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Dynamics of Nanoparticles in Fluids and at Interfaces

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Abstract

Dynamics of Nanoparticles in Fluids and at Interfaces

by

Weikang Chen

Adviser: Professor Ilona Kretzschmar, Professor Joel Koplik

In this thesis, we use molecular dynamics simulation to study three basic behaviors or properties of nanoparticles: deposition during droplets evaporation, slip boundary condition and Brownian motion. These three problems address the need for an in-depth understanding of the dynamics of nanoparticles in fluids and at interfaces. In the first problem, evaporation of the droplets dispersed with particles, we investigated the distribution of evaporative flux, inner flow field, density and temperature. And we use these numerical experiments to check on our hydrodynamic theory of the “coffee ring” phenomenon. The simulations reveal the connection between the particle interactions and the deposit structure, and indicate some limitations in continuum modeling. In the second problem, we explore the slip boundary conditions for curved surfaces, which is one of the desired information in modeling the hydrodynamics of micro-fluidic objects. The conclusion we draw is strong: the slip length, defined in a consistent tensorial manner, depends only on the physical properties of the solid and fluid involved and does not vary with the flow configuration. The final part is devoted
to the Brownian motion of Janus particle, where we use a simple model to explain
the increase of diffusivity of self-propelling Janus particles. We also show that the
hydrodynamic image could be used to account for the self-aligning phenomenon at
liquid-solid interfaces. The coupling between the translation and rotation is investi-
gated by Brownian simulation, where we modify the standard Langevin equation with
coupling terms which derive from the hydrodynamic interaction with the liquid-solid
interfaces. The resultant individual trajectories and their diffusivities are consistent
with both the laboratory observations and theoretical calculations.
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Chapter 1

Introduction

In scientific research, molecular dynamics (MD) simulation play one of the central roles to fulfill the gap between observation and comprehension. It is often used to check our understanding of natural processes by virtually reproducing physics process we are interested in. More often, we adopt these numerical experiments to predict the unknowns of experiments in real world, because we have confidence in our tested theories and codes. In the first chapter, we introduce mainly the molecular dynamics simulation technique. After that, we will briefly discuss some properties of Janus particles, which is a special type of nanoparticles. The outline of the thesis is summarized in the last part of this chapter.

1.1 Methology

The basic theory of MD simulation [1–3] involves two fundamental parts of physics: *analytical mechanics* and *statistical mechanics*. The first part was well developed before 1900 [4]. Newtons’s second law laid down the principles for the motion of atoms and molecules. Euler equation or the quaternion variables are used to describe the rotational motion of rigid bodies. In MD, dynamics of particles are directly obtained by solving these differential equations. Sometime we need the Lagrange method or
the Hamilton principle to transform geometric or thermodynamic constraints to some additional differential equations. This routine is quite general, which we always follow to solve the \( N \)-body problem in MD. The cornerstone, which characterizes different system types, is the pair interaction function. We are using the following generalized Lennard-Jones potential interaction between a pair of neutral atoms of two different species \( i \) and \( j \)

\[
U_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - c_{ij} \left( \frac{\sigma}{r} \right)^{6} \right] \quad r \leq r_c
\]

in which \( \sigma \) is the characteristic length scale, \( \epsilon \) the potential depth and \( r \) the atom-atom distance. The potential is cut off at distance \( r_c \). The adjustable parameters \( c_{ij} \) are the interaction coefficients between species \( i \) and \( j \). These \( c_{ij} \) are the keys, they measure the relative strength of repulsion and attraction and are often used to control the wettability between the solid and liquid. Of course, there are other forms of interaction used, but the Lennard-Jones potential is a very good approximation for its simplicity. We will heavily utilized this form of interaction in our simulations, and the details are explained in latter chapters when encountered.

To compare with the experiments, we need the second part of the theory, statistical mechanics [5–7]. We need to do summations and then averaging so as to squeeze out the essential information of the \( N \)-body system. For example, in the canonical ensemble where the temperature \( T \) and the number of particles \( N \) are fixed, the
measurable quantity $V$ is calculated by the following form of ensemble average:

$$\langle V \rangle = \frac{\int V(r_1, \cdots, r_N)e^{-\beta U(r_1, \cdots, r_N)}dr_1 \cdots dr_N}{\int e^{-\beta U(r_1, \cdots, r_N)}dr_1 \cdots dr_N}$$

The ergodic hypothesis says that the above ensemble average of phase space of micro states equals the time average of the equilibrium system in experiments. For the system obeying the ergodic hypothesis, the long time average over evolution of the simulated system are anticipated to be equal to the macroscopic thermodynamic properties. We use this fundamental principle to calculate physics quantities and make comparing them with real experiments.

Another simulation method often quoted and compared with MD is Brownian dynamics simulation [93], which treats the surrounding liquid solution as continuum rather than discrete atoms as done in MD, and the forces are no longer calculated by adding up the pair interactions but by evaluation of stochastic quantities. These stochastic variables are, actually, beyond chaos. Their time correlation function and long time average are related to the properties of system. We will detail these ideas in Chapter 4.

We are going to use molecular dynamics to study the dynamics of nanoparticles suspended in a liquid or self-propelling in the vicinity of liquid-solid interfaces. It is of great advantage to use molecular dynamics to study these small scale hydrodynamics. It provides the most detailed information of a physical system. Molecular dynamics also bridges the gap between theory and experiments. Following the procedure of modeling, coding, simulating and calculating, endows us with the ability to rebuild
the experiments virtually and answer the unsolved questions through varying the parameters of simulation. We will look into Janus particles a lot, which is one special type of nanoparticle.

1.2 Janus particles

Janus particles, named after the Roman god Janus for their two different chemical functional surfaces, are now of wide interest and have many applications in micro-fluid and chemical engineering. Interestingly, they are just one type of patchy particle, a big family of micrometer sized particles with surface modifications and decorating patches, manufactured purposely as building blocks for the assembly of complex structures. One of the method to make patchy particles, being used in our laboratory, is the template-assisted Glancing Angle Vapor Deposition method [8]. The surface anisotropy endows these patchy particles with many new abilities, which we are interested to analyze, model and simulate.

Due to the very distinguish the responses of the two hemispheres to an external electric field or magnetic field, Janus particles possess new properties, such as self-assembly and self-propulsion. The applications reported are self-propelled micro-motor [9,10] and flexible display screen pixels [11]. Current studies of Janus particles stimulate the potential application in photonics crystals [12], targeted drug delivery [13,14] and electronic devices [15].

Both electric and magnetic fields are good tools to control the assembly structure
of Janus particles. For magnetic field, the different capping materials (Ferromagnetic, Ferrimagnetic and anti-ferromagnetic) allow Janus particles to form several different chain structures: staggered chains for Fe$_{1-x}$O, double chains for Fe$_3$O$_4$ and no assembly for $\alpha$–Fe$_2$O$_3$, see references [16–18] for more details.

In this thesis, we treat Janus particle as a mathematic model composed of a series of dipoles.

1.3 Outline

The research of this thesis is devoted to the study of the dynamics of nanoparticles in fluids and at interfaces. We are interested in modeling the Janus particles so as to mimic those physical processes in the laboratory, comparing the simulations with observed behavior under microscopes. Once we remodel these phenomena in our computer, we will be able to check the underlying physics and hope to guid future experiments and predict additional behavior. The thesis will present the following materials.

Chapter 2 investigates MD simulations of sessile droplets evaporating in the presence of dispersed particles. During droplets evaporation, like many other nano or micro-particles, Janus particles deposit to the bottom wall because of the flow field inside the droplets. We check the current continuum theories for “coffee rings”, analyze the profile of the evaporative flux and inner flow field, and investigate factors impacting the deposition structures of Janus particles as well.
Chapter 3 presents the results for the slip boundary condition of curved surfaces, which is an important and desired property of micro-fluidic devices. We will treat several types of surface geometries, including spherical particles. The slope of the surface is one of the keys to understand the hydrodynamics of micro-particles. We will show that the Navier’s slip boundary condition is a very good one. The slip length defined in a consistent tensorial manner, depends only on the physical properties of the solid and fluid involved and does not vary with the flow configuration.

Chapter 4 will provides a preliminary study the stochastic theory of Brownian motion. We first review the historic development of Brownian motion and derive the Fokker-Planck equation for translational and rotational Fokker-Plank equation. Then, we try to model a Langevin equation to explain why self-propelling Janus particles will have a larger diffusivity, and why they tend to align themselves parallel to nearby surfaces. After that, we will model the coupling behavior between translational and rotational Brownian motion, which is a very fascinating phenomenon observed in the laboratory. The results of simulation consistent with the findings are shown at the end.
Chapter 2

Evaporation of Particle-laden Droplets

In this chapter, we use molecular dynamics simulations to study the evaporation of particle-laden droplets on a heated surface. The droplets are composed of a Lennard-Jones fluid containing rigid particles, which are spherical sections of an atomic lattice, and heating is controlled through the temperature of an atomistic substrate. We observe that sufficiently large (but still nano-sized) particle-laden drops exhibit contact line pinning, measure the outward fluid flow field which advects particles to the drop rim, and find that the structure of the resulting aggregate varies with inter-particle and droplet-wall interactions. The profile of the evaporative fluid flux is measured with and without particles present, and is also found to be in qualitative but not quantitative agreement with earlier theory. The compatibility of the deposit patterns in simple nanoscale calculations and micron-scale experiments indicates that molecular simulation may be used to predict aggregate structure in evaporative growth processes.

The main body of this chapter is published, see Ref. [19].
2.1 Introduction

The evaporation of a sessile droplet on a hot surface is a key problem in fluid mechanics, relevant both to theoretical issues in heat transfer and to practical questions in materials processing. The evaporation of a particle-laden droplet raises the additional issue of the structure of the resulting solid aggregate, and, going further, offers the possibility of controlling this structure by means of anisotropic (e.g., Janus) surface properties [20]. A familiar and paradigmatic example of this process occurs in coffee stains, where the residue of evaporated droplets takes the form of a ring-like deposit of grains at the rim. Experiments by Deegan and collaborators [21] focused attention on this “coffee ring problem” several years ago, and subsequent work [22–25] established the ubiquity of the process, while numerous theoretical studies have addressed the dynamics [26–29,32,33]. A complete understanding of the problem is not yet available however: experiments cannot measure everything in a small, time-dependent, multiphase droplet, while most theoretical treatments require approximations to deal with an evaporating particle-laden drop.

The difficulty of understanding the droplet evaporation mostly comes from the complex interaction between the three phases: the solid wall, the liquid droplet itself and its vapor. The interaction of solid and liquid gives rise to a thermal effect: heat transfer from the wall to the droplet. The interactions within the liquid cause a hydrodynamic effect: particle convection due to the internal flow. Interactions between liquid and vapor, and in particular the temperature contrast, produces an
evaporative flux from the droplet surface. In addition, temperature variation along
the liquid-vapor interface may yield a Marangoni flow due to surface tension variation.
The interplay of these effects control the structure of the particle deposit.

In this chapter, we use MD simulations to simulate the evaporation of droplets
containing colloidal particles, having either uniform or Janus-like surface properties.
One goal is to test whether the phenomena found in micron-sized particle systems
persist down to nanometer scales; in this way we hope to extend the size range in
which controlled aggregate structures may be produced by droplet evaporation. A
second goal is to test the validity of some of the underpinnings of the theoretical
analyses used in the problem. Since MD simulations provide detailed atomic-scale
information: concentration, temperature and fluid flow fields are available even dur-
ing the rapid heterogeneous processes occurring in evaporation. Furthermore, key
parameters such as the strength of the interaction between wall and liquid, liquid
and liquid, and liquid and particles are easily varied here, serving as a convenient vir-
tual laboratory for addressing the questions raised above. The difficulties of applying
uncertain constitutive relations are absent, although replaced to some degree by the
problem of extracting a robust signal from a relatively small sample in a fluctuating
environment. More generally, our goal is to establish the ability of these relatively ba-
sic simulations of moderate scale systems to predict phenomena occurring in droplet
evaporation and guide experimental investigations. As usual in MD simulations, the
length and time scales of the simulations are much shorter than those of laboratory
experiments, but the phenomena of deposition and pattern formation studied here are quite similar.

2.2 Modeling assumptions

The simulations use standard molecular dynamics (MD) techniques [1–3] and generic interactions of Lennard-Jones form,

$$V(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - c_{ij} \left( \frac{\sigma}{r_{ij}} \right)^{6} \right]$$

(2.1)

The parameter $c_{ij}$ can be used to adjust the strength of the interaction between atomic species $i$ and $j$, but for simplicity in most simulations we set it to unity and we assume that all fluid-fluid and fluid-particle interactions have the same interaction potential, along with the same mass $m$ and approximate atomic diameter $\sigma$. The calculations are nondimensionalized using $\epsilon$, $\sigma$ and $m$ as energy, length and mass scales, respectively, and the resulting time scale is $\tau = \sigma (m/\epsilon)^{1/2}$. Typical numerical values are $\sigma \sim 0.3 \text{nm}, \tau \sim 2 \text{ps}$ and $\epsilon \sim 120k_B$, where $k_B$ is Boltzmann’s constant, and temperatures are measured in units of $\epsilon/k_B$. The fluid atoms in the liquid or vapor obey ordinary Newtonian dynamics with the force arising from the interaction with other atoms (within a cutoff radius of $2.5 \sigma$). Newton’s equations are integrated using a predictor-corrector method with a time step of $0.005\tau$. The suspended particles are spherical sections of an atomic cubic lattice containing all atoms within a certain radius of a center; here the atomic density is 0.8, the radius is 2 and the particles contain 32 atoms. Two types of particles are considered here – “plain,” with uniform
surface properties, and “Janus”, which have different interactions on each hemisphere. To implement Janus particles, we make the atoms in only one hemisphere of a particle attractive to other particle atoms while those in the other hemisphere have only the repulsive $r^{-12}$ interaction; all particle atoms attract the fluid and wall atoms with unit strength. (Specific examples might be a particle with a uniform shell in which one half has a magnetic component, or a gold-coated polystyrene particle where the contact angles on gold and polystyrene are comparable but the charge distribution differs.) The particles move as rigid bodies, where the net force and torque on each particle is computed by summing the interatomic forces between its atoms and the neighboring fluid atoms, and the motion is given by Newton’s and Euler’s equations. Quaternion variables are used to describe the particle orientations [1]. The solid substrate is made of atoms coupled to lattice sites by a linear spring of stiffness $100\epsilon/\sigma^2$.

Initially the drop consists of a hemispherical cap of 72,236 fluid atoms placed above a solid wall consisting of a single layer of fcc unit cells. The drop contains 119 particles of 32 atoms each, centered at random positions within the cap. The simulation box dimensions are 130x130 in the $x-y$ plane of the wall, and 90 in the vertical $z$-direction. The entire system is prepared by gradually raising the temperature from 0.5 to 1.0 over a $10\tau$ interval, following which the liquid is maintained at this temperature for an additional $100\tau$, using a Nosé-Hoover thermostat. During this period the walls of the simulation box are reflecting. The structure of the system at this stage is shown in Fig. 2.1 in terms of time-averaged density profiles of fluid atoms and particles,
and a snapshot is given in Fig. 2.2a. These densities are computed by counting the number of atoms or particles in a three-dimensional array of concentric hemispherical sampling bins centered at the middle of the drop at the wall (subsequent profiles in this chapter are given in cylindrical coordinates). The density profile for the fluid atoms shows a liquid hemisphere of density 0.85 surrounded by vapor of density 0.04. These values are roughly consistent with the measured phase diagram for the Lennard-Jones system [35], but some deviation occurs because of the presence of the wall. Note that during the preparation stage the particles remain approximately uniformly distributed in the interior of the drop, as indicated in the figure, although there are too few particles present to produce a smooth curve.

Figure 2.1: Equilibrated drop structure before evaporation: time-averaged density of fluid (main figure) and particles (inset) as a function of (three-dimensional) distance from the center of the drop at the wall.
The drop actually tends to spread slightly during preparation, because when the fluid-wall interaction has unit strength \( (c_{fw} = 1 \text{ in Eq. 3.9}) \) the liquid is completely wetting and would eventually spread to cover the substrate [57]. However, this spreading is very slow, with drop contact radius varying as \( t^{1/10} \) [37], and is preempted by the more rapid evaporation process. As a check, we have also simulated a partially-wetting liquid, with \( c_{fw} = 0.75 \) and a 90° contact angle [57], and found no significant change in the evaporation dynamics reported below. Another potential complication is that the atoms in the particles attract each other and the particles would eventually form clusters, but this process is driven by the slow Brownian motion of the particles and also occurs on time scales well beyond those of evaporation.

Figure 2.2: Stages in the evaporation of a Janus particle-laden droplet: (a) after 50\( \tau \), (b) 500\( \tau \) and (c) 1000\( \tau \). The fluid atoms in the drop are shown as cyan (light) dots, the solid atoms in the substrate are red (dark) dots, and the Janus particles are filled circles whose two sides are red (medium grey) and blue (dark grey).

To evaporate the drop, the temperature of the wall is ramped further to 1.2 over a 10\( \tau \) interval and maintained at that value by a constant kinetic energy thermostat, while the fluid temperature is allowed to vary. (The simplest thermostat is used for the wall since our focus is the dynamics of the liquid in the unthermostatted
drop.) The liquid expands slightly during the temperature ramp and then, as seen in Fig. 2.2, the drop shrinks monotonically as it emits vapor, and eventually disappears due to evaporation. The structure of the deposit is discussed below; see in particular Fig. 2.8. The time-dependent vapor density is monitored during the simulation, and evaporating fluid atoms which arrive at the boundary of the simulation box are either bounced back or deleted so as to maintain a constant vapor environment for the drop at the equilibrium density 0.04.

2.3 Analysis of evaporation

Our concern here is the shape evolution and particle flux produced during evaporating of a droplet placed on a heated surface, and in particular the effects of suspended particles. We observe that there is little difference between plain and Janus particles in this regard (only) and in this subsection we refer for simplicity to Janus particles alone.

We first consider the temperature and density distributions within the system. The drop is observed to maintain an approximate spherical cap shape as it evaporates, so in the analysis we use a cylindrical \((r, \phi, z)\) coordinate system with the vertical \(z\)-axis through the center of the drop, and divide the simulation domain into a two-dimensional array of concentric circular rings in the radial \(r\) and vertical directions. We record the number of particles and their velocity and temperature in each ring and average over a 10\(\tau\) time interval. The result for a typical simulation is shown
in Fig. 2.3. We see that both density and temperature are fairly uniform within the drop despite the presence of the particles, with higher fluctuations in the vapor region due to having fewer molecules there to average over. The temperature at the rim is slightly higher than in the interior due to the fact that the escaped vapor atoms need a higher kinetic energy on average. Note however that the temperature variation along the liquid-vapor interface is fairly weak, and we therefore neglect Marangoni effects in the subsequent discussion. The density varies smoothly between the bulk liquid and bulk vapor values, with most of the transition occurring near the interfacial region, and the latter maintains a nearly-constant thickness along the drop surface. An important observation is that the liquid-vapor interface is not a perfect spherical cap and deviates notably at the foot of the drop, reflecting the completely-wetting nature of the liquid.

During evaporation, the particles are advected first towards the substrate and
subsequently to the rim of the droplet where they deposit. The contact line itself remains pinned. The connection between liquid and particle motion is indicated by the velocity field shown in Fig. 2.4: the fluid moves downward over most of the drop and radially outward near the substrate. The origin of the flow that drives particles to the rim is, it is believed [21], contact line pinning coupled to the fact that the evaporative flux is largest at the edges of the drop. The liquid must supply this flux as the droplet shrinks down, and the geometry of the situation requires a strong outward flow field, as seen in Fig. 2.4.

We have measured the evaporative flux both for pure liquid and particle-laden drops, and obtained Fig. 2.5, which shows $j$ at the three successive times indicated. Each plot is an average over a short ($10\tau$) interval centered at 300, 400 and 500$\tau$. Averaging is necessary to smooth the fluctuations, and longer averaging periods would
be more effective, but the drop shape changes too much over longer intervals. The entire evaporation process lasts for about 1000\(\tau\) (roughly 2 ns) for the Janus case, and slightly longer for pure fluid evaporation, but the data at later times involves fewer and fewer evaporating atoms and is too noisy for analysis. The results shown above are based on an ensemble average of 5 realization. The ordinate in Fig. 2.5 is radial position divided by the current drop \((x-y)\) radius, and varies between 0 and 1. While the radius is constant (except for fluctuations) in the particle-laden case, the radius of the pure fluid drop decreases with time. Note the rapid increase in flux as the contact line is approached \((r \to 1)\).
We have attempted to relate the simulation data to a popular “Lens” model from the literature. This approach assumes that the vapor concentration satisfies a steady-state diffusion equation with an evaporative flux proportional to the concentration gradient, and solves the resulting boundary value problem by analogy to the electrostatics of a lens held at fixed potential \([30–33]\). The outcome is

\[
j(r; \theta) = j_0(\theta) \left(1 - \frac{r^2}{R^2}\right)^{-\lambda(\theta)} \quad \lambda(\theta) = \frac{1}{2} \left(1 - \frac{\theta}{\pi - \theta}\right)
\]  

(2.2)

where the flux \(j(r; \theta)\) is the number of atoms crossing a sampling ring just outside and parallel to the drop surface, centered at (cylindrical coordinate) radius \(r\), per unit time and per unit area. The flux depends on the drop contact radius \(R\) and the contact angle \(\theta\), the latter varying as the droplet evaporates. The key point is that for \(\theta < \pi/2\) the (mathematical) vapor flux diverges at the edge of the droplet. Of course, there is no real singularity in a physical problem, and one expects \(j\) to be cut off at a small (molecular) scale. The Lens model qualitatively accounts for the behavior of the evaporative flux: the functional form in Eq. 2.2 fits the data in Fig. 2.5 well. The simulations are also consistent with the other aspects of the theory such as the variation of contact angle and drop volume with time, shown in Fig. 2.6 for both the pure and particle-laden fluid cases. (The contact angle is obtained by fitting snapshots of the drop to a spherical cap, and the volume is estimated by counting the number of atoms within it, and using the measured density.) However, the formula fails to quantitatively describe the simulations. The exponents \(\lambda(\theta)\) obtained in fitting the pure fluid data are 0.48, 0.55 and 0.65 at times 300, 400 and 500\(\tau\), respectively,
but Eq. 2.2 does not permit values $\lambda > 1/2$. The flux is slightly more singular for the particle-laden drop: the fitted values of $\lambda$ are 0.61, 0.71 and 0.83 for the same three times. The stronger divergence is presumably the outcome of the contact line pinning, since the particles at the edge prevent the liquid from receding.

Figure 2.6: Variation of (a) contact angle and (b) droplet volume with time, for evaporating drops with (lower curves, □) and without (upper curves, ○) Janus particles.

The origin of the discrepancy requires some discussion. One possibility is that the flux is not measured accurately at the edge of the drop, where evaporating atoms travel nearly parallel to the surface, and indeed the error bars in our flux measurements are distinctly larger at the edge. However, the fit is quite good at lower values of radius $r$, and even if we delete the less-certain points at large $r$ from the fitting procedure, the resulting exponents change only by about 4%. Along the same line, the density contour plot indicates that the drop shape deviates from a circular cap at the three-phase contact line at the foot of the drop, a feature not accounted for in the theoretical prediction. In Fig 2.7 examples of this region are shown in molecular
detail for both pure-liquid and particle-laden drops. The liquid drop shows a fairly smooth circular interface with a transition zone of modest thickness along most of the surface, and a small foot which reflects the fact that the liquid is completely wetting and the drop would spread under isothermal conditions. In the presence of particles, however, the liquid-vapor interface is distinctly less regular everywhere. If the details of the interface shape were responsible for the discrepancy between theory and simulation in the evaporative flux one would expect the results for pure and particle-laden drops to differ significantly, but in fact they do not.

![Figure 2.7](image_url)

Figure 2.7: Views of the edge of evaporating droplets at molecular resolution: (a) pure liquid and (b) particle-laden drops.

A second possible source of discrepancy is that the simulation conditions may deviate from the assumptions leading to Eq. 2.2. In particular, the liquid density and interface temperature are assumed to be uniform and the drop shape is assumed to be a spherical cap, whereas the simulation protocol does not explicitly enforce this behavior. Nonetheless, as shown in Fig. 2.3, we do observe a roughly spherical shape.
and constant density and temperature throughout most of the evaporating drop. Slight variations occur at the foot of the drop, but as noted above this region does not control the fitted exponents. A more likely explanation is that the evaporation process is poorly approximated by the Laplace equation used in the theoretical analysis. In particular, the Péclet number $Pe = vR/D$ in these simulations is appreciable: a peak value can be estimated as $Pe \sim (1.0) \cdot (50)/(0.2) \sim 250$ using the measured largest fluid velocity $v \sim 1.0$, the drop contact radius $R$, and an earlier calculation of the molecular diffusivity $D$ [39]. In consequence, the advective derivative term $\mathbf{v} \cdot \nabla c$ in the full concentration equation is required here, which would alter the predicted exponents in Eq. 2.2. In larger (millimeter-sized) drops, the velocities are likely to be smaller since the relative temperature differences are less, and this complication may be absent.

A common alternative approach to the evaporative flux assumes that vapor diffusion is rapid and instead transport processes within the liquid control evaporation [27, 40]. The resulting nonequilibrium one-sided (“Neos”) model is most often used in modeling thin liquid films in the limit of weak surface height variation, which is not entirely appropriate to the geometry of nano-size droplets. Furthermore, the starting point is an assumption that the local evaporative flux is proportional to the difference between the interface temperature and the saturation temperature of the liquid. In our simulations, however, we observe a nearly constant interfacial temperature and the model would predict a constant flux along the interface, which we do
not observe. If we nonetheless attempt to fit our flux data to the Neos expression for the flux, \( j(r) = j_0/(K + h(r)) \), where \( j_0 \) and \( K \) are constants and \( h(r) \) is the local height of the drop, the result is a very poor fit.

### 2.4 Deposition pattern

The pattern formed by deposited particles after evaporation is sensitive to the interaction between the particles, and in this subsection we indicate the distinctions between the plain and Janus cases.

An essential requirement for particles to deposit at the rim of an evaporating drop is that the drop be large enough: if the drop is too small it evaporates, or at least decays into a thin pancake, before the flow field is established and the particles are able to move to the rim. This behavior was first observed experimentally by Shen et al. [38], and we have reproduced it in simulations. The drop shown in Fig. 2.2 has a radius of about 15 nm, whereas in similar simulations for drops whose initial radius is around 5 nm, we see that the particles deposit roughly uniformly over the drops interior: see Fig. 2.8. Initially small evaporating droplets produce a somewhat uniform deposition pattern for plain particles, but some chain-like structure is evident in the Janus case. For larger droplets the deposit occurs preferentially at the rim, and in the Janus deposits chain formation is very evident.

A second requirement for deposition to occur at the drop rim is that the liquid must have adequate thermal contact with the solid to set up the flow field seen
Figure 2.8: Top row: Janus particle deposit for evaporated drops of initial radius (a) 5 nm and (b) 15 nm. Bottom row: same for plain particles with initial radii (c) 5 nm and (d) 15 nm.

above [41]. We have investigated this issue by adjusting the interaction between the liquid and the wall: in Eq. 3.9 we varied the coefficient of the attractive $r^{-6}$ term $c_{fw}$ between 0 (pure short-distance repulsion – hydrophobic wall) and 1 (standard strength attraction – completely wetting wall) [57] and observed the resulting solid pattern. Independently, we measured the thermal conductance for each value of interaction strength by simulating a slab of liquid completely filling the gap between two atomic walls held at different temperatures. As the attractive strength decreased from 1 to
0, the amount of temperature slip (or, equivalently, Kapitza resistance) at the wall increased so that the thermal conductance decreased, approximately linearly, and ultimately by a factor of nearly 10 – see the left frame in Fig. 2.9). Correspondingly, as the wall attractive strength decreased the resulting pattern of solid particles varied from the rim deposit shown above to a random distribution, which is quite like that shown in the left panel of Fig. 2.8. More quantitatively, in the right frame of Fig. 2.9 we compare the (ensemble-averaged) radial distributions of the deposited particles for two different fluid-solid interaction strengths. Lowering the value of $c_{fw}$ from 1.0 to 0.8 shifts the distribution from a sharp peak at the rim to a broader shape centered in the interior. In contrast, the strength of the fluid-particle interaction has very little effect on the structure of the deposit: varying its value from 0.5 to 1.0, for example, is observed to have almost no effect on the radial distribution. The effects of substrate thermal resistance and conductance on evaporation have been studied more systematically by Dunn et al. [42,43].

The detailed structure of the deposit is an important consideration in potential applications to evaporative self-assembly. We saw above that particles with Janus surface properties would, under the right conditions, form a rim deposit with chain-like structures. This behavior is confirmed by experimental observations of gold-capped sulfated-polystyrene Janus particle-laden droplets during drying [44]. The chaining behavior is a result of the attractive interaction between the gold caps and the sulfated polystyrene half of the Janus particles.
Additional experiments investigated the effect of particle surface charge on the deposition behavior [44, 45]. The presence of sulfate groups on the surface of the particles results in an overall negative surface charge, which can be screened by the addition of salt. Sulfated polystyrene particles in deionized water form hexagonal close-packed, highly ordered layers at the rim, whereas formation of randomly packed particle layers is observed in 10 mM aqueous NaCl solution. In contrast, Janus particles show random assembly at all electrolyte concentrations. These results motivated us to study the effect of charge on the deposit structure of uniform particles. In Fig. 2.10, we show the deposits that result when the charge on a symmetric particle increases from 0 to 4 and then to 8. In the simulations, a charge of the appropriate magnitude is placed on randomly chosen individual atoms within each particle, and a Coulomb interaction is added to the Lennard-Jones potential. The neutral case
Figure 2.10: Effects of adding a charge to a plain particle: deposition patterns for (a) charge 0, (b) charge 4 and (c) charge 8.

resembles the random packing observed in the 10 mM case. The charge 8 situation models the case where the particles carry a charge, i.e., deposition in deionized water. It is apparent from the right panel of Fig. 2.10 that the particles tend toward assembling at the rim and a regular packing [46], but that the drop volume is not sufficient to enable long enough evaporation times to achieve close packing at the rim.

2.5 Discussion and conclusion

We have shown that straightforward, medium-scale MD simulations could be used to rebuild the process of evaporation of particle-laden droplets. Aside from demonstrating that nano-scale and micron-scale systems behave in a similar way with regard to the behavior of the particles, we were able to measure continuum fields such as velocity within the droplet, along with the profile of the evaporative flux, which drives the process. Using standard methods, we have also measured the density, temperature and stress fields (but not reported here) within the droplet. In addition, we were
able to show the existence of a minimum drop size for rim deposition, and verify the importance of adequate thermal coupling between liquid and solid. Furthermore, the simulations reveal the connection between particle interactions and deposit structure, and indicate some limitations in continuum modeling for nanodrops. The significance of these results is that simple simulations provide a viable method for both testing the theoretical underpinnings of the process and for predicting the nature of the outcome – the structure of the resulting particle deposit. Indeed, Cheng and Grest [47] have recently used similar MD simulations to examine the defect and grain boundary structure of the deposit formed by an evaporating particle-laden liquid film. In this chapter, we have focused on the most important aspect of the continuum flow, the velocity field and the evaporative flux, but any other quantity which can be determined from atomic variables is equally accessible.
Chapter 3

Velocity Slip on Curved Surfaces

The Navier boundary condition for velocity slip on flat surfaces, when expressed in tensor form, is readily extended to surfaces of any shape. We test this assertion using molecular dynamics simulations of flow in channels with flat and curved walls and for rotating cylinders and spheres, all for a wide range of solid-liquid interaction strengths. We find that the slip length as conventionally measured at a flat wall in Couette flow is the same as that for all other cases with curved and rotating boundaries, provided the atomic interactions are the same and boundary shape is properly taken into account. These results support the idea that the slip length is a material property, transferable between different flow configurations.

The main body of this chapter is published on Ref. [48].

3.1 Introduction

The explosive growth in the development and application of micro-fluidic devices requires accurate modeling of fluid flow in irregular and convoluted regions with curved bounding surfaces. At the same time, the traditional no-slip boundary condition (BC) for the velocity of a liquid at a solid surface has come into question [49] and attention has focused on alternatives, and in particular the velocity slip boundary
condition first proposed by Navier [50] in 1823. In its usual form for flow past a flat solid surface, one introduces a slip length $\xi$ as the distance from the surface where the linearly-extrapolated fluid velocity field coincides with the surface velocity. Explicitly, the discontinuity $\Delta V$ between the fluid and solid tangential velocities at the surface is assumed to be proportional to the local strain rate:

$$\xi \left( \frac{\partial u_x}{\partial y} \right)_S = \Delta V$$

(3.1)

where $x, y$ are Cartesian coordinates parallel and normal to the surface $S$, respectively.

This Navier slip BC has been widely used in gas dynamics [51] since the work of Maxwell [52], and in the last decade or two slip has been observed for liquid flows both in experiments (see the reviews in [49,53–56]) and molecular dynamics computer simulations. The latter have indicated that the slip length in liquids depends critically on three factors – wettability, roughness and strain rate. A fluid is more likely to slip in the presence of a weak liquid-solid interaction (indicated by a high contact angle) [57–62], surface roughness at the atomic scale influences the degree of slip in a complex way [63–65] and the slip length tends to grow and perhaps diverge at high strain rate flows [66–68].

Going beyond flat surfaces, in 1990 Einzel, Panzer, and Liu [69] introduced a curvature correction to the Navier slip length, which was pursued in some gas dynamics studies [70–73], and later expressed in a general tensor form by Barber et al. [74]. If one regards velocity slip as the linear response of the fluid to the shear stress exerted
at the fluid-solid interface, then a coordinate invariant generalization of Eq. 3.1 is

\[
\frac{\xi}{\mu} \mathbf{\tau} : \mathbf{\hat{n}} \mathbf{\hat{t}} = \Delta V \tag{3.2}
\]

where \(\mathbf{\tau}\) is the shear stress tensor, \(\mu\) is the fluid viscosity and \(\mathbf{\hat{n}}\) and \(\mathbf{\hat{t}}\) are normal and tangent unit vectors at the surface, respectively. The generalization assumes that the solid is impenetrable and the normal fluid velocity vanishes at the surface, and the two boundary conditions agree when the surface is flat. More generally, as we shall see, if we choose a coordinate system “aligned” with the surface the curvature corrections emerge naturally.

We will use molecular dynamics (MD) simulations of simple liquids to test the above form of the Navier BC for curved surfaces. The slip length can be extracted directly from the velocity field obtained in simulations of flow past various solid boundary shapes, including planes, cylinders and spheres. Alternatively, we can compare the force and torque on moving solids to solutions of the Navier-Stokes equations with a Navier BC imposed and thereby infer the slip length. We address the influence of wettability by varying the strength of the interaction between liquid and solid atoms, and test the assumed linearity in strain rate by varying the forcing of the flow. The effects of roughness are avoided by using model solids with atomically-smooth surfaces with a fixed lattice structure, and likewise we do not explore the variation of slip length with other solid properties such as the atomic mass or the stiffness of the binding potential [75]. The key feature of the Navier condition which is tested here is whether the slip length is a genuine material parameter, dependent on the nature of
the solid and liquid involved but otherwise a constant transferable between different flow configurations. Note we include the surface structure as a material property. Aside from the variation in slip length resulting from roughness mentioned above, it is well known that other transport properties such as thermal conductance and dielectric response are highly sensitive to surface structure.

A somewhat exceptional situation occurs in carbon nanotubes, which are known experimentally to exhibit a highly enhanced flow permeability in comparison to other materials [76], and which have been the subject of MD simulations by Falk et al. [77] among others. These authors find that the friction coefficient for flow along the axis of model carbon nanotubes has a significant variation with the tube radius. Normally, the friction coefficient friction coefficient $\lambda$ is related to the slip length $\xi$ and the fluid viscosity $\mu$ by $\xi = \mu/\lambda$, and one might conclude that a significant variation of slip length with radius of curvature occurs. However, the same simulations find that the fluid velocity profile, both inside and outside the tube, is completely flat with no variation at all as a function of the distance from the tube. Since the slip length is defined as the distance from the solid surface where the parallel component of the velocity extrapolates to zero, the slip length is formally infinite! Since the same behavior is found independently of tube radius, their results in a sense provide a confirmation of our claim. Realistically of course, it makes more sense to state that carbon nanotubes exhibit anomalous behavior not seen in other fluid mechanical systems. where among the things the usual connection between slip and friction
coefficient fails.

3.2 Slip length in curvilinear coordinates

We assume that the fluid is Newtonian and incompressible, so that the stress is proportional to the deviatoric stress tensor, \( \tau = 2\mu E \). In Cartesian coordinates, the Navier slip law Eq. 3.2 reduces to

\[
\xi \left( \frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right)_s t_i n_j = \Delta V \tag{3.3}
\]

For a plane wall, the Cartesian coordinates can be aligned with the wall, and if the wall tangent and normal directions are \( \hat{x} \) and \( \hat{y} \), respectively, the slip law reduces to the common form

\[
\xi \left. \frac{\partial u_x}{\partial y} \right|_{y=Y} = \Delta V \tag{3.4}
\]

where the wall is located at \( y = Y \) and the condition of impenetrability \( u_y(y = Y) = 0 \) has been used to drop the second term.

A trivial generalization to a curved wall would replace \( \partial u_x / \partial y \) by \( \partial u_t / \partial r_n \). Einzel et al. Ref. [69] pointed out the correct procedure is to begin with Eq.3.3 and work out the derivatives carefully, leading to an extra term related to curvature. A simpler and more systematic procedure is to directly evaluate the general form of the boundary condition Eq.3.2 in a curvilinear coordinate system aligned with the boundary. For a cylinder of radius \( R \), for example, in cylindrical coordinates \( (r, \phi, z) \) with the \( z \)-axis
along the cylinder axis, Eq. 3.3 reduces to
\[ r \left. \frac{\partial(u_\phi/r)}{\partial r} \right|_{r=R} = \frac{\Delta V}{\xi} \]  
(3.5)

where a term \((\partial u_r/\partial \phi)_{r=R}\) is dropped because the cylinder is impenetrable to the fluid. If the derivative is expanded, we have
\[ \frac{\partial u_\phi}{\partial r} \bigg|_{r=R} = \frac{\Delta V}{\xi} + \frac{V}{R} \equiv \frac{\Delta V}{\Xi} \]  
(3.6)

where \(V = u_\phi(r = R)\), and in the last equality defined an effective slip length \(\Xi\) by
\[ \frac{1}{\Xi} = \frac{1}{\xi} + \frac{V}{\Delta V} \cdot \frac{1}{R} \]  
(3.7)

If the cylinder is stationary, \(\Delta V = V\) and we recover the result of Ref. [69]. However, a more convenient version of the boundary condition follows if we introduce the angular velocity \(\omega(r) = u_\phi(r)/r\) and the angular velocity slip \(\Delta \omega = \Delta V/R\):
\[ \xi \left. \frac{\partial \omega}{\partial r} \right|_{r=R} = \Delta \omega \]  
(3.8)

Furthermore, these boundary conditions are also valid for spheres. If a sphere of radius \(R\) rotates about its z-axis, we can choose a spherical coordinate system \((r, \theta, \phi)\) oriented along this axis and evaluate the strain tensor, and obtain an equation of the same form as Eq. 3.5, but with a different definition of radius \(r\). The boundary condition in the form of Eqs. 3.6 and Eq. 3.7 follow immediately. In this case, the fluid’s angular velocity with respect to the sphere axis is \(\omega(r) = u_\phi(r)/(r \sin \theta)\), and if we define the angular velocity slip as \(\Delta \omega = \Delta V/(R \sin \theta)\) the result is Eq. 3.8.
To sum up, we regard the tensor equation Eq. 3.2 as the general form of the slip boundary condition, which is made explicit for a plane surface in Eq. 3.4 and for a cylindrical or spherical surface in Eq. 3.8. The subsequent calculations test whether the single slip length parameter $\xi$ depends on fluid and solid properties alone.

### 3.3 Simulation method

We employ standard molecular dynamics (MD) techniques [1–3] and generic interactions of Lennard-Jones form for all interactions between atoms

$$V_{ij}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - c_{ij} \left( \frac{\sigma}{r} \right)^{6} \right]$$ (3.9)

The parameter $c_{ij}$ is used to adjust the interaction strength between atomic species $i$ and $j$. Here, we have 2 species of atoms in the simulations, fluid (f) and solid (w). The solid atoms will constitute the walls in channel flows and the cylindrical and spherical particles in other cases. The interaction coefficient between atoms of the same species is always set to unity, $c_{ff} = c_{ww} = 1$, while the fluid-solid interaction strength $c_{fw}$ varies to adjust the wettability. In Table I in the Appendix we record the equilibrium contact angle for a drop of liquid placed on a plane atomistic surface, as a function of the interaction strength. Since the liquid and solids simulated here are generic, this is not the contact angle of any particular laboratory materials, but is intended to provide a guide to the wettability variation. The interaction scale $\epsilon$, the (common) atomic mass $m$ and approximate atomic diameter $\sigma$ set the energy, mass and length units, respectively. The calculations are non-dimensionalized accordingly.
and the resulting time scale is $\tau = \sigma (m/\epsilon)^{1/2}$. Representative numerical values are
$\sigma = 0.34\text{nm}$, $m = 40.0\text{ a.u.}$, $\epsilon/k_B = 120\text{ K}$ and thus $\tau \sim 2\text{ ps}$, where $k_B$ is Boltzmann’s constant, and temperatures ($T$) are expressed in units of $\epsilon/k_B$. The fluid atoms in the liquid obey ordinary Newtonian dynamics with the force arising from the interaction with other atoms (within a cutoff radius of $2.5 \sigma$). Newton’s equations are integrated using a predictor-corrector method with a time step of $0.002\tau$. A “profile-unbiased” Nosé-Hoover thermostat [5] is applied to the fluid atoms to fix the temperature at $T = 0.8$ without disturbing the flow field.

A flat solid boundary wall is made of four layers of a cubic lattice of atoms, which are coupled to their fixed lattice sites by a linear spring of stiffness $100\epsilon/\sigma^2$. The particles are cylindrical or spherical sections of the same lattice, all with the same atomic number density as the fluid, $0.8\sigma^{-3}$. Plane walls are fixed in place, while cylinders and spheres are treated as rigid bodies which rotate rigidly about an axis. Velocity rescaling is used to maintain the wall and solid particles at the same temperature as the fluid atoms; this simpler thermostat suffices since the dynamics of the solid is of no interest here.

All simulations start with the atoms on lattice sites, and the fluid is equilibrated with no forcing for $250\tau$ to produce an equilibrium steady state. Subsequently either the fluid or the solid is set into motion, and the flow fields, forces, torques, etc. are averaged over a $5000\tau$ interval. These quantities are further averaged over an ensemble of 10-20 realizations, and in the figures below most points have statistical
3.4 Simulation results

The principal result of this chapter is the master curve Fig. 3.1 for slip length vs. solid-liquid interaction strength, which encapsulates the outcome of all of our simulations for flow past planar and curved surfaces. In the remainder of this section, the various calculations are described individually.

![Figure 3.1: Slip length vs. solid-liquid interaction strength.](image)

**Figure 3.1**: Slip length vs. solid-liquid interaction strength.

3.4.1 Planar flows

We first determine the slip length for our model fluid and solid systems using MD simulations of Couette and Poiseuille in a channel between two flat walls. Although
numerous previous papers have done this, the precise numerical results depend on many specific modeling assumptions (interactions, density, temperature, etc.) and we require benchmark values before proceeding to curved surfaces. In addition, it is useful to discuss some general points in the simplest situation, for comparison to the curved boundary cases.

The simulation cell in this case contains 8000 fluid atoms, has dimensions \((X,Y,Z) = (20,30,20)\) and is periodic in the \(x\) and \(z\) directions, and the fluid density as a function of distance normal to the walls is shown in Fig. 3.2, for two choices of fluid-solid interaction strength. The nominal or geometrical position of the walls might be taken as the \(y\)-coordinates of the innermost solid layers, at \(Y_{0}^{\text{bot}} = 3.82\) and \(Y_{0}^{\text{top}} = 26.34\), which are indicated by vertical gray lines in subsequent figures. The density profiles illustrate the inherent ambiguity in defining the position of a bounding wall. The wall atoms fluctuate about their lattice positions, and in fact present a somewhat corrugated wall, and there is a gap between the fluid and wall atoms whose magnitude depends on the interaction strength. (Likewise, the degree of layering – the heights of the density oscillation peaks in the fluid – increase with \(c_{fw}\).) In this chapter, we choose a “hydrodynamic radius” as the midpoint of the gap between the density peak of two phases, \(i.e., Y_{h}^{\text{bot}} = Y_{0}^{\text{bot}} + \delta/2\), where \(\delta\) is the distance between the adjacent peaks of solid and liquid density. Note that \(Y_{h}\) therefore is interaction or material dependent. Other choices are possible; for example \(Y_{0}\) is used in [58].

For Couette flow the top wall is translated at a constant velocity, ranging from
0.1 to 0.5, while the bottom wall moves at the same speed in the opposite direction. Poiseuille flow is generated by applying a constant body force $mg$ in the $x$-direction, with $g$ ranging from 0.005 to 0.03. In Fig. 3.2 the velocity profile for Couette flow is shown for one choice of interaction strength, $c_{fw} = 0.4$, which happens to lead to significant slip. Note that it is the linear profile in the center of the channel that determines the slip length, since this is the solution of the Navier-Stokes equation to which the boundary condition is applied, and the up- and down-ticks near the walls would be macroscopically unobservable. The Poiseuille flow profiles in this geometry are parabolas in $y$ which change their shape as the interaction strength and resulting degree of slip vary.

To extract the slip length, the measured velocity profiles are fit to the appropriate general solution of the Navier-Stokes equation, linear and quadratic functions of $y$ for Couette and Poiseuille, respectively, and Eq. 3.4 is applied. The result is plotted in
Fig. 3.1, and the numerical values and statistical errors are given in Table 2 in the Appendix. The slip length is expected to be constant only in the Newtonian fluid regime (see, e.g., [66]) so we have also recorded the strain rate for each simulation in Table 3 in the Appendix. We see that if limit ourselves to simulations with \( \dot{\gamma} \lesssim 0.03 \) the slip length is indeed constant, and it is only these results which appear in the figure. The slip length is negligibly small (less than an atomic diameter) for strong solid-fluid interaction strength \( c_{fw} \geq 0.8 \), increases as the interaction weakens, and is large but finite as \( c_{fw} \to 0 \). The special case of no solid-fluid attraction has some subtleties: an unconfined liquid drop or film tends to float off or bounce along such a surface, and might be said to have infinite slip length, as suggested in [59], but a dense fluid confined in a channel still experiences some wall friction in the sense that atoms near the surface are slowed because their motion is obstructed by the atomic corrugations of the surface. The result is a shallow parabolic profile and a finite slip length (and relatively large statistical fluctuations) rather than a plug flow with infinite \( \zeta \).

### 3.4.2 Flow past cylinders

A cylinder is a simple model of a curved surface with constant curvature, and cylindrical surfaces are frequently present in microfluidic devices. For computational reasons it is more convenient to consider a rotating cylinder which generates a vortical flow rather than a stationary cylinder in an imposed flow. In the former case sampling
is improved by averaging around the cylinder circumference, taking advantage of the angular independence of the velocity. In the latter case, the velocity varies along the circumference and each polar angle would experience a different strain rate and require a separate analysis based on a relatively small sample of surface. We also consider a separate configuration of flow parallel to a cylinder axis, where the boundary condition takes a different form.

**Cylindrical Couette flow**

We first consider the flow external to a rotating solid cylinder. The simplest method to produce a nano-sized cylinder particle in an MD simulation is to select the atoms in a cylindrical selection of simple cubic lattice, a “type I” cylinder, as indicated in the inset to the left frame of Fig. 3.4. However, the surface is evidently much rougher than a plane surface at the same atomic density, and its slip properties are likely to differ since experiments indicate a sensitivity to roughness. To minimize the effect of surface irregularity, we adjust the atomic positions so that each surface atom is at the same radial distance from the cylinder axis, giving the much smoother “type II” cylinder depicted in the inset to the right frame of the figure, which more closely resembles the planar surface treated previously. The smooth cylinder has the property that the spacing between the outer atoms along its surface is the same as for the planar case, which suffices to produce the same potential energy landscape. We quantify this behavior by evaluating $V_{\text{eff}}(d,s)$, the net potential energy of interaction
between the entire solid and a single fluid atom located at a distance \( d \) from the surface and at position or arclength \( s \) along it. As seen in Fig. 3.3, the results for the planar and smooth cylinder surfaces match closely, whereas the landscape for the rough cylinder is entirely different.

Figure 3.3 : Effective potential energy seen by a fluid atom at distance \( d \) from a solid surface as a function of \( s \), the position (planar) or arclength (cylinder) along the surface. Left to right: planar surface, smooth cylinder and rough cylinder.

For the simulation, we place the cylinder in the center of a fully-periodic box of dimensions \((X, Y, Z) = (86.18, 86, 18, 10.77)\) with its axis along \( z \)-direction, and surround it with 63560 fluid atoms. The geometric radius of both cylinders is 3.52, much less than the distance to the box edges, but for safety we will test the dependence on box size below. The cylinders are rotated at angular velocity \( \omega_0 = 0.0571 \), corresponding to a surface velocity \( u_0 = R \omega_0 = 0.2 \), which is within the regime where the planar slip length is constant, and compute the fluid radial density and velocity profiles.

The fluid density profile is strongly influenced by the surface structure variation, as seen in Fig. 3.4. The sharp density peak adjacent to the surface in the planar case is present in the smoother type II cylinder, but the surface interstices in type
I trap some fluid atoms and broaden the interfacial region, and make it difficult to assign a single radius to the cylinder. Furthermore, the trapped atoms always have a strong attraction to the rest of the fluid, independent of $c_{fw}$, and tend to drag it along with the cylinder as it rotates. Thus, we expect less slip in the type I case. The general solution of the Navier-Stokes equation for this geometry, assuming cylindrical symmetry and a velocity which decays at large distances, is

$$\omega(r) = u_\phi(r)/r = k/r^2,$$  \hspace{1cm} (3.10)

where $k$ is a constant. As seen in Fig. 3.5, the measured angular velocity fits this function quite well, and the boundary condition Eq. 3.8 determines the slip length. The results are tabulated in Table 4 in the Appendix, and included in Fig. 3.1, along with the previous slip length as determined from the channel flows. The agreement is excellent for the (smoothed) type II cylinder, and as expected the slip lengths for the rougher type I cylinder are systematically lower. We have verified that the strain...
rates for these simulations are sufficiently low as to be in the Newtonian regime, but do not record the numbers here.

The finite size of the simulation is a possible source of concern, because periodic boundary conditions force the fluid velocity to vanish at the edges of the simulation box rather than decaying to zero as $1/r$. To test the sensitivity of the results to size we carried out two variant simulations involving either the same (type II) cylinder in a smaller box $(X,Y,Z) = (86, 86, 10.77)$ or a larger cylinder $(R = 4.5)$ in the original box. The results are presented in Table 4, and are in agreement with the previous values.

![Figure 3.5](image)

Figure 3.5: Left: Angular velocity profile for rotating cylinders, for different values of $c_{fw}$ at $\omega = 0.0571$. Right: Torque vs. $c_{fw}$ for a cylinder rotating with angular velocity $\omega = 0.0571$. Simulation results for both cylinder types compared to the Navier-Stokes prediction with the slip length determined from Couette flow. The horizontal gold line is the ideal hydrodynamic (no-slip) result.

We can confirm these results via an independent measurement by determining the torque on the rotating cylinder in two ways: first summing the individual torques exerted on the cylinder atoms, and second by evaluating it from the solution of
the Navier-Stokes equation for a rotating cylinder with a slip boundary condition. Equating the two results determines the slip length. The direct torque measurements are plotted in Fig. 3.5. Using the Navier-Stokes solution Eq. 3.10, and the boundary condition Eq. 3.8 gives \( k = u_0 R^2 / (R + 2\xi) \). The resulting torque is

\[
\mathcal{T} = \frac{4\pi \mu u_0 R^3 L}{R + 2\xi} \tag{3.11}
\]

This expression, using the previously determined values for \( \xi \) for each \( c_{fw} \), and \( \mu = 2.2 \) as determined from the channel flow simulations for this fluid, is also plotted in Fig. 3.5, and agrees well with the direct torque measurement for the smoothed type II sphere. The slip length values themselves are included in Fig. 3.1. The torque values measured directly for the rough cylinder give larger values (by about 30%) as one might expect.

**Cylindrical Poiseuille flow**

For a variant form of flow along a curved boundary, we consider fluid in the interior of a hollow cylinder driven along the axis by a pressure gradient, as depicted in the inset to Fig 3.4.2. The cylinder is again made of a section of a cubic lattice by selecting all atoms between an inner radius of 16.16 and an outer radius 17.14. In contrast to the previous case of a thin solid cylinder, here the inner radius is large enough that the roughness induced by curvature is insignificant. The cylinder has length 43.09 and contains 25600 fluid atoms at number density 0.8, and the flow is driven by a body force of magnitude \( g \) along the axis. In this situation the tensor boundary condition
Eq. 3.2 reduces to the simple form

$$\xi \left. \frac{\partial u_z}{\partial r} \right|_{r=R} = \Delta V_z$$

(3.12)

because there is no curvature in the flow direction. Although there is a superficial resemblance to flow along a flat boundary, the curvature of the wall can alter the structure of the nearby fluid layer and there is no guarantee that the slip is the same.

Figure 3.6: Left: Fluid density distribution for cylindrical Poiseuille flow for different fluid-solid interaction strengths $c_{fw}$; Inset: system as viewed along the flow direction. Right: Velocity profile for cylindrical Poiseuille flow for various $c_{fw}$ at $g = 0.01$

Simulations of this flow for a range of forcing values $g$: 0.002-0.02 in the low strain rate regime ($\dot{\gamma} < 0.03$) produce a parabolic velocity profile, with a typical case illustrated in Fig 3.4.2. The appropriate general solution of the Navier-Stokes equation (which is regular at $r = 0$) is $u_z = k_1 r^2 + k_2$, and by fitting the data to this function and applying the boundary condition Eq. 3.12 we obtain the data points for this case in Fig. 3.1 and Table 5 in the Appendix. The slip lengths are again the same, within statistical uncertainty.
3.4.3 Spheres

Lastly, we turn to the slip characteristics of flow around a spherical particle, a very common situation in numerous applications at all length scales. We consider the simplest configuration, a sphere with a fixed center rotating about a diameter. As in the cylinder case, the relevant boundary condition is Eq. 3.8 and the same issue of surface roughness arises. We focus on the type II smooth sphere case alone, where the atoms are first selected from a spherical region of a cubic lattice, and then those near the boundary are displaced outwards to form a smoothed shell at radius \( R = 3.52 \).

The fluid density profile around the sphere is shown in Fig.3.7, and the inset shows its atomic structure. When the sphere rotates at fixed angular velocity \( \omega_0 \), the velocity at the surface varies with polar angle as \( \omega_0 \sin \theta \), so each angle requires a separate analysis. A typical example of the angular velocity variation with \( r \) is shown in Fig.3.7 for one angle, where the curves for different values of \( c_{fw} \) are fit to the Navier-Stokes solution \( \omega(r) = c_2/r^3 \).

The resulting slip lengths are plotted in Fig. 3.1 and tabulated in Table 6, and once more the results are consistent with the earlier determinations. The statistical errors are larger in this case, up to 8%, because only a disk-shaped region of the sphere surface is available at a given angle and the sample is smaller.
Figure 3.7: Left: fluid density around a type II sphere for various $c_{fw}$; the inset shows the atomic structure of the sphere. Right: Angular velocity distribution about a sphere rotating at $\omega_0 = 0.1$, at polar angle $\theta = 90^\circ$.

3.5 Discussion

We have used molecular dynamics simulations of flow past stationary surfaces and around rotating solids to study the variation of slip length with surface curvature. Provided the slip length is defined in a consistent tensorial manner, the resulting numerical values depend only on the physical properties of the solid and fluid involved and do not vary with the flow configuration. These calculations support (but of course do not prove) the belief that the slip length $\xi$ is an intrinsic material property suitable for a fluid mechanical boundary condition. The present experimental situation is not completely clear, with widely disparate results cited in the literature [49], but at least one recent and precise experimental test [79] supports our conclusions.

The methods here can be applied directly to particles such as ellipsoids, whose shape is bounded by coordinate axes in some curvilinear system, rotating about a symmetry axis. For other rotation axes, or for particles of more complicated shape,
the general boundary condition Eq. 3.2 is relevant, but an MD analysis along the present lines would be difficult because of sampling issues – long runs would be needed to accumulate accurate data on a small surface region. Likewise, although our method is restricted to the low strain rate regime where the slip length is constant, the methods could easily be extended to that case, but there is no reason to expect the conclusions to change. Surface roughness on large length scales is not an issue here because the slip boundary condition is applied locally, but small-scale roughness is problematic. We have seen that atomic roughness of the type I cylinder changes the slip length significantly, for example. In this case approaches involving effective surfaces [78] may provide a useful way to characterize slip.
Chapter 4

Brownian Motion

In this chapter, we will discuss the Brownian motion of Janus particles, which is a key aspect of the behavior of these micro-particles when suspended in a fluid. We begin with a short review of the history of Brownian motion.

4.1 Background

After Einstein’s other famous paper published in 1905 [80] (the one better known to the public is special relativity), Brownian motion [81] became a focus of academic discussion. This atomistic view, which attributed the random motion of flower pollen to rapid collisions with the surrounding molecules of air rather than some mysterious organic origin, was a great success. Although Einstein’s heuristic theory of Brownian motion was approximate, the method he used is both general and enlightening. The innovative aspect of his work, a first systematic treatment of stochastic processes, was quickly accepted by his peers, while the deeper meaning was gradually realized later. Many concepts contained in this pioneering work have been developed into important theories in modern mathematics and physics during the next decades [? , 82–85].

We begin with a rapid summary of the main ideas, which we will elaborate upon subsequently. First is the underlying assumption that the probability distribution of
future states is independent of all of the system’s history except the current state, the *Markov Postulate*, which leads to the *Chapman-Kolgomorov Equation* [82–85].

Secondly, one key step in the derivation, which leads to a simple differential equation for the spatial probability distribution, is now called the *Kramers-Moyal expansion*. The resulting “diffusion” equation, in its simplest form for a one dimensional case, reads:

\[
\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} \implies P(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \tag{4.1}
\]

was later identified as a special case of the *Fokker-Planck equation* which governs the distribution function of *Markov Processes*. As in Eq. (4.1), the solution is a standard normal distribution whose the key variable \(D\), called the diffusion coefficient or briefly as *diffusivity*, measures the position variance. It can be easily shown from the above probability distribution that the diffusivity has the following property which is often taken as its definition:

\[
\langle x^2 - \langle x \rangle^2 \rangle = 2Dt \tag{4.2}
\]

In 1908, Langevin [88] proposed a dynamical equation for the motion of micro-particles in a fluid, afterwards named after him, and showed that its solution gave the same diffusive properties as Einstein’s model:

\[
m \ddot{x}(t) = -m\gamma \dot{x} + \xi(t) \implies \langle x^2 - \langle x \rangle^2 \rangle = 2(k_B T/m\gamma) t \tag{4.3}
\]

Here, \(m\gamma = 6\pi\eta R\), where \(\eta\) is the liquid’s shear viscosity and \(R\) is the radius of the spherical particle, and \(-6\pi\eta R\dot{x}\) is the *Stokes’ drag*, derived from the Navier-Stokes
equation for a viscous fluid in the limit of small Reynolds number [91–93]. From Eq. (4.2) and Eq. (4.3), we identify the diffusion coefficient as

\[ D = \frac{k_b T}{m \gamma} \]  

(4.4)

which is called the Stokes-Einstein relation. This relation between the thermal fluctuations and the Stokes’ force was later understood to be an example of the general fluctuation-dissipation theorem of Callen, Green, Kubo and others [5–7]. We will use the theorem later in this chapter.

From the Langevin equation, a single trajectory of Brownian motion can be calculated, provided the random force is known at all times. The resulting time evolution of the position of a Brownian particle, \( X(t) \), satisfies several common properties of Brownian motions

1. \( X(0) = 0 \)
2. \( X(t) \) is almost surely continuous
3. For any \( 0 < s < t \), \( X(t) - X(s) \) is independent of each other
4. For all \( 0 < s < t \), \( X(t) - X(s) \) are normally distributed as \( \mathcal{N}(0, t - s) \)

The last entry connects the probability Eq. (4.1) with the trajectory. These four requirements in fact comprise a mathematical definition of Brownian motion. Outside of the problem in which it originated, Brownian motion is a general phenomenon with numerous applications in other fields, such as the stock market [90].
4.2 The Fokker-Planck equation

In this section we sketch the derivation of the Fokker-Planck (FP) equation, which is essential for a better understanding of Brownian motion. Further details may be found in numerous textbooks on stochastic processes such as [82–86].

Our first aim is to derive the connection between the Langevin equation Eq. (4.3) and Einstein’s diffusion equation Eq. (4.1). The basic quantity of interest is the probability distribution $P(x,t)$ for the particle to be at phase space point $x$ at time $t$. Its time evolution is controlled by the transition probability $P(x_2,t_2|x_1,t_1)$ from point $x_1$ at time $t_1$ to point $x_2$ at the later time $t_2$. For a Markov process we can write [85,86]

$$P(x_2,t_2) = \int \, dx_1 P(x_2,t_2|x_1,t_1) P(x_1,t_1), \quad (4.5)$$

and using the above relation twice over three sequential time points ($t_3 > t_2 > t_1$) we have

$$P(x_3,t_3) = \int \, dx_2 dx_1 P(x_3,t_3|x_2,t_2) P(x_2,t_2|x_1,t_1) P(x_1,t_1) \quad (4.6)$$

An alternate form of Eq. (4.6) is called the Chapman-Kolmogorov equation:

$$P(x_3,t_3|x_1,t_1) = \int \, dx_2 P(x_3,t_3|x_2,t_2) P(x_2,t_2|x_1,t_1) \quad (4.7)$$

The time evolution of $P(x,v)$ is given by the master equation,

$$\frac{\partial}{\partial t} P(x,t) = \int \, dx' [W(x|x') P(x',t) - W(x'|x) P(x,t)] \quad (4.8)$$

in which $W(x|x')$ is the transition rate from $x'$ to $x$, which simply expresses the fact that the the probability of being at $x$ changes due to transitions from or to
other points. (See [82–85] for details.) The Kramers-Moyal expansion of the master equation is given by

\[
\frac{\partial P(x, t)}{\partial t} = \sum_{m=1}^{\infty} \frac{(-1)^m}{m!} \frac{\partial^m}{\partial x^m} \left[ a^{(m)}(x, t) P(x, t) \right]
\]  

where the coefficients \(a^{(m)}\) at each order are given by

\[
a^{(m)}(x, t) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \langle [x(t + \Delta t) - x(t)]^m \rangle \big|_{x(t) = x}
\]  

If for \(m > 2\), \(a^{(m)}\) is zero or negligible, which can be shown to occur in a Markov Process, we have the so-called Fokker-Planck equation

\[
\frac{\partial P(x, t)}{\partial t} = -\frac{\partial}{\partial x} \left[ a^{(1)}(x, t) P(x, t) \right] + \frac{1}{2} \frac{\partial^2}{\partial x^2} \left[ a^{(2)}(x, t) P(x, t) \right]
\]  

where \(a^{(1)}\) and \(a^{(2)}\) are the drift and diffusion coefficients, respectively. While this argument applies to a one-dimensional system, higher dimensional cases involve no additional concepts and generalizes as follows.

Consider now a general Langevin equation for a multi-component stochastic process \(Y_x(t)\), with phase space \(x = (x_1, x_2, \ldots, x_n)\), of the form:

\[
\frac{dx_i}{dt} = A_i(x, t) + \sum_j B_{ij}(x, t) \xi_j(t)
\]  

where the ensemble average of these random variables \(\xi_j(t)\) given by:

\[
\langle \xi_i(t) \rangle = 0 \quad \text{and} \quad \langle \xi_i(t)\xi_j(t') \rangle = 2\Delta \delta_{ij} \delta(t - t')
\]  

We should calculated each \(a^m\) by the above definition Eq. (4.10), which will keep using the ensemble averaged behavior of above random force. Consequently, due to
the second Dirac delta function, all $a^{(m)}$, $m > 2$ will vanish (see Risken’s book [85] for details), which renders the stochastic process $Y_x(t)$ a Markov process. We call this $\delta(t - t')$ correlation (actually uncorrelated) behavior white noise since the spectral density (Fourier transform into frequency domain) is constant in frequency. Thus, we could apply the Kramers-Moyal expansion as in Eq. (4.9), the coefficients for each order are:

$$a_i^{(1)} = A_i(x, t) + \Delta \sum_{j,k} B_{jk}(x, t) \frac{\partial B_{ik}(x, t)}{\partial x_j}$$

$$a_{ij}^{(2)} = 2\Delta \sum_k B_{ik}(x, t) B_{jk}(x, t)$$

$$a_{(m)} = 0 \quad \text{(for } m > 2)$$

It end up with the desired Fokker-Planck equation differential equation for a general Langevin equation:

$$\frac{\partial P(x, t)}{\partial t} = -\sum_i \frac{\partial}{\partial x_i} \left\{ A_i(x, t) + \Delta \sum_{j,k} B_{jk}(x, t) \frac{\partial B_{ik}(x, t)}{\partial x_j} \right\} P(x, t) + \Delta \sum_{i,j} \frac{\partial^2}{\partial x_i \partial x_j} \left\{ \sum_k B_{ik}(x, t) B_{jk}(x, t) \right\} P(x, t)$$

or more briefly

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x_i} (A_i P) + \Delta \frac{\partial}{\partial x_i} \left[ B_{ik} \frac{\partial}{\partial x_j} (B_{jk} P) \right]$$

Where we have simplified the equation by adopting the Einstein summation convention and combining the last two terms. The above equation ends the general derivation from Langevin equation to Fokker-Planck equation.
4.2.1 Translation and Rotation

First simple generalization of above basic derivation is the most common three dimensional Brownian motion with an external field $U(r)$:

$$m \frac{d^2 r}{dt^2} = F_{fr} + F_{ext} + F_{th} \quad (4.17)$$

Where $F_{fr} = -m \gamma \dot{r}(t)$ is the Stokes' drag force, $F_{ext} = -\nabla U$ is the force due to the external fields and the white noise thermal fluctuation $F_{th} = \xi(t)$, chosen to be

$$\langle \xi_i(t) \rangle = 0 \quad \text{and} \quad \langle \xi_i(t) \xi_j(t') \rangle = 2 k_B T m \gamma \delta_{ij} \delta(t - t') \quad (4.18)$$

Rewriting the above equation in Langevin equation form as in Eq. (4.12) and choosing the phase space $(x_i, v_i)$, $i = 1, 2, 3$, leads to

$$\frac{dx_i}{dt} = v_i \quad (4.19a)$$
$$\frac{dv_i}{dt} = -\gamma v_i - \partial_i U/m + \xi_i(t)/m \quad (4.19b)$$

Applying Eq. (4.16), we arrive at the Fokker-Planck equation

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x_i} (v_i P) + \frac{\partial}{\partial v_i} (\gamma v_i + \partial_i U/m) P + \frac{k_B T \gamma}{m} \frac{\partial^2}{\partial v_i^2} P \quad (4.20)$$

For the over-damped limit of Langevin equation, the phase space $(x_i)$, $i = x, y, z$

$$\frac{d\mathbf{r}}{dt} = -\frac{\nabla U}{m \gamma} + \frac{\mathbf{\xi}(t)}{m \gamma}$$

with the same thermal fluctuation condition, we have

$$\frac{\partial P}{\partial t} = \frac{1}{m \gamma} \frac{\partial}{\partial x_i} (\partial_i U P) + \frac{k_B T \gamma}{m \gamma} \frac{\partial^2}{\partial x_i^2} P$$
This is also called Smoluchowski equation. By the way, if there is no external field (i.e.: $U = 0$), we will recover the diffusion equation, i.e.: Eq. (4.1).

The second generalization, which interests us more, is the three dimension rotational dynamics of a rigid body. The rotation of a rigid body should obey the Newtonian dynamics in classical mechanics, more specifically the Euler equation, as shown in reference [4]. The dynamic variable is $\hat{n}$, which specifies the orientation of the rigid body and defined to be a unit vector. Thus, the Euler equation of rotation is

$$\frac{d\hat{n}}{dt} = \omega \times \hat{n}$$  \hspace{1cm} (4.21)

$$I \cdot \frac{d\omega}{dt} = -\zeta_r \omega + N_{\text{ext}} + \eta(t)$$  \hspace{1cm} (4.22)

in which $\zeta_r$ is rotational drag coefficient, $N_{\text{ext}} = -\hat{n} \times \nabla \hat{n} U$ is the net torque due to the external potential field, $\eta(t)$ is the stochastic torque due to the surrounding solution, and $I$ is the inertial tensor.

For the over-damped limit, or the drag force dominate, the second equation right above gives

$$\omega_i = \frac{1}{\zeta_r} (N_i + \eta_i)$$  \hspace{1cm} (4.23)

Inserting Eq. (4.23) into Eq. (4.21) above, we have

$$\frac{d\hat{n}}{dt} = \frac{1}{\zeta_r} \left[ -\left( \hat{n} \times \frac{\partial U}{\partial \hat{n}} \right) \times \hat{n} + \eta \times \hat{n} \right]$$  \hspace{1cm} (4.24)

Eq. (4.24) is one type of Langevin equation. Using Eq. (4.16) again, the corresponding
Fokker-Planck equation will be (see Appendix A for more details):

$$\frac{\partial P}{\partial t} = \frac{D_r}{k_BT} \frac{\partial}{\partial \hat{n}} \cdot \left( \Pi \cdot \frac{\partial U}{\partial \hat{n}} P \right) + D_r \left[ \Pi : \frac{\partial}{\partial \hat{n}} \frac{\partial}{\partial \hat{n}} - 2\hat{n} \cdot \frac{\partial}{\partial \hat{n}} \right] P \quad (4.25)$$

in which $D_r = k_BT/\zeta_r$, and operator $\Pi = I - \hat{n} \hat{n}$. This is the same Fokker-Planck equation derived by Doi and Edwards [87] using intuitive reasoning. (also see Appendix A for a proof),

$$\frac{\partial P}{\partial t} = D_r \Re \cdot \left[ \frac{P}{k_BT} \Re U + \Re P \right] \quad (4.26)$$

where the rotation operator is $\Re = \hat{n} \times \nabla \hat{n}$. The above question is often referred as the Smoluchowski equation for rotational diffusion.

### 4.2.2 Colored noise in Brownian motions

In the standard Langevin equation Eq. (4.17), the friction force is assumed to be proportional to the instantaneous velocity. Generally, the friction force could depend on history, and should be written as:

$$F_{fr}(t) = - \int_{-\infty}^{t} \gamma(t-t') \dot{x}(t')dt' \quad (4.27)$$

where $\gamma(t-t')$ is called the kernel. The fluctuation–dissipation (FD) theorem [5–7] tells that the kernel of dissipation force is related to the auto-correlation function of the thermal force by:

$$k_BT \gamma(t-t') = \langle F_{th}(t)F_{th}(t') \rangle \quad (4.28)$$

In the extreme uncorrelated situation or say that the correlation function go limits to Dirac-Delta function, i.e.: $\langle F_{th}(t)F_{th}(t') \rangle = 2k_BTm\delta(t-t')$, the FD theory gives
\[ \gamma(t - t') = 2m\gamma \delta(t - t'). \] Then, we recover the constant coefficients in the Stokes’ drag force.

\[ F_{fr}(t) = -\int_{-\infty}^{t} \gamma(t - t') \dot{x}(t') dt' = -m\gamma \dot{x}(t) \quad (4.29) \]

The above simple Langevin equation with constant drag and uncorrelated thermal force predicts that the particles’ velocity auto-correlation function will decay exponentially in time

\[ \langle \dot{r}(t) \dot{r}'(t') \rangle \sim e^{-\gamma(t-t')} \quad (t > t') \quad (4.30) \]

However, early famous MD simulations by Alder and Wainwright [94], found that it is instead a \((t - t')^{-3/2}\) decay in velocity auto-correlation function. This, analyzed by the early theories [95], is due to the fact that the motion of the particle alters the local fluid environment by producing a dipole flow field, characterized by temporal delay in boundary layer development. Most recently, experimental observation [100, 101] confirmed that the correlation behavior is long time correlated or white noise as

\[ \langle F_{th}(t) F_{th}(t') \rangle = -k_B T m\gamma \sqrt{\frac{\tau_f}{4\pi}} (t - t')^{-3/2} \quad (4.31) \]

where, \( \tau_f = R^2 \rho_f / \eta \), \( \rho_f \) is the density of solution. \( \tau_f \) describes the time scale for flow diffusing over the distance in magnitude of object’s radius. This result is consistent with the Basset force [96, 97], meaning the two terms in the fluctuation-dissipation theorem, the left kernel term from Basset force, and the right auto-correlation term measured from the experiments above, are identical.

To sum up, the auto-correlation function of the thermal fluctuation force is colored
rather than white. Put in another way, friction force is history dependent and the Stokes’ drag is not complete due to the hydrodynamic memory in the solvent. While for rotation dynamics, we believe it will be the same case since the auto-correlation function of torque from thermal fluctuation is also colored and the friction torque is history dependent as well.

We are interested in using molecular dynamics simulation to investigate these problems, especially with Janus particles near an interface. We will model the above problem using the same standard MD method as used in previous droplet evaporation problem. And we want to find the colored noise in the auto-correlation function of thermal fluctuation torque.

4.3 Coupling two Brownian motions

In the last sections, we assumed the independence of translation and rotation, which is a valid assumption for inert particles in bulk fluids. However for self-propelling Janus particles, this will not be the case since the direction of propulsion depends on the particle’s instantaneous orientation, as observed in experiments [102, 103]. In this section we introduce a simple model in order to explain address two questions in intuitive terms: (1) What causes the increase of diffusivity of self-propelling Janus particles? (2) Why is the time scale of velocity correlations increased in some cases but not others?
4.3.1 Toy model

We start from the standard Langevin equation as in Eq. (4.12), describing independent motion in two spatial directions, and add a new coupling term $\alpha v_y$ to the $x$-equation, giving

$$
\begin{align*}
\frac{dv_x}{dt} &= -\gamma v_x + \alpha v_y + \xi(t) \\
\langle \xi(t)\xi(t') \rangle &= q \delta(t - t') \\
\frac{dv_y}{dt} &= -\gamma y + \eta(t) \\
\langle \eta(t)\eta(t') \rangle &= q_y \delta(t - t') 
\end{align*}
$$

(4.32)

In the absence of the new drift term $\alpha v_y$, the motion in the $xy$-plane would be two independent Brownian motions, each with correlation function $\langle v(t)v(0) \rangle = \frac{q}{\gamma} e^{-\gamma t}$, and the diffusivity would be isotropic with value $D = \frac{q}{2\gamma}$ [85].

Numerical solutions of the coupled Langevin equations are shown in Fig. (4.3.1), where the data points are obtained through a long-time average of one particle over $10^6$ time steps (corresponding to maximum $x$-displacement of $10^3$). The solid curves are obtained theoretically, as discussed in the following section. Two conclusions can be drawn from the figure: firstly, the diffusivity is enlarged, which the effect seen in references [102, 103] that we wish to understand. Secondly, the amount of velocity correlation is enlarged.

4.3.2 Analytic solution of the toy model

The governing equation in $y$ is standard Brownian motion, so the diffusion coefficient in $y$ is just $D_0 = \frac{q_y}{2\gamma_y} = \frac{k_BT}{m^y}$. The increased diffusion in $x$ must then arise from the additional term $\alpha v_y$. The fact that $v_y$ and $y$ are random variables suggests treating
the additional term in $x$ as a random force:

$$\tilde{\xi}(t) = \xi(t) + \alpha v_y(t)$$

Reformatting the governing equation Eq. (4.32) accordingly, we have:

$$\begin{align*}
\frac{dv_x}{dt} &= -\gamma v_x + \tilde{\xi}(t) \\
\langle \tilde{\xi}(t)\tilde{\xi}(t') \rangle &= q \delta(t - t') + \alpha^2 \langle v_y(t)v_y(t') \rangle \\
\frac{dv_y}{dt} &= -\gamma_y v_y + \eta(t) \\
\langle \eta(t)\eta(t') \rangle &= q_y \delta(t - t')
\end{align*}$$

The velocity in $y$-axis is formally given by:

$$v_y(t) = v_y(0)e^{-\gamma_y t} + \int_0^t e^{-\gamma_y (t-t')}\eta(t')dt'$$  \hspace{1cm} (4.33)$$

and its autocorrelation function (ACF) is

$$\begin{align*}
\langle v_y(t_1)v_y(t_2) \rangle &= v_y^2(0)e^{-\gamma_y(t_1+t_2)} + \int_0^{t_1} \int_0^{t_2} e^{-\gamma_y(t_1+t_2-t_1'-t_2')} \langle \eta(t_1')\eta(t_2') \rangle dt_1'dt_2' \\
&= v_y^2(0)e^{-\gamma_y(t_1+t_2)} + \frac{q_y}{2\gamma_y} \left( e^{-\gamma_y(t_1-t_2)} - e^{-\gamma_y(t_1+t_2)} \right)
\end{align*}$$
where we have calculated the double integral by inserting the \( \eta \) correlation function.

At large times \( \gamma_y(t_1 + t_2) \gg 1 \), the first and last terms vanish, giving a function of the time difference \( (t_2 - t_1) \) alone:

\[
\langle v_y(t_1)v_y(t_2) \rangle = \frac{q_y}{2\gamma_y} e^{-\gamma_y|t_1-t_2|} \quad \text{when} \quad \gamma_y(t_1 + t_2) \gg 1 \quad (4.34)
\]

The value \( q_y = 2\gamma_y \langle v_y^2 \rangle = \frac{2\gamma_y k_B T}{m} \) is known from the equipartition theorem, \( \frac{1}{2} m \langle v_y^2 \rangle = \frac{1}{2} k_B T \). Furthermore, we can approximate \( \frac{1}{2} e^{-\gamma|t_1-t_2|} \sim \delta(t_1-t_2) \) for large time intervals \( \gamma_y(t_1 - t_2) \gg 1 \), giving

\[
\langle v_y(t_1)v_y(t_2) \rangle = \frac{q_y}{\gamma_y^2} \delta(t_1 - t_2) \quad \text{when} \quad \gamma_y(t_1 - t_2) \gg 1 \quad (4.35)
\]

This limit is satisfied in practice here, since the observation time scale is always much larger than the diffusion time scale. It is convenient to define \( \frac{q_y}{\gamma_y} = \Delta_{vy} \) for later use.

Next, we calculate the mean squared displacement (MSD) \( \langle y^2(t) \rangle \). Assuming \( y(0) = 0 \), we have:

\[
\langle y^2(t) \rangle = \left\langle \int_0^t v_y(t_1)dt_1 \int_0^t v_y(t_2)dt_2 \right\rangle = \int_0^t \int_0^t dt_1 dt_2 \langle v_y(t_1)v_y(t_2) \rangle \quad (4.36)
\]

Inserting Eq. (4.34) gives

\[
\langle y^2(t) \rangle = \frac{q_y}{\gamma_y^3} \left( e^{-\gamma_y t} - 1 + \gamma_y t \right) \quad (4.37)
\]

The behavior of MSD\((t)\) at short and long times is then:

\[
\langle y^2(t) \rangle = \begin{cases} 
\frac{q_y}{2\gamma_y} t^2 & \text{when} \quad \gamma t \ll 1 \\
\frac{q_y}{\gamma_y^2} t & \text{when} \quad \gamma t \gg 1 
\end{cases} \quad (4.38)
\]
We refer to the early time behavior as ballistic motion, $\text{MSD} \sim t^2$, and the late-time behavior as diffusive motion, $\text{MSD} \sim t$. Defining the diffusivity via

$$\langle y^2(t) \rangle = 2D_y t,$$

we have

$$D_y = \frac{q_y}{2\gamma_y^2}.$$

The motion in $x$ can also be solved formally as:

$$v_x(t) = v_x(0)e^{-\gamma t} + \int_0^t e^{-\gamma(t-t')}\tilde{\xi}(t')dt' \quad \text{where} \quad \tilde{\xi}(t) = \alpha v_y(t) + \xi(t)$$

As stated earlier, we assume $\gamma(t_1 + t_2) \gg 1$ and also set $\gamma_y = \gamma$ and $q_y = q$ for convenience. The ACF of $v_x(t)$ differs from that of $v_y$ due to the additional term

$$\langle v_x(t_1)v_x(t_2) \rangle = \frac{q}{2\gamma}e^{-\gamma|t_1-t_2|} + \alpha^2\int_0^{t_1}\int_0^{t_2}e^{-\gamma(t_1+t_2-t_1'-t_2')}\langle v_y(t_1')v_y(t_2') \rangle dt_1'dt_2'$$(4.39)

Using Eq. (4.34) for the ACF of $v_y(t)$, the ACF(t) of $v_x(t)$ is:

$$\langle v_x(t_1)v_x(t_2) \rangle = \frac{q}{2\gamma}e^{-\gamma|t_1-t_2|}\left[1 + \frac{\alpha^2}{2\gamma^2}(1 + \gamma|t_1 - t_2|)\right]$$ (4.40)

Proceeding in the same way, the MSD(t) of $x(t)$ can be found:

$$\langle x^2(t) \rangle = \frac{q}{\gamma^3}\left[\left(1 + \frac{\alpha^2}{2\gamma^2}\right)e^{-\gamma t} - 1 + \gamma t + \frac{\alpha^2}{2\gamma^2}\left(e^{-\gamma(2 + \gamma t)} - 2 + \gamma t\right)\right]$$ (4.41)

At large times $\gamma t \gg 1$, this result simplifies to

$$\langle x^2(t) \rangle = \frac{q}{\gamma^3}\left[\left(1 + \frac{\alpha^2}{\gamma^2}\right)\gamma t - \frac{3\alpha^2}{2\gamma^2} - 1\right]$$ (4.42)
and we can identify the diffusivity in $x$:

$$D_{\text{eff}} = \frac{q}{2\gamma^2} \left(1 + \frac{\alpha^2}{\gamma^2}\right) = D_0 \left(1 + \frac{\alpha^2}{\gamma^2}\right) \quad (4.43)$$

where $D_0 = \frac{q}{2\gamma^2}$ is the standard diffusivity.

These analytic results are compared to the simulations in Fig. (4.3.1), where they are seen to agree quite well except for the fluctuating region in the ACF.

While the increase in diffusion is quantitatively explained by the above argument, we can understand the effect by the following heuristic reasoning. It could be interpreted this way: the randomness of $v_y(t)$ adds additional white noise to the original stochastic variable $\xi(t)$:

$$\langle \tilde{\xi}(t_1)\tilde{\xi}(t_2) \rangle = \langle \xi(t_1)\xi(t_2) \rangle + \alpha^2 \langle v_y(t_1)v_y(t_2) \rangle = q \delta(t_1 - t_2) + \alpha^2 \Delta_{v_y} \delta(t_1 - t_2)$$

where we have assumed the statistical independence of $v_y(t)$ and $\xi(t)$. Using $\Delta_{v_y} = \frac{q}{\gamma^2}$, we have

$$\langle \tilde{\xi}(t_1)\tilde{\xi}(t_2) \rangle = \tilde{q} \delta(t_1 - t_2) = q \left(1 + \frac{\alpha^2}{\gamma^2}\right) \delta(t_1 - t_2)$$

which means that the effective diffusivity in the $x$-direction increases to

$$D_{\text{eff}} = \frac{\tilde{q}}{2\gamma^2} = D_0 \left(1 + \frac{\alpha^2}{\gamma^2}\right)$$

which is the previous result Eq. (4.44).
4.3.3 Application to self-propelling rotating particles

A standard model of the self-propelling problem, as in [102, 103], is based on the Langevin equation

$$m \frac{dv}{dt} = -m\gamma v + m\gamma v_0 \hat{n} + m\xi(t)$$

where the second term represents the propulsion force. The unit vector $\hat{n}$ specifies the particle’s orientation, and satisfies the equation of rotation Eq. (4.21)

$$\frac{d\hat{n}}{dt} = \omega \times \hat{n}$$

$$\mathbf{I} \cdot \frac{d\omega}{dt} = -\zeta_r \omega + \eta(t)$$

To simplify the analysis, we consider a one-dimensional version:

$$\frac{dx}{dt} = -\gamma v + \gamma v_0 \hat{n}_x + \xi(t)$$

This problem now has the same form as the toy model equation in $x$, so the previous argument indicates that the effective diffusion coefficient will increase to

$$D_{\text{eff}} = D_0 + \frac{v_0^2}{2} \Delta_{u_x}$$

The autocorrelation correlation function for one component of $\langle \hat{n}(t_1) \hat{n}(t_2) \rangle$ is calculated in (the supplementary material for the paper) [104] as

$$\langle \hat{n}_x(t_1) \hat{n}_x(t_2) \rangle = \frac{1}{3} e^{-2D_r |t_1 - t_2|} \sim \frac{1}{3D_r} \delta(t_1 - t_2)$$

where $D_r$ is the rotational diffusivity $D_r = \tau_r^{-1}$. Thus we find the same result as in [102, 103].

$$D_{\text{eff}} = D_0 + \frac{v_0^2 \tau_r}{6} \tag{4.44}$$
We will use MD and Brownian simulation to verify the above relation in a later section.

4.3.4 Relation to the autocorrelation function

As we see in Fig. (4.3.1), in the short time regime the slope of the log-log plot of mean-squared distance $\text{MSD}(t) = \langle y^2(t) \rangle$ is 2, which means a standard ballistic regime of independent particle motion at constant velocity. At longer times, the slope becomes 1 and simultaneously the velocity autocorrelation function $\text{ACF}(t) = \langle v_y(t)v_y(0) \rangle$ becomes small and randomly fluctuating. This is the very point at which we might use the Dirac delta function as an approximation to Eq.(4.35).

One factor impacting the correlation time of the ACF is the magnitude of $\alpha$. When we enlarge the coupling constant $\alpha$, the transition point will be delayed further. This observation is confirmed by numerical simulation, as seen in Fig. (4.3.4).

Figure 4.2: Log-Log plots for the velocity autocorrelation function (ACF) and the mean squared displacement (MSD), with except $\alpha = 0.5$ rather than 0.15 as in Fig. (4.3.4).
The derivation of the Fokker-Planck equation from the Langevin equation as in [82–85] makes use of the Kramers-Moyal expansion. In particular, we assumed that for a Markov process, where the correlation function of the Langevin force is a delta function, which has the property that all the higher order coefficients $n \geq 3$ vanish. The preceding discussion implies that the transition point $\tau_c$ on the time axis where we could regard $\langle x(t)x(0) \rangle$ as a Markov process is enlarged by the coupling term $v_y$.

### 4.4 Self-propelling Janus particles at interfaces

This section is motivated by the experimental finding that self-propelling Janus particles tend to keep their orientation parallel to the solid wall [106]. We wish to understand the dynamics of Janus particles in the vicinity of a liquid-solid interface. The fascinating conclusion from the experiments is that the translational and rotational dynamics are correlated, which means that the off-diagonal terms of the resistance matrix are non-zero. An important consideration is the fact that the boundary imposes a no-slip velocity condition which must be maintained continuously, since the velocity field reacts instantaneously to particle motion in the quasi-static, Stokes flow limit. In practice, the effect of the wall is included by use of image terms.

We first present some basic derivations and then carry out some Brownian dynamics simulations to check our understanding of the problem.
4.4.1 Greens functions and multipole expansion

For incompressible flow at small values of the Reynolds number and Stokes number we have creeping or Stokes flow, described by the following equations:

\[-\nabla p + \mu \nabla^2 v = -f(r) \quad \nabla \cdot v = 0\] (4.45)

where \(p\) is the pressure, \(\mu\) is the viscosity, \(v\) is the flow velocity, \(f\) is the body force as a distribution function of position.

The first (Navier-Stokes) equation comes from momentum conservation while the second (Continuity) equation arises from mass conservation. Since the Stokes equation is linear, we can attack this general problem of flow subject to an arbitrary body force through the fundamental solution (Greens Function) for a point force:

\[-\nabla p + \mu \nabla^2 v = -F\delta(r) \quad \nabla \cdot v = 0\] (4.46)

which incorporates the boundary condition that the flow field should vanish at infinity.

As shown in textbooks [96,97], the solution is

\[v(r) = \frac{F}{8\pi\mu} \cdot \left( \frac{I}{r} + \frac{rr}{r^3} \right) = F \cdot \frac{G(r)}{8\pi\mu}\]

\[p(r) = \frac{F \cdot r}{4\pi r^3} = F \cdot \frac{P(r)}{8\pi\mu}\]

The Greens function \(G(r) = \frac{I}{r} + \frac{rr}{r^3}\) here is actually a second order tensor, which is often called the Oseen tensor

\[T(r) = \frac{G(r)}{8\pi\mu} = \frac{1}{8\pi\mu} \left( \frac{I}{r} + \frac{rr}{r^3} \right)\]
After obtaining the fundamental solution for Eq.(4.46), the general integral representation of flow field for Eq.(4.45) is written as

\[ \mathbf{v}(\mathbf{r}) = \int \mathbf{f}(\mathbf{r}') \cdot \mathbf{T}(\mathbf{r} - \mathbf{r}') \, d\mathbf{r}' \]  

(4.47)

As a side remark, if we relax the restriction of mass conservation and add an outflow source term \( M \) (volume per unit time) such as:

\[ \nabla \cdot \mathbf{v} = M \delta(\mathbf{r}), \]

We have a corresponding velocity source field:

\[ \mathbf{v}(\mathbf{r}) = \frac{M}{4\pi} \frac{\mathbf{r}}{r^3} \]

If we perform a multipole expansion on a system with more than one point force source, the velocity field would be \([96–99]\)

\[ \mathbf{v}(\mathbf{r}) = \sum_{\alpha} \mathbf{F}(\mathbf{r}_\alpha) \cdot \mathbf{T}(\mathbf{r} - \mathbf{r}_\alpha) = \sum_{n} \sum_{\alpha} \mathbf{F}(\mathbf{r}_\alpha) \left( -\frac{r_\alpha}{n!} \right)^n \cdot \nabla^n \mathbf{T}(\mathbf{r}) \]

\[ = \left( \sum_{\alpha} \mathbf{F}(\mathbf{r}_\alpha) \right) \cdot \mathbf{T}(\mathbf{r}) - \left( \sum_{\alpha} \mathbf{F}(\mathbf{r}_\alpha) r_\alpha \right) \cdot \nabla \mathbf{T}(\mathbf{r}) + \cdots \]

Written in component form, using the Einstein summation convention, the velocity is:

\[ v_i(\mathbf{r}) = F_j \mathbf{T}_{ij}(\mathbf{r}) - D_{jk} \mathbf{T}_{ij,k}(\mathbf{r}) + \cdots \]  

(4.48)

The first “stokeslet” term is physically the flow resulting from the total force. The second term involves a second order tensor, called the Stokes doublet.

\[ \mathbf{D} = \sum_{\alpha} \mathbf{F}(\mathbf{r}_\alpha) r_\alpha \]
To see the physics more clearly, we split it into a symmetric part and an antisymmetric part.

\[ S_{jk} = \frac{1}{2} (D_{jk} + D_{kj}) \]

\[ A_{jk} = \frac{1}{2} (D_{jk} - D_{kj}) = -\frac{1}{2} \epsilon_{jkl} A_l \]

Then the second term in Eq.(4.48) is be

\[ -D_{jk} G_{ij,k}(r) = -\frac{1}{2} (D_{jk} + D_{kj}) G_{ij,k}(r) + \frac{1}{2} \epsilon_{jkl} A_l G_{ij,k}(r) \]

We easily recognize that the vector \( A \) in the second antisymmetry part is the torque on the fluid field. Physically, the first term here is a symmetric force dipole related with straining motion, which is called the *stresslet*, the second term are related with torque, called the *rotlet*. See the book [96] for more details.

In the same way, we could carry out a multipole expansion on the source term to get a source doublet term:

\[ v_i(r) = -\frac{M}{4\pi} r_j \frac{\partial}{\partial x_j} \left( \frac{r_i}{r^3} \right) \]

### 4.4.2 Oseen tensor for no-slip plane wall

Blake [98,99] considered a stationary wall at \( z = 0 \), which is equivalent to a non-slip boundary wall condition: \( \mathbf{v} = 0 \) at \( z = 0 \). The new Greens function incorporating the effect of the wall is

\[ T_{ij} = \]

\[ \frac{1}{8\pi\mu} \left\{ \left( \frac{\delta_{ij}}{r} + \frac{r_i r_j}{r^3} \right) - \left( \frac{\delta_{ij}}{R} + \frac{R_i R_j}{R^3} \right) + 2h(\delta_{jk} - \delta_{j3}\delta_{3k}) \frac{\partial}{\partial R_k} \left[ \frac{h R_i}{R^3} - \left( \frac{\delta_{i3}}{R} + \frac{R_i R_3}{R^3} \right) \right] \right\} \]
In the above Blake tensor, the first term is a stokeslet due to the point force itself, the second term is a stokeslet due to the image in the wall and the third term is a combination of source doublet and Stokes doublet in the wall. An important feature of this expression is the combination \( \delta_{jk} - \delta_{j3} \delta_{3k} = 1 \), when \( j = k = 1, 2 \) or \( x, y \).

### 4.4.3 Force point and force dipole at interfaces

Let us consider one spherical particle moving slowly in the vicinity of a wall due to an imposed force and experiencing a drag force as well. A practical example could be a particle settling in a viscous liquid under gravity or being dragged in a fluid by an electrical field. Using the flow field due to Blake’s image solution, we calculate the local vorticity:

\[
\omega = \nabla \times v = \nabla \times \left( -\frac{F}{8\pi \mu} \cdot \left( \frac{I}{R} + \frac{RR}{R^3} \right) \right)
\]

or in component form

\[
\omega_i = \epsilon_{ijk} \partial_j v_k = \epsilon_{ijk} \partial_j F_i \mathbb{T}_{kl} = -F_i \epsilon_{ijk} \partial_j \left( \frac{\delta_{kl}}{R} + \frac{R_k R_l}{R^3} \right)
\]

For large separation, we ignore both doublet terms because they are higher order in \( 1/R \). Noting that \( F \cdot R = FR \cos(\theta - \phi) \), where \( \theta \) is the angle between the direction of \( R \) and \( \hat{x} \) and \( \phi \) is the angle between the direction of \( F \) and \( \hat{x} \),

\[
v = -\frac{F}{8\pi \mu} \cdot \left( \frac{I}{R} + \frac{RR}{R^3} \right) = -\frac{F}{8\pi \mu R} - \frac{R}{8\pi \mu R^2} F \cos(\theta - \phi)
\]

The radial velocity is

\[
v_r = v \cdot R/R = -\frac{F}{4\pi \mu R} \cos(\theta - \phi)
\]
The negative sign above tells us that the image attracts its partner. The local vorticity due to the image at \( R = 2z \) away is thus

\[
\omega_y = (\nabla \times \mathbf{v})_y = \frac{F}{4\pi\mu R} \left( -\frac{1}{R} \frac{\partial}{\partial \theta} \right) \cos(\theta - \phi) \big|_{\theta = \frac{\pi}{2}, R = 2z} = \frac{F}{16\pi\mu z^2} \sin\left( \frac{\pi}{2} - \phi \right) = \frac{F}{16\pi\mu z^2} \cos(\phi)
\]

Or

\[
\omega_y = \frac{F}{16\pi\mu h_z^2} \cos(\phi) > 0 \quad -\frac{\pi}{2} < \phi < \frac{\pi}{2} \tag{4.49}
\]

where \( h_z = z \) is the distance between particle and wall. If the particle is dragged in the \( x \)-direction, the local vorticity will always have a counter-clockwise swirl about the particle.

Next, we consider a dipole force exerted on the particle. Following reference [106], we write:

\[
\sum_i F(r_i) = 0, \quad \sum_i F(r_i)r_i = p e_F e_r
\]

The velocity due to an image force dipole will be (assuming \( e_F = e_r \))

\[
\mathbf{v} = -(p e_F e_F) : \frac{-1}{8\pi\mu} \nabla \left( \frac{\mathbf{I}}{R} + \frac{\mathbf{R R}}{R^3} \right) = \frac{p}{8\pi\mu R^3} \left[ 1 - 3 \left( \frac{\mathbf{R} \cdot \mathbf{e_F}}{R} \right)^2 \right] \mathbf{R}
\]

The radial velocity will be

\[
v_r = \frac{p}{8\pi\mu R^2} \left[ 1 - 3 \cos^2(\theta - \phi) \right]
\]

and the local vorticity will be:

\[
\omega_y = (\nabla \times \mathbf{v})_y = \frac{p}{8\pi\mu R^2} \left( -\frac{1}{R} \frac{\partial}{\partial \theta} \right) [3 \cos^2(\theta - \phi)] \big|_{\theta = \frac{\pi}{2}, R = 2z} = \frac{3p}{32\pi\mu h_z^3} \cos \phi \sin \phi
\]
or

$$\omega_y \sim \cos \phi \sin \phi \sim \begin{cases} > 0 & 0 < \phi < \frac{\pi}{2} \\ < 0 & -\frac{\pi}{2} < \phi < 0 \end{cases}$$

(4.50)

As discussed in reference [106], the above results indicate that the hydrodynamic force from the wall will always keep the dipole force carrier parallel to the wall surface. This explain the phenomena we discussed at the beginning of this chapter.

### 4.4.4 Brownian simulations

For a spherical particle with radius $a$ in a liquid of viscosity $\mu$, we have uncoupled translational and rotational dynamics:

$$\sum F = -6\pi \mu a \ U + \xi(t) = -\mathcal{R}^{FU} \ U + \xi(t)$$

$$\sum N = -8\pi \mu a^3 \ \Omega + \eta(t) = -\mathcal{R}^{MU} \ \Omega + \eta(t)$$

where $\xi(t)$ and $\eta(t)$ denote the stochastic force and stochastic torque, respectively.

To model self-propelling Janus particles, we add an additional force term $f\hat{n}$, where $\hat{n}$ denote the orientation of the propulsion drive, along with the coupling between translation and rotation:

$$\sum F = -\mathcal{R}^{FU} U - \mathcal{R}^{HO} \Omega + f\hat{n} + \xi(t)$$

$$\sum N = -\mathcal{R}^{MU} U - \mathcal{R}^{MO} \Omega + \eta(t)$$

The damping terms collectively form a big matrix with some off-diagonal terms, often called the resistance matrix. The above equations may be combined in a grand matrix form, but often many terms are zero due to symmetries; see [97] for a nice discussion.

Here, specifically,

\[
\begin{pmatrix}
F_x \\
F_y \\
F_z \\
N_x \\
N_y \\
N_z
\end{pmatrix}
= -
\begin{pmatrix}
\mathcal{R}^{FU}_{xx} & 0 & 0 & 0 & \mathcal{R}^{\Omega}_{xy} & 0 \\
0 & \mathcal{R}^{FU}_{yy} & 0 & -\mathcal{R}^{\Omega}_{yx} & 0 & 0 \\
0 & 0 & \mathcal{R}^{FU}_{zz} & 0 & 0 & 0 \\
0 & -\mathcal{R}^{NU}_{xy} & 0 & \mathcal{R}^{\Omega}_{xx} & 0 & 0 \\
\mathcal{R}^{NU}_{yx} & 0 & 0 & 0 & \mathcal{R}^{\Omega}_{yy} & 0 \\
0 & 0 & 0 & 0 & 0 & \mathcal{R}^{FU}_{zz}
\end{pmatrix}
\begin{pmatrix}
U_x \\
U_y \\
U_z \\
\Omega_x \\
\Omega_y \\
\Omega_z
\end{pmatrix}
+ 
\begin{pmatrix}
f n_x + \xi_x \\
f n_y + \xi_y \\
f n_z + \xi_z \\
\eta_x \\
\eta_y \\
\eta_z
\end{pmatrix}
\]
4.4.5 Some Brownian simulation results

We have used numerical simulations of the previous set of equations to study the effects of self-propulsion and a bounding wall on Janus particle motion. They are first written in dimensionless form, based on rescaling lengths by $a$, the particle radius, time by $a^2/2D$, the diffusion time across the particle, and energy by $k_B T$, the thermal energy. In above figures, we show the trajectories of several individual Janus particles moving in a plane at fixed distances, $h_z = 4$ and 200, from a planar wall, a different self-propulsion velocities $V_s$. Two obvious qualitative features are that diffusion is enhanced considerably by propulsion, but the wall does not seem to have a significant effect.

For a more quantitative analysis, we average over many such particles and compute the diffusivity as a function of the self-propulsion velocity. The variation is quadratic, and to cast the result in terms of relevant variables we fit the simulation diffusivity
to Eq. (4.43), written in terms of the rotation diffusivity $D_r = \tau^{-1}_r$:

$$D_{\text{eff}}(v_s) = D_0 + \frac{v_s^2}{6D_r}$$  \hspace{2cm} (4.51)

The rotation diffusivity $D_r$ is expected to be a function of the distance to the wall. Although computable in simulations, in this analysis we treat it as a fitting parameter, and obtain the curve shown in Fig. (4.4.5) which fit the data quite well. The resulting values are $D_r = 0.7454$ for $h_z = 200$ and $0.7133$ for $h_z = 4$, which should be compared to the theoretical value $3/4$ for bulk fluid. The results indicate only a weak $5\%$ suppression of rotational diffusion due to a wall. Although this calculation could be extended to smaller distances from the wall, a more accurate evaluation of the resistance matrix elements is likely required.

4.5 Discussion and future work

As presented in previous sections, we first reviewed the Fokker-Planck equation for isotropic particles and as well derived the rotational version of Fokker-Planck equa-
Figure 4.5: Effective diffusivity vs. $V_s$ relation in Brownian simulation, we plot two cases of $h_z$ for comparing: $D_r = 0.7454$ for $h_z = 200$ (blue curve) and $D_r = 0.7133$ for $h_z = 4$ (red curve).

Next, we used a simple toy model to explain the enlargement of diffusivity for self-propelling Janus particles and analyzed its relationship with the velocity autocorrelation function. Then, we used the hydrodynamic image method to account for the self-aligning of a Janus particle at liquid-solid interfaces. The coupling between the translation and rotation is modeled by adding appropriate terms to the standard Langevin equation. Finally, we used MD and Brownian simulation to study the individual trajectory and diffusivity, and ensemble averaging provides statistically significant results. These simulations are a powerful tool to study this topic, helping us to deepen our understanding of the particles dynamics and interaction with an interface. In the future, it is worthwhile to model more complex systems which are closer to these in the laboratory. The following specific calculations would
be relevant: (1) Beyond one point force or dipole force, modeling multipole force of a particle interacting with a wall. (2) Particle clusters: simulation of many particles interacting with each other. (3) Modeling the liquid-liquid interfaces, rather than liquid-solid interfaces we used. The main difference is the boundary condition.
In this thesis, we do modeling and simulation of nanoparticles on three problems, which are deposition during droplets evaporation, slip boundary condition and Brownian motion. They address the need for an in-depth understanding of the dynamics of nanoparticles in fluids and at interfaces.

For the problem of evaporation, we have shown that medium-scale MD simulations can easily capture most of the salient features in the evaporation of particle-laden droplets. We have measured the evaporative flux, inner flow field, density and temperature. The simulations reveal the connection between particle interactions and deposit structure, and indicate some limitations in continuum modeling.

For the problem of slip boundary condition, we used MD simulations to realize the flow past stationary surfaces and around rotating solids to study the relation of slip length with surface curvature. Starting from preliminary that the slip length is defined in a consistent tensorial manner, the resulting numerical values of the length depend only on the physical properties of the solid and fluid involved and do not vary with the flow configuration.

For the problem of Brownian motion, we have explained the increase of diffusivity for self-propelling Janus particles, we used the hydrodynamic image to account for
the self-aligning at interfaces. The coupling between the translation and rotation is modeled by adding cross terms to the standard Langevin equation. Finally, we used Brownian simulation to study their individual trajectories and diffusion constants.
Appendix A

The Fokker-Planck Equation for Rotational Brownian Motion

In this appendix, we derive a special type of Fokker-Planck equation for rotational Brownian motion. We have the Langevin equation for over-damped rotation motion as

\[
\frac{d\hat{u}}{dt} = \frac{1}{\zeta_r} \left[ -\left( \hat{u} \times \frac{\partial U}{\partial \hat{u}} \right) \times \hat{u} + \xi \times \hat{u} \right]
\]

Or equivalently in component form

\[
\frac{du_i}{dt} = \frac{1}{\zeta_r} \left[ -\epsilon_{ijk} \epsilon_{jmn} u_m u_k \frac{\partial U}{\partial u_n} + \epsilon_{ijk} u_k \xi_j \right]
\]

Or equivalently in component form

\[
\frac{du_i}{dt} = \frac{1}{\zeta_r} \left[ -\left( \delta_{km} \delta_{ni} - \delta_{im} \delta_{kn} \right) u_m u_k \frac{\partial U}{\partial u_n} + \epsilon_{ijk} u_k \xi_j \right]
\]

Where we have adopted the Einstein sum rule, and used \(u_i u_i = 1\) in last step.

Then, the first term in the Fokker-Planck equation 4.16 will become

\[
\frac{1}{\zeta_r} \frac{\partial}{\partial u_i} \left[ (\delta_{ij} - u_i u_j) \frac{\partial U}{\partial u} \right]
\]

\[
= \frac{1}{\zeta_r} \frac{\partial}{\partial \hat{u}} \cdot (I - \hat{u} \hat{u}) \cdot \frac{\partial U}{\partial \hat{u}} = \frac{1}{\zeta_r} \frac{\partial}{\partial \hat{u}} \cdot \Pi \cdot \frac{\partial U}{\partial \hat{u}}
\]
where we adopt symbol $\mathbf{\Pi} = \mathbf{I} - \mathbf{\hat{u}}\mathbf{\hat{u}}$. The second term will be

$$
\frac{1}{\zeta_r^2} \frac{\partial}{\partial \hat{u}_i} \left[ \epsilon_{ikm} \hat{u}_m \frac{\partial}{\partial \hat{u}_j} (\epsilon_{jkn} \hat{u}_nP) \right]
$$

$$
= \frac{1}{\zeta_r^2} \epsilon_{ikm} \epsilon_{jkn} \hat{u}_m \frac{\partial}{\partial \hat{u}_i} \left[ \hat{u}_n \frac{\partial P}{\partial \hat{u}_j} + \delta_{nj} P \right]
$$

$$
= \frac{1}{\zeta_r^2} (\delta_{mn}\delta_{ij} - \delta_{in}\delta_{mj}) \hat{u}_m \left[ \hat{u}_n \frac{\partial^2 P}{\partial \hat{u}_j \partial \hat{u}_i} + \delta_{ni} \frac{\partial P}{\partial \hat{u}_j} + \delta_{nj} \frac{\partial P}{\partial \hat{u}_i} \right]
$$

$$
= \frac{1}{\zeta_r^2} \left[ \frac{\partial^2 P}{\partial \hat{u}_i^2} - \hat{u}_i \hat{u}_j \frac{\partial^2 P}{\partial \hat{u}_i \partial \hat{u}_j} - 2 \hat{u}_i \frac{\partial P}{\partial \hat{u}_i} \right]
$$

$$
= \frac{1}{\zeta_r^2} \left[ \mathbf{\Pi} : \frac{\partial^2 P}{\partial \hat{u}^2} - 2 \mathbf{\hat{u}} \cdot \frac{\partial P}{\partial \mathbf{\hat{u}}} \right]
$$

Adding the above two pieces together, we got

$$
\frac{\partial P}{\partial t} = \frac{1}{\zeta_r} \frac{\partial}{\partial \mathbf{\hat{u}}} \cdot \left( \mathbf{\Pi} : \frac{\partial \mathbf{U}}{\partial \mathbf{\hat{u}}} P \right) + \frac{\Delta}{\zeta_r^2} \left[ \mathbf{\Pi} : \frac{\partial}{\partial \mathbf{\hat{u}}} \frac{\partial}{\partial \mathbf{\hat{u}}} - 2 \mathbf{\hat{u}} \cdot \frac{\partial}{\partial \mathbf{\hat{u}}} \right] P \quad (A.2)
$$

with $\Delta = k_B T \zeta_r$ and $D_r = k_B T / \zeta_r$, we arrive at Eq. (4.25).

The following equation is often referred as Smoluchowski equation for rotational motion [87]:

$$
\frac{\partial P}{\partial t} = D_r \mathbf{R} \cdot \left[ \frac{P}{k_B T} \mathbf{R} \mathbf{U} + \mathbf{R} P \right] - \mathbf{R} \cdot (\mathbf{u} \times \mathbf{\kappa} \cdot \mathbf{u} P) \quad (A.3)
$$

where $\mathbf{R} = \mathbf{\hat{u}} \times \nabla \mathbf{\hat{u}}$. We could verify that the first term with square bracket is actually the two pieces we have derived right above, while the additional term comes from the
velocity gradient \( \kappa = \nabla \mathbf{v} \) in surrounding solutions.

\[
\mathbf{R} \cdot \left[ P \mathbf{R} \mathbf{U} \right] = \left( \hat{\mathbf{u}} \times \frac{\partial}{\partial \hat{\mathbf{u}}} \right) \cdot \left( \hat{\mathbf{u}} \times \frac{\partial \mathbf{U}}{\partial \hat{\mathbf{u}}} \right) P
\]

\[
= \epsilon_{ijk} \hat{u}_j \frac{\partial}{\partial \hat{u}_k} \left[ \epsilon_{ilm} \hat{u}_l \frac{\partial \mathbf{U}}{\partial \hat{u}_m} P \right]
\]

\[
= \epsilon_{ijk} \epsilon_{ilm} \frac{\partial}{\partial \hat{u}_k} \left[ \hat{u}_j \hat{u}_l \frac{\partial \mathbf{U}}{\partial \hat{u}_m} P \right]
\]

\[
= \frac{\partial}{\partial \hat{\mathbf{u}}} \cdot \left( \mathbf{\Pi} \cdot \frac{\partial \mathbf{U}}{\partial \hat{\mathbf{u}}} P \right)
\]

and

\[
\mathbf{R} \cdot \mathbf{R} P = \left( \hat{\mathbf{u}} \times \frac{\partial}{\partial \hat{\mathbf{u}}} \right)^2 P
\]

\[
= (\epsilon_{ijk} u_j \partial_k \epsilon_{ilm} u_l \partial_m) P
\]

\[
= \left[ (\delta_{ji} \delta_{km} - \delta_{kl} \delta_{jm}) u_j (\delta_{kl} \partial_m + u_l \partial_k \partial_m) \right] P
\]

\[
= \left[ \frac{\partial^2}{\partial \hat{u}_i^2} - \hat{u}_i \hat{u}_j \frac{\partial^2}{\partial \hat{u}_i \partial \hat{u}_j} - 2 \hat{u}_i \frac{\partial}{\partial \hat{u}_i} \right] P
\]

\[
= \left[ \mathbf{\Pi} : \frac{\partial^2 P}{\partial \hat{\mathbf{u}}^2} - 2 \hat{\mathbf{u}} \cdot \frac{\partial P}{\partial \hat{\mathbf{u}}} \right]
\]

which is identical to the terms in the Fokker-Planck equation for rotational Brownian motion as we expected.
Appendix B

Data Tables for Slip Boundary Condition

<table>
<thead>
<tr>
<th>$c_f w$</th>
<th>0</th>
<th>0.4</th>
<th>0.67</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$</td>
<td>180°</td>
<td>134°</td>
<td>96°</td>
<td>73°</td>
<td>50°</td>
<td>0°</td>
</tr>
</tbody>
</table>

Table B.1 : Relation between liquid-solid interaction strength and equilibrium contact angle.

<table>
<thead>
<tr>
<th>$\xi$</th>
<th>$c_f w$</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Couette</td>
<td>$v=0.1$</td>
<td>10.4 ± 0.9</td>
<td>6.17 ± 0.56</td>
<td>2.81 ± 0.21</td>
<td>1.35 ± 0.12</td>
<td>0.50 ± 0.11</td>
<td>−0.11 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>$v=0.3$</td>
<td>11.0 ± 0.8</td>
<td>6.22 ± 0.88</td>
<td>3.07 ± 0.53</td>
<td>1.11 ± 0.19</td>
<td>0.42 ± 0.22</td>
<td>−0.22 ± 0.18</td>
</tr>
<tr>
<td></td>
<td>$v=0.5$</td>
<td>11.5 ± 1.1</td>
<td>6.46 ± 0.72</td>
<td>3.16 ± 0.32</td>
<td>1.27 ± 0.15</td>
<td>0.54 ± 0.17</td>
<td>−0.09 ± 0.12</td>
</tr>
<tr>
<td>Poiseuille</td>
<td>$g=0.005$</td>
<td>9.39 ± 0.88</td>
<td>5.79 ± 0.63</td>
<td>2.96 ± 0.46</td>
<td>1.35 ± 0.32</td>
<td>0.13 ± 0.21</td>
<td>−0.28 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>$g=0.01$</td>
<td>10.3 ± 1.1</td>
<td>6.45 ± 0.54</td>
<td>3.13 ± 0.42</td>
<td>1.39 ± 0.26</td>
<td>0.14 ± 0.14</td>
<td>−0.26 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>$g=0.02$</td>
<td>12.7 ± 1.8</td>
<td>7.24 ± 0.66</td>
<td>3.24 ± 0.31</td>
<td>1.42 ± 0.23</td>
<td>0.24 ± 0.12</td>
<td>−0.24 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>$g=0.03$</td>
<td>15.9 ± 2.2</td>
<td>9.62 ± 0.98</td>
<td>3.90 ± 0.38</td>
<td>1.65 ± 0.21</td>
<td>0.35 ± 0.17</td>
<td>−0.26 ± 0.11</td>
</tr>
</tbody>
</table>

Table B.2 : Slip length for planar channel flow from Eq. (3.4).
Table B.3: Strain rate $\dot{\gamma}$ for planar surface, obtained by fitting the velocity distribution.

<table>
<thead>
<tr>
<th>$\dot{\gamma} \times 10^2$</th>
<th>$c_{f_w}$</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Couette</td>
<td>v=0.1</td>
<td>0.47 ± 0.05</td>
<td>0.59 ± 0.02</td>
<td>0.73 ± 0.03</td>
<td>0.82 ± 0.05</td>
<td>0.92 ± 0.02</td>
<td>0.98 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>v=0.3</td>
<td>1.37 ± 0.08</td>
<td>1.76 ± 0.11</td>
<td>2.16 ± 0.07</td>
<td>2.52 ± 0.10</td>
<td>2.80 ± 0.06</td>
<td>2.99 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>v=0.5</td>
<td>2.24 ± 0.08</td>
<td>2.90 ± 0.15</td>
<td>3.59 ± 0.08</td>
<td>4.15 ± 0.14</td>
<td>4.62 ± 0.13</td>
<td>4.91 ± 0.13</td>
</tr>
<tr>
<td>Poiseuille</td>
<td>g=0.005</td>
<td>1.44 ± 0.10</td>
<td>1.52 ± 0.08</td>
<td>1.58 ± 0.07</td>
<td>1.61 ± 0.15</td>
<td>1.70 ± 0.15</td>
<td>1.80 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>g=0.01</td>
<td>2.76 ± 0.18</td>
<td>2.99 ± 0.19</td>
<td>3.12 ± 0.11</td>
<td>3.31 ± 0.18</td>
<td>3.53 ± 0.14</td>
<td>3.61 ± 0.24</td>
</tr>
<tr>
<td></td>
<td>g=0.02</td>
<td>5.58 ± 0.46</td>
<td>5.99 ± 0.52</td>
<td>6.21 ± 0.24</td>
<td>6.61 ± 0.43</td>
<td>6.96 ± 0.28</td>
<td>7.29 ± 0.45</td>
</tr>
<tr>
<td></td>
<td>g=0.03</td>
<td>8.10 ± 0.78</td>
<td>8.95 ± 0.81</td>
<td>9.40 ± 0.37</td>
<td>9.96 ± 0.50</td>
<td>10.4 ± 0.40</td>
<td>10.9 ± 0.80</td>
</tr>
</tbody>
</table>

Table B.4: Slip length for a rotating cylinder, obtained by using Eq. (3.8).

<table>
<thead>
<tr>
<th>$\xi$</th>
<th>$c_{f_w}$</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>type I</td>
<td>v=1.0</td>
<td>2.59 ± 0.26</td>
<td>1.29 ± 0.10</td>
<td>0.59 ± 0.08</td>
<td>0.13 ± 0.04</td>
<td>−0.30 ± 0.02</td>
<td>−0.54 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>v=2.0</td>
<td>2.53 ± 0.28</td>
<td>1.34 ± 0.13</td>
<td>0.69 ± 0.09</td>
<td>0.18 ± 0.02</td>
<td>−0.24 ± 0.02</td>
<td>−0.53 ± 0.02</td>
</tr>
<tr>
<td>type II</td>
<td>v=1.0</td>
<td>10.8 ± 0.83</td>
<td>5.23 ± 0.52</td>
<td>2.87 ± 0.34</td>
<td>1.07 ± 0.12</td>
<td>0.18 ± 0.07</td>
<td>−0.34 ± 0.05</td>
</tr>
<tr>
<td>Smaller Box</td>
<td>v=2.0</td>
<td>11.3 ± 0.83</td>
<td>5.82 ± 0.45</td>
<td>3.03 ± 0.22</td>
<td>1.11 ± 0.13</td>
<td>0.20 ± 0.09</td>
<td>−0.27 ± 0.07</td>
</tr>
<tr>
<td>Bigger Cyl.</td>
<td>v=3.0</td>
<td>12.2 ± 0.98</td>
<td>6.12 ± 0.58</td>
<td>3.10 ± 0.20</td>
<td>1.24 ± 0.23</td>
<td>0.22 ± 0.12</td>
<td>−0.30 ± 0.08</td>
</tr>
<tr>
<td>From Torque</td>
<td></td>
<td>11.8 ± 0.76</td>
<td>6.29 ± 0.48</td>
<td>2.87 ± 0.23</td>
<td>1.06 ± 0.19</td>
<td>0.08 ± 0.12</td>
<td>−0.48 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>v=3.0</td>
<td>12.6 ± 0.88</td>
<td>6.11 ± 0.49</td>
<td>3.16 ± 0.18</td>
<td>1.25 ± 0.17</td>
<td>0.28 ± 0.14</td>
<td>−0.27 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>From Torque</td>
<td>10.4 ± 1.34</td>
<td>6.15 ± 0.87</td>
<td>3.10 ± 0.56</td>
<td>1.16 ± 0.43</td>
<td>0.19 ± 0.24</td>
<td>−0.32 ± 0.23</td>
</tr>
</tbody>
</table>
Table B.5: Slip length for Poiseuille flow along a cylinder axis, obtained by using Eq. (3.12).

<table>
<thead>
<tr>
<th>ξ</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>g=0.002</td>
<td>6.84 ± 0.77</td>
<td>3.24 ± 0.38</td>
<td>1.08 ± 0.32</td>
<td>0.17 ± 0.14</td>
<td>−0.42 ± 0.13</td>
<td></td>
</tr>
<tr>
<td>Axial</td>
<td>g=0.006</td>
<td>7.14 ± 0.64</td>
<td>3.58 ± 0.43</td>
<td>1.63 ± 0.42</td>
<td>0.23 ± 0.12</td>
<td>−0.26 ± 0.04</td>
</tr>
<tr>
<td>g=0.010</td>
<td>7.11 ± 0.68</td>
<td>3.77 ± 0.24</td>
<td>1.50 ± 0.21</td>
<td>0.36 ± 0.07</td>
<td>−0.29 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>g=0.020</td>
<td>9.83 ± 0.72</td>
<td>4.36 ± 0.34</td>
<td>1.84 ± 0.12</td>
<td>0.57 ± 0.08</td>
<td>−0.19 ± 0.05</td>
<td></td>
</tr>
</tbody>
</table>

Table B.6: Slip length for a rotating sphere (with ω₀ = 0.1), obtained by using Eq. (3.8).

<table>
<thead>
<tr>
<th>ξ</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ= 90</td>
<td>11.02 ± 0.85</td>
<td>5.92 ± 0.46</td>
<td>3.05 ± 0.34</td>
<td>1.33 ± 0.22</td>
<td>0.59 ± 0.08</td>
<td>0.08 ± 0.05</td>
</tr>
<tr>
<td>Particle</td>
<td>θ= 60</td>
<td>9.87 ± 0.82</td>
<td>5.38 ± 0.47</td>
<td>3.10 ± 0.28</td>
<td>1.61 ± 0.18</td>
<td>0.75 ± 0.09</td>
</tr>
<tr>
<td>θ= 30</td>
<td>10.07 ± 1.20</td>
<td>6.59 ± 0.58</td>
<td>3.45 ± 0.23</td>
<td>1.54 ± 0.22</td>
<td>0.68 ± 0.12</td>
<td>0.16 ± 0.03</td>
</tr>
</tbody>
</table>
Bibliography


[34] F. Guzman and I. Kretzschmar, Unpublished, City College of New York (2010).


