table>
captures the two minima in the wall-fluid PMF quite accurately. These two minima cause the splitting of the density profile in the interfacial region into two sub-layers. $u^{CGSS}_{\text{CO}_2-\text{CO}_2}$ also captures the minima in the fluid-fluid PMF profile quite accurately. These minima positions correspond to the density peaks in the central region of the channel. There is a small error in the magnitude of the CG fluid-fluid PMF profile in the region up to 0.3 nm from the walls. Due to the highly repulsive nature of the wall-fluid PMF in this region ($U^{CGSS}_{\text{wall-\text{CO}_2}}(z) > 5 K_BT$; $K_B$ is the Boltzmann constant), this error does not affect the structural prediction in the interfacial region. It is important to understand that this parameterization procedure ensures that given a set of equilibrium trajectories, $u^{CGSS}_{\text{wall-\text{CO}_2}}$ and $u^{CGSS}_{\text{CO}_2-\text{CO}_2}$ will reproduce the wall-fluid and the fluid-fluid PMF profiles of the confined fluid, respectively. It does not guarantee that given any random initial configuration, these potentials would evolve the system to its equilibrium configuration the same way as AA-MD simulation. This issue is checked later when we use these potentials to perform CG-MD simulations.

### 2.2.3 CGSS Potentials: Transferability

To check the transferability of the functional form of $u^{CGSS}_{\text{wall-\text{CO}_2}}$ and $u^{CGSS}_{\text{CO}_2-\text{CO}_2}$, they were parameterized for four different thermodynamic states ($T = 323$ K, $P = 10.1$ MPa; $T = 323$ K, $P = 1.01$ MPa; $T = 348$ K, $P = 9.05$ MPa; $T = 308$ K, $P = 5.5$ MPa). The first two states are chosen to check the transferability of the functional form to high and low pressure confinements. The last two states are representative of high pressure confinement at supercritical temperatures. During parameterization, the variation of the coarse-graining parameters was studied to obtain their functional dependence with the thermodynamic variables and associate a physical meaning where ever possible. While parameterizing the wall-fluid interaction potential, $u^{CGSS}_{\text{wall-\text{CO}_2}}$, for high-pressure confinements (pressure values for which the first layer splits into two sub-layers), it was observed that the values of the parameters $\sigma_1$ and $\sigma_2$ were quite close to the distance values at which the two minima occur in the wall-$\text{CO}_2$ PMF profile. For the three high-pressure states ($P \geq 5.5$ MPa) considered in this work, the first and the second minima occur at approximately 0.335 nm and 0.405 nm away from the wall, respectively. Hence, to parameterize $u^{CGSS}_{\text{wall-\text{CO}_2}}$, the values $\sigma_1 = 0.335$ nm and $\sigma_2 = 0.405$ nm were used and they worked well in all the three high-pressure thermodynamic states. Interestingly, the usage of the same values ($\sigma_1 = 0.335$ nm and $\sigma_2 = 0.405$ nm) also worked fine in the parameterization of the fluid-fluid interaction potential, $u^{CGSS}_{\text{CO}_2-\text{CO}_2}$, for these high-pressure states. Also, for $u^{CGSS}_{\text{wall-\text{CO}_2}}$, it was observed that once it is parameterized for a high-pressure state ($T = 323$ K, $P = 10.1$ MPa), only the coarse-graining parameter $R_{\text{trans}}$ needs to be changed to re-parameterize it for a low-pressure state at the same temperature ($T = 323$ K, $P = 1.01$ MPa). The potentials were not found to be physically sensitive to the coarse-graining
parameters $\Delta$, $c_1$ and $c_2$, whose variations were mostly considered to fine tune the results. $c_1 = c_2 = 0.5$ and $\Delta$ value in the range 0.03 to 0.05 nm were found to be working fine for all the four thermodynamic states considered in this study. Figure 2.8 shows the comparison of the CG wall-fluid PMF, $U_{\text{wall-CO}_2}^{\text{CG}}$, (left) and the CG fluid-fluid PMF, $U_{\text{CO}_2-\text{CO}_2}^{\text{CG}}$, (right) profiles obtained from CGSS potentials (solid line) with their respective target AA-MD PMF profiles (open circle) at different thermodynamic states. The parameters for the CGSS potentials are obtained following the procedure outlined in Algorithm 1, and are reported in Table 2.1. It can be observed that the proposed functional form of $u_{\text{wall-CO}_2}^{\text{CGSS}}$ performs well for all the thermodynamic states and reproduces the wall-fluid PMF quite accurately. The functional form of $u_{\text{CO}_2-\text{CO}_2}^{\text{CGSS}}$ performs better for high pressure (or density) states than for low pressure states. At high densities, short range inter-molecular repulsions are typically the dominant interactions, and $u_{\text{CO}_2-\text{CO}_2}^{\text{CGSS}}$, which is designed as a combination of 12-6 LJ potentials, reproduces the PMF profiles quite accurately. At low densities,
long range electrostatic interactions also become important and \( u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2} \) does not capture these long range effects quite efficiently. The performance of \( u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2} \) for low density confinements could be improved by supplementing its functional form with a slowly varying function (e.g. a Gaussian or a smaller exponent LJ potential) that can capture the long range effects more efficiently.

### 2.2.4 Quasi-continuum potential models for Carbon Dioxide

We use \( u_{\text{wall}}^{\text{wall-\text{CO}_2}} \) and \( u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2} \) to develop the quasi-continuum potential models for confined carbon dioxide, i.e.,

\[
U(r) = U_{\text{wall-\text{CO}_2}}(r) + U_{\text{CO}_2-\text{CO}_2}(r),
\]

\[
U_{\text{wall-\text{CO}_2}}(r) \approx \int_{\Omega} u_{\text{wall-\text{CO}_2}}^{\text{CGSS}}(|r - r'|) \rho_{\text{wall}}(r') \, dr',
\]

\[
U_{\text{CO}_2-\text{CO}_2}(r) \approx \int_{\Omega} u_{\text{CO}_2-\text{CO}_2}^{\text{CGSS}}(|r - r'|) \rho_{\text{CO}_2}(r') \, dr'.
\]

Here, \( \rho_{\text{wall}} \) and \( \rho_{\text{CO}_2} \) are the wall and the fluid density, respectively. \( U_{\text{wall-\text{CO}_2}}(r) \) and \( U_{\text{CO}_2-\text{CO}_2}(r) \) are the wall-fluid and the fluid-fluid interaction energy, respectively. The wall-fluid interaction energy, \( U_{\text{wall-\text{CO}_2}} \) (Eq. (2.22)), is computed by assuming the graphite surface as a continuum graphene layer with \( \rho_{\text{wall}} = 35 \) atoms/nm\(^2\) and an inter-layer spacing of 0.335 nm. Similar to LJ type fluids, fluid-fluid interaction energy, \( U_{\text{CO}_2-\text{CO}_2} \), is computed using a truncated softer repulsive core potential \( u_{\text{CO}_2-\text{CO}_2}^{t} \) as

\[
U_{\text{CO}_2-\text{CO}_2}(r) \approx \int_{\Omega} u_{\text{CO}_2-\text{CO}_2}^{t}(|r - r'|) \rho_{\text{CO}_2}(r') \, dr'.
\]

where \( u_{\text{CO}_2-\text{CO}_2}^{t}(r) \) is defined as

\[
u_{\text{CO}_2-\text{CO}_2}^{t}(r) = \begin{cases} 0 & r \leq R_{\text{crit}} \\ b_0 + b_1 r + b_2 r^2 & R_{\text{crit}} < r \leq R_{\text{min}} \\ u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}(r) & r > R_{\text{min}} \end{cases}
\]

\( R_{\text{min}} \) and \( R_{\text{crit}} \) define the softer repulsive region and the zero potential core, respectively. The coefficients \( b_0 \), \( b_1 \) and \( b_2 \) are computed by enforcing the continuity of the softer potential and its first and second derivative at \( R_{\text{min}} \). The parameters \( R_{\text{min}} \) and \( R_{\text{crit}} \) are also obtained through PMF matching algorithm, which is summarized in Algorithm 2. The parameterization of the quasi-continuum fluid-fluid interaction potential (finding \( R_{\text{min}} \) and \( R_{\text{crit}} \)) is performed using the same AA-MD simulation data that is used to parameterize the CGSS pair-potentials. In addition to the wall-fluid and the fluid-fluid PMF, the COM density profile
\( \rho_{CO_2}(r) \) is needed to perform this optimization. Once the quasi-continuum potential is optimized for a given thermodynamic state, it is used in EQT to predict the COM density and potential profiles of CO\(_2\) in different size nanochannels. Figure 2.9 shows the comparison of the COM density and potential profiles obtained by using the quasi-continuum models in EQT (solid line) with the AA-MD simulation results (open circle) for supercritical carbon dioxide (T = 348 K and P = 9.05 MPa) confined inside \( H = 2.232 \) nm and \( H = 1.488 \) nm wide graphite slit nanochannels. The parameters used in \( u_{CGSS}^{CO_2} \) and \( u_{CGSS}^{CO_2-CO_2} \) for this thermodynamic state are reported in Table 2.1. Parameters \( R_{min} \) and \( R_{crit} \) used in \( u_{CO_2-CO_2}^{t} \) are reported in Table 2.2. It can be observed that the results obtained from EQT are in good agreement with those obtained from AA-MD simulations.
Algorithm 2 Parametrization of fluid-fluid quasi-continuum potential.

1: Input: $\rho_{CO_2}(r)$ and target PMF, $U^{AA}(r)$, from AA-MD simulation.
2: Compute the wall-fluid PMF, $U_{wall-CO_2}(r)$, using Eq. (2.22).
3: Take initial guess for $R_{\text{min}}$ and $R_{\text{crit}}$.
4: Compute the fluid-fluid PMF, $U_{CO_2-CO_2}(r)$, using $\rho_{CO_2}(r)$ and $u_{CO_2-CO_2}(r)$ in Eq. (2.24).
5: Calculate $U(r) = U_{wall-CO_2}(r) + U_{CO_2-CO_2}(r)$ (Eq. (2.21)).
6: Obtain $R_{\text{min}}$ and $R_{\text{crit}}$ by solving the non-linear equation $U(R_{\text{min}}, R_{\text{crit}}, r) - U^{AA}(r) = 0$.

<table>
<thead>
<tr>
<th>Thermodynamic State</th>
<th>$R_{\text{crit}}$ (nm)</th>
<th>$R_{\text{min}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T=323K, P=10.1MPa</td>
<td>0.174</td>
<td>0.364</td>
</tr>
<tr>
<td>T=323K, P=1.01MPa</td>
<td>0.201</td>
<td>0.364</td>
</tr>
<tr>
<td>T=348K, P=9.05MPa</td>
<td>0.174</td>
<td>0.362</td>
</tr>
<tr>
<td>T=308K, P=5.50MPa</td>
<td>0.164</td>
<td>0.365</td>
</tr>
</tbody>
</table>

2.3 COM density profiles from EQT

We now use the quasi-continuum potentials in EQT to predict the COM density profile of CO$_2$ confined inside different width (1.05 to 3.72 nm) graphite slit nanochannels. Figure 2.10 shows the comparison of the COM density profiles at a high and a low pressure confinement state (P = 10.1 MPa and 1.01 MPa; T = 323 K). For both these states the potentials are parameterized using the AA-MD data of $H = 2.232$ nm wide graphite slit. The parameters are reported in Tables 2.1 and 2.2. It can be observed that the density profiles obtained from EQT (solid line) match well with those obtained from AA-MD simulations (open circle). For bigger nanochannels ($H = 3.72$ and 2.976 nm), the potentials capture both the density layering in the interfacial region and the bulk like behavior in the central region of the nanochannels. For smaller nanochannels ($H = 1.488$ and 1.116 nm), confinement makes the density inhomogeneous across the entire length of the nanochannel, which is also captured well with these potentials. At low pressure (low density) confinements, most of the fluid confinement occurs near the wall. Also, the density layer in the interfacial region does not split into two sub-layers and resembles like that of confined simple LJ type fluids. Figure 2.11 shows the COM density profiles at two different supercritical temperature states (T = 348 K, P = 9.05 MPa and T = 308 K, P = 5.50 MPa) as obtained from EQT. For T = 348 K state, the potentials are parameterized using the AA-MD data of $H = 2.232$ nm wide slit, while for T = 308 K state, AA-MD data of $H = 1.850$ nm wide slit is used to parameterize the potentials. The parameters are reported in Tables 2.1 and 2.2. Again, the results obtained from EQT are in good agreement with those obtained from AA-MD simulations. The general structural behavior at these two states looks quite similar to each other.
Figure 2.10: COM density profile of carbon dioxide confined inside different width graphite slit nanochannels at a high pressure (left) and a low pressure (right) confinement state. Solid line represents the results from EQT and open circle are the AA-MD results. $\rho_{\text{avg}}$ is reported in units of molecules/nm$^3$.

Figure 2.11: COM density profile of carbon dioxide confined inside different width graphite slit nanochannels at two different supercritical temperature states. Solid line represents the results from EQT and open circle are the AA-MD results. $\rho_{\text{avg}}$ is reported in units of molecules/nm$^3$. 

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2.4 COM density profiles from CG-MD Simulations

The CGSS wall-CO\(_2\) and CO\(_2\)-CO\(_2\) interaction potentials developed in this work are also used to perform CG-MD simulations. The objective of performing CG-MD simulations is to check their performance in a particle based CG simulation method. Figure 2.12 shows the comparison of the density profiles obtained from the CG-MD simulations (solid line) with the AA-MD (open circle) results for the four thermodynamic states considered in this work. It can be observed that the results obtained from CG-MD simulations are in reasonable agreement with those obtained from AA-MD simulations. The developed potentials work well in the interfacial region (reproduce the splitting of the density layer) but slightly underestimate the magnitude of the density profile in the central region of the nanochannels. The performance of the potentials for CG-MD simulations could be further improved by using parameterization techniques (especially for the fluid-fluid interaction potential \(u^{CGSS}_{CO_2-CO_2}\)) that are more suitable to particle based coarse-graining. Also, the functional form of the fluid-fluid interaction potential could be supplemented with a slowly varying function to capture the long range electrostatic effects more efficiently. Since the developed potentials are single-site potentials and do not contain any partial charges, the CG-MD simulations are computationally much faster than the AA-MD simulations. Further, to check the applicability of the potential models (applicability of the proposed functional form, parameterization procedure and the EQT formulation) to very small nanochannels (\(H < 1\) nm), they are used to predict the COM density profiles of carbon dioxide inside 0.60 nm and 0.744 nm wide slit nanochannels. Figure 2.13 shows the comparison of the density profiles obtained from the CG-MD simulation (broken line) and EQT (solid line) with those obtained from AA-MD simulations (open circle). It can be observed that the results obtained from both CG-MD and EQT are in good agreement with those obtained from AA-MD simulations.

2.5 Simulation Details

In this section, we provide the simulation parameters and settings used to perform AA-MD and CG-MD simulations. All MD simulations are performed in the NVT ensemble using the simulation package GROMACS 3.3.1[61]. In AA-MD simulations, carbon dioxide is modeled as a linear (O-C-O angle = 180°), rigid (fixed bond lengths) 3-site LJ molecule with partial charges. The parameters are taken from the model proposed by Zhang and Duan (2005) [2] with the values \(\sigma_{O-O} = 0.30\) nm, \(\epsilon_{O-O} = 0.68724\) KJ/mol, \(\sigma_{C-C} = 0.27918\) nm, \(\epsilon_{C-C} = 0.23983\) KJ/mol, and point charges of \(q_O/e = -0.2944\) and \(q_C/e = 0.5888\). The O-O bond length is 0.2326 nm, and C-O bond length is 0.1163 nm. To properly handle the 180° angle constraint in GROMACS, two dummy mass particles are used. The dummy mass particles are constructed such that
Figure 2.12: Comparison of the COM density profile obtained from CG-MD simulations (solid line) with those obtained from AA-MD simulations (open circle).
their mass and moment of inertia is identical to that of the CO$_2$ molecule. The position of the massless C and O atoms is constructed from the position of the dummy mass particles using the concept of virtual interaction-sites [61]. Electrostatic interactions are computed using the particle mesh Ewald (PME) method [63, 64] with Fourier spacing of 0.15 nm. The LINCS algorithm is used to maintain the shape of the molecule. The graphite wall is modeled as four graphene layers with lateral dimensions 4.550 × 4.331 nm$^2$ ($\rho_{\text{wall}} \approx 35$ atoms/nm$^2$) and an inter-layer spacing of 0.335 nm. The interaction parameters for graphite wall atoms have the values $\sigma_{w-w} = 0.34$ nm, $\epsilon_{w-w} = 0.23279$ KJ/mol [65, 66]. The Lorentz-Berthelot rules are used to estimate the cross interaction parameters. In CG-MD simulations, CO$_2$ is represented as a single-site molecule placed at its COM position. The wall-fluid and fluid-fluid interactions are defined by $u_{\text{wall-CO}_2}^{\text{CGSS}}$ and $u_{\text{CO}_2\text{-CO}_2}^{\text{CGSS}}$, respectively, and are specified using the table option [62] in the mdrun program of GROMACS. For both AA-MD and CG-MD simulations, Nosé-Hoover thermostat [67] with a time constant of 0.1 ps is used to maintain the temperature of the fluid. LJ cutoff distance is set to 1.2 nm and a time step of 1 fs is used to simulate the system. For a given thermodynamic state, MD simulation of the fluid in different size slit nanochannels requires the density of the fluid within the nanochannel as an input. The density of carbon-dioxide inside different width graphite slit nanochannels is obtained from the adsorption isotherms reported by Zhou and Wang (2000) [1] and Samios et al. (2000) [68]. In EQT, the wall-fluid PMF, $U_{\text{wall-CO}_2}$ (Eq. (2.22)), is computed by assuming the graphite surface as a continuum graphene layer with $\rho_{\text{wall}} = 35$ atoms/nm$^2$ and an inter-layer spacing of 0.335 nm. Fluid-fluid PMF, $U_{\text{CO}_2\text{-CO}_2}$, is computed using Eq (2.24). A finite-volume implementation to numerically solve the 1-D NP equation is discussed in Ref. [47].
2.6 Summary

The key results from this chapter can be summarized as follows:

- For poly-atomic fluids, the CGSS pair-potentials developed for the bulk state do not predict the correct microstructure at nanoscale confinements. The geometric shape and the relative orientation of the poly-atomic fluid can give rise to unique structuring/packing of the molecules near the confining surface. Also, unlike spherical LJ type fluids, for poly-atomic fluids, the wall-fluid interaction energy is a function of the thermodynamic state of the confined fluid.

- For confined carbon-dioxide, we proposed a two-minima 12-6 LJ type piecewise polynomial functional form to describe CGSS wall-fluid and fluid-fluid interactions. The proposed functional form successfully captures the distance-dependent preferred relative orientation of carbon-dioxide in nanoscale confined environments. PMF matching technique is used to parameterize the CGSS pair-potentials. Also, the proposed functional form is found transferable across a wide range of high and low pressure thermodynamic states.

- CGSS pair-potentials are used to develop quasi-continuum potential models, which are used in EQT to predict the COM density and potential profiles of carbon-dioxide confined inside different width graphite slit nanochannels at four different thermodynamic states. The predictions from EQT are found in good agreement with those obtained from AA-MD simulations.
Chapter 3

Thermal noise in confined fluids

3.1 Introduction

To develop multiscale models for dynamical properties of confined fluids, it is important to understand the interplay of thermal noise in the nanofluidic dynamics and transport. Thermal noise is the spontaneous microscopic fluctuations that occur naturally in a molecular system at finite temperature. In the last decade, few theoretical and molecular dynamics (MD) simulation studies have been performed that report the unforeseen role of thermal fluctuations in nanofluidic transport. Kalra et al. (2003) [8] in their MD simulation of osmotic flow through a carbon-nanotube (CNT) report that the water flow is stochastic in nature and the flow rate is governed by thermal fluctuations. Detcheverry and Bocquet (2012) [17, 18] explored the impact of hydrodynamic fluid fluctuations on the transport of mass and charge in nanochannels. Recently, Wan et al. (2012) [69] using a toy model showed that thermal noise may induce a biased (unidirectional) transport in a spatially asymmetric nanoscale dimension system, provided the correlation time of the thermal fluctuations is comparable to the characteristic time scale of the system. Though, these studies highlight the relevance of thermal fluctuations in nanofluidic dynamics and transport, a general methodology that can be used to characterize and understand thermal fluctuations in nanofluidic systems is, however, lacking.

Conventionally, equilibrium thermal fluctuations are modeled as “White” noise [70], which means that thermal fluctuations do not have any time scale associated with them and exist independently of the underlying physical process. This assumption provides a reasonable description in systems where the correlation time of thermal noise is much smaller than the characteristic time scales of the system (see Ref. [71] for discussion on different time scales associated with molecular motion). However, in many fluidic systems, specifically for fluids confined inside nanometer scale geometries, the White noise assumption might be insufficient or invalid. In this chapter, we discuss a combined memory function equation (MFE) and generalized Langevin equation (GLE) approach (MFE/GLE formulation) to characterize thermal noise in confined fluids.
3.2 MFE/GLE Formulation

In MFE/GLE formulation, we use the Langevin theory to characterize thermal noise in confined fluids. We assume that for confined systems in thermal equilibrium, the velocity \( v_q \) and position \( r_q \) of the fluid molecule of mass \( m \) in the direction \( q \) at time \( t \) can be described by the GLE \([72–74]\) as

\[
m \frac{dv_q(t)}{dt} = -m \int_0^t K_q(t - t') v_q(t') dt' + F_q(r_q(t)) + R_q(t),
\]

\[
\frac{dr_q(t)}{dt} = v_q(t),
\]

where \( K_q \) is the memory function that characterizes the velocity dependent dissipative force, \( F_q \) is the position dependent mean force that characterizes the structural inhomogeneity of the confined fluid and \( R_q \) is an additive random force that mimics the thermal noise. Further, as \( R_q \) represents equilibrium thermal fluctuations, no instant plays a preferential role (starting sampling time is referred to as \( t = 0 \)), and we assume that it obeys the following statistical relations

\[
\langle R_q(t) \rangle = 0,
\]

\[
\langle v_q(0) R_q(t) \rangle = 0,
\]

\[
\langle F_q(r_q(0)) R_q(t) \rangle = 0.
\]

Relation (3.2a) assumes that the mean value of the random force is zero as it does not disturb or destroy the equilibrium. Relations (3.2b) and (3.2c) assume that the thermal force is uncorrelated with the velocity and the mean force, respectively \([72]\). If we multiply Eq. (3.1a) by \( v_q(0)/\langle v_q(0)^2 \rangle \) and perform the ensemble averaging (angular brackets denote ensemble average) using Eq. (3.2b), we get

\[
\frac{d\Psi_q(t)}{dt} = -\int_0^t K_q(t - t') \Psi_q(t') dt' + \Theta_q(t),
\]

\[
\Psi_q(t) = \langle v_q(0) v_q(t)/\langle v_q(0)^2 \rangle \rangle,
\]

\[
\Theta_q(t) = \langle v_q(0) F_q(r_q(t))/m\langle v_q(0)^2 \rangle \rangle,
\]

where \( \Psi_q(t) \) is the normalized velocity autocorrelation function (\( v \)-ACF) and \( \Theta_q(t) \) is the time-dependent cross-correlation function between the mean force and the velocity of the fluid molecule. The above integro-differential equation (Eq. (3.3a)) that describes the time evolution of the \( v \)-ACF of a fluid molecule inside the confined system is the memory function equation (MFE) for a confined fluid. This equation reduces to the MFE for bulk fluids \((F_q = 0, \Theta_q(t) = 0)\), which is an exact equation that can be formally derived from
the Liouville equation using the projection operator formalism [73, 74]. Thus, Θ_q(t) can be interpreted as a measure of the additional memory that a confined fluid molecule carries because of its interaction with the confining surface. The utility of this equation is that given Ψ_q(t) and Θ_q(t) (from experiments or MD simulations), it can be used to compute the memory function K_q(t).

For fluids in thermal equilibrium, the fluctuation-dissipation (FD) theorem relates the memory function K_q(t) to the autocorrelation function of the random force used in the Langevin equation [74]. Now, we discuss that relationship. The GLE (Eq. (3.1a)) can be used to compute the autocorrelation function of the random force, \( \langle R_q(0)R_q(t) \rangle \), as

\[
\langle R_q(0)R_q(t) \rangle = m^2 \left[ \langle \dot{v}_q(0)\dot{v}_q(t) \rangle + \int_0^t K_q(t-t')\langle \dot{v}_q(0)v_q(t') \rangle dt' \right] - m\langle \dot{v}_q(0)F_q(r_q(t)) \rangle,
\]

(3.4)

where the dot (.) represents the derivative with respect to time. We have used the property defined in Eq. (3.2c) to obtain Eq. (3.4). Now, using the properties of the derivative of stationary autocorrelation functions, [74, 75] and performing the algebra using Laplace transform, the above equation can be solved for \( \langle R_q(0)R_q(t) \rangle \) as

\[
\langle R_q(0)R_q(t) \rangle = m^2\langle v_q(0)^2 \rangle \left[ K_q(t) - \Theta_q(0)\delta(t) \right],
\]

(3.5)

where δ is the Dirac delta function and the rest of the symbols have the same meaning as defined above.

Further, using the equipartition theorem that relates the variance of the velocity to temperature \( T \) as \( \langle v_q(0)^2 \rangle = m^{-1}k_B T \) (\( k_B \) is the Boltzmann constant), and realizing that \( \Theta_q(0) = 0 \) (since \( \Psi_q(t) \) is an even function in time, \( \frac{d\Psi_q}{dt} \bigg|_{t=0} = 0 \) and from Eq. (3.3a) we get \( \Theta_q(0) = 0 \)), we can simplify the relation as

\[
\langle R_q(0)R_q(t) \rangle = mk_BTK_q(t).
\]

(3.6)

The utility of this relation is that the knowledge of the memory function \( K_q(t) \) that describes the v-ACF of a molecular fluidic system can provide an understanding of the autocorrelation function of the thermal noise in that system. We use this relationship to compute the correlation time of the thermal noise, \( \tau_R \), as [70]

\[
\tau_R \equiv \frac{\int_0^\infty |\langle R_q(0)R_q(t) \rangle| dt}{\langle R_q(0)R_q(t) \rangle^2} = \frac{1}{K_q(0)} \int_0^\infty |K_q(t)| dt,
\]

(3.7)

which can be compared with other characteristic time scales to understand its interplay with the underlying physical process. In this work, we compare the thermal noise correlation time with the momentum relaxation time of the fluid. Momentum relaxation time is the average time it takes for a molecule to completely randomize its state in momentum. The momentum relaxation time, \( \tau_v \), can be estimated by using the
velocity autocorrelation function in place of the thermal noise autocorrelation function in Eq. (3.7). Such an analysis lets one understand the interplay of thermal noise in the self diffusion dynamics of the fluid. We now apply this approach to characterize thermal noise in molecular fluids.

3.3 Thermal noise in molecular fluids

3.3.1 Bulk fluids

We first use the MFE/GLE formulation to compute the correlation time of thermal noise in bulk fluids ($F_\eta = 0$, $\Theta_\eta(t) = 0$). Figures 3.1(a) and 3.1(b) show the comparison of the time decay of the center-of-mass (COM) $v$-ACF and the corresponding thermal noise autocorrelation function ($R$-ACF) for bulk carbon-dioxide (CO$_2$) [2] and extended simple point charge (SPC/E) [76] water, respectively. Both the $v$-ACF and the $R$-ACF are normalized by their initial value. The thermodynamic state for these fluids is reported in Table 3.1. $v$-ACFs are obtained from MD simulations. MD simulation is performed using the simulation package GROMACS [61]. Once $v$-ACF is known, Eq. (3.3a) is solved numerically to obtain $K(t)$, which is related to $R$-ACF through Eq. (3.6). The numerical procedure to solve Eq. (3.3a) is discussed in Ref. 74. It can be observed that for CO$_2$ the $v$-ACF and the $R$-ACF are widely separated in time, while for SPC/E water they have a significant overlap. Further, the $v$-ACF of CO$_2$ has an exponential type decay, which is typical of the relaxation mechanism in low density fluids where the fluid relaxes without experiencing significant
Table 3.1: Thermal noise correlation time, $\tau_R$, and the momentum relaxation time, $\tau_v$ in fluidic systems.

<table>
<thead>
<tr>
<th>System</th>
<th>$\rho$ (#/nm$^3$)</th>
<th>$T$ (K)</th>
<th>$\tau_R$ (ps)</th>
<th>$\tau_v$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk CO$_2$</td>
<td>9</td>
<td>323</td>
<td>0.03</td>
<td>0.51</td>
</tr>
<tr>
<td>Bulk SPC/E Water</td>
<td>33.3</td>
<td>300</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>SPC/E Water (6,6) CNT</td>
<td>-</td>
<td>300</td>
<td>0.35</td>
<td>0.22</td>
</tr>
<tr>
<td>SPC/E Water (16,16) CNT</td>
<td>-</td>
<td>300</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>SPC/E Water (30,30) CNT</td>
<td>-</td>
<td>300</td>
<td>0.06</td>
<td>0.06</td>
</tr>
</tbody>
</table>

backscattering from the neighboring molecules. For SPC/E water, the $v$-ACF shows a rapid initial decay, becomes negative because of backscattering and then slowly decays to zero. Also, it can be observed that the $v$-ACF of SPC/E water has a small bump at $t \sim 0.16$ ps before it becomes negative. It has been reported in the literature that this feature is universal to bulk water $v$-ACF at 1 bar pressure and 300 K temperature, and is independent of the interaction potential model used to simulate the water dynamics [77]. Its origin can be related to the rotational induced translation due to a combined effect of Lennard-Jones (LJ) and Coulomb interactions.

We use the $v$-ACFs and $R$-ACFs to compute the noise correlation time ($\tau_R$) and the momentum relaxation time ($\tau_v$) for these fluids. The correlation times are computed using Eq. (3.7) and are reported in Table 3.1. It can be observed that for CO$_2$ the correlation time of thermal noise is about an order of magnitude smaller than the momentum relaxation time ($\tau_v/\tau_R \sim 15$), while for bulk water the noise and the momentum relaxation times are of the same order ($\tau_v/\tau_R \sim 1$). It is only when the thermal noise correlation time is much smaller than the characteristic time scale of the system, it can be assumed uncorrelated with the underlying physical process and “White” noise description is valid. When the two time scales are of comparable order, the memory effects become important and the finite correlation time of the thermal noise must be taken into account to understand the interplay of thermal noise. Our conclusion for bulk water is consistent with the results of Liu et al. (2004) [78], where they show the inability of the Gaussian White-noise in capturing the short-time self-diffusion dynamics of TIP4P water molecules in the bulk state. Also, we want to point out that the noise correlation time for bulk SPC/E water computed here ($\tau_R \sim 0.06$ ps) is lower than the value of $\sim 2$ ps reported in Ref. [79]. The reason for this discrepancy is that in Ref. [79] the autocorrelation function of the force that the oxygen atom of the water molecule experiences in a MD simulation is used to compute the correlation time of thermal noise.

3.3.2 Confined fluids

We now use the MFE/GLE formulation to study thermal noise in confined fluids. For fluids confined inside nanometer scale geometries, due to the strong interaction of the fluid molecules with the confining wall, the
fluid becomes inhomogeneous and its static and dynamical properties are different in the direction parallel and perpendicular to the confining surface [14]. We study the properties of thermal noise in both the directions.

The first system we study is SPC/E water confined inside a 11\(\sigma_{oo}\) wide (\(\sigma_{oo}\) is the LJ interaction distance parameter of the oxygen atom of SPC/E water molecule; \(\sigma_{oo} = 0.317\) nm [76]) semi-infinite graphite slit nanochannel. The system is loaded at a reference bulk state of 33.3 molecules/nm\(^3\) and 300 K temperature. Figure 3.2(a) shows a schematic diagram of the semi-infinite slit nanochannel system (slit is infinite in \(x\) and \(y\) directions and \(z\) is the confining direction). The molecular modeling and MD simulation details for all the confined SPC/E water systems considered in this work can be found in Refs. [35, 80]. Figure 3.2(b) shows the variation of the local number density \(\rho(z)\) of the water molecules across the confinement. To understand the effect of confinement, we divide the slit into three regions, Reg. I, II and III, based on their perpendicular distance from the confining wall. Figures 3.2(c) and 3.2(d) show the variation of the mean force, \(F_q\), in the three regions along the perpendicular (\(q = z\)) and the parallel (\(q = x\)) directions, respectively. It can be observed that \(F_z\) is oscillatory in Regs. I and II, and is a constant \(\sim 0\) in Reg. III, thus giving rise to an inhomogeneous density profile near the confining surface and a bulk-like homogeneous density in the central region of the nanochannel. The variation of \(F_x\) is very small (\(\sim 0\)) in all the three regions, which suggests that the lattice structure of the graphite wall does not induce structural inhomogeneity along the parallel direction. Figure 3.2(e) shows the comparison of the COM \(v\)-ACF of water along \(x\) (broken line) and \(z\) (solid line) directions in the three regions. The \(v\)-ACFs are normalized by their initial value. It can be observed that in Reg. I, which is nearest to the wall, the time decay of the \(v\)-ACF in \(x\) and \(z\) directions is significantly different from each other, confirming that the dynamical behavior of the fluid molecules is highly anisotropic.

In Regs. II and III, the \(v\)-ACFs in both directions look quite similar to each other. It is interesting to observe that in Reg. II, though the density profile is quite inhomogeneous (see Fig. 3.2(b)), the two \(v\)-ACFs are not significantly different from each other.

With \(v\)-ACFs known from MD simulation, we now use the MFE to compute the memory function in each region. It can be observed from Eq. (3.3a) that for confined fluids the time evolution of \(v\)-ACF is governed by a combined effect of the dynamical response due to the interaction of the fluid molecules with the confining surface (\(\Theta_q(t)\)) and the thermal noise (\(K_q(t)\)). To solve Eq. (3.3a) for \(K_q(t)\), we also need to compute the function \(\Theta_q(t)\) in each region. To compute \(\Theta_q(t)\), we need the positions \(r_q\) (to compute the mean force \(F_q\)) and the velocity \(v_q\), both of which are directly obtained from MD simulation. Since \(F_x\) is \(\sim 0\), in all the three regions, the cross-correlation function \(\Theta_x(t)\) is also negligible in all the three regions. Figure 3.2(f) shows the variation of the function \(\Theta_z(t)\) in the three regions. It can be observed that \(\Theta_z(t)\) provides a significant short time contribution (until 0.5 ps) in Reg. I, while it is almost zero in Reg. II and III. We use \(\Theta_q(t)\) and \(v\)-ACF of each region and direction (total 6 cases) in Eq. (3.3a) and
Figure 3.2: (a) Schematic of a semi-infinite slit nanochannel, (b) Number density $\rho(z)$, (c)-(d) Mean force profiles (Force is in kJ/mol-nm), (e) $v$-ACFs along $x$ (broken line) and $z$ (solid line) directions, (f) Variation of $\Theta_z(t)$ and (g) Memory functions $K_x(t)$ (broken line) and $K_z(t)$ (solid line) of SPC/E water confined inside a graphite slit.
numerically compute $K_q(t)$. Figure 3.2(g) shows the comparison of the memory functions, $K_{x/z}(t)$, along $x$ (broken line) and $z$ (solid line) directions in the three regions. Similar to $v$-ACFs, the memory functions are also normalized by their initial value ($K_{x/z}(0)$). It can be observed that the time decay of the memory functions along $x$ and $z$ directions in each region is quite similar to each other. Also, the time decay of the memory functions in the three regions do not differ significantly from each other. The correlation time of the thermal noise (computed using Eq. (3.7)) in the three regions along both the directions is found to be quite similar and is $\sim [0.05 - 0.06]$ ps. These observations suggest that even though the $v$-ACF is spatially anisotropic, the correlation time and the time decay of the thermal noise autocorrelation function are not significantly different across the confinement. Further, from Eq. (3.3a) we can deduce that it is the strong cross-correlation of the mean force with the molecular velocity (characterized by the function $\Theta_q(t)$) that gives rise to the spatial anisotropy in the $v$-ACF of the confined fluid.

To investigate further on the statistical properties of the thermal noise in each region, we use the computed memory functions in the GLE and extract the thermal force from the total force that a particle experiences in a MD simulation. If $F^\text{tot}_q(t)$ is the total instantaneous force at time $t$ along the direction $q$, then Eq. (3.1a) can be written for $R_q(t)$ as

$$R_q(t) = [F^\text{tot}_q(t) - F_q(r_q(t))] + m \int_0^t K_q(t - t') v_q(t') dt'.$$

The total force, velocity and position at each instant can be directly obtained from MD simulation and the above equation can be solved numerically to obtain $R_q(t)$. To minimize the artificial effects of MD thermostats, MD simulation was performed in the NVE ensemble, where $N$ is the number of particles, $V$ is the volume and $E$ is the total energy of the system. We extract the thermal force and estimate the frequency distribution and statistical moments of the thermal force for each region and direction. Figure 3.3 shows the comparison of the frequency distribution and Table 3.2 reports the mean, variance, skewness and Kurtosis value of the thermal force extracted from the MD simulation. It can be observed that the distribution

---

Table 3.2: Statistical moments of the thermal force $R_q(t)$ as extracted from the MD simulation.

<table>
<thead>
<tr>
<th>Reg.</th>
<th>Direction</th>
<th>Mean</th>
<th>Variance</th>
<th>Skewness</th>
<th>Kurtosis</th>
<th>$K_q(0)$</th>
<th>$m k_B T K_q(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$x$</td>
<td>-3.7±52.3</td>
<td>5.71E+04±4.9E+03</td>
<td>-0.012±0.08</td>
<td>3.65±0.22</td>
<td>1211</td>
<td>5.44E+04</td>
</tr>
<tr>
<td>I</td>
<td>$z$</td>
<td>11.2±36.8</td>
<td>4.85E+04±6.9E+03</td>
<td>-0.29±0.20</td>
<td>4.29±0.47</td>
<td>1123</td>
<td>5.04E+04</td>
</tr>
<tr>
<td>II</td>
<td>$x$</td>
<td>1.01±47.3</td>
<td>5.39E+04±2.8E+03</td>
<td>0.004±0.07</td>
<td>3.65±0.23</td>
<td>1231</td>
<td>5.53E+04</td>
</tr>
<tr>
<td>II</td>
<td>$z$</td>
<td>-3.37±51.4</td>
<td>5.23E+04±4.2E+03</td>
<td>-0.034±0.20</td>
<td>3.66±0.24</td>
<td>1261</td>
<td>5.66E+04</td>
</tr>
<tr>
<td>III</td>
<td>$x$</td>
<td>1.74±45.9</td>
<td>5.42E+04±2.5E+03</td>
<td>0.002±0.08</td>
<td>3.62±0.24</td>
<td>1233</td>
<td>5.54E+04</td>
</tr>
<tr>
<td>III</td>
<td>$z$</td>
<td>-1.97±45.2</td>
<td>5.41E+04±2.7E+03</td>
<td>0.004±0.08</td>
<td>3.63±0.22</td>
<td>1240</td>
<td>5.57E+04</td>
</tr>
</tbody>
</table>
function of the thermal force in all three regions qualitatively resemble a zero mean Gaussian distribution, which is typically assumed to model thermal noise in molecular fluids. It can be observed from Table 3.2 that the mean of the thermal force is \( \sim 0 \) for all regions and directions. Also, for Reg. I, which is nearest to the confining surface, the variance of the thermal force along the \( z \) direction is lower than that of the \( x \) direction. For Regs. II and III, the variance along \( x \) and \( z \) directions are quite similar to each other. Further, it is interesting to note that for all regions and directions, the skewness value (third moment) is not strictly zero and the Kurtosis value (fourth moment) is greater than 3. A non-zero skewness value and a Kurtosis value greater than 3 suggest that thermal noise is not strictly Gaussian. We also report in Table 3.2 the initial value of the memory function \( K_q(0) \) and the theoretical variance value (\( \langle R_q(0)^2 \rangle = m k_B T K_q(0) \)) for each region and direction. It can be observed that within statistical uncertainty, the variance of the thermal force extracted from the MD simulation for all directions and regions is in agreement with their respective theoretical values. Thus, the noise extraction from MD simulation suggests that frequency distribution of the thermal force is non-Gaussian and its distribution near the confining surface is different in the direction parallel and perpendicular to the confinement. We also repeated our calculations by performing a MD simulation for this system using the simulation package LAMMPS [81]. The aim was to ensure that the MD inputs to the MFE/GLE formulation are the same from both LAMMPS and GROMACS. The \( v \)-ACFs, cross-correlation functions \( \Theta_q(t) \) and memory functions \( K_q(t) \) obtained from LAMMPS were found to be
almost identical to those obtained from GROMACS. To check if the non-Gaussian features observed in the confined fluid are also observed in the bulk fluid, we extracted and analyzed thermal noise in the bulk SPC/E water at the same thermodynamic state. For bulk water too the Kurtosis value was found greater than 3. It has been reported in the literature that non-Gaussian behavior is also observed in the velocity autocorrelation function of dense bulk fluids [82, 83].

To show the generality of these observations to a different confining surface, we use the formulation to study thermal noise for SPC/E water confined inside a 4σoo wide semi-infinite silicon slit-shape nanochannel. This system is also loaded at a reference bulk state of 33.3 molecules/nm³ and 300 K temperature [80]. Figure 3.4(a) shows the variation of the local density ρ(z) across the confinement. It can be observed that for this system the density profile of water is completely inhomogeneous across the confinement. Here again we divide the slit into two regions (Reg. I and II) to understand the effect of the confinement. Figures 3.4(b) and 3.4(c) show the variation of the mean force along z and x directions, respectively. It can be observed that...
observed that for this system, $F_x$ varies periodically in Reg. I. This periodic variation of $F_x$ characterizes the effect of the lattice structure of the silicon wall and gives rise to structural inhomogeneity along the parallel direction. Figures 3.4(d)-(f) show the COM $v$-ACFs, cross-correlation functions $\Theta_{x/z}(t)$ and memory functions $K_{x/z}(t)$, respectively, for this system. It can be observed that even for this system the time decay of the memory functions (Fig. 3.4(f)) in the two regions along both directions is quite similar to each other. For this system too, it is the strong cross-correlation of the mean force with the molecular velocity that gives rise to the dynamical anisotropy in the $v$-ACF near the confining surface. It is interesting to note that though the magnitude of $F_x$ oscillates with a finite non-zero magnitude in Reg. I, function $\Theta_x(t)$ (Fig. 3.4(e)) is quite small in comparison to $\Theta_z(t)$. This is because the magnitude of $F_x$ is much smaller than that of $F_z$. We also performed this study for SPC/E water confined inside different size graphene slit nanochannels, and for CO$_2$ and LJ argon confined inside different size graphite slit nanochannels. The physical findings obtained for these systems were also found to be consistent with the findings reported above.

Now, we use the MFE/GLE approach to compute the correlation time of thermal noise for water confined inside a (6,6) CNT. The motivation of this study is to understand if the preferential orientation of the hydrogen bond of water molecules inside a (6,6) CNT can effect the correlation time of thermal noise. In the bulk state, water forms on an average 4 hydrogen bonds, but the molecules are pulled or pushed by their hydrogen bonds isotropically without any preferential direction. Inside smaller size CNTs, specifically (6,6) CNT, the average number of hydrogen bonds that a water molecule forms is between 1 and 2 but they act mainly along the axis of the CNT and present a very strong correlation between the neighboring water molecules [9]. Because of these highly coordinated hydrogen bonds, water forms a twisted spiral-like single-file chain where two water molecules cannot cross each other [10]. Though water forms a single-file chain, it has been reported in several MD simulation studies that the diffusion mechanism of water inside (6,6) CNT exhibits an initial ballistic motion, which, in the long run, changes to Fickian [11]. As long as the mean-square-displacement (MSD) exhibits a Fickian dynamics at long times, the GLE (Eq. (3.1a)) can be used to model the stochastic dynamics of water inside a (6,6) CNT [84]. We apply the MFE/GLE approach to compute the noise correlation time for SPC/E water confined inside (6,6), (16,16) and (30,30) CNTs, which are loaded at the same thermodynamic state. The CNTs are infinitely long and are loaded at 1 bar pressure and 300 K temperature. The molecular modeling and MD simulation details for water-CNT systems can be found in Ref. [85]. Figures 3.5(a) and 3.5(b) show the comparison of the COM $v$-ACFs and the corresponding memory functions $K(t)$, respectively, of the water molecules along the axial direction for each CNT. Also, for comparison, we plot the $v$-ACF and the memory function of bulk water at 1 bar pressure and 300 K temperature. Both the $v$-ACF and the memory function are normalized by their initial value. It can be observed that the time decay of both the $v$-ACFs and the memory functions of the water molecules
inside (30,30) and (16,16) CNTs (see insets) are very similar to that of bulk water. For (6,6) CNT, it can be observed that both the short time (see insets) and the long time behavior of the \( \nu \)-ACF and the memory function are significantly different from that of bulk water. The \( \nu \)-ACF shows a distinctive hump starting at \( \sim 4 \) ps, which reoccurs at \( \sim 8 \) ps, albeit with a smaller magnitude before eventually decaying to zero. We have time averaged the \( \nu \)-ACF up to 6 ns to ensure that these humps are not statistical noise. Also, the \( \nu \)-ACF is computed using the molecules in the middle of the tube (tube is 17.192 nm long and contains 99 water molecules) to ensure that these humps are not a periodic boundary condition (PBC) artifact. These long time non-zero correlations, which are absent in the bulk state and bigger size CNTs are the characteristics of the highly concerted single-file motion of the water molecules inside a (6,6) CNT. We use the computed memory functions to estimate the noise correlation time for these systems. The thermal noise correlation times are reported in Table 3.1. Also, for comparison, we report the momentum relaxation time of water in these systems. It can be observed from Table 3.1 that for (6,6) CNT, the noise correlation time is \( \sim 0.35 \) ps.
which is around 5 times bigger than that of bulk water (0.06 ps). For (16,16) and (30,30) CNT, the noise correlation time is same as that of bulk water. Also, it can be observed from Table 3.1 that the ratio of the noise and momentum relaxation times in these systems is \( \sim 1 \), suggesting that thermal noise cannot be assumed uncorrelated and its finite correlation time must be accounted for to understand the interplay of thermal noise in these systems.

### 3.4 GLE simulation for self-diffusion dynamics of confined fluids

In this section, we discuss a combined GLE+EQT approach to simulate self-diffusion dynamics of fluids in nanoscale confined systems. We show that using the PMF profile obtained from EQT and assuming the thermal noise to be spatially isotropic and Gaussian distributed in GLE reproduces several important single-particle dynamical properties of confined fluids. Though the noise extraction from MD reveals that thermal force is not strictly Gaussian distributed, we still assume it to be Gaussian. The reason for assuming the noise to be Gaussian is purely a mathematical simplicity as a correlated Gaussian distribution can be easily generated numerically. Further, such an exercise will let us understand what sort of discrepancies can occur in the computed quantities if the non-Gaussian features are ignored in modeling thermal noise.

The system we choose is a high density LJ argon (Ar) (average density 18.5 atoms/nm\(^3\) and temperature 300 K) confined inside a 5\( \sigma_{\text{Ar,Ar}} \) wide (\( \sigma_{\text{Ar,Ar}} \) is LJ interaction distance parameter; \( \sigma_{\text{Ar,Ar}} = 0.34 \text{ nm} \) [48]) semi-infinite graphite slit. The reason for choosing this system is that in one of our earlier studies [86] this system showed maximum quantitative difference in the computed single-particle quantities when the finite correlation time of thermal noise was ignored and thermal fluctuations were modeled as Gaussian White noise. Figures 3.6(a) and 3.6(b) show the mean force profile \( F_z \) and the memory function \( K(t) \), respectively, for this system. The mean force profile \( F_z \) is obtained from an empirical potential based quasi-continuum theory (EQT) [47, 48]. Memory function \( K(t) \) is obtained by using the MFE/GLE formulation and we take the memory function of Reg. II (see Fig. 3.6(a)) to be the representative memory function for the entire system. Also, it is found that the memory function of the confined fluid at a particular thermodynamic state is not significantly different than that of the corresponding bulk fluid in the same state. Thus, the memory function for a confined fluid can be obtained by performing a quick bulk fluid MD simulation at the reference state. The thermal noise correlation time of LJ Ar in this system can be estimated using Eq. (3.7) and is \( \sim 0.08 \text{ ps} \). With the mean force profile and the memory function known, we solve Eqs. (3.1a) and (3.1b) to compute the position and velocity of the confined fluid molecule in the perpendicular (\( q = z \)) direction. We use an approximate frequency domain method to generate correlated Gaussian random numbers \( R_z(t) \). The algorithm is discussed in Ref. [87]. A stochastic version of the Verlet algorithm is used to numerically integrate
the GLE in time. This integration scheme is discussed in Ref. [88]. The numerical procedure to generate correlated Gaussian random numbers and time integration of GLE are briefly discussed in Appendix A. The simulation is used to compute the MSD and survival probability of argon in different regions across the confinement (see Fig. 3.6(a)). To compute static quantities such as equilibrium density, the assignment of a molecule to a particular region can be unambiguously done based on its position alone, and is independent of the time. However, the assignment of a molecule for the computation of dynamic quantities such as MSD (or self-diffusion coefficient) is tricky as the molecule can move out of the region during the sampling time. For computing dynamic quantities, two tagging strategies are generally used; a) Initial position based tagging in which a molecule is assigned to a region if it is in the region at the initial time \( t_0 \), regardless of its position at subsequent times, b) Occupation-time based tagging in which a molecule is assigned to a particular region only if it stays in that region for certain percentile (say 60%) of the sampling time. The relative merits of these two approaches are discussed by Pinnick et al. (2010) [89]. Here, we use the initial position based strategy to compute the MSD in different regions. In confined fluids, the position dependent MSD, \( \langle [r_q(t) - r_q(t_0)]^2 \rangle \), along the direction \( q \) can be computed as [86]

\[
\langle [r_q(t) - r_q(t_0)]^2 \rangle = \frac{1}{J} \sum_{j=1}^{J} \frac{1}{N_j(t_0)} \sum_{i=1}^{N_j(t_0)} [r_q^i(t) - r_q^i(t_0)]^2,
\]

(3.9)

where \( r_q^i(t_0) \) is the position of a molecule \( i \) at the starting time \( t_0 \), \( r_q^i(t) \) is its position at a later time \( t \) and \( N_j(t_0) \) is the number of particles present in the region of interest at the starting time \( t_0 \). The simulation time is partitioned into blocks and the sampling process is repeated \( J \) times to perform block averaging. Survival probability is defined as the average probability that a particle which was inside a region at time \( t_0 \) still remains inside that region at a later time \( t \). For a region, \( q_L \leq q \leq q_U \), the survival probability, \( P([q_L, q_U], t; [q_L, q_U], t_0) \), can be defined as [90]

\[
P([q_L, q_U], t; [q_L, q_U], t_0) = \int_{q_L}^{q_U} dq \int_{q_L}^{q_U} dq_0 \ P([q_L, q_U], t|[q_L, q_U], t_0)g(q_0)
\]

(3.10)

where \( P([q_L, q_U], t|[q_L, q_U], t_0) \) is the conditional probability that the particle was located in the region \( q_L \leq q \leq q_U \) at time \( t \), given that it was in the region \( q_L \leq q \leq q_U \) at time \( t_0 \). \( g(q_0) \) is the probability for the particle to be in \( q_L \leq q \leq q_U \) at time \( t_0 \). In a particle based simulation, it is computed as [78, 86]

\[
P([q_L, q_U], t; [q_L, q_U], t_0) = \frac{1}{J} \sum_{j=1}^{J} \frac{N_j(t)}{N_j(t_0)}.
\]

(3.11)
where \( N_j(t_0) \) is the number of particles present in the region at time \( t_0 \), and \( N_j(t) \) is the number of those particles which still remain in the region after time \( t - t_0 \). Survival probability is a boundary dependent quantity and its accuracy is quite sensitive to the resolution of the short time dynamics [78]. Figures 3.6(c) and 3.6(d) show the comparison of the MSD and survival probability, respectively, in different regions as obtained from GLE and MD simulations. It can be observed that the results obtained by assuming the thermal noise to be isotropic and Gaussian distributed are in reasonably good agreement with those obtained from MD simulation. What quantities and what length and time scale can get effected by ignoring the non-Gaussian features of thermal noise is under investigation.

### 3.5 Summary

The key results from this chapter can be summarized as follows:

- In this chapter, we discussed a combined MFE/GLE formulation to characterize thermal noise in confined fluids. Our study revealed that the correlation time and the time decay of the autocorrelation function of the thermal noise are not significantly different across the confinement. We showed that
it is the cross-correlation of the mean force with the molecular velocity that gives rise to the spatial anisotropy in the velocity-autocorrelation function of the confined fluids.

- We also used the MFE/GLE formulation to extract the thermal force that a single particle experiences in MD simulations. Noise extraction from MD simulation revealed that for both bulk and confined fluids the distribution function of the thermal force is not strictly Gaussian. Also, the frequency distribution of the thermal force near the confining surface is found to be different in the direction parallel and perpendicular to the confinement.

- We used the MFE/GLE formulation to compute the noise correlation time for water confined inside different size CNTs. It is found that inside the (6,6) CNT, in which water arranges itself in a highly concerted single-file arrangement, the correlation time of thermal noise is an order of magnitude larger than that of bulk water.

- We also discussed an example which demonstrated that using the PMF profile from EQT, and assuming the thermal noise to be spatially isotropic and Gaussian distributed in the GLE can be used to simulate important single-particle dynamical properties of confined fluids.
Chapter 4

A GLE based approach to estimate interfacial friction at liquid-solid interfaces

4.1 Introduction

In this chapter we discuss a two-dimensional (2-D) GLE formulation that can be used to estimate the interfacial friction coefficient at liquid-solid interfaces. Interfacial friction coefficient is an important macroscopic modeling parameter that provides the atomistic to continuum bridge by incorporating the effect of the wall-lattice structure and the nature of wall-fluid interactions on the fluid transport. The results obtained from the proposed GLE formulation are used in a quasi-continuum hydrodynamical transport theory proposed by Bhaduria and Aluru \cite{91, 92} to study the transport of water in slit-shaped nanochannels.

4.2 Interfacial friction coefficient

To compute the interfacial friction coefficient, $\zeta_0$, we follow the approach presented by Huang and Szlufarska (HS) in Ref. \cite{93}. HS argue that the friction experienced by the fluid particles in the interfacial region is an intrinsic property of the system, and that the friction coefficient is additive. In this approach, using the linear response theory, first the friction coefficient $\zeta_j^0$ of an individual fluid particle $j$ (see Fig. 4.1) near the interface is computed in terms of single-particle equilibrium time correlation functions as \cite{93}

$$
\zeta_j^0 = \int_0^\infty \int_0^\infty \left\langle \frac{\langle f_{x,j}^{wf}(0) f_{x,j}^{wf}(t) \rangle dt}{k_B T + \langle v_{x,j}(0) f_{x,j}^{wf}(t) \rangle dt} \right\rangle,
$$

where $f_{x,j}^{wf}$ and $v_{x,j}$ are the instantaneous streaming direction wall-fluid force and velocity of the particle $j$ near the solid wall. The time correlation in the numerator is the single-particle wall-fluid force autocorrelation function (FACF) and denominator contains wall-fluid force–velocity cross-correlation function (FVCCF). Then, the contributions from all the interfacial fluid particles is added to obtain the total interfacial friction

46
coefficient $\zeta_0$ as

$$\zeta_0 = \sum_j \zeta_0^j.$$  

(4.2)

The derivation of Eq. (4.1) is provided in Appendix B.

### 4.3 GLE formulation

The FACF and FVCCF in Eq. (4.1) can be evaluated either from equilibrium molecular dynamics (EMD) simulation or any other particle sampling method that can simulate the single-particle dynamical motion of confined fluids in equilibrium. We propose a 2D GLE formulation to compute these equilibrium correlation functions. We have shown in our previous works [86, 94] that using the structural information (PMF profile) obtained from EQT and using the memory function of the reference bulk state fluid, GLE can be used as a computationally efficient means to simulate the single-particle properties of confined fluids. With this knowledge, to compute the interfacial friction coefficient, we formulate a 2D GLE model as

$$m \frac{dv_{z,j}(t)}{dt} = -m \int_0^t K(t-t')v_{z,j}(t')dt' + f_{z,j}^{tot}(z_j(t)) + R_z(t),$$  

(4.3a)

$$m \frac{dv_{x,j}(t)}{dt} = -m \int_0^t K(t-t')v_{x,j}(t')dt' + f_{x,j}^{tot}(x_j(t), z_j(t)) + R_x(t),$$  

(4.3b)

$$\frac{dz_j(t)}{dt} = v_{z,j}(t), \quad \frac{dx_j(t)}{dt} = v_{x,j}(t).$$  

(4.3c)
Here \( m \) is the mass of the fluid particle \( j \), while \( v_{z,j}, v_{x,j} \) are, respectively, the velocities in the confined (\( z \)) and streaming (\( x \)) directions. \( f_{z,j}^{\text{tot}} \) and \( f_{x,j}^{\text{tot}} \) are the instantaneous forces in \( z \) and \( x \) directions, respectively, experienced by the particle due to the structural inhomogeneity, while \( R_{z}(t) \) and \( R_{x}(t) \) are the random forces in confined and streaming directions, respectively. The random force satisfies the following statistical properties

\begin{align}
\langle R_{\alpha}(t) \rangle &= 0, \\
\langle v_{\alpha,j}(0) R_{\beta}(t) \rangle &= 0, \\
\langle f_{\alpha,j}^{\text{tot}}(0) R_{\beta}(t) \rangle &= 0, \\
\langle R_{\alpha}(0) R_{\beta}(t) \rangle &= m k_B T K(t) \delta_{\alpha\beta},
\end{align}

where \( \alpha \) and \( \beta \) are the directions in the 2D system (\( x \) and \( z \)), and \( \delta_{\alpha\beta} \) is the Kronecker delta, which is unity only when \( \alpha = \beta \) and zero otherwise. The memory function \( K(t) \) in both confined (Eq. (4.3a)) and streaming (Eq. (4.3b)) direction equations is the same. Since the memory function is same in the two directions, the thermal force also has identical statistical properties in both directions (noise is assumed isotropic, Eq. (4.4d)). Also, the memory function for this confined system is assumed to be the same as the memory function of the corresponding bulk water state. To justify this assumption, we compare the memory function \( K(t) \) of bulk water and water confined within the first interfacial layer of \( 4 \sigma_f \) wide silicon slit channel in Fig. 4.2(a). The confined water is in equilibrium with bulk water at density 33.46 molecules/nm\(^3\). It can be observed from the plot that the time decay characteristics and the correlation time of the memory function is not significantly different from corresponding bulk state even under high degree of confinement.

The instantaneous force values on particle \( j \), i.e., \( f_{z,j}^{\text{tot}} \) and \( f_{x,j}^{\text{tot}} \), are realized from the static mean force maps \( F_{z}^{\text{tot}}(z) \) and \( F_{x}^{\text{tot}}(x,z) \). Since the magnitude of \( F_{z}^{\text{tot}} \) is very large near the interface, its variation along \( x \) is ignored, and it is directly obtained from EQT as \( F_{z}^{\text{tot}}(z) = -dU^{\text{tot}}(z)/dz \). This means that the dynamics along the confined direction is primarily dictated by a 1D GLE formulation (Eq. (4.3a)), as demonstrated in our earlier works [86, 94]. However, it is necessary to consider the variation of \( F_{x}^{\text{tot}} \) in both directions, since its variation in the streaming direction is necessary to capture the effect of surface corrugations on the friction coefficient, and its magnitude changes very sharply along the confined direction near the interface. Also, the total mean force map along the streaming direction can be approximated as the wall-fluid force map \( (F_{x}^{\text{tot}}(x,z) \approx F_{x}^{\text{wf}}(x,z)) \). This approximation means that the spatial inhomogeneity in the fluid density profile in the streaming direction primarily results due to the variation in the wall-fluid potential. Figures 4.2(b) and 4.2(c) show the comparison of the streaming direction total force and the
Figure 4.2: (a) Memory function of SPC/E bulk water (blue line) at 298 K and density 33.46 molecules/nm$^3$. Also plotted are memory function of water in the streaming (green dash-dot line) and confined (red dashed line) direction for 4$\sigma_B$ wide Silicon-water system. Mean wall-fluid (solid blue line) and total (red open circles) force in the streaming direction for (b) graphene-water, and (c) silicon-water interface.
wall-fluid force profile for graphene-water and silicon-water interfaces, calculated using EMD, at the location of the first density peak. It can be observed that the wall-fluid force profile does not differ significantly from the total force profile near the interface. The advantage of this approximation is that the two-dimensional wall-fluid force map can be computed analytically using the structure of the wall as

$$U_{wf}^{3D}(x,y,z) = \sum_{r_i < R_{cut}} u_{LJ}^{wf}(r_i),$$  \hspace{1cm} (4.5a)

$$\frac{dU_{wf}^{3D}}{dx} = \sum_{r_i < R_{cut}} \frac{du_{LJ}^{wf}}{dr_i} \cdot \frac{x - x_i}{r_i},$$  \hspace{1cm} (4.5b)

$$F_{wf}^x(x,z) = -\frac{\int_0^{L_y} \frac{dU_{wf}^{3D}}{dx} \exp(-\beta U_{wf}^{3D}) \, dy}{\int_0^{L_y} \exp(-\beta U_{wf}^{3D}) \, dy},$$  \hspace{1cm} (4.5c)

where $r_i = ((x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2)^{1/2}$ is the distance between the wall particle centered at $(x_i, y_i, z_i)$ to the point of interest $(x, y, z)$, $u_{LJ}^{wf}$ is the 12–6 LJ wall-fluid interaction potential, $U_{wf}^{3D}$ is the three dimensional wall-fluid interaction energy, $\beta = 1/k_B T$, and $L_y$ is the box length in the $y$ direction. The wall particles which are inside the cutoff length $R_{cut} = 1.4$ nm are considered in the summation, similar to the confined MD simulations. Therefore, all the inputs needed to compute the interfacial friction coefficient are obtained without using computationally expensive EMD. 2D GLE simulations are performed with a time step of 0.01 ps, with the production trajectory of 400 ps, with data saved every other step (0.02 ps). The numerical procedure to obtain the memory function $K(t)$ and the time integration of the GLE are discussed in Ref. [94]. First 100 ps of the simulation trajectory was discarded to allow the equilibration of the fluid particle. We used $\sim 2 \times 10^4$ instances of particle trajectories to compute the time correlations in Eq. (4.1). A typical GLE simulation for 100 ps equilibration and 400 ps production run takes about 144 seconds in CPU time. In contrast, a typical EMD simulation is orders of magnitude slower (approximately 24 CPU hours to simulate a 500 ps run for graphene water $10\sigma_f$ system). Also, as GLE is a single particle formulation, it can be run on a personal workstation, as opposed to EMD/NEMD, which require suitable parallelization and High Performance Computing Cluster environments to reduce the wall-time. Therefore, the GLE simulation provides a massive speedup over EMD to obtain the interfacial friction coefficient.
4.4 Results

In this section, we compare the accuracy of the correlation functions obtained using the proposed GLE approach with the EMD results. For EMD calculations of the friction coefficient, a perpendicular distance of $1\sigma_{ff}$ from the wall in the confined direction is chosen as cutoff distance, and the region between the wall and the cutoff distance is defined as interfacial region. Initial time occupancy based tagging [86, 89] is used to compute the time correlations. This means that only the particles that are present in the interfacial region at an initial time contribute to the interfacial friction. This is done because for large cutoff lengths, the friction coefficient will include both the viscous and the slip effects and therefore will not remain an intrinsic property of the wall-fluid interface, as assumed in the formulation. This point has been discussed in detail by Hansen et al. [95]. Also, HS [93] have acknowledged the issue, and have verified the formulation by computing the friction coefficient inside 2 molecular diameter wide channel, where the entire body of the fluid becomes a wall-fluid interface. In GLE, the single particle friction is multiplied by the average number of particles in the cutoff region instead of the summation, which is obtained from the 1D density profiles from EQT. Figures 4.3(a) and 4.3(b) show the comparison of the single-particle force autocorrelation function (FACF) calculated from EMD and GLE formulations for graphene and silicon walls, respectively. Initial time occupancy based tagging [86, 89] is used to compute the time correlations. In this strategy, a particle is tagged at an initial time if it belongs to the interfacial region. Then, for a specified length of time, its trajectory data such as velocity and forces are used to compute one ensemble of time correlations, and their final value is reported by taking the ensemble average. It can be observed from these figures that the correlations computed from the GLE trajectories are in good quantitative agreement to their EMD counterpart. Silicon interface offers higher friction than graphene [91], which is clearly evident from the FACF plots where its variance is significantly higher in the case of silicon. Figure 4.3(c) displays the comparison of the FVCCF for the two interfaces as obtained from GLE and EMD simulations. It can be observed from the plot that the silicon interface presents a strong short-time force–velocity cross-correlation while it is negligible for the graphene interface. As a result, the contribution to the friction coefficient from the FVCCF term is only significant for the silicon interface (its integral value is $-0.536 \text{ kJ/mol}$, comparable to the thermal energy $k_B T \approx 2.5 \text{ kJ/mol}$). Table 4.1 shows the comparison of the friction coefficient computed using the GLE approach with those obtained from EMD simulations. Assuming the EMD value as a benchmark, the deviation in the friction coefficient calculated from the GLE is within 3%. Thus, the proposed GLE formulation provides a robust and computationally efficient alternative to compute the interfacial friction.
Figure 4.3: Wall-fluid FACF from GLE (bold line, blue) and EMD (circles, red) for (a) graphene-water and (b) silicon-water interfaces. (c) FVCCF from GLE and EMD for water with graphene and silicon interfaces.
Table 4.1: Friction coefficient $\zeta_0$ (kJ-ps/mol/nm$^2$)

<table>
<thead>
<tr>
<th>Surface</th>
<th>EMD</th>
<th>GLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene-Water</td>
<td>123.73</td>
<td>125.14</td>
</tr>
<tr>
<td>Silicon-Water</td>
<td>$4.05 \times 10^4$</td>
<td>$3.93 \times 10^4$</td>
</tr>
</tbody>
</table>

4.5 Summary

The key results from this chapter can be summarized as follows:

- We proposed a 2D GLE formulation to estimate the interfacial friction coefficient at liquid-solid boundaries. The attractive feature of this approach is that all the inputs to the GLE formulation are obtained from the EQT and the simulation data of the reference bulk state fluid, thereby eliminating the need to perform computationally expensive EMD simulation of the confined fluidic system to estimate the interfacial friction.

- Single-particle equilibrium correlation functions and the friction coefficient of SPC/E water confined inside graphite and silicon slit channels are found in good quantitative agreement with those obtained from EMD simulations.
Chapter 5

Memory effects in nanoparticle dynamics and transport

5.1 Introduction

Understanding the dynamics and transport of natural and engineered nanoparticles in a host fluid environment is necessary for various nanofluidic applications. Nanoparticles lie at the boundary between the macroscopic and atomistic regimes and multiscale techniques are required to understand their behavior. In this work, we use the generalized Langevin equation (GLE) formulation to understand memory effects in nanoparticle diffusion and transport. The description of a nanoparticle’s motion by a GLE provides a powerful coarse-grained multi-scale approach to simulate its dynamics and transport in a host fluid environment. With the advent of nanobiotechnology, there has been a growing interest in using GLE based stochastic simulations as a viable alternative to a) investigate the so-called rare events whose timescales are still out of reach of conventional molecular dynamics (MD) simulation, and b) efficiently simulate processes such as self-assembly or agglomeration of nanoparticles in solvent/host environment, which become computationally very expensive in MD simulations because of explicit atomistic treatment of the solvent/host environment molecules [96–98]. On the basis of GLE formulation, we extract the memory function and investigate its scaling with the mass, size and shape of the nanoparticle. The systems we investigate are fullerene based nanoparticles (see Fig. 5.1) immersed in water. Fullerenes are among the most widely studied nanoparticles owing to their potential uses in electronics, photonics and medical applications [99–102].

5.2 GLE formulation and memory effects

Using Mori-Zwanzig projector operator techniques, the Hamilton’s equation of motion for a nanoparticle (solute) of mass $M$ interacting with $N$ particles of mass $m$ (host fluid/solvent) can be written in the math-
Figure 5.1: Fullerene nanoparticles studied: (a) C60, (b) C100, (c) C180, (d) C240.

Mathematically equivalent form as [72, 103]

\[ \dot{X}(t) = V(t), \]  
\[ M\dot{V}(t) = -M \int_0^t K(t - t')V(t')dt' + R(t). \]

Here \( X \) and \( V \) are, respectively, the position and the velocity, \( K(t) \) is the memory function and \( R(t) \) is a "projected or random" force with statistical properties [72, 103]

\[ \langle R(t) \rangle = 0, \]  
\[ \langle V(0)R(t) \rangle = 0, \]  
\[ R(0) = F(0), \]

where, \( F(0) = M\dot{V}(0) \) is the total force acting on the nanoparticle at the initial time and angular brackets, \( \langle \cdot \rangle \), denote ensemble average. The relation that \( V(0) \) is uncorrelated with \( R(t) \) (Eq. (5.2b)) means that there is no feedback between the nanoparticle’s motion and the projected force exerted by the molecules of the host fluid. All feedback information or the memory is contained in the memory function \( K(t) \), which connects the current value of the velocity with its values in the past. Further, the fluctuation-dissipation
(FD) theorem provides the relation between the autocorrelation function of the projected force in terms of memory function as

$$\langle R(0)R(t) \rangle = \langle P^2 \rangle K(t), \quad (5.3)$$

where $\langle P^2 \rangle$ is the mean squared momentum ($P = MV$) of the nanoparticle. The practical use of GLE can only be made if we have a means to compute the memory function and assign a statistical model to the projected force. Though Mori’s microscopic derivation provides the expressions for the memory function and the projected force, they are extremely involved and are often difficult to evaluate analytically, except for certain limiting situations. Furthermore, determination of the memory function and extraction of the projected force from MD simulation, in-which the Hamilton’s equations of motion for the entire system are solved numerically, is also not straightforward. The difficulty arises from the fact that the projection dynamics entering the definitions of the memory function and the projected force requires the propagation of the observables instead of configurations [104].

The common approaches used to extract these quantities from MD simulation is either through inversion of the GLE using Laplace transform or through rewriting the GLE as a Volterra type equation, commonly referred to as the memory function equation. Multiplying both sides of Eq. (5.1b) by $MV(0)$, and performing the ensemble average using the statistical properties of the random force (Eq. (5.2b)), one obtains a memory function equation for the momentum autocorrelation function $C(t) = \langle P(0)P(t) \rangle$ in terms of $K(t)$ as

$$\dot{C}(t) = - \int_0^t K(t - s)C(s)ds. \quad (5.4)$$

The momentum autocorrelation function $C(t)$ is an observable that is easily computed from the MD simulation, and then Eq. (5.4) is inverted numerically to obtain the memory function $K(t)$. Similarly, using Laplace transform, a closed form equation for the autocorrelation of the projected force can be written in terms of the autocorrelation function of the total force as [105]

$$\langle R(0)R(s) \rangle = \langle F(0)F(s) \rangle \left[ 1 - \frac{\langle F(0)F(s) \rangle}{s\langle P^2 \rangle} \right]^{-1}, \quad (5.5)$$

where $s$ is the Laplace variable and $\langle R(0)R(s) \rangle$, $\langle F(0)F(s) \rangle$ are, respectively, the Laplace transform of the projected and the total force autocorrelation. Also, once the memory function is known, the FD relation (Eq. (5.3)) can be used to estimate the autocorrelation of the projected force. Higher order correlation functions of the projected force and consequently higher than second moments of the relevant GLE variables ($X$ and $V$) remain unspecified within Mori’s theory. The detailed microscopic derivation of the GLE and the corresponding microscopic expressions for the projected force and the memory function can be found in
Before we study the memory function of nanoparticles, we discuss the generalized equipartition theorem for finite-size MD ensembles with applied periodic boundary condition (PBC). The generalized equipartition theorem is utilized to compute the mean square momentum \( \langle P^2 \rangle \) of the nanoparticle. In MD simulations, PBC are typically applied to mimic the behavior of the bulk fluids. When PBC are applied during equilibrium MD simulations, the total linear momentum is maintained equal to zero to prevent the drifting of the center of mass of the system. Due to this total linear momentum conservation constraint, the momentum of one of the particle is no longer independent of the momenta of the remaining particles, and the usual unconstrained result of \( \langle P^2 \rangle = dMk_B T \) (\( d \) is the system dimensionality, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature of the host-fluid environment) gets modified. This modification can be significant in magnitude if there are unequal mass particles in the system. In a canonical or NVT ensemble with the constraint that the total linear momentum of the system is zero, the mean squared momentum of the nanoparticle is given by [107, 108]

\[
\langle P^2 \rangle = 2M \left( 1 - \frac{M}{M_{\text{Total}}} \right) \frac{dk_B T}{2} \equiv dk_B T \mu, \tag{5.6}
\]

where \( M_{\text{Total}} = M + Nm \) is the total mass and \( \mu = M \left( 1 - \frac{M}{M_{\text{Total}}} \right) \) is the reduced mass of the system. The imposition of the zero total linear momentum constraint reduces the mean squared momentum of the nanoparticle by an amount equal to \( M/M_{\text{Total}} \), a factor which depends both on the mass \( M \) of the nanoparticle and the size \( N \) of the system. For identical mass particles (\( M = m \), \( M/M_{\text{Total}} = 1/N + 1 \)), the reduction is negligible (less than 1% for \( N > 100 \)). However, for unequal mass particles, this reduction can be quite large, especially when \( M \gg m \). Similarly, in a microcanonical or NVE ensemble, the additional constraint of zero total linear momentum modifies the mean squared momentum as [105, 107, 108]

\[
\langle P^2 \rangle = 2M \left( 1 - \frac{M}{M_{\text{Total}}} \right) \frac{\langle E - U \rangle}{N} \equiv 2\mu \frac{\langle E - U \rangle}{N}, \tag{5.7}
\]

where \( E \) is the total energy, \( U \) is the potential energy and \( \langle E - U \rangle \) is the average kinetic energy of the system. If we replace \( \langle E - U \rangle = dNk_B T/2 \), we see that the canonical distribution given by Eq. (5.6) is attained. These results will be used to both access the accuracy of MD simulations and understand the scaling of the memory function with the mass of the nanoparticle.
5.3 Simulation Details

In this section we discuss the MD simulation details. MD simulations are performed using LAMMPS [81]. Each fullerene molecule is modeled as rigid body using the fix “rigid/NVE” in LAMMPS, which integrates the equation of motion such that the body moves and rotates as a single entity. Simple point charge-extended (SPC/E) [76] model is used for water. Particle-Particle Particle-Mesh (PPPM) method is used to compute the long range electrostatic interactions. To model water-fullerene non-bonded interactions, we use the water-carbon interaction parameters proposed recently by Wu and Aluru [109]. These parameters are developed entirely from ab-initio calculation data and predict the graphite-water contact angle and water-carbon nanotube radial breathing mode frequency shift in close agreement with experimental results. For equilibrium MD simulations, initial 2-5 ns equilibration of the nanoparticle-water system is performed in the NVT ensemble with Nosé–Hoover thermostat [67]. After equilibration, computations are performed in the NVE ensemble. For transport simulations, the external force on the fullerene molecule and the potential barrier are, respectively, defined using the fix “gravity and addforce” and partial thermostat is applied on the water molecules in the non-streaming directions.

5.4 Results

5.4.1 Different mass nanoparticles

In this section, we use the GLE formulation to compute the memory function $K(t)$ and investigate its scaling with the mass of the nanoparticle. The systems we study are different mass C60 fullerene molecules (Fig. 5.1(a)) immersed in bulk water ($m = 18$ amu) at 1 bar pressure and 298 K temperature. The mass $M$ of the C60 molecule is varied by changing the mass of its constituent carbon atoms by a factor of 1, 10 and 100, corresponding to the mass ratio $M/m$ of 40, 400 and 4000, respectively. Figure 5.2(a) shows the center of mass (COM) momentum autocorrelation function, $C(t)$, of the C60 molecule for different mass ratios. $C(t)$ are normalized by their initial values. It can be observed that as the mass ratio is increased, the behavior of $C(t)$ changes from a non-linear oscillatory type decay to a featureless exponential decay. Once $C(t)$ is obtained from MD simulation, Eq. (5.4) is used to compute its memory function $K(t)$. Figure 5.2(b) shows the comparison of the memory function $K(t)$ for different mass ratios. The first thing to observe is that the initial value $K(0)$ decreases with the increase in the mass ratio. This can be explained as follows: Eq. (5.4) can be differentiated with respect to time to obtain $K(0)$ as

$$K(0) = -\frac{\ddot{C}(0)}{C(0)}.$$ (5.8)
Figure 5.2: Comparison of (a) Momentum autocorrelation function, $C(t)$, (b) Total force autocorrelation, $F$-ACF, (c) Memory function, $K(t)$, (Inset: Normalized $K(t)$), (d) Projected force autocorrelation, $F^+$.-ACF, (Inset: Comparison of $F$-ACF and $F^+$.-ACF for $M/m=4000$) for different mass C60 immersed in water.
Using the properties of the derivatives of stationary autocorrelation functions, we have $\dot{C}(0) = -\langle F^2(0) \rangle$. [75] Figure 5.2(c) shows the total force autocorrelation function F-ACF of the C60 molecule for different mass ratios. It can be observed that though the time decay of F-ACF is different, the variance $\langle F^2(0) \rangle$ is almost same and is independent of the mass of the nanoparticle. This is physically expected as the solvent accessible surface area is same for different mass C60. From FD relation (Eq. (5.6)), we know that $C(0)$ is directly proportional to the mass of the nanoparticle. Thus, $K(0)$ is inversely proportional to the mass of the nanoparticle and decreases with increase in the mass ratio. Now, we compare the functional-form of the memory function. The inset of Fig. 5.2(b) shows the comparison of the time decay of the normalized memory functions. The memory functions are normalized by their initial values. It can be observed that the time decay, hence the functional-form, of $K(t)$ is very similar for the three mass ratios. As $\dot{C}(0)$ does not change with mass, changing the mass of the nanoparticle from $M$ to $\tilde{M}$ simply rescales the memory function as

$$\frac{K_{\tilde{M}}(0)}{K_M(0)} = \frac{C_M(0)}{\tilde{C}_M(0)},$$

$$K_{\tilde{M}}(t) = \frac{\mu_M}{\mu_{\tilde{M}}} K_M(t).$$

(5.9a)

(5.9b)

Here subscripted symbols have their usual meaning and refer to the quantities associated with the masses $M$ and $\tilde{M}$. We have used the generalized equipartition theorem result (Eq. (5.6)) in Eq. (5.9a) to obtain Eq. (5.9b). Thus, changing the mass of the nanoparticle leads to a simple rescaling of the memory function with the reduced mass of the system. We now show the validity of the generalized equipartition theorem results for finite-size MD ensemble of unequal mass particles and applied PBC. Table 5.1 reports the mean squared momentum $\langle P^2 \rangle$ of the nanoparticle computed using Eq. (5.7) with $C(0)$ value obtained from MD simulation data. It can be observed that the two values are in good agreement with each other. It should be noted that for mass ratio of 4000 ($N = 10,027$), the imposition of zero total linear momentum constraint reduces the mean squared momentum of the nanoparticle by $\sim$ 30% in comparison to the value $\langle P^2 \rangle = 3MK_B T$. Once $C(t)$ and $K(t)$ are known, a simple measure of the memory can be defined through a non-dimensional parameter $\delta$ as [110]

$$\delta = \frac{\tau_C^2}{\tau_K^2},$$

$$\tau_C^2 = \left| \int_0^\infty t \dot{C}(t) dt \right|, \quad \tau_K^2 = \left| \int_0^\infty t \ddot{K}(t) dt \right|,$$

$$\tilde{C}(t) = \frac{C(t)}{C(0)}, \quad \tilde{K}(t) = \frac{K(t)}{K(0)}.$$

(5.10a)

(5.10b)

(5.10c)
Table 5.1: Scaling of memory with the mass of nanoparticle.

<table>
<thead>
<tr>
<th>$M/m$</th>
<th>$\langle P^2 \rangle$</th>
<th>$C(0)$</th>
<th>$\tau^2_C$ (ps)</th>
<th>$\tau^2_K$ (ps)</th>
<th>$\delta = \tau^2_C/\tau^2_K$</th>
<th>$D$ (nm$^2$/ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>5.34E+03</td>
<td>5.27E+03</td>
<td>0.042</td>
<td>0.11</td>
<td>2.61</td>
<td>5.0E-04</td>
</tr>
<tr>
<td>400</td>
<td>5.15E+04</td>
<td>5.14E+04</td>
<td>0.045</td>
<td>1.287</td>
<td>28.6</td>
<td>4.8E-04</td>
</tr>
<tr>
<td>4000</td>
<td>3.83E+05</td>
<td>3.76E+05</td>
<td>0.036</td>
<td>186</td>
<td>5166.6</td>
<td>4.7E-04</td>
</tr>
</tbody>
</table>

where $\tau^2_C$ and $\tau^2_K$ are the squared characteristic relaxation scales of the momentum autocorrelation function and its memory function, respectively. The limit $\delta \to \infty$ corresponds to memoryless behavior ($\tau^2_C \gg \tau^2_K$) while strong memory effects correspond to the limit $\delta \to 0$ ($\tau^2_C \ll \tau^2_K$). The relaxation times and the $\delta$ values for the three mass ratios are reported in Table 5.1. Since the time decay of the memory function is almost same for all the three mass ratios, $\tau^2_C$ values are very similar. However, $\tau^2_K$ increases with increase in the mass ratio and the relaxation process changes from one with strong-memory (smaller $\delta$ value) for smaller mass ratio to memoryless (bigger $\delta$ value) for larger mass ratios. This observation is contrary to the usual Brownian dynamics assumption that with mass ratio $M/m \to \infty$, the memory relaxation time $\tau^2_K \to 0$ ($K(t)$ is approximated as a Dirac-delta distribution), giving rise to $\delta \to \infty$ memoryless behavior. This observation can be explained as follows: Since the memory relaxation time remains same and only its initial value is changed for different mass ratios, we can approximate the memory function as $K(t) = K(0) \exp(-\lambda t)$, where $\lambda$ is the time constant. Now, differentiating Eq. (5.4) with respect to time, and using $K(t) = K(0) \exp(-\lambda t)$, one can obtain an equation for $\ddot{C}(t)$ as

$$
\ddot{C}(t) = -K(0)C(t) - \int_0^t \dot{K}(t-t')C(t')dt',
$$

$$
\dot{K}(t) = -\lambda K(t),
$$

$$
\ddot{C}(t) + \lambda \dot{C}(t) + K(0)C(t) = 0.
$$

Eq. (5.11c) is the familiar equation of motion of a damped harmonic oscillator, where $K(0)$ defines the frequency and $\lambda$ is the damping constant. As the damping constant $\lambda$ is the same for all mass ratios, it is essentially $K(0)$ that determines the behavior of $C(t)$. When $K(0)$ is small ($K(0) \to 0$), as it is for larger mass ratios, $C(t)$ exhibits an exponentially decaying behavior with time constant $\lambda$, while for larger values of $K(0)$, $C(t)$ exhibits non-linear oscillatory decay, as observed for smaller mass ratios. We also report in Table 5.2 the diffusion coefficient $D$ of the nanoparticle for the three mass ratios. The diffusion coefficient can be computed from the memory function $K(t)$ as [73]

$$
D = \frac{k_B T}{M} \left[ \int_0^\infty K(t)dt \right]^{-1}.
$$

61
It can be observed that diffusion coefficient does not change significantly (6% deviation) with change in the mass of the nanoparticle. For consistency check, we compare in Fig. 5.2(d), the autocorrelation function of the projected force $R$-ACF, which is the force that the host fluid molecules exert on the nanoparticle. It can be observed that it is almost identical for the three mass ratios, which is expected as projected force does not depend on the mass of the nanoparticle [103]. Also, we show in inset of Fig. 5.2(d) the comparison of $F$-ACF and $R$-ACF for the mass ratio 4000. It can be observed that $F$-ACF and $R$-ACF are very close to each other, thus confirming the assumption that as the true Brownian limit [105] is approached ($M/m \to \infty$ and $N \to \infty$, giving $\langle P^2 \rangle \to \infty$ in Eq. (5.5)), the autocorrelation of the projected and the total force start to coincide with each other. Though we report the results for different mass C60 molecule immersed in water, this global scaling of the memory function with the reduced mass is observed for other fullerene molecules immersed in water.

5.4.2 Different shape and size nanoparticles

In this section we investigate the scaling of memory effects with the change in the shape and the size of the nanoparticles. We consider C60, C100, C180 and C240 molecules (see Fig. (5.1)) immersed in bulk water at 1 bar pressure and 298 K temperature. For multi-atom clusters like fullerenes, both the arrangement of the constituent atoms and the size influence their dynamics and transport in host fluid environment. It has been reported that shape anisotropy and initial orientation of a nanoparticle significantly effect its translocation across biological membranes and are used as controlling factors to design efficient nanoscale drug delivery systems. [102] Also, unlike a smooth spherical particle, the interaction of these multi-atom cluster with the surrounding fluid generates a net torque which gives rise to rotational motion. To understand the memory effects due to shape and size change, we scale the mass of these different shape and size fullerene molecules to maintain a constant mass ratio $M/m$ of 40. Figures 5.3(a) and 5.3(b) show the comparison of the COM $C(t)$ and $F$-ACF, respectively, of different size fullerene molecules for $M/m = 40$. It can be observed that both $C(t)$ and $F$-ACF show a complicated non-linear behavior for different shape and size molecules. An increased size or solvent accessible surface area increases the variance $\langle F^2(0) \rangle$ of the total force. This is expected as an increased size allows more fluid molecules to interact with the nanoparticle. Fig. 5.3(c) shows the comparison of the memory function $K(t)$. Since the initial value of the memory function is directly proportional to the variance of the total force (Eq. (5.8)), $K(0)$ increases with increase in the size of the nanoparticle. The inset of Fig. 5.3(c) shows the time decay of the normalized memory function for these molecules. It can be observed that the functional form of the memory function is quite different for different shape and size nanoparticles. Thus, the shape and the size of the nanoparticle influence both the initial value
Figure 5.3: Comparison of (a) Momentum autocorrelation function, $C(t)$, (b) Total force autocorrelation, $F$-ACF and (c) Memory function, $K(t)$ for different shape and size nanoparticles ($M/m=40$) immersed in water.
and the functional form of the memory function. No simple rescaling relation is observed for the memory functions when the size of the nanoparticle is changed for a fixed mass ratio. Only the initial value $K(0)$ of the memory function is found to qualitatively scale with the solvent accessible surface area of the fullerene molecule. We report in Table 5.2, the momentum and memory relaxation times and the $\delta$ values for these fullerene molecules. It can be observed that the momentum and memory relaxation times are of comparable magnitude and all these different shape and size nanoparticles exhibit strong memory effects at the mass ratio of 40. Also, from the $\delta$ values it can be inferred that for a fixed mass ratio, the memory effects are relatively enhanced with increase in the size of the nanoparticle. We also report in Table 5.3 the diffusion coefficient $D$ of these different shape molecules. It can be observed that $D$ decreases with increase in the size of the nanoparticle. We also studied the dynamics of these different shape and size fullerene molecules at the mass ratio of 400 and similar conclusions were obtained.

### 5.4.3 GLE simulation

In this section, we use GLE simulations to investigate the role of memory in nanoparticle dynamics and transport. To highlight the role of memory, we compare the results obtained from GLE simulation with those obtained from static-Langevin equation (SLE), which is extensively used in conjunction with MD to simulate the long time scale behavior of ions/nanoparticles in biological systems [96–98, 111]. SLE is obtained by substituting the memory function $K(t)$ by $\gamma \delta(t)$ in Eq. (5.1b), where $\gamma = \int_0^\infty K(t) dt$ is a time-independent friction coefficient and $\delta(t)$ is the Dirac-delta function. The Markovian or “memoryless” property of the projected force in the SLE can be seen through the FD relation (Eq. (5.3)), which becomes $\langle R(0) R(t) \rangle = \langle P^2 \rangle \gamma \delta(t)$ when $K(t) = \gamma \delta(t)$. A consequence of Markovian assumption is that the momentum autocorrelation of the nanoparticle exhibits an exponential decay with time constant $\gamma^{-1}$. However, the momentum autocorrelation of fullerenes such as C60 in water exhibits non-exponential decay and contain strong memory effects. As pointed earlier, the practical use of GLE requires knowing the memory function $K(t)$ and assigning a statistical model to the projected force $R(t)$. A standard choice for $R(t)$ is to assume that it is Gaussian distributed. There are some studies [83, 94, 112] where MD simulation is used to study the

<table>
<thead>
<tr>
<th>Fullerene</th>
<th>$\tau^K_C$ (ps)</th>
<th>$\tau_C^K$ (ps)</th>
<th>$\delta = \tau_C^K / \tau^K_C$</th>
<th>$D$ (nm$^2$/ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C60</td>
<td>0.042</td>
<td>0.11</td>
<td>2.61</td>
<td>5.0E-04</td>
</tr>
<tr>
<td>C100</td>
<td>0.04</td>
<td>0.03</td>
<td>0.75</td>
<td>4.3E-04</td>
</tr>
<tr>
<td>C180</td>
<td>0.03</td>
<td>0.02</td>
<td>0.66</td>
<td>3.3E-04</td>
</tr>
<tr>
<td>C240</td>
<td>0.02</td>
<td>0.015</td>
<td>0.75</td>
<td>2.9E-04</td>
</tr>
</tbody>
</table>
statistical properties of the projected force in fluidic systems. All the studies report that for both bulk and confined fluids, the distribution of the projected force is not strictly Gaussian. However, using a Gaussian model for the projected force in the GLE simulations is found to reproduce several important single-particle properties of both bulk and confined fluids in good agreement with MD simulation results [86, 94]. So, we assume a zero mean correlated Gaussian model for the projected force, with correlation defined through the FD relation (Eq. (5.3)). Thus, once the memory function \( K(t) \) is known, GLE can be used to simulate the dynamics and transport of nanoparticles in host fluid environment. Here, we want to point out that though the projected force is assumed to be Gaussian, it is still non-Markovian. Doob’s theorem [113] states that a correlated Gaussian process is Markovian, if and only if its correlation function is a single exponential. Thus, the trajectories generated from GLE using an arbitrary memory function are in general non-Markovian. The numerical procedure to solve GLE is discussed in Appendix A. Numerical solution of the SLE requires a trivial modification of the Verlet algorithm and is discussed in Ref. [86].

We first use the GLE simulation to demonstrate the scaling of the memory effects with the change in the initial value of the memory function. We consider two memory functions with different initial values. The first memory function \( K(t) \) is that of the C60 fullerene molecule immersed in bulk water and the second is obtained by scaling \( K(t) \) by a factor of 1/10. This scaling only reduces the magnitude of the second memory function and its correlation time \( \tau^2_K \) is exactly same as that of the first memory function. The mass \( M \) of the nanoparticle is 720.16 amu. Figure 5.4 shows the comparison of the normalized momentum autocorrelation function \( C(t) \) as obtained from GLE simulation for these two memory functions. The first observation to be made is that using the memory function for C60, and assuming a Gaussian distribution for the projected force, GLE simulation reproduces the momentum autocorrelation function \( C(t) \) (solid line) in excellent agreement with that obtained from MD simulation (open circle). Second, it can be observed that rescaling the memory function changes the behavior of \( C(t) \) from a non-linear oscillatory type decay to an exponential type decay, thus, exhibiting the above observed transition from a strong-memory to a memoryless behavior with the decrease in the initial value of the memory function. Since the momentum autocorrelation function \( C(t) \) is an ensemble averaged quantity, it does not give a very detailed information about the effect of memory on the molecular motion. To analyze the effect of memory on the microscopic motion of the nanoparticle, we study the probability distribution \( W(\theta, t) \) of the angle \( \theta \) formed by the velocity \( V(t) \) of the nanoparticle at time \( t \) with its velocity at an initial time \( V(0) \),

\[
\theta(t) = \cos^{-1} \left[ \frac{V(0) \cdot V(t)}{||V(0)|| \ ||V(t)||} \right].
\]  

(5.13)

Here \( ||V|| \) is the magnitude of the vector \( V \). The distribution, \( W(\theta, t) \Delta \theta \), defines the probability that the
Figure 5.4: Scaling of the momentum autocorrelation function with the magnitude of the memory function in GLE simulation.

angle between the velocity vectors $V(0)$ and $V(t)$ is in the interval $\theta + \Delta \theta$ at time $t$ [114, 115]. $\theta$ in the range $0^\circ < \theta < 90^\circ$ signifies the forward direction motion, while $90^\circ < \theta < 180^\circ$ indicates the backward direction motion with respect to $V(0)$ ($W(\theta, t = 0) = 0$). Figure 5.5 shows the time dependence of $W(\theta, t)$ for a C60 molecule immersed in water at four different $\theta$ values ($30^\circ$, $60^\circ$, $120^\circ$, $150^\circ$, $\Delta \theta = 10^\circ$) as obtained from GLE (solid line), SLE (broken line) and MD (open circle) simulations. MD simulation results are used as a benchmark to check the accuracy of the trajectories generated by GLE simulation, while SLE simulation is used to highlight the discrepancies that can occur when memory effects are neglected. It can be observed from Fig. 5.5 that the presence of memory gives rise to a preferred direction ($\theta$ value) at different times. At short times (until $t \sim 0.5$ ps), $\theta < 90^\circ$ values are the preferred direction, giving rise to a correlated motion in the forward direction. At intermediate times ($t \sim 0.5-1.5$ ps), $\theta > 90^\circ$ directions start to build up giving rise to a correlated backward motion. It is only at longer times ($t > 1.5$ ps) that $W(\theta, t)$ becomes flat signifying a loss of memory with respect to the initial velocity $V(0)$. This correlated forward and backward direction motion can give rise to interesting dynamical and transport behavior in nanofluidic applications. SLE simulation trajectories, which assume that there is no memory associated with the molecular motion completely fail to reproduce this behavior. The time variation of $W(\theta, t)$ obtained from SLE trajectories is a featureless flat line giving a near uniform distribution at all the times. It is only at longer times ($t > 1.5$ ps) that time variation of $W(\theta, t)$ from GLE, LE and MD simulations converge to the same value. It is remarkable to observe that the GLE simulation trajectories reproduce the time dependence of $W(\theta, t)$ for different $\theta$ values in very good agreement with MD simulation results. We want to point out that this is a non-trivial result and is one of the most critical test of the accuracy of the GLE simulation. This is because
unlike momentum autocorrelation function $C(t)$ or mean-square-displacement (MSD), which are computed by averaging over several trajectories (ensemble average), $W(\theta, t)$ is calculated from the time evolution of a single trajectory. This exercise demonstrates that GLE can be used as a reliable stochastic simulation tool to generate microscopic trajectories of a nanoparticle in the host fluid environment. Now, we discuss a simple barrier crossing example to highlight the effect this memory induced forward and backward motion can have on nanoparticle transport. Using GLE and SLE we simulate the transport of C60 though a one-dimensional (1D) Gaussian potential energy barrier $U$ defined as

$$U = U_0 \exp(-X^2/2b^2),$$

(5.14)

where $U_0$ is the barrier height and $b$ is its width. Such Gaussian energy barriers are used as basis function to model the potential of mean force (PMF) for studying the transport of fullerene-like nanoparticles across lipid bilayers and ion channels [97, 98, 111]. We compute the average barrier crossing time of a C60 molecule through the barrier, when it is immersed in water and is acted upon by a constant external force $F_{\text{ext}} = Ma$, where $a$ is the applied acceleration. A schematic of the system is shown in Fig. 5.6. Barrier crossing time is defined as the time of transport of the nanoparticle from an initial position $X(t = 0)$ on the left of the barrier to the center of the barrier ($X = 0$). Before we discuss the effect of memory on the barrier crossing time, we first show that the steady-state velocity attained by the C60 molecule in the bulk water
under the application of a constant external force $F_{ext}$ (no potential barrier, $U = 0$) is same from both GLE and SLE simulation. Table 5.3 shows the comparison of the steady-state velocity of the C60 molecule for the applied acceleration $a$ of 0.01 nm/ps$^2$ as obtained from GLE, SLE and MD simulation. It can be observed that the steady-state velocity obtained from GLE and SLE simulation are same and match well with the value obtained from all-atom MD simulation. It is physically expected because within the linear response regime, the steady state velocity is given by the expression $F_{ext}/\gamma$, which is by construction same in both GLE and SLE simulation. Thus, the memory induced forward/backward motion does not alter the long-time steady-state velocity. It only effects the short-time transient motion that characterizes the response or the resistance offered to the C60 molecule by the surrounding water molecules. This short time memory induced transient motion could be significant when studying the transport of the nanoparticle across potential barriers. Table 5.3 also reports the average barrier crossing time of a C60 molecule as obtained from GLE, SLE and MD simulations for the barrier potential parameters of $U_0 = 2k_BT$, $b = 0.4$ nm, $a = 0.01$ nm/ps$^2$. For GLE and SLE simulations, the average barrier crossing time is calculated from the average of 20 simulations, where each simulation is run for 10 ns. MD simulation result is obtained from 5 simulations where each simulation is run for 9 ns. It can be observed that the average barrier crossing time predicted from SLE is much higher (> 1 ns) than that obtained from GLE simulation. Also, the average barrier crossing time obtained from all-atom MD simulation is much closer to the GLE simulation result. The inclusion of the memory allows the nanoparticle to cross the barrier in lesser time and increases its probability of barrier crossing. This phenomena of increased probability of barrier crossing with the inclusion of memory is also reported in transport of ions through biological pores [111]. Thus, memory effects are important and should be included in the stochastic-simulation based multi-scale approaches used to study the dynamics and transport of fullerene-like nanoparticles in aqueous solution/biological environment.

### 5.5 Summary

In this work, we used the generalized Langevin equation (GLE) to characterize and understand memory effects in nanoparticle dynamics and transport. Using the GLE formulation, we computed the memory function and investigated its scaling with the mass, shape and size of the nanoparticle. The key results from
this chapter can be summarized as follows:

- It is observed that changing the mass of the nanoparticle leads to a rescaling of the memory function with the reduced mass of the system. Further, we found that for different mass nanoparticles, it is the initial value of the memory function and not its relaxation time that determines the “memory” or “memoryless” dynamics.

- The size and the shape of the nanoparticle are found to influence both the functional-form and the initial value of the memory function. For a fixed mass nanoparticle, increasing its size enhances the memory effects.

- Using GLE simulations we showed that the memory effects lead to a correlated backward and forward motion which can significantly alter the barrier crossing time of the nanoparticle in host fluid environment.
Chapter 6

Interacting-particle generalized Langevin dynamics

6.1 Introduction

In this chapter, we check the suitability of the generalized Langevin equation (GLE) to describe the dynamical behavior of a system of interacting particles. We discuss a generalized Langevin dynamics (GLD) based methodology to simulate the time evolution of Lennard-Jones fluids. Generalized Langevin equation (GLE) is a very well suited stochastic simulation methodology to study single-particle dynamical properties of a solute particle immersed in a very large and complex host-fluid environment (solvent). It includes the effect of the microscopic details and the complicated solvent-solute interactions through random and friction forces and can be used as a substitute for the Newton’s equation used in the classical molecular dynamics (MD) simulations. The GLE based approach is very helpful in studying the long time atomic behavior of the solute in a big and complex multi-component solvent as the need for expensive computational resources required to model the solvent is avoided. In this work we discuss a generalized Langevin dynamics (GLD) based methodology to study the dynamics of a system of interacting solutes. This research effort is motivated from our success in using the single-particle GLE with an empirical potential based quasi-continuum theory (EQT) [47] to study the single-particle dynamical properties of the confined fluids. EQT is a coarse-grained multiscale approach that can be used to predict the equilibrium structure and thermodynamic properties of confined fluids [24, 35, 47, 48, 80, 116]. In our previous works, using the structural information from EQT, we used GLE to simulate the single-particle properties such as position dependent mean-square-displacement (MSD), survival probability, velocity-force correlation functions and interfacial friction coefficient of confined fluids [86, 92, 94]. In these confined systems, the solute and the solvent are identical particles. The aim here is to try to design a GLD based methodology that can reproduce the collective properties of bulk fluids and then combine it with EQT to study the collective properties of confined fluids. Further, such an approach could be used to design stochastic simulation based computationally efficient alternatives to MD simulation for studying the self-assembly of interacting nanoparticles such as fullerenes in aqueous solution or other complex biological environments. We wish to mention that unlike the single-particle GLE, which
can be formally derived using the Mori-Zwanzig projection operator formalism [72, 103], this generalization is phenomenological in nature. The statistical-mechanical derivation of the GLE for a system of interacting solute particle is not very simple. The application of the Mori-Zwanzig projection technique results in a GLE in which random forces loose some of their characteristic properties and the memory functions become so complex that they are not easily modeled and used in a computer simulation [117–121].

Figure 6.1 shows a cartoon level description of the inter-particle interactions in a MD and a GLD simulation. In a MD simulation, the position \( r_i \) and velocity \( v_i \) of a particle \( i \) in a \( N \) interacting-particle system are updated using the force \( f_{MD}^i(r_1, \ldots, r_{i-1}, r_{i+1}, \ldots, r_N, t) \), which is the total force the particle \( i \) experiences due to other \( N - 1 \) particles. For fluids, this multi-particle force \( f_{MD}^i(r_1, \ldots, r_{i-1}, r_{i+1}, \ldots, r_N, t) \) is typically computed as the sum of the two-body interactions (pair-wise additive approximation) using the pair interaction potentials/force-fields such as 12-6 LJ potential, which are the fundamental inputs required to perform a MD simulation. In an interacting-particle GLD, only \( n \) solute particles are explicitly retained, and the effect of the remaining \( N - n \) particles on the dynamics of the particle \( i \) is incorporated as the sum of a conservative force \( f_i(r_1, \ldots, r_{i-1}, r_{i+1}, \ldots, r_n, t) \), which is the total force it experiences due to its “explicit” interaction with \( n - 1 \) solute particles, and a combination of a velocity dependent dissipative force characterized by the memory function \( K_i \), and a random force \( R_i \), which together characterize the effect of the force fluctuations exerted by the coarse-grained or eliminated \( (N - n) \) degrees of freedom exert on the particle \( i \). It is an attempted generalization of the single-particle GLE to describe the dynamics of a system of interacting-particles.
6.2 Formalism

In generalized Langevin dynamics (GLD), we assume that the dynamics of a particle \( i \) of mass \( m \) interacting with \( n - 1 \) identical solute particles (see Fig. 6.1) can be described by \( n \) coupled GLE type equations as

\[
m_i \dot{v}_i(t) = -m \int_0^t K_i(t - t')v_i(t')dt' + R_i(t) + f_i(r_1, ..., r_{i-1}, r_{i+1}, ..., r_n, t),
\]

\[\dot{r}_i(t) = v_i(t), \quad i = 1, 2, ..., n.\]  

(6.1a)

(6.1b)

Here \( i \) is the particle index, \( r_i \) and \( v_i \) are respectively, its position and velocity, \( K_i(t) \) is the time-dependent memory function, \( R_i(t) \) is a random force that characterizes the effect of the force fluctuations exerted by the coarse-grained or eliminated \((N - n)\) degrees of freedom and \( f_i(r_1, ..., r_{i-1}, r_{i+1}, ..., r_n, t) \) is the conservative force that the particle \( i \) experiences because of its explicit interaction with the remaining \( n - 1 \) solute particles. Inputs required for this approach are the memory function \( K_i \), a pair-wise interaction potential to compute the total conservative force \( f_i \) and a model to sample thermal fluctuations \( R_i \). The methods to obtain these inputs are discussed below.

6.2.1 Pair-wise interaction potential

Similar to MD, we assume that the total conservative force \( f_i \) in a GLD is also pair-wise decomposable (pair-wise additive approximation) and can be written as the sum of two-body interactions

\[
f_i = \sum_{i \neq j}^n F^{GLD}_{12}(|r_i - r_j|),
\]

(6.2)

where \( F^{GLD}_{12} \) is an isotropic, mean pair-interaction force that describes the interaction between two solute particles in a GLD simulation. Like MD, GLD also requires a choice of the model for \( F^{GLD}_{12} \). We define \( F^{GLD}_{12} \) as the negative derivative of the potential of mean force determined from the radial-distribution function \( g(r) \)

\[
F^{GLD}_{12}(r) = \begin{cases} 
F^{MD}_{12}(r) - F^{MD}_{12}(r_c) + F^{GLD}_{12}(r), & r \leq r_c; \\
-k_B T \frac{d}{dr} \log(g(r)), & r \geq r_c.
\end{cases}
\]

(6.3)

Here, \( r \) is the inter-particle separation distance, \( g(r) \) is the solute-solute radial distribution function, \( r_c \) is the excluded volume distance (distance until which \( g(r) \) is < 1e-2) between two particles, \( k_B \) is the Boltzmann constant and \( T \) is the temperature of the fluid. To define the interaction potential in the excluded volume region \( r_c \), we use \( F^{MD}_{12}(r) \), which is the single-site interaction potential used in the MD simulation. For simple LJ type molecules, \( F^{MD}_{12}(r) \) can be computed from the 12-6 LJ interaction potential, while for poly-atomic
molecules, $F_{12}^{MD}(r)$ can be computed from the coarse-grained single-site (CGSS) interaction potentials that are used in EQT [24, 80, 116]. Thus, $F_{12}^{GLD}(r)$ gives the average net force on particle 1 when particle 2 is a given $r$ distance away and includes the effect of both the direct pair interaction and the multi-body solvent-mediated indirect contributions. We want to point out that although $F_{12}^{GLD}$ is computed from the exact two-particle correlation function ($g(r)$), there is no guarantee that the total interaction force $f_i$, which is defined as the sum of two-body interaction defined through $F_{12}^{GLD}$ would preserve the static-atomic structure in a multi-particle GLD simulation. Further, as $F_{12}^{GLD}(r)$ contains the effect of both direct and solvent mediated indirect interactions, computing the total conservative force $f_i$ using Eq. (6.2) for a system of more than two particles ($n > 2$) would result in double counting of the indirect contributions for retained degrees of freedom, and could significantly affect both the structural and dynamical properties in a GLD simulation. There are some structural properties based coarse-graining studies where the pair-wise additivity of the isotropic CGSS potentials is tested. It is reported that for reproducing the structural properties, pair-wise additivity is a good approximation when the solute concentration is low, and it becomes less accurate at higher concentrations [122, 123]. We check this issue later when we use this force model to perform GLD simulations at several low and high density LJ fluids. To remove the effect of the double counting of the indirect contributions on the dynamical properties, we propose a self-consistent GLD simulation based iterative methodology which is discussed in the interacting-particle memory function section. Figure 6.2 shows the radial distribution function $g(r)$ (top) and the comparison of the $F_{12}^{GLD}$ and $F_{12}^{MD}$ (bottom) for bulk LJ argon at density of 26 atoms/nm$^3$ and temperature of 300 K. For simple LJ fluids, $F_{12}^{MD}$ is the usual 12-6 LJ potential.

6.2.2 Random force

The random force $R_i(t)$ in Eq.(6.1a) is usually modeled as a Gaussian random variable. As mentioned above, it characterizes the effect of the force fluctuations exerted by the coarse-grained or eliminated ($N-n$) degrees of freedom on the dynamics of the particle $i$. Besides assigning a Gaussian character, the following supplementary hypotheses about the random force are made; since the fluid is in thermodynamic equilibrium, no instant plays a preferential role, and the fluctuation force can be modeled as a stationary random process. As a result, its mean does not depend on time and its autocorrelation does not change when shifted in time. Further, fluctuation dissipation (FD) theorem relates the autocorrelation of the random force to the memory function. Thus, the random force $R_i(t)$ is modeled as a stationary, additive Gaussian variable, with

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statistical properties

\[
\langle R_i(t) \rangle = 0, \quad (6.4a)
\]
\[
\langle v_i(0)R_i(t) \rangle = 0, \quad (6.4b)
\]
\[
\langle f_i(0)R_i(t) \rangle = 0, \quad (6.4c)
\]
\[
\langle R_i(0)R_i(t) \rangle = mk_BTK_i(t). \quad (6.4d)
\]

The numerical generation of the random force in a GLD simulation require the knowledge of the memory function \(K_i(t)\), which is discussed in the next section.

### 6.2.3 Interacting-particle memory function

Memory function characterizes the retardation effect of the coarse-grained degrees of freedom on the dynamics of the solute particle. The common approaches used to extract memory function in single-particle GLE is through inversion of the GLE using Laplace transform or through rewriting the GLE as a Volterra type equation, commonly referred to as the memory function equation (MFE). For single-particle GLE, the MFE
can be written as

\[
\dot{C}_i(t) = - \int_0^t K_i(t-s)C_i(s)ds,
\]

(6.5)

where \(C_i(t)\) is the velocity autocorrelation function. Using \(C_i(t)\) as the input (obtained either from MD simulations or experiments), Eq. (6.5) is solved numerically to compute the memory function \(K_i(t)\). Unlike, single-particle GLE, there is no general procedure to extract the memory function for an interacting-particle GLD. Moreover, the interacting-particle memory function will depend on the number of particles \(n\) that are explicitly retained in the GLD. Starting with Eq. (6.1a), and using the statistical properties of the random force defined in Eqs. (6.4a)-(6.4c), we can derive an interacting-particle MFE as (see Ref. [94] for the derivation)

\[
\dot{C}_i(t) = - \int_0^t K_i(t-s)C_i(s)ds + \frac{1}{k_BT}\langle v_i(0)f_i(t)\rangle,
\]

(6.6)

where, \(\langle v_i(0)f_i(t)\rangle\) is the force-velocity cross correlation function (FVCCF) in the GLD simulation and rest of the symbols have the same meaning as defined above. It can be observed that Eq. (6.6) reduces to the single-particle MFE if FVCCF =0 (\(f_i(t)=0\), for single-particle GLE). Thus, the FVCCF can be thought of the additional memory that a particle carries in a GLD because of its interaction with the remaining \(n-1\) solute particles. To compute \(K_i(t)\) from Eq. (6.6), both the velocity autocorrelation function and the FVCCF are required as inputs. FVCCF in Eq. (6.6) depends on the number of particles explicitly retained in the GLD simulation. We now discuss a self-consistent GLD simulation based iterative procedure to compute the memory function \(K_i(t)\). In the first step, the FVCCF is assumed zero and the memory function \(K_i(t)\) for interacting-particle GLD is taken same as that obtained from the single-particle MFE (Eq. (6.5)) (infinite-dilution approximation). Using the single-particle memory function, an interacting-particle GLD is performed and the velocity autocorrelation function \(C_i(t)^{GLD}\) and FVCCF are computed. Figure 6.3 shows the comparison of the velocity autocorrelation function, FVCCF (FVCCF is zero in MD simulation) and the radial distribution function as obtained from GLD and MD simulation for LJ methane at the thermodynamic state of 2.138 atoms/nm\(^3\) and 300 K. The GLD simulation is performed using 40 explicit particles in a 4x4x4 nm\(^3\) box. The numerical algorithm of the three-dimensional coupled GLEs is a trivial extension of the one-dimensional GLE procedure discussed by Berkowitz et al. in Ref. [88]. Correlated Gaussian random numbers are generated using an approximate frequency domain method discussed in Ref. [87]. It can be observed from Fig. 6.3(a) that the velocity autocorrelation obtained from the GLD simulation using the single-particle memory function does not match well with that of MD simulation. This is physically expected as single-particle memory function completely ignores the contribution of the FVCCF (Fig. 6.3(b)) present in the GLD simulation. However, it is interesting to note that the radial distribution function \(g(r)\) (Fig. 6.3(c)) obtained from GLD is in good agreement with the MD simulation result. This observation suggests that the
pair-wise decomposition of the total force $f_i$ using the inter-particle interaction force $F_{12}^{GLD}$ preserves the static-atomic structure of the fluid. We now use the target single-particle velocity autocorrelation $C_{i}^{MD}(t)$ (obtained from MD) and FVCCF obtained from the GLD in Eq. (6.6) to compute the new memory function $K_i(t)$ for the interacting system. Figure 6.4 shows the comparison of the single-particle and the interacting-particle memory function. It can be observed that the interacting-particle memory function has a smaller initial value ($K_i(0)$) than the single-particle memory function. The solute-solute interactions in the GLD reduce the initial value of the memory function. This behavior can be understood from the FD theorem (Eq. (6.4d)) that relates the initial-value of the memory function to the variance of the random force. Single-particle memory function contains the effect of the force-fluctuations of a larger number of coarse-grained degrees of freedom ($N - 1$) in comparison to interacting-particle memory function ($N - n$). Thus, subtracting the FVCCF from the single-particle memory-function eliminates the contribution of the $n$ degrees of freedom that are explicitly retained in the GLD simulation and reduces its variance. We now run a new GLD simulation using the interacting-particle memory function and repeat the above process until a good match between the GLD and MD velocity-autocorrelation is obtained. For the several high and low different thermodynamic-states tested in this work, it never took more than one iteration of GLD simulation to obtain the interacting-particle memory function that reproduced the velocity autocorrelation function. Similar to single-particle GLE, this procedure also requires the single-particle velocity autocorrelation function $C_i(t)$ as the only input. Also, this procedure is independent of the number of particles $n$ explicitly retained in the GLD simulation. The procedure is summarized in Algorithm 3. Figure 6.5 shows the comparison of velocity autocorrelation function, radial-distribution function and mean-square displacement as obtained from GLD using the interacting-particle memory function with that of MD simulation. It can be observed that using the interacting-particle memory function in GLD reproduces the velocity-autocorrelation function, radial distribution function and MSD in very good agreement with those obtained from MD simulation. Thus, the GLD formalism using the above proposed models for $F_{12}^{GLD}$, $R_i(t)$ and $K_i(t)$ preserves the static-atomic structure ($g(r)$) and reproduces the single-particle dynamical properties of bulk fluids in excellent agreement with the corresponding MD system. We now check the validity of the GLD formalism in reproducing the collective properties of bulk LJ fluids.

Algorithm 3 Computation of the interacting-particle memory function.

1: Use $C_{i}^{MD}$ and compute the single-particle memory function $K_i(t)$ using Eq. (6.5).
2: Perform a GLD simulation (Eqs. (6.1a)-(6.1b)) using $K_i(t)$ and compute $C_{i}^{GLD}$ and FVCCF$^{GLD}$.
3: Re-compute $K_i(t)$ by using $C_{i}^{MD}$ and FVCCF$^{GLD}$ in Eq. (6.6).
4: Repeat steps 2-3 until $C_{i}^{MD}(t)$-$C_{i}^{GLD}(t) < tol$. 

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Figure 6.3: Comparison of (a) velocity autocorrelation function, $C_i(t)$, (b) force-velocity cross-correlation function, FVCCF, and (c) radial distribution function, $g(r)$, as obtained from GLD (using single-particle memory function) and MD simulation.
In this section we use the interacting-particle GLD framework to compute the collective properties of the bulk fluid. The two properties we particularly focus on are (a) van-Hove function \( G(r, t) \) and (b) shear viscosity \( \eta_s \). For a \( n \) particle bulk fluid system of density \( \rho \) and time dependent position coordinates \( r_i(t) \), van Hove correlation function is the probability of finding a particle at position \( r \) at time \( t \), given that there was a particle at the origin at time \( t = 0 \) and is defined as \[124\]

\[
G(r, t) = \frac{1}{n} \left\langle \sum_{i=1}^{n} \sum_{j=1}^{n} \delta(r + r_j(0) - r_i(t)) \right\rangle, \tag{6.7}
\]

where \( \langle \cdot \rangle \) represents an ensemble average and \( \delta(\cdot) \) is the three-dimensional Dirac delta function. \( G(r, t) \) can be separated into two terms, conventionally referred to as its “self” and “distinct” part, by distinguishing the cases \( i = j \) and \( i \neq j \), as

\[
G(r, t) = \frac{1}{n} \left\langle \sum_{i=1}^{n} \delta(r + r_i(0) - r_i(t)) \right\rangle + \frac{1}{n} \left\langle \sum_{i \neq j}^{n} \delta(r + r_j(0) - r_i(t)) \right\rangle, \tag{6.8a}
\]

\[
\equiv G_s(r, t) + G_d(r, t), \tag{6.8b}
\]
Figure 6.5: Comparison of (a) velocity autocorrelation function, $C_i(t)$, (b) radial distribution function, $g(r)$, and (c) mean-square displacement (MSD), as obtained from GLD (using interacting-particle memory function) and MD simulation.
where, the self part, $G_s(r, t)$ describes the average motion of the particle that was initially at the origin (single-particle dynamics), whereas the distinct part, $G_d(r, t)$ describes the motion of the remaining $n - 1$ particles (inter-particle correlation dynamics). It can be seen from Eq. (6.8a) that at $t = 0$

$$G_s(r, t = 0) = \delta(r) \quad (6.9a)$$

$$G_d(r, t = 0) = \rho g(r), \quad (6.9b)$$

For homogeneous fluids, distinct part of the van-Hove function $G_d(r, t)$ can be thought of as a time dependent radial distribution function that contains the information about inter-particle correlations and their time evolution. Figure 6.6 shows the comparison of the $G_d(r, t)$ for a low and high density LJ fluid as measured in GLD and MD simulation. It can be observed that the result obtained from GLD is in good agreement with that obtained from MD simulation. This result is quite encouraging and suggests that the interacting-particle GLD also preserves the dynamical time scale of the inter-particle correlations. Further, it can be observed that at the initial time, $G_d(r, t)/\rho$ resembles the two-particle correlation function $g(r)$, while at longer times the correlation diminishes and $G_d(r, t)/\rho$ converges to 1. Figure 6.6 shows the comparison of the $G_d(r, t)$ for a low and high density LJ fluid as measured in GLD and MD simulation. It can be observed that the results obtained from GLD are in good agreement with that obtained from MD simulation. This result is quite encouraging and suggests that the interacting-particle GLD also preserves the dynamical time scale of the inter-particle correlations. Further, it can be observed that at the initial time, $G_d(r, t)/\rho$ resembles the two-particle correlation function $g(r)$, while at longer times the correlation diminishes and $G_d(r, t)/\rho$ converges to 1. Now, we compute and compare the shear viscosity $\eta_s$ obtained from GLD with that obtained from MD simulation. We use Green-Kubo relation to compute the shear viscosity. The Green-Kubo formulae relate the transport coefficient to a time integral of a time dependent correlation function of the appropriate dynamic variable. For the shear viscosity $\eta_s$, such an expression can be written as [125]

$$\eta_s = \frac{1}{V k_B T} \int_0^\infty z_{\alpha\beta}(\tau) d\tau, \quad (6.10)$$

where $V$ is the box volume and $z_{\alpha\beta}(\tau)$ is the stress-autocorrelation function (SACF). The SACF is defined as

$$z_{\alpha\beta}(\tau) = \langle \sigma_{\alpha\beta}(t) \sigma_{\alpha\beta}(t + \tau) \rangle, \quad (6.11)$$
Figure 6.6: Comparison of distinct van-Hove function $G_d(r, t)$ for (a) LJ Methane, and (b) LJ Argon, from interacting-particle GLD and MD simulation.
where $\sigma_{\alpha\beta}(t)$ are the off-diagonal elements of the microscopic tensor and is defined as

$$
\sigma_{\alpha\beta}(t) = \sum_{i=1}^{n} \frac{p_{i\alpha}p_{i\beta}}{m} + \sum_{j \neq i} r_{ij\alpha} F_{ij\beta}; \alpha \neq \beta.
$$

Here, $\alpha$ and $\beta$ denote the vector components, $p_{i\alpha}$, $p_{i\beta}$ are the $\alpha$ or $\beta$ component of the momentum of the particle $i$, $r_{ij\alpha}$ is the $\alpha$ component of the inter-particle separation between particle $i$ and $j$ and $F_{ij\beta}$ is the $\beta$ component of the force on particle $i$ due to particle $j$. The rest of the symbols have the same meaning as defined above. In MD, $F_{ij}$ is computed from the pair-potential used in the simulation, while in GLD, $F_{ij}$ is computed using $F_{12}^{GLD}$. Using Eq. (6.12) into Eq. (6.11), the SACF and the shear viscosity can be written as sum of four contributions

$$
\begin{align*}
z_{\alpha\beta}^{kk}(\tau) &= \left\langle \sum_{i=1}^{n} p_{i\alpha}(t)p_{i\beta}(t) \sum_{i=1}^{n} \frac{p_{i\alpha}(t+\tau)p_{i\beta}(t+\tau)}{m} \right\rangle, \\
z_{\alpha\beta}^{kp}(\tau) &= \left\langle \sum_{i=1}^{n} p_{i\alpha}(t)p_{i\beta}(t) \sum_{j \neq i} r_{ij\alpha}(t+\tau) F_{ij\beta(t+\tau)} \right\rangle, \\
z_{\alpha\beta}^{pk}(\tau) &= \left\langle \sum_{i=1}^{n} \sum_{j \neq i} r_{ij\alpha}(t) F_{ij\beta(t)} \sum_{i=1}^{n} \frac{p_{i\alpha}(t+\tau)p_{i\beta}(t+\tau)}{m} \right\rangle, \\
z_{\alpha\beta}^{pp}(\tau) &= \left\langle \sum_{i=1}^{n} \sum_{j \neq i} r_{ij\alpha}(t) F_{ij\beta(t)} \sum_{i=1}^{n} \sum_{j \neq i} r_{ij\alpha}(t+\tau) F_{ij\beta(t+\tau)} \right\rangle,
\end{align*}
$$

$$
\eta_s = \eta_s^{kk} + \eta_s^{kp} + \eta_s^{pk} + \eta_s^{pp},
$$

where the superscripts $kk$, $kp$, $pk$ and $pp$ denote the kinetic-kinetic, kinetic-potential, potential-kinetic and potential-potential terms, respectively. The $kp$ and $pk$ terms are identical for reasons of symmetry ($z_{\alpha\beta}^{kp}(\tau) = z_{\alpha\beta}^{pk}(\tau); \eta_s = \eta_s^{kk} + 2\eta_s^{kp} + \eta_s^{pp}$). We examine the performance of GLD by comparing these contributions individually with those obtained from MD simulation. Figures 6.7 and 6.8 show the comparison of the time decay of $z_{\alpha\beta}^{kk}(\tau)$, $z_{\alpha\beta}^{pp}(\tau)$ and $z_{\alpha\beta}^{kp}(\tau)$ for a low and high-density LJ fluid, respectively, as obtained from GLD and MD simulation. Table 6.1 reports the computed shear viscosity $\eta_s$, for 4 different high and low density thermodynamic states as obtained from GLD and MD simulation. Shear viscosity is computed by integrating the SACF with time (Eq. (6.10)). It can be observed that the time decay of SACFs obtained from GLD are not in good accordance with those obtained from MD simulation.

Although the present GLD formulation preserves the static atomic-structure and the dynamical time scales of the inter-particle correlation, there are significant quantitative discrepancies in the computed SACF and the shear viscosity values. One possible reason for the quantitative discrepancy could be the inability of the isotropic interacting-particle memory function $K_i(t)$ to accurately model the effect of the solvent (coarse-
Table 6.1: Shear viscosity $\eta_s$ (kJ·ps/mol·nm$^3$).

<table>
<thead>
<tr>
<th>Fluid</th>
<th>State Point</th>
<th>Simulation</th>
<th>$\eta_{sk}^{kk}$</th>
<th>$\eta_{sk}^{pp}$</th>
<th>$\eta_{sk}^{kp}$</th>
<th>$\eta_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LJ Methane</td>
<td>10.0 atoms/nm$^3$, 300 K</td>
<td>GLD</td>
<td>3.31</td>
<td>18.14</td>
<td>2.66</td>
<td>24.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MD</td>
<td>4.49</td>
<td>14.11</td>
<td>5.74</td>
<td>24.36</td>
</tr>
<tr>
<td>LJ Methane</td>
<td>2.138 atoms/nm$^3$, 300 K</td>
<td>GLD</td>
<td>4.83</td>
<td>0.74</td>
<td>1.36</td>
<td>6.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MD</td>
<td>5.79</td>
<td>0.36</td>
<td>0.91</td>
<td>7.06</td>
</tr>
<tr>
<td>LJ Argon</td>
<td>5.0 atoms/nm$^3$, 300 K</td>
<td>GLD</td>
<td>8.64</td>
<td>4.70</td>
<td>3.29</td>
<td>16.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MD</td>
<td>12.04</td>
<td>1.77</td>
<td>3.08</td>
<td>16.91</td>
</tr>
<tr>
<td>LJ Argon</td>
<td>26.0 atoms/nm$^3$, 300 K</td>
<td>GLD</td>
<td>4.72</td>
<td>229.44</td>
<td>1.66</td>
<td>235.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MD</td>
<td>6.95</td>
<td>251.78</td>
<td>6.957</td>
<td>265.69</td>
</tr>
</tbody>
</table>

grained $N - n$ degrees of freedom) on the dynamics of the solute particles. A complete description might require the use of a non-local model for the memory function, $K_i(r_{ij}(t), t)$, which depends on the relative-position $r_{ij}(t)$ of the solute particles. Another possible reason could be the inability of the pair-interaction force model $F_{12}^{GLD}$ to correctly reproduce the effect of the many-body correlations, which significantly affect properties like shear viscosity. One way to incorporate the multi-body correlations is through the Yvon-Born-Green (YBG) integral equation [123, 126] that provides a means of decomposing the mean pair force on particle 1 at $r_1$ when second particle is located at position $r_2$ ($F_{12}^{GLD}(r_1, r_2) = -\nabla_1 k_B T g(r_1, r_2); g(r_1, r_2)$ is the two-body correlation function) into direct and solvent mediated indirect contributions as

$$F_{12}^{GLD}(r_1, r_2) = -\nabla_1 U(r_1, r_2) + \int dr_3 (-\nabla_1 U(r_1, r_3)) \rho_{3|2}(r_3|r_1, r_2). \quad (6.14)$$

Here, $U$ is the inter-particle interaction potential used in MD simulation, $-\nabla U(r_1, r_2)$ is the force due to direct interaction and $\rho_{3|2}(r_3|r_1, r_2)$ is the three-body correlation function that signifies how the presence of two particles impact the packing of the surrounding particles. The integral term in the above equation represents the indirect contribution of the surrounding particles to the average force. Weather using a non-local model for the memory function or a more advanced model for the mean force that properly incorporates the multi-body effects would help improve the quantitative accuracy in collective properties without increasing the computational complexity is an open question and could be a possible direction for future work.

### 6.4 Summary

The key results from this work can be summarized as follows:

- We discuss a generalized Langevin dynamics (GLD) based methodology to simulate the time evolution
Figure 6.7: Comparison of the time decay of (a) kinetic-kinetic SACF, $z_{\alpha\beta}^{kk}(\tau)$, (b) potential-potential SACF, $z_{\alpha\beta}^{pp}(\tau)$, and (c) kinetic-potential SACF, $z_{\alpha\beta}^{kp}(\tau)$, for LJ Methane as obtained from GLD and MD simulation.
Figure 6.8: Comparison of the time decay of (a) kinetic-kinetic SACF, $z_{kk}^{\alpha\beta}(\tau)$, (b) potential-potential SACF, $z_{pp}^{\alpha\beta}(\tau)$, and (c) kinetic-potential SACF, $z_{kp}^{\alpha\beta}(\tau)$, for LJ Argon as obtained from GLD and MD simulation.
of Lennard-Jones fluids. The inter-particle interaction potential is defined using the radial-distribution function and a self-consistent GLD simulation based iterative procedure is proposed to compute the interacting-particle memory function.

- The formalism is used to compute the collective properties (van-Hove function and the shear viscosity) of bulk LJ fluids. Although the GLD simulation preserves the dynamical time scale of the inter-particle correlations and reproduces the van-Hove function in good accordance with MD simulation results, quantitative discrepancies are observed for the stress-autocorrelation functions and the shear viscosity.
Chapter 7
Conclusions

The primary contributions of this research work are as follows:

• We first discussed the extension of the empirical potential based quasi-continuum theory (EQT) to study the equilibrium structure of confined poly-atomic fluids. Using carbon-dioxide as the example fluid, we developed coarse-grained single-site (CGSS) wall-fluid and fluid-fluid interaction potential models to predict the correct microstructure in confined environments. We first showed that CGSS pair-potentials developed for the bulk state do not predict the correct microstructure at nanoscale confinements. It is observed that the geometric shape and the relative orientation of the poly-atomic fluid gives rise to unique structuring/packing of the molecules near the confining surface. Also, unlike spherical LJ type fluids, for poly-atomic fluids, the wall-fluid interaction energy is found to be a function of the thermodynamic state of the confined fluid. We proposed a two-minima 12-6 LJ type piecewise polynomial functional form to describe CGSS wall-fluid and fluid-fluid interactions. The proposed functional form successfully captured the distance-dependent preferred relative orientation of carbon-dioxide in nanoscale confined environments.

• We proposed a combined memory function equation (MFE) and generalized Langevin equation (GLE) based approach (referred to as MFE/GLE formulation) to characterize thermal noise in molecular fluids. Using MFE/GLE formulation in conjunction with MD simulation, we extracted and analyzed the statistical properties of thermal noise in confined fluids. We found that the thermal noise correlation time of the confined fluid does not vary significantly across the confinement and is quite similar to that of the corresponding reference bulk state fluid. We showed that it is the correlation of the mean force with the molecular velocity that gives rise to the spatial anisotropy in the velocity-autocorrelation function of the confined fluids.

• We proposed a combined EQT/GLE methodology to simulate the single-particle properties of confined fluids. The method is used to compute the interfacial friction coefficient at solid-liquid interfaces. The interfacial friction coefficient characterizes the influence of solid-fluid interactions on the fluid transport,
and is used to estimate the slip velocity and design slip boundary conditions for nanoscale transport. The results obtained from the formulation are used in a quasi-continuum hydrodynamical transport theory proposed by Bhaduria and Aluru to study the transport of water in slit-shaped nanochannels.

- We also used the GLE formulation to characterize the memory effects in nanoparticle (Fullerenes) dynamics and transport. Using the GLE formulation, we computed the memory function and investigated its scaling with the mass, shape and size of the nanoparticle. It is observed that changing the mass of the nanoparticle leads to a rescaling of the memory function with the reduced mass of the system. Further, we found that for different mass nanoparticles, it is the initial value of the memory function and not its relaxation time that determines the memory or memoryless dynamics. The size and the shape of the nanoparticle are found to influence both the functional-form and the initial value of the memory function.
Appendix A

A.1 Numerical solution of GLE

Numerical solution of GLE requires generation of zero mean correlated Gaussian random numbers and a time integration scheme to solve the equations

\[
\dot{x}(t) = v(t), \quad (A.1a)
\]

\[
m\dot{v}(t) = -m \int_0^t K(t - t')v(t')dt' + R(t), \quad (A.1b)
\]

Here \(x\) and \(v\) are, respectively, the position and the velocity of the particle of mass \(m\), \(K(t)\) is the memory function and \(R(t)\) is a “projected or random” force with statistical properties [72, 103]

\[
\langle R(t) \rangle = 0, \quad (A.2a)
\]

\[
\langle v(0)R(t) \rangle = 0, \quad (A.2b)
\]

\[
\langle R(0)R(t) \rangle = mk_BTK(t), \quad (A.2c)
\]

\[
R(0) = F(0), \quad (A.2d)
\]

where, \(F(0) = m\dot{v}(0)\) is the total force acting on the nanoparticle at the initial time and angular brackets, \(\langle .. \rangle\), denote ensemble average. We use an approximate frequency domain method to generate a sequence \(\{R\}\) of zero mean Gaussian random numbers with a specified autocorrelation function \(s_R = mk_BT K(t)\). The method is as follows: First, using the autocorrelation function \(s_R\), the spectral density \(S_R\) is computed as

\[
S_R(f_j) \equiv \sum_{\tau=-(\frac{Q}{2}-1)}^{\frac{Q}{2}} s_R e^{-i2\pi f_j \tau}, \quad 0 \leq j \leq \frac{Q}{2}, \quad (A.3)
\]
where $Q$ is any even positive number (typically a power of 2) greater than or equal to the desired length of the sequence and $f_j = j/Q$. Then, using a sequence $\{W_j\}, j = 0, \ldots, Q - 1$ of $Q$ independent and identically distributed Gaussian random numbers with zero mean and unit variance, the sequence $\{R\}$ is generated as

$$R \equiv \frac{1}{\sqrt{Q}} \sum_{j=0}^{Q-1} R_j e^{-i2\pi f_j t}, \quad t = 0, \ldots, Q - 1,$$

where $R_j$ is defined as

$$R_j = \begin{cases} \sqrt{S_R(0)}W_0, & j = 0; \\ \sqrt{\frac{1}{2}S_R(f_j)}(W_{2j-1} + iW_{2j}), & 1 \leq j < \frac{Q}{2}; \\ \sqrt{S_R(1/2)}(W_{Q-1}), & j = \frac{Q}{2}; \\ R^{*}_{Q-j}, & \frac{Q}{2} < j \leq Q - 1. \end{cases}$$

Here asterisk (*) denotes the complex conjugate. The frequency domain method is computationally faster ($O(Q \log Q)$) than traditional time domain methods such as Cholesky factorization and Levinson-Durbin recursion ($O(Q^2)$) [87]. To integrate the GLE in time, we use a modified Verlet algorithm proposed by Berkowitz et al. in Ref. [88]. We briefly review the algorithm here. The Verlet algorithm [127] updates the position and velocity of a particle of mass $m$ as

$$x_{n+1} = -x_{n-1} + 2x_n + \frac{F_n}{m} \Delta t^2, \quad (A.6a)$$
$$v_n = \frac{x_{n+1} - x_{n-1}}{2\Delta t}, \quad (A.6b)$$

where $x_n, v_n$ and $F_n$ are, respectively, the position, velocity and total force at step $n$ ($n > 0$), and $\Delta t$ is the time step of the integration. In GLE (Eq. (A.1b)), the total force at time $t$ is given as

$$F(t) = -m \int_0^t K(t')v(t - t')dt' + R(t). \quad (A.7)$$

By approximating the integral in Eq. (A.7) by a quadrature formula such as trapezoidal rule, the total force $F_n$ at step $n > 0$ can be computed as

$$F_n = -m\Delta t \sum_{j=0}^{n} K_j v_{n-j} w_j + R_n, \quad (A.8a)$$
$$F_n = -m\Delta t K_0 v_0 w_0 + \sum_{j=1}^{n} K_j v_{n-j} w_j + R_n, \quad (A.8b)$$
where $K_0 = K(t = 0)$, $w_j$ is the weight factor of the integrand at discrete point $j$ (for trapezoidal rule, the weights $w_j$ are 1/2 for $j = 0, n$ and 1 for $j = 1, \ldots, n - 1$), and $R_n$ is a particular realization of the random force at step $n$. Substituting Eq. (A.8b) in Eq. (A.6a) and using the expression for $v_n$ (Eq. (A.6b)), one obtains an expression for the position at $n + 1$ step as

$$x_{n+1} \left[ 1 + K_0 \Delta t^2 w_0/2 \right] = -x_{n-1} \left[ 1 - K_0 \Delta t^2 w_0/2 \right] + 2x_n - \Delta t^3 \sum_{j=1}^{n} K_j v_{n-j} w_j + R_n \Delta t^2 / m. \quad (A.9)$$

To use Eq. (A.9), $x_0$ and $x_1$ are needed. One can choose any value for $x_0$ and compute $x_1$ using Eq. (A.6a) as

$$x_1 = x_0 + v_0 \Delta t + \frac{F_0}{m} \Delta t^2, \quad (A.10)$$

where $v_0$ is drawn from a maxwellian distribution corresponding to temperature $T$, and $F_0 = R(0)$. Once $x_1$ is computed, Eqs. (A.9) and (A.6b) are used to compute the position and the velocity, respectively. The numerical procedure to solve Eq. (A.1b) with the addition of an external force $F_{ext}(x, t)$ requires a trivial modification to the verlet algorithm discussed above.
Appendix B

B.1 Application of linear response theory to compute interfacial friction

In this appendix we discuss the application of the linear response theory to compute the expressions for estimating the interfacial friction at solid-liquid interface. When a system at thermal equilibrium is slightly perturbed by an external force \( f \), the response of the system can be predicted from the time correlation function of its thermal fluctuations at the equilibrium state. For any physical observable \( B \) of interest, its thermal average at the perturbed non-equilibrium state can be expressed as the convolution of the external force and the generalized susceptibility \( \chi_{AB} \) as

\[
\Delta \langle B(t) \rangle = \int_{-\infty}^{\infty} \chi_{AB}(t-t')f(t')dt'.
\] (B.1)

Here, \( A \) is the internal variable that is conjugate to \( f \). \( \Delta \langle B(t) \rangle = \langle B(t) \rangle_{NE} - \langle B(t) \rangle_{EC} \), where \( \langle \cdot \rangle_{NE} \) and \( \langle \cdot \rangle_{EC} \) denote ensemble averages at non-equilibrium and equilibrium conditions, respectively. The relation between the susceptibility \( \chi_{AB} \) and the corresponding time correlations of \( \delta A \) and \( \delta B \) at equilibrium is given by

\[
\chi_{AB} = \begin{cases} 
- \frac{1}{k_B T} \frac{d}{dt} \langle \delta A(0) \delta B(t) \rangle_{EC}, & t \geq 0; \\
0, & t < 0,
\end{cases}
\] (B.2)

where \( \delta A = A - \langle A \rangle_{EC} \) and \( \delta B = B - \langle B \rangle_{EC} \) are thermal fluctuations in variables \( A \) and \( B \), respectively. For the liquid-solid interface, under the perturbation by external force along the direction parallel to the solid wall, a liquid particle \( j \) will respond with a drift velocity, \( u_j \), the magnitude of which is determined by the balance between the external drag force and the friction force exerted by the solid wall as

\[
F_j = \zeta_0^j u_j.
\] (B.3)
Here $F_j$ is the friction force exerted by the solid wall on the interfacial particle $j$ and $\zeta_j^0$ is the interfacial friction coefficient. Interfacial friction coefficient is by definition equal to the ratio between the friction force and the drift velocity. To estimate $\zeta_j^0$ using linear response theory, we obtain the expressions for drift velocity $u_j$ and friction force $F_j$ in terms of the time correlation functions in the equilibrium system. For drift velocity, we choose $A = x_j$, $B = u_j$, and define the external force as $f e^{i \omega t}$, where $x_j$ is the particle’s displacement along the direction parallel to the wall, $\omega$ is the frequency, and $t$ is the time. Substituting Eq. (B.2) into Eq. (B.1) and taking the Fourier transform, one finds that the drift velocity is proportional to the velocity autocorrelation function determined in the equilibrium system as

$$\langle u_j \rangle_\omega(t) = \frac{f e^{i \omega t}}{k_B T} \int_0^\infty \langle u_j(0)u_j(t) \rangle_{EC} e^{-i \omega t} dt. \quad (B.4)$$

Similarly, for friction force, by choosing $A = x_j$ and $B = F_j$, one finds that $F_j$ is related to the correlation between the particle’s velocity and the friction force experienced by the particle at equilibrium as

$$\langle F_j \rangle_\omega(t) = \frac{f e^{i \omega t}}{k_B T} \int_0^\infty \langle u_j(0)F_j(t) \rangle_{EC} e^{-i \omega t} dt. \quad (B.5)$$

Using Eqs. (B.4) and (B.5), one obtains the expression for friction coefficient as

$$\zeta_j^0 \equiv -\frac{\langle F_j \rangle_{\omega=0}(t)}{\langle u_j \rangle_{\omega=0}(t)} = -\frac{\int_0^\infty \langle F_j(0)F_j(t) \rangle_{EC} dt}{\int_0^\infty \langle u_j(0)u_j(t) \rangle_{EC} dt}. \quad (B.6)$$

Equation (B.6) is not particularly well suited to compute the interfacial friction coefficient at the liquid-solid interface as particles diffuse away from the interface in a finite amount of time, which might not be necessarily sufficient to obtain a well-converged estimate of the velocity autocorrelation function that appears in the denominator. To avoid this problem, using generalized Langevin equation formulation, Eq. (B.6) can be recasted as

$$\zeta_j^0 = -\frac{\int_0^\infty \langle F_j(0)F_j(t) \rangle_{EC} dt}{k_B T + \int_0^\infty \langle u_j(0)F_j(t) \rangle_{EC} dt}. \quad (B.7)$$

It is a very straightforward derivation, which can be found in Ref. [93]. As the frictional force $F_j$ becomes zero away from the interface, single-particle wall-fluid force autocorrelation function (FACF) in the numerator and the wall-fluid force-velocity cross-correlation function (FVCCF) in the denominator of Eq. (B.7) are comparatively better converged quantities than the velocity autocorrelation function of Eq. (B.6).
References


