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MASTER THESIS

**Multi-Scale Modeling of Star
Polymers using the Mori-Zwanzig
Formalism**

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Abstract

In this Master thesis, we study the different scales of modeling, and we specifically focus on methods that aim to bridge the microscopic and macroscopic scale. The mesoscopic length scale applies to structures that occur on between the atomic and the macroscopic length scales. Such a method is the Dissipative Particle Dynamics (DPD), a technique invented to carry out particle based simulations of hydrodynamic behavior. The DPD method is based on the Langevin dynamics and the lattice gas algorithms, with respect to fulfilled the Galilean invariance and the conservation of the momentum.

This thesis is organized as follows: we begin from scratch, reviewing the basic properties of dynamical systems, and the basic concepts of Statistical Mechanics, in *Section 1*. Then in *Section 2*, we give an introduction on the multi-scale modeling. In *Section 3*, we provide a review of the the basic modeling techniques we mention in this thesis, the Molecular Dynamics, the Langevin equation and the DPD model. An alternative simulation technique is presented in *Section 4*, based on the Generalized Langevin Equation (GLE). We present the derivation of GLE from the microscopic equations of motions using the Mori-Zwanzig projection operator formalism. Moreover, we discuss two common approximations made in practical applications of the GLE, the Markovian approximation and the Modified Projected Dynamics method, which give rise to the DPD type of equations. In *Section 5*, we carry out and present the results of the computer simulations of two case studies, of coarse-grained systems, most specifically systems of star polymers, part of an on-going work. Finally, in *Section 6*, we summarize the work that have be done so far, and discuss the relative on going projects. In the *Appendix*, in which we provide some theoretical foundations that are used in this work.

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Chapter 1

Introduction

1.1 Dynamical system theory

The systems that we are interested in in this work belong to the wide category of dynamical systems. A dynamical system deals with the evolution of a system in which some or all variables evolve in time. It is a system whose state is uniquely specified by a set of variables and whose behavior is described by predefined rules. Even though, the application of dynamical systems in the development process is relatively new, it is in many ways a modern continuation of a long tradition of developmental process theories and general systems theories.

In every day life, we are coming across a vast amount of problems, that they actually could be studied as dynamical systems. Some examples of such systems include population growth, a swinging pendulum, a predator-prey model, molecular interactions, the movements a player follows in a game of chess, and the behavior of individuals while negotiating a deal, only to name a few. We can see that dynamical systems can even be used to describe human behavior as a deterministic dynamical system; we formulate the model using relevant assumptions, then decision process becomes deterministic, and therefore the interactions among them may be modeled as a deterministic dynamical system.

Following the same concept, every dynamical system can be described over a model system. In a wide sense of speaking, dynamic systems are composed of three parts,

- the state of a system; a representation of all the information about the system at some particular moment in time, denoted as $X(t) = [x_1(t), \dots, x_n(t)]$, where t is the time.

- The state-space of a system; a set that contains all of the possible state to which a system can be assigned, denoted Ω and $X(t) \in \Omega$.
- The state-transition function; used to update and change the state from one moment to another. The symbol \mathbf{T} is used to denote the state-transition function that maps an initial state, $X(t)$ after some period of time h into a new state $X(t+h)$:

$$X(t+h) = \mathbf{T}(\mathbf{X}(\mathbf{t}), \mathbf{t}, \mathbf{t} + \mathbf{h}).$$

The transition function can be either a discrete-time function or a differential function of time. Discrete-time dynamical system is denoted as:

$$\mathbf{T}_{\mathbf{t}} = \mathbf{f}(\mathbf{X}_{\mathbf{t}-1}, \mathbf{t}),$$

which is a difference equation. Whenever the state transition function is assumed to be a differentiable function of time, then we can define the time derivative:

$$\frac{d\mathbf{T}}{dt} = \lim_{h \rightarrow 0} \left(\frac{X(t+h) - X(t)}{h} \right) = \mathbf{f}(\mathbf{X}(\mathbf{t}), \mathbf{t}).$$

This time derivative, given a starting state $X(0)$, is used to generate a trajectory, $X(t)$ for all $t > 0$. In either case, $\mathbf{T}_{\mathbf{t}}$ or $\frac{d\mathbf{T}}{dt}$ is the state variable of the system at time t .

The dynamic system theory concerns continuous state, deterministic systems. It includes both discrete and continuous time systems as well as linear and nonlinear systems. The theory was developed with the hope that the complexity exhibited by low dimensional nonlinear systems might somehow lead to ways of understanding the complex dynamics of high dimensional systems. But, in the end that was not the case. Most approaches to high dimensional systems involve deriving a reduction to a low dimensional system.

1.2 Complex systems

Complex system is a dynamical system that its components interact with each other, typically in a non-linear fashion. There are multiple causes of complexity and although more complexity metrics may be found, these are few typical characteristics often attributed to complex systems:

- State space complexity (number of possible system states, number and value range of model parameters)

- Structural complexity (relationships and dependencies of system components)
- Behavioral and algorithmic complexity (intricate behavior and interaction patterns of system components)
- Temporal complexity (time and state dependent behavior of system components)

One of the most important properties of such systems, is that no single component controls the system behavior. Instead, the system behavior results from multiple interactions between the components. They often use the term *emergence* to refer to the fact that the system's overall behavior may widely differ from the behavior suggested by its components. Interactions of its components have to be taken into account, as well as effects of non-linearity.

Many systems fall in this category, from physical and biological, to financial and social. Generally, when a system connects and/or interacts, complexity will emerge. Closed systems can not spontaneously become differentiated and show complex organization, form or structure. The interactions between real complex systems and their environment can induce changes on various degrees on all scales, setting fit the use of multi-scale models for the analysis of such systems. The complex systems that we are interesting in this work belong to the category of many-body systems.

There are many modeling approaches that someone can follow to create a model for a complex system. As we already discuss, a complex system can be used to describe a vast variety of problems, in different scales. The choice of the model that someone may use to solve these problems, depends on these characteristics.

To understand the properties and the behavior of the complex systems, we carry out computer simulations. This serves as a complement to conventional experiments, enabling us to learn some information about the system, that otherwise will have been impossible to learn. Moreover, in many case computer simulations bridge the gaps between microscopic length and time scales, and the macroscopic scales. Here, since our main subject is the analysis of a complex network of chemical entities that evolve dynamically at the molecular level, we will focus on the techniques that simulates such systems. The two main families of the simulation technique are Molecular Dynamics and Monte Carlo, and of course all the hybrid techniques that may occur by combining features of both. For this work, we used model that belong in the Molecular Dynamics family. In the next chapters, we look into the Molecular Dynamics simulation techniques and then we address more complicated and advanced techniques; Langevin Dynamics and Dissipative Particle Dynamics, which are methods used to described system in the mesoscopic scale.

1.3 Introduction to Statistical Mechanics

Complex systems usually refer to systems with many particles. It is better to describe such system using their macroscopic properties, e.g. pressure, temperature etc., instead of using every particles' trajectory. Statistical Mechanics is the theory that provides the basic tools for explaining the macroscopic observations using the molecular motion of the system. In this section, we review some of the fundamental concepts of Statistical Mechanics that we using in this work.

1.3.1 Classical Mechanics

Almost every methodology on this work is based on the laws of Classical Mechanics, i.e. neither relativistic nor quantum effects will be taken into account.

In classical mechanics, the time evolution of a system of particles is given by the Euler-Lagrangian equation of motion

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) - \frac{\partial L}{\partial q_i} = 0,$$

where q_i , \dot{q}_i are generalized coordinates and velocities, respectively. The Lagrangian L is a function of $(\mathbf{q}, \dot{\mathbf{q}})$, given in terms of the kinetic energy K and the potential V

$$L = K - V$$

Using Cartesian coordinates \mathbf{r}_i and the usual definition of the kinetic energy

$$K = \frac{1}{2} \sum_i m_i \dot{\mathbf{r}}_i^2$$

and the forces \mathbf{f}_i

$$f_i = \nabla_{\mathbf{r}_i} L = -\nabla_{\mathbf{r}_i} V.$$

The Euler-Lagrange equation yields Newton's equation of motion

$$m_i \ddot{\mathbf{r}}_i - \mathbf{f}_i = 0 \tag{1.3.1}$$

Introducing generalized momenta p_i conjugate to the coordinates

$$p_i = \frac{\partial L}{\partial \dot{q}_i},$$

we define the Hamiltonian for the system

$$H = \sum_i \dot{q}_i p_i - L.$$

If the potential does not depend on the velocities \dot{q}_i and the time t , the Hamiltonian resembles the energy. The Hamiltonian equation of motion are

$$\begin{aligned} \dot{q}_i &= \frac{\partial H}{\partial p_i}, \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i}. \end{aligned}$$

For Cartesian coordinates, we get

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} = \mathbf{v}_i, \\ \dot{\mathbf{p}}_i &= \mathbf{f}_i \end{aligned} \tag{1.3.2}$$

While the Newton's equation is a system of $3N$ second-order differential equations, eq. (1.3.2) is a system of $6N$ first order differential equations. Both systems are equivalent but they can lead to different discrete algorithms for their solution.

1.3.2 Phase space

The description of a three-dimensional N -particle system at any given time is not complete if we do not specify the $3N$ coordinates and $3N$ momenta. The $6N$ dimensional space of coordinates and momenta is called phase space. As time progresses the phase space $\Gamma \equiv (q, p)$ traces out a path which we call the phase-space trajectory of the system. As the equations of motion for Γ is a $6N$ first-order differential equations, there are $6N$ constants of integration. The trajectory of Γ is completely determined by specifying these $6N$ constants.

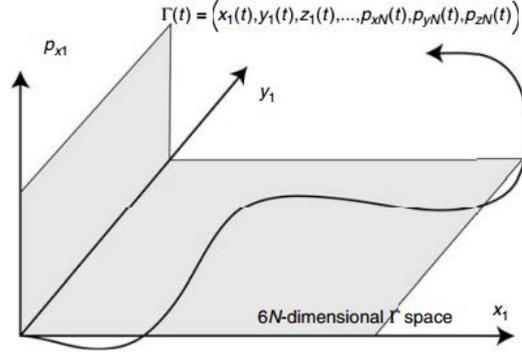


Figure 1.1: Phase space trajectory in $6N$ -dimensional phase space is a path parameterized by the time .

Ensembles, Ergodicity, Averages, Partition Function

The time-average of any quantity over the trajectory in phase space can be replaced by an average over phase space, in which the different volumes are weighted with a distribution function $\rho(\{p_i, q_i\}; t)$. The distribution function may depend on the point of phase space $\{p_i, q_i\}$, and may also depend on the time t .

An *ensemble*, is a large number of points in the phase-space that can be described by a distribution function $\rho(\{p_i\}, \{q_i\})$, for $i = 1, \dots, N$, and N is the number of particles in the system. The distribution function gives the probability of picking any particular point out of the entire ensemble.

Probability Distribution Function

The probability distribution function $\rho(\{p_i, q_i\}; t)$ could, in principle, be measured by measuring the microstates of the system composing an ensemble at time t and determining the relative number of systems which are found in microstates in the volume $d\Gamma$ of phase space around the point $\{p_i, q_i\}$. In the limit that the number of systems in the ensemble goes to infinity, this ration reduces to a probability. So, if the probability denoted as $dP(t)$ is expected to be proportional to the volume of phase space $d\Gamma$, then we expect that

$$dP(t) = \rho(\{p_i, q_i\}; t)d\Gamma,$$

where $\rho(\{p_i, q_i\})$ is the probability distribution function (PDF). The PDF is only finite for accessible volume of phase space.

Ensemble averages

Once $\rho(\{p_i, q_i\}; t)$ is determined for the ensemble, the measured value of any physical quantity $A(\{p_i, q_i\}; t)$ of a system in a macroscopic state at time t can be represented by an ensemble average. The ensemble average is the average over phase space weighted by the probability function

$$\langle A \rangle = \int d\Gamma \rho(\{p_i, q_i\}; t) A(\{p_i, q_i\}; t). \quad (1.3.3)$$

Liouville theorem

As we mention before, in a microscopic system, all positions and momenta together form the phase space $\mathbf{\Gamma} = \{\mathbf{r}_i, \mathbf{p}_i\}$. A trajectory in phase space is denoted by $\mathbf{\Gamma}(t)$, and the density distribution in phase-space is denoted by $\rho(\mathbf{\Gamma}; t)$. Let us also denote the arbitrary function $A(\mathbf{\Gamma})$ in phase-space. The time evolution can be derived from the equations of motion:

$$\frac{d}{dt} A(\mathbf{\Gamma}) = \sum_i \left(\frac{\partial A}{\partial \mathbf{r}_i} \dot{\mathbf{r}}_i + \frac{\partial A}{\partial \mathbf{p}_i} \dot{\mathbf{p}}_i \right) = i\mathcal{L}A(\mathbf{\Gamma}),$$

where:

$$i\mathcal{L} = \sum_i \left(\dot{\mathbf{r}}_i \frac{\partial}{\partial \mathbf{r}_i} + \dot{\mathbf{p}}_i \frac{\partial}{\partial \mathbf{p}_i} \right) \quad (1.3.4)$$

is the Liouville operator. From the equation of motion we can write:

$$\nabla_{\mathbf{\Gamma}} \dot{\mathbf{\Gamma}} = 0.$$

The phase-space density along a trajectory is conserved

$$\frac{d}{dt} \rho(\mathbf{\Gamma}; t) = 0.$$

By applying the chain rule, the Liouville's equation yields

$$\frac{\partial}{\partial t} \rho(\mathbf{\Gamma}; t) + i\mathcal{L} \rho(\mathbf{\Gamma}; t) = 0$$

The Liouville equation is used to describe how solutions of ODEs with random data evolve this randomness in time.

Ergodic Hypothesis

The *ergodic hypothesis* states that the system will come arbitrary close to any point in the accessible phase space, i.e. almost every trajectory will cover almost the entire accessible phase space. If a system is ergodic, time averages can be replaced by *ensemble averages*:

$$\langle A \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt A(\Gamma) = \int d\Gamma \rho(\Gamma) A(\Gamma), \quad (1.3.5)$$

where T a sufficiently large time.

Partition function

We introduce *the partition function* that contains all necessary information about the system. In the canonical ensemble it is

$$Z_K = \frac{1}{N! h^{3N}} \int d\Gamma e^{-\beta H(\Gamma)}, \quad (1.3.6)$$

where $H(\Gamma)$ is the Hamiltonian of the system, h is a constant to make Z dimensionless, and the inverse temperature β is

$$\beta = \frac{1}{k_B T}. \quad (1.3.7)$$

where k_B is the Boltzmann constant. With the partition function we can rewrite the average of eq. 1.3.3:

$$\langle A \rangle = \frac{1}{Z_K} \int d\Gamma A(\Gamma) e^{-\beta H(\Gamma)}.$$

1.3.3 Fokker Planck and Chapman-Kolmogorov equations

Consider a continuous time Markov chain $z(t)$, $t \leq 0$, taking values in the state space $\mathcal{I} \subseteq 0, 1, 2, \dots$, and the probability that the process is in state j at the time i at time zero:

$$p_{ij}(t) = (P)z(t) = j|z(0) = i,$$

where $p_{ij}(t)$ is the transition probability from state i to j . The Markov property implies that for all $\Delta t \leq 0$,

$$p_{ij}(t + \Delta t) = \sum_k p_{ik}(t)p_{kj}(\Delta t).$$

We can write:

$$\frac{p_{ij}(t + \Delta t) - p_{ij}(t)}{\Delta t} = \sum_k p_{ik}(t)l_{kj}(\Delta t),$$

where

$$l_{kl}(\Delta t) = \frac{1}{\Delta t} \times \begin{cases} p_{kj}(\Delta t), & \text{for } k \neq j, \\ p_{jj}(\Delta t) - 1, & \text{for } k = j. \end{cases}$$

Suppose that the limit $l_{kj} = \lim_{\Delta t \rightarrow 0} l_{kj}(\Delta t)$ exists, then we can obtain:

$$\frac{dp_{ij}}{dt} = \sum_k p_{ik}l_{kj}. \quad (1.3.8)$$

Because p_{ij} is the transition probability, we have $\sum_j p_{ij}(\Delta t) = 1$, and consequently $\sum_j l_{ij}(\Delta t) = 0$, and we expect that $\sum_j l_{ij} = 0$. This implied that for the limit equation (1.3.8), $\sum_j p_{ij} = 1$.

Now, consider the matrices P, L with entries p_{ij}, l_{ij} , respectively, where $i, j \in I$. Then the limit equation (1.3.8), can be written using the matrix notation:

$$\frac{dP}{dt} = PL, \quad P(0) = I.$$

We call the matrix L generator of the process. One solution of the equation is $P(t) = e^{Lt}$ and $P(t)$ also solves $\frac{dP}{dt} = LP$, $P(0) = I$. The last two equations are called the forward and the backward equations of the Markov chain.

Now, let $\mu(t) = (\mu_0(t), \mu_1(t), \dots)^T$ be the row of $P(t)$, i.e. a column vector whose entries $\mu_j(t) = p_{ij}(t)$ are the probabilities that a system starting in the state i will end up, at time t , in each of the states $j \in \mathcal{I}$. We can write the forward equation as

$$\frac{d\mu}{dt} = L^T \mu, \quad \mu(0) = e_i, \quad (1.3.9)$$

where e_i is the i^{th} unit vector, zero in all entries except the i^{th} , in which it is equal to one.

Let $w : \mathcal{I} \mapsto \mathbb{R}$ be a real valued function defined on the state space, so it can be represented as a vector with entries w_j , $j \in \mathcal{I}$, and let $v(t) = (v_0(t), v_1(t), \dots)^T$ denote the vector with i^{th} entry:

$$v_i(t) = \mathbb{E}\{w_{z(t)} | z(0) = i\},$$

where \mathbb{E} denotes expectation with respect to the Markov transition probabilities. The function $v_i(t)$ denotes the expectation value at time t of a function of the state space, i.e. an observable, given that the process started in the i^{th} state. This function can be written explicitly in terms of the transition probabilities:

$$v_i(t) = \sum_j p_{ij}(t) w_j.$$

If w is a set such as $w = (w_0, w_1, \dots)^T$, then this can be written in vector form as $v(t) = P(t)w$. Differentiating with respect to time and using the backward equation, $v(t)$ satisfies the following system of ordinary differential equations:

$$\frac{dv}{dt} = Lv, \quad v(0) = w. \quad (1.3.10)$$

This is the discrete version of the Chapman-Kolmogorov.

To extend the Fokker-Planck equation in the continuous time Markov processes over countable observables, consider the case where $W(t)$ is a multi-dimensional Brownian motion and the noise-driven differential equation

$$\frac{d\mathbf{u}}{dt} = h(\mathbf{u}) + \gamma(\mathbf{u}) \frac{dR}{dt}, \quad \mathbf{u} \in \mathcal{Z}, \quad (1.3.11)$$

where \mathcal{Z} is a Hilbert space of d dimension, $R(t)$ is a noise process, chosen so that $\mathbf{u}(t)$ is Markovian. Let $R(t)$ to be a standard Brownian motion, then the equation is an Itô stochastic differential equation. Consider a gradient that act on both scalar valued functions ϕ , or vector valued functions v as follows:

$$\begin{aligned} (\nabla\phi)_i &= \frac{\partial\phi}{\partial\mathbf{u}_i} \\ (\nabla v)_{ij} &= \frac{\partial v_i}{\partial\mathbf{u}_j} \end{aligned}$$

Note, that in this section we have used the Einstein summation convention, i.e. whereby repeated indexes imply a summation. Also for the remaining analysis, we use ∇_x, ∇_y to denote gradient or divergence with respect the co-ordinates x and y .

With the functions $h(\mathbf{u})$ and $\gamma(\mathbf{u})$ given in the SDE, we define

$$\Gamma(\mathbf{u}) = \gamma(\mathbf{u})\gamma(\mathbf{u})^T,$$

and the generator \mathcal{L} by

$$\mathcal{L}\phi = h \cdot \nabla\phi + \frac{1}{2}\Gamma : \nabla(\nabla\phi),$$

where \cdot denotes the inner product on \mathbb{R}^d and $:$ denotes the inner product on $\mathbb{R}^{d \times d}$, which induces the Frobenius norm $A : B = \text{trace}(A^T B)$. We define the operator \mathcal{L}^* such as

$$\mathcal{L}^*\rho = -\nabla \cdot (h\rho) + \frac{1}{2}\nabla \cdot [\nabla \cdot (\Gamma\rho)],$$

which is the adjoint of \mathcal{L} , with respect to the scalar product

$$\langle \phi\rho \rangle = \int \phi(\mathbf{u})\rho(\mathbf{u})d\mathbf{u},$$

which can be also written as $\langle \mathcal{L}\phi, \rho \rangle = \langle \phi, \mathcal{L}^*\rho \rangle$.

If we consider solutions of the SDE, (1.3.11), with initial data distributed according to the measure with density $\rho_0(\mathbf{u})$, then at time $t < 0$, $\mathbf{u}(t)$ is distributed according to a measure with density $\rho(\mathbf{u}, t)$, satisfying the **Fokker-Planck equation**:

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \mathcal{L}^*\rho, \quad (\mathbf{u}, t) \in \mathbb{R}^d + \times(0, \infty), \\ \rho &= \rho_0, \quad (\mathbf{u}, t) \in \mathbb{R}^d + \times 0. \end{aligned} \tag{1.3.12}$$

Note, that the smooth density ρ depends on the properties of \mathcal{L} . In cases where no noise is present, the latter equation form the Liouville equation.

The adjoint counterpart of the Fokker-Planck equation is the **Chapman-Kolmogorov equation**:

$$\begin{aligned} \frac{\partial v}{\partial t} &= \mathcal{L}v, \quad (\mathbf{u}, t) \in \mathbb{R}^d + \times(0, \infty), \\ v &= w, \quad (\mathbf{u}, t) \in \mathbb{R}^d + \times 0, \end{aligned} \tag{1.3.13}$$

where $v(\mathbf{u}, t)$ is a solution of this equation, for which we considered that $v(\mathbf{u}_0, t) = \mathbb{E}[w(\mathbf{u}(t)) | \mathbf{u}(0) = \mathbf{u}_0]$. The expectation value is considered to be set with respect to all Brownian driven paths satisfying $\mathbf{u}(0) = \mathbf{u}_0$. The Chapman-Kolmogorov equation is the analogue of the Fokker-Planck, in the countable state space case.

Following the semi-group notation, we can denote the solution of the Fokker-Planck equation by $\rho(\mathbf{u}, t) = e^{\mathcal{L}^*t}\rho_0(\mathbf{u})$, and respectively the solution of the Chapman-Kolmogorov $\mathbf{v}(\mathbf{u}, t) = e^{\mathcal{L}t}w(\mathbf{u})$. The connection between the two evolution operators is:

$$\int \rho_0(\mathbf{u})(e^{\mathcal{L}t}w)(\mathbf{u})d\mathbf{u} = \int (e^{\mathcal{L}^*t}\rho_0)(\mathbf{u})w(\mathbf{u})d\mathbf{u}.$$

For $\rho_0(\mathbf{u}) = \delta(\mathbf{u} - y)$:

$$e^{\mathcal{L}t}w(y) = \int (e^{\mathcal{L}^*t}\rho_0)(\mathbf{u})w(\mathbf{u})d\mathbf{u}.$$

The last equation represents the expectation value at time t of $w(\mathbf{u}(t))$ with respect to the distribution of the trajectories that originate at the point y .

In section (4.4), we use the GLE equation to derive a SDE equation, which will contain a memory matrix that does not suffer from the plateau problem. It is one of the main subjects of this work.

The reduction corresponds to a situation where the generator takes the form

$$\mathcal{L} = \mathcal{L}_0 + \frac{1}{\epsilon}\mathcal{L}_1 + \frac{1}{\epsilon^2}\mathcal{L}_2,$$

for some $\epsilon \ll 1$, with \mathcal{L}_3 being the generator of an ergodic process. Systematic expansions in ϵ then simplify the problem.

Chapter 2

Multi-scale Modeling

When dealing with the problem of modeling the behavior of a physical phenomenon, the tradition approach requires to focus on a single scale. Depending on which behavior we want to focus, we model in the appropriate scales. For example, if we want to exam in detail the microscopic mechanism of a process, we model the effect in smaller scales and we assume that nothing interesting is happening in larger scales. Respectively, in problems where we are focusing on the macroscale behavior. By choosing to ignore or homogenize the processes that are not crucial for our approach, we simplify and accelerate the whole process of the simulation.

If we are going to deal with more complex systems, we have to evolve more advanced tools. For example, in the case of non-Newtonian fluids - fluids whose molecular structure has a non-trivial consequence on its macroscopic behavior - there have been many efforts to try to obtain the constitutive relations by guessing or fitting a small set of experimental data. The results of these efforts are quite mixed. In most cases, the resulting functional form becomes too complicated or there are too many parameters to fit. Overall, empirical approaches have had limited success for complex systems or small scale systems for which the discrete or finite size effects are important. Similar issues arising from the use of ab initio calculations. Even though these calculations are extremely accurate, there are many limitations and difficulties in these approaches. For example, the mathematical complexity of the quantum mechanics principles, that are used on such calculations, makes them almost impossible to use directly to study engineering problems. By considering simultaneously models at different scales, we aim to create an approach that shares the efficiency of the macroscopic models as well as the accuracy of the microscopic models.

The multi-scale viewpoint offers a more unified view to modeling, by focusing on

scale levels and the relations between them. There are still many fundamental issues that one has to consider when using these models. Some of these issues include the relation between the different levels of physical models, the boundary conditions for atomistic models and systematic and accurate procedures of coarse-graining. We call coarse-graining the transition from a description with many degrees of freedom on a small scale to a description on a larger scale with eliminated degrees of freedom. This method “lies” between the microscopic description of classical mechanics, and the macroscopic description of thermodynamics. The scale between A given system may have many mesoscopic levels, which connect through the coarse-graining procedure, which eliminate some degrees of freedom from the description. In some cases, there is a clear separation between time scales of the relevant variables and the times scales of the eliminated degrees of freedom. In these cases, the evolution equations of the relevant variables are Markovian, i.e. the future state of the system is determined by the present, and independent from the past states of the relevant variables. Otherwise, the equations are non-Markovian, i.e. integro-differential, which are much more difficult to treat than the usual differential equations that result from a Markovian description.

It is expected, that will occur a loss of information when going from one level of description to a more coarser one. This loss is reflected in a stochastic description of coarse-grained levels, so even if the evolution equations are Markovian, it still not enough information to predict future, coarse states with certainty. In order to deal with these uncertainties, one must use a statistical description based on the probability distribution function for the relevant variables.

The importance of a coarse-graining method is definite. It is a tool that can be used to exam big system, that otherwise they will be to computational expensive to study. Moreover, since the degrees of freedom represent larger time scales, a much larger time span can be simulated.

One of the challenge of constructing a coarse-grain model is to figure a satisfying way to link simulations of detailed models with simulations of coarse-grained ones, in such a way that the behavior of the system can be resolved at multiple scales and the interactions at different scales inform each other. There are two techniques to do that:

- bottom-up: information are propagated by using fundamental physical principles at the more detailed scale, and using them to parametrize a model at a coarse-grained scale.
- top-down: subsequently, the behavior on larger scales are used to inform the interactions at more detailed scales. In this category, we consider also the simulations for which we take the input from experiments, such as molecular

structures, and then use them to guide the development of molecular models.

Example: Ab initio materials design

It is of a great interest in the field of solid state chemistry to find a way to change the field from an inductive to a deductive science by developing a general route to the rational planning of syntheses in the solid state. This way, we may be able to produce new materials with specific physical properties, such as materials for high-temperatures, batteries, sensors, which are base on widely available raw materials and have only a low impact to the environment. This can be achieved by being able to predict all possible stable crystalline and amorphous modifications in a given chemical system and by optimize various synthesis routes that can be tuned to produce the desired compound, combined with the ability to compute the physical properties of the predicted compounds.

Modeling syntheses in the solid state, requires the analysis of many processes occurring over a wide range of scales, such as chemical reactions between molecules, atoms and surfaces, diffusion in bulk and on surfaces. Predicting new compounds require to explore the energy landscape of chemical systems, to determinate the minima, the energetic and entropic barriers, and the locally ergodic regions of the landscape corresponding to stable and metastable compounds. All these calculations are obtained by performing simulations in the atomistic scale, using empirical potentials depending on only the ionic degrees of freedom and high-level ab initio methods taking the electronic structure into account.

Example: Soft matter design through multi-scale models

The term soft materials includes a wide variety of materials. From colloids, polymers, membranes, complex fluids, and all their possible combinations, to biological structures as proteins, DNA, and other biological assemblies, there are all systems of great interest. Though all these materials are rather different in their structures thus require in part different modeling tools, there is one unifying aspect, which makes it very reasonable to treat such systems from a common point of view. The characteristic energy density of soft matter is much smaller compared to hard matter. That basically means that the bonded and the non bonded interactions are of different order, allowing strong fluctuations, even though the molecular connectivity

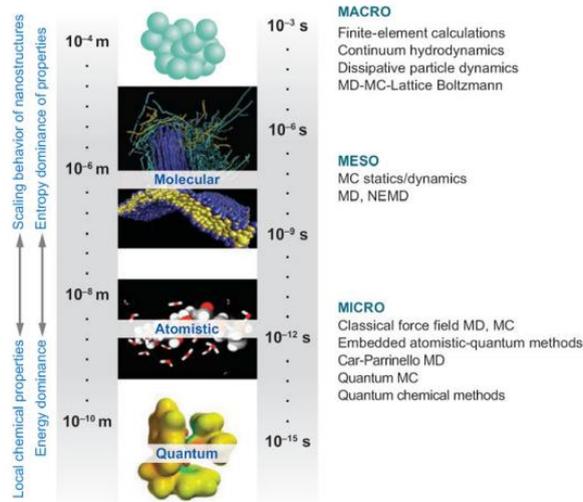


Figure 2.1: Examples of the different time and space scales encountered in the field of the soft matter structure and properties such as polymers.

is never affected. To give a rough reasoning for this, imagine that the ratio between the elastic constant of hard matter and the elastic constant of soft matter shows that the polymeric systems are typically 100 to 10000 times softer than classical crystals. As a consequence the thermal energy $k_B T$ is no longer a small energy for the systems, but it defines the essential energy scale. Subsequently, the entropy, usually of order of $k_B T$ per degree of freedom, plays a much more important role. So, in soft matter systems, the quantum chemical approaches as well as simulations with atomistic details are not a good option on describing these materials or predict their macroscopic properties.

In many cases when dealing with soft matter materials, we use simplified models, which if properly scaled, give good qualitative understanding of its properties. One way is to start from an all atom description and derive from that directly a coarse grained model, which is efficient enough to study both structural properties and long time dynamics. By applying an inverse mapping back to the atomistic model, one can actually use the simulation on the coarse grained level to efficiently equilibrate all atom models of huge size.

One part of the development of a coarse-grain model for soft matter systems that is of great interest, is the construction of the potentials that will describe the interaction between the coarse-grained particles, i.e. the mesoscale system. The coarse-grain potentials must be complex enough to represent the molecule in the intended mesoscopic simulation. The goal is to utilize the fewest and simplest potentials as

possible that represent the structures of the system, as well as its mechanical properties, and interactions. The potential of mean force can be either simulated using approximate forms, such as non-bonded pairs potentials, Lennard-Jones potential (see Appendix), tabulated potentials, and more, or by **parametrization methods**, such as Boltzmann inversion, force matching, relative entropy [1], [2], [3].

Chapter 3

Computer simulations techniques

Computer simulations is used to reduce the risk associated with creating new systems or with making changes to existing ones. A wide number of fields - economy, social science, manufacture, meteorology, physics and more - use mathematical models to predict the development of unpredictable variables. Computer simulation combined with statistical analysis techniques have evolved to give us perspective to problems that otherwise will be really costly, inconvenient to validate through experiment techniques, or even impossible to study. So, by using simulations we can give sufficient information to allow us to, at least partially, achieve what the experiment was aimed to do, or to be used on the planning stage in order to optimize the scientific or financial outcome of an experiment. On a more theoretical side, computer simulations are frequently used to handle complex non-linear systems and systems with a large number of degrees of freedom. That is, systems where traditional analytical methods fail to provide a comprehensive solution. Computer simulations, combined with a strong theoretical frame work and experimental data, is an important scientific tool.

Focusing on the mathematical point of view, we use computer simulations to solve high dimensional integrals. As we mention before, these techniques are Monte Carlo and Molecular Dynamics. Monte Carlo method uses stochastic dynamics. The idea is to perform random generated configurations and use them as supporting points for a numerical integration. The challenging part of developing a Monte Carlo simulation is to generate the random configurations in a clever way. There are several methods for stochastic sampling used in Mode Carlo, along of which are the simple sampling, where the configurations are drawing just randomly, and the importance sampling, which uses a Markov chain to generate the configurations according to a prescribed distribution. The most commonly used sampling algorithm is the Metropolis, which is mostly used to generate a Boltzmann distribution. If one,

though, is interested in the real trajectory of the system, Monte Carlo simulations are not the most practical tool. That is mostly because these simulations perform a stochastic sampling of the phase space, which eventually does not generate a real trajectory of the system, and therefore these methods are unsuitable for evaluating the dynamic and transport properties of the system. When we are interested in the real trajectory of the system, Molecular Dynamics is the best option. But the problem of finding a exact and efficient scheme remains.

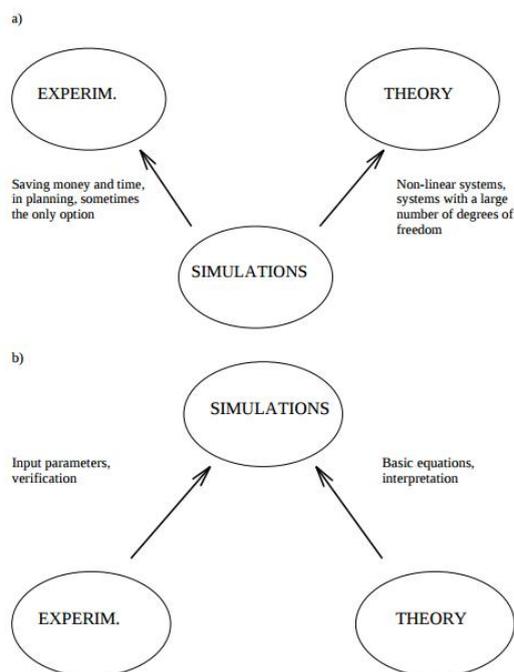


Figure 3.1: Graph of the interaction taking place between the three pillars of science and engineering.

3.1 Molecular Dynamics

Molecular Dynamics (MD) is a simulation technique, base on the solution of the classical equations of motion we discussed in the *Section 1.3.1* . It provides a simulation of the time evolution of a system by numerically integrating the classical equations of motion. According to [Allen and Tildesley, 1987], an algorithm for this purpose should meet the following requirements:

- it should produce the best possible trajectory approximation,

- is should satisfy the conservation laws and the symmetries of the system,
- it should be computationally efficient,
- is should be easy to implement.

These points may look obvious, but they deserve a closer look. In a lot of cases, the two first points conflict with the latter two. This is mainly because the integrations schemes are derived from a series expansion, which usually means that the more exact the integration schemes, the more complicated and less efficient the algorithm. Another interesting point, is about the exactness of an algorithm. To be more specific, we are interesting in two kinds of stability; short-term and long-term. Since we deal with complex systems, the real trajectories are likely to be in the regime of Lyapunoc instability; when two trajectories that are initially close, diverge exponentially in later times. Therefore, in simulations, where numerical deviations always will occur, the simulated trajectory will always diverge exponentially form the real trajectory. This is not as big issue as it may sounds, since we are interesting in the average behavior of the system. We only have to make sure that the second point is fulfilled.

The last point of the list, which talks about the ease of the implementation of the algorithm, may not affects the simulation directly, but nevertheless should be taken into consideration. There are often sophisticated, impressive algorithms, which implementation turns out to be too complicated to implement. Such errors usually lead to spurious effects in the results and errors that are hard to find.

We can summarize the basic steps for the implementation of a standard MD algorithm in the following steps:

- We choose, or if it necessary construct, a model configuration that will represent a molecular-level snapshot of the corresponding system, and set the initial positions and velocities of each particle within the system.
- We compute the total force acting on each particle of the system.
- Using an appropriate method, we integrate the equations of motion.
- After the system has reach equilibrium, we perform actual measurements of positions, velocities, energies etc, periodically every N_k steps.
- After the main loop is finished, we calculate the averages of the measured quantities.

There are two classes of MD algorithms that perform the integration of the equations of motion: Verlet-like algorithms and higher-order algorithms. We use the higher-order algorithms to calculate higher moments. Verlet-like algorithms only need the

positions, the velocities and the forces to determine their respective new values. We will discuss the Verlet-like algorithms in more detail.

As we mention before, MD simulation are based in the Newton's equations of motion.

Verlet algorithm

The Verlet algorithm is a simulation method initially formed by utilizing a Taylor expansion at times $t - dt$ and $t + dt$:

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \frac{\Delta t^2}{2m_i} \mathbf{F}_i(t) \\ &+ \frac{\Delta t^3}{3!} \ddot{\mathbf{r}}_i(t) + \mathcal{O}(\Delta t^4), \end{aligned} \quad (3.1.1)$$

$$\begin{aligned} \mathbf{v}_i(t + \Delta t) &= \mathbf{v}_i(t) + \frac{\Delta t^2}{m_i} \mathbf{F}_i(t) + \frac{\Delta t^2}{2} \ddot{\mathbf{v}}_i(t) \\ &+ \frac{\Delta t^3}{3!} \ddot{\mathbf{v}}_i(t) + \mathcal{O}(\Delta t^4). \end{aligned} \quad (3.1.2)$$

Verlet-like algorithms have proven to be a very useful computational tools since they are simple, accurate and time reversible. They used to solve the second order system 1.3.1 based on the current positions $\mathbf{r}_i(t)$, forces $\mathbf{F}_i(t)$ and the previous positions $\mathbf{r}_i(t - \Delta t)$.

Consider the Taylor expansion for $\mathbf{r}_i(t - \Delta t)$:

$$\mathbf{r}_i(t - \Delta t) = \mathbf{r}_i(t) - \Delta t \mathbf{v}_i(t) + \frac{\Delta t^2}{2m_i} \mathbf{F}_i(t) - \frac{\Delta t^3}{3!} \ddot{\mathbf{r}}_i(t) + \mathcal{O}(\Delta t^4). \quad (3.1.3)$$

We can update the equation for the positions by adding (3.1.3) and (3.1.2), and the velocities are subtracting, respectively. So, we have:

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) &= 2\mathbf{r}_i(t) - \Delta t \mathbf{v}_i(t) + \frac{\Delta t^2}{2m_i} \mathbf{F}_i(t) \\ &- \frac{\Delta t^3}{3!} \ddot{\mathbf{r}}_i(t) + \mathcal{O}(\Delta t^4), \end{aligned} \quad (3.1.4)$$

$$\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t - \Delta t)}{2\Delta t} + \mathcal{O}(\Delta t^2). \quad (3.1.5)$$

To calculate the trajectories, we only need to know the positions of the molecules. We use the velocities for the calculation of the some observables like the kinetic energy. It is important to mention that in the Verlet algorithm the velocities $\mathbf{v}(t)$ are available only after $\mathbf{r}(t + \Delta t)$ is calculated, i.e. one time step later. Moreover, updating the positions using 3.1.4 often leads to numerical imprecision, due to a small term of order Δt^2 that is been added to a difference of $\mathcal{O}(1)$ -terms.

There are many modified versions of the Verlet scheme. Some of them are modified in order to help us overcome the shortcomings of the original algorithm. The most widely used are the *Leap frog* method and the *velocity-Verlet* method.

Leap-frog algorithm

In the leap-frog method, the positions and velocities are not evaluated at half-integer time step, instead on calculated in the same time. The updating steps for the leap-frog algorithm are:

$$\mathbf{v}_i(t + \frac{\Delta t}{2}) = \mathbf{v}_i(t - \frac{\Delta t}{2}) + \frac{\Delta t}{m_i} \mathbf{F}_i, \quad (3.1.6)$$

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t + \frac{\Delta t}{2}) \quad (3.1.7)$$

Here, the velocities are updated first, and they are evaluated at half time steps ahead the positions. In order to calculate the Hamiltonian H we need to know the current velocities, which can be obtained from:

$$\mathbf{v}_i(t) = \frac{\mathbf{v}_i(t - \frac{\Delta t}{2}) + \mathbf{v}_i(t + \frac{\Delta t}{2})}{2} \quad (3.1.8)$$

The numerical imprecision that was notice in the simple Verlet scheme is minimized in the leap-frog scheme, but the velocities are still not accessible in an ad-hoc manner.

Velocity-Verlet algorithm

This algorithm yields the positions, velocities and forces at the same time. Again the positions are obtained through the usual Taylor expansion:

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \delta t \mathbf{v}_i(t) + \frac{\Delta t^2}{m_i} \mathbf{F}_i(t) + \mathcal{O}(\Delta t^3), \quad (3.1.9)$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{\Delta t}{2m_i} (\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t)) + \mathcal{O}(\Delta t^3). \quad (3.1.10)$$

This scheme, is algebraically equivalent to the original Verlet algorithm. Equations 3.1.4 can be derived from 3.1.9 by elimination of the velocities in the position update. The velocity-Verlet is a simple but the same time very stable algorithm, and probably in this way is the most widely used Molecular Dynamics algorithm. While the short-term precision is only moderate, it exhibits little long-term energy drift. The reason for the stability of the velocity-Verlet algorithm is that it is a symplectic algorithm, i.e. it preserves the volume in phase-space.

```

.....
do i = 1, N
  r(i) = r(i) + dt*v(i) + dt*dt/2*F(i)           ! update positions at t+dt using
                                                    velocities and forces at t
  v(i) = v(i) + dt/2*F(i)                       ! update velocities at t+dt using
                                                    forces at t
end do

call get_forces (F)                             ! calculate forces at t+dt

do i = 1, N
  v(i) = v(i) + dt/2*F(i)                       ! update velocities at t+dt
                                                    using forces at t+dt
end do

```

Figure 3.2: Velocity-Verlet integration scheme (as seen on “Molecular Dynamics Simulations for Polymers”, V.Harmandaris, V.G.Mavrantzas)

An exact and stable Molecular Dynamic algorithm are heavily depends on time reversibility and phase-space conservation. Phase-space conservation is formally expressed in Liouville’s theorem (see section [A]). So, the Liouville formulation of classical mechanics the time evolution of an arbitrary function of positions and momenta can be written as

$$\frac{d}{dt} A\Gamma = i\mathcal{L}A(\Gamma), \quad (3.1.11)$$

where \mathcal{L} is the Liouville operator defined in section [A]. Notice that the decomposition of the Liouville operators is arbitrary. One could also use other decompositions,

than the one we present below. Different decompositions will lead to different algorithms.

Integrate the equation above

$$A(t) = \exp(i\mathcal{L}t)A(0).$$

We split the Liouville equation into a position part and a momentum part:

$$i\mathcal{L} = i\mathcal{L}_r + i\mathcal{L}_p \quad (3.1.12)$$

where

$$i\mathcal{L}_r = \sum_i \dot{\mathbf{r}}_i \frac{\partial}{\partial \mathbf{r}_i}, \quad i\mathcal{L}_p = \sum_i \dot{\mathbf{p}}_i \frac{\partial}{\partial \mathbf{p}_i}.$$

These operators yields shifts of coordinate and momenta, respectively. Using the Trotter expansion of the Liouville operator:

Second order Trotter expansion:

$$e^{A+B} = \lim_{n \rightarrow \infty} (e^{A/2n} e^{B/n} e^{A/2n})^n$$

Trotter expansion of the Liouville operator:

$$e^{i(\mathcal{L}_r + \mathcal{L}_p)\Delta t} = e^{i\frac{\Delta t}{2}\mathcal{L}_p} e^{i\Delta t\mathcal{L}_r} e^{i\frac{\Delta t}{2}\mathcal{L}_p} + \mathcal{O}(\Delta t^3).$$

By applying the single terms of this expansion to the positions and momenta, we get:

$$\begin{aligned} e^{i\frac{\Delta t}{2}\mathcal{L}_p}\mathbf{r}_i &= \mathbf{r}_i & e^{i\frac{\Delta t}{2}\mathcal{L}_p}\mathbf{p}_i &= \mathbf{p}_i + \frac{\Delta t}{2}\dot{\mathbf{p}}_i \\ e^{i\frac{\Delta t}{2}\mathcal{L}_p}\dot{\mathbf{r}}_i &= \dot{\mathbf{r}}_i + \Delta t\ddot{\mathbf{r}}_i & e^{i\Delta t\mathcal{L}_r}\mathbf{p}_i &= \mathbf{p}_i, \end{aligned}$$

which are the integration equations of the Velocity-Verlet algorithm. We can see that the volume of the phase-space is preserved, because the operators \mathcal{L}_r and \mathcal{L}_p are hermitian, and thus the operators $e^{i\frac{\Delta t}{2}\mathcal{L}_p} e^{i\Delta t\mathcal{L}_r} e^{i\frac{\Delta t}{2}\mathcal{L}_p}$ is a unitary operator. Due to deviations, the true Hamiltonian H of the system is not strictly conserved. Since the conservation is rigorous, it explains the absence of energy drift, which is in fact the reason the velocity-Verlet algorithm is stable for longer times. If one apply the decomposition repeatedly will get a multiple-time-step algorithms, which will also be time reversible and phase-space preserving.

The Molecular Dynamic algorithm described so far is designed to simulate the dynamics on the microcanonical ensemble (NVE). Of course, we want to be able to perform MD simulations in other ensembles, where the conditions of temperature and/or pressure is specified. In order to do so, there are several methodologies for performing MD simulations under such conditions. In the majority of these methods, there is a need of reformulation of the equations of motion to include the constraints of constant T and/or P . Specifically, for the simulation of constant temperature, one has to use a thermostat which allows for heat exchange with the system. In this work, the focus is on the DPD method, which is a method combines ideas from Langevin dynamics and lattice gas algorithms. In order to understand better DPD method, we briefly review the Langevin dynamics method. The advantage of a Langevin thermostat, compare with other widely used thermostats e.g. Nosse-Hoover thermostat, is that it can be derived directly from the microscopic dynamics of the system. This make the simulations of non-equilibrium Molecular Dynamics possible.

3.2 The Langevin equation

In MD simulations methods, we compute all microscopic degrees of freedom explicitly. But there are simulations where this approach is not very effective. For example, in systems where the dynamics shows timescale separation, which means that some degrees of freedom evolve fast and some slow. There are cases where the motion of fast variables are not of any interest themselves, but rather their effect on the slow phenomena is what we want to study. An prominent example for such system is a Brownian particle in a solvent. The reader can find more details of the Brownian motion the complimentary, theoretical chapter. Systems that follow Brownian motion are colloidal systems, polymer solutions, and biological systems such as membranes and blood. Since there usually is a large number of particles, it is difficult to calculate explicitly the fast degrees of freedom. In order to simulate such systems, approximation techniques were introduce in order to eliminate the fast degrees of freedom. Langevin methods and Dissipative Particle Dynamics methods are two approaches to do so. In the Langevin dynamics method, the fast degrees of freedom are substituted by stochastic terms in the equation of motion. The reduction of degrees of freedom is achieved by the projection operator technique, introduced by Mori and Zwanzig, which we will discuss in more detail in the next chapter.

The main idea behind the Langevin dynamics, is based on the description of the Brownian motion. Consider a large particle (Brownian particle) immersed in a fluid

of much smaller particles (atoms). The motion of the large particle is much slower than that of the atoms and is the result of random and rapid collisions due to density fluctuations in the fluid. There are three different timescales in a colloidal system τ_s, τ_B and τ_r : the short atomic scale ($\approx 10^{-12}s$), the Brownian timescale for the relaxation of the particle velocity ($\approx 10^{-3}$) and the relaxation time for the Brownian particle, i.e. the time that particle have diffused its own radius ($\tau = \frac{a^2}{D}$). In general $\tau_s \ll \tau_B \ll \tau_r$.

While the motion of a dust particle performing Brownian motion appears to be quite random, it must nevertheless be describable by the same equation of motion as is any other dynamical system. In classical mechanics these are Newton's or Hamilton's equations. Here, we will consider motion in one dimension.

Newton's equation of motion for the particle in a fluid medium is:

$$m \frac{dv(t)}{dt} = F(t)$$

where $F(t)$ is the total instantaneous force on the particle at time t , $x(t)$ is the position, $v(t)$ is the velocity in fluid medium (viscosity η), m is the mass and α is the radius. This force is due to interaction if the Brownian particle with the surrounding medium. If the positions of the molecules in the surrounding medium are known as a function of time, then the force is a known function of time. In this sense it is not a random force. But usually, it is not practical to look for an exact expression for $F(t)$. In typical cases this force is represented by a friction force $-\gamma v(t)$, proportional to the velocity of the Brownian particle. γ is the friction coefficient is given by Stokes law $\gamma = 6\pi\eta\alpha$.

Also, we expect a random force $\xi(t)$ due to random density fluctuations in the fluid. The Langevin equation is given:

$$\frac{d\mathbf{v}_i}{dt} = -\gamma \frac{\mathbf{v}_i}{mi} + \mathbf{F}_i(t) + \xi(t), \quad (3.2.1)$$

where \mathbf{F}_i can be also called conservative force The Langevin model requires some complementary hypothesis about the random force $\xi(t)$:

– Average value

We assume that the average value of the Langevin force vanishes:

$$\langle \xi(t) \rangle = 0,$$

This hypothesis is necessary in order ensure that the average value of the Brownian particle's velocity vanish at equilibrium.

– Autocorrelation function

The autocorrelation function of the random force is given by

$$g(\tau) = \langle \xi(t)\xi(t + \tau) \rangle$$

is an even function of τ , decreasing over a characteristic time τ_c (correlation time). We set:

$$\int_{-\infty}^{\infty} g(\tau) d\tau = 2Dm^2. \quad (3.2.2)$$

where parameter D is a diffusion coefficient. The correlation time is of the order of the mean time interval separating two successive collisions of the fluid's molecules on the Brownian particle. If this time is much shorter than the characteristic times, we can assimilate $g(\tau)$ to a delta function of weight $2Dm^2$:

$$g(\tau) = 2Dm^2\delta(\tau). \quad (3.2.3)$$

– Gaussian approximation of the Langevin force

In most cases, we assume that $\xi(t)$ is a Gaussian process. Under this rather convenient assumption, we can calculate all the statistical properties of the Langevin force, given only its average and its correlation function.

The physical interpretation of the Langevin equation is easy to understand. The term $\gamma \frac{\mathbf{v}_i}{m_i}$ represents a dissipative force, caused by the friction between the particles and the fluid and the random force is caused by the random collisions from the surrounding solvent particles.

The Langevin dynamics method is most often used in simulations in the canonical ensemble (NVT). Hence, the equilibrium distribution should be the Boltzmann distribution. This fact implies that the friction and the random force have to somehow be related. The relation between friction and random force is obtain by considering the phase-space distribution $\rho(\Gamma; t)$. It satisfies the equation

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= - \sum_i \left(\frac{\partial \rho}{\partial \mathbf{r}_i} \dot{\mathbf{r}}_i + \frac{\partial \rho}{\partial \mathbf{p}_i} \dot{\mathbf{p}}_i \right) \\ &= - \sum_i \left(\frac{\partial \rho}{\partial \mathbf{r}_i} \dot{\mathbf{r}}_i + \frac{\partial \rho}{\partial \mathbf{p}_i} \mathbf{F}_i \right) + \sum_i \frac{\partial}{\partial \mathbf{p}_i} \left(\gamma \frac{\mathbf{p}_i}{m_i} \rho + \frac{\sigma^2}{2} \frac{\partial \rho}{\partial \mathbf{p}_i} \right) \\ &= - \sum_i \left(\frac{\partial \rho}{\partial \mathbf{r}_i} \frac{\partial H}{\partial \mathbf{p}_i} - \frac{\partial \rho}{\partial \mathbf{p}_i} \frac{\partial H}{\partial \mathbf{r}_i} \right) + \sum_i \frac{\partial}{\partial \mathbf{p}_i} \left(\gamma \frac{\partial H}{\partial \mathbf{p}_i} \rho + \frac{\sigma^2}{2} \frac{\partial \rho}{\partial \mathbf{p}_i} \right) \\ &= (\mathcal{L} + \mathcal{L}_{LD})\rho, \end{aligned} \quad (3.2.4)$$

where \mathcal{L} is the classical Liouville operator and

$$\mathcal{L}_{LD} = \sum_i \frac{\partial}{\partial \mathbf{p}_i} \left(\gamma \frac{\partial H}{\partial \mathbf{p}_i} + \frac{\sigma^2}{2} \frac{\partial}{\partial \mathbf{p}_i} \right)$$

which includes both friction and random terms. The equation 3.2.4 is also known as the Fokker-Planck equation for the phase-space density of the Langevin dynamics. Applied to the Boltzmann distribution we get:

$$(\mathcal{L} + \mathcal{L}_{LD})e^{-\beta H} = \mathcal{L}_{LD}e^{-\beta H} = \sum_i \frac{\partial}{\partial \mathbf{p}_i} \left(\gamma \frac{\partial H}{\partial \mathbf{p}_i} + \frac{\sigma}{2} \frac{\partial}{\partial \mathbf{p}_i} \right) e^{-\beta H}. \quad (3.2.5)$$

In order to obtain the Boltzmann distribution as the stationary distribution, we read off the condition

$$\sigma^2 = 2m\gamma k_B T, \quad (3.2.6)$$

which is the ‘‘fluctuation dissipation theorem’’. The fluctuation-dissipation theorem is a consequence of the requirement that the system tend to equilibrium for long times and it relates the dissipation and the random force to the thermal fluctuations at the ultimate equilibrium. The larger the input, the higher the equilibrium temperature, while the more dissipation there is, the lower the final temperature.

Earlier, we briefly discussed the use of Langevin dynamics as a thermostat for non-equilibrium Molecular Dynamics. Although, there are some advantages to this approach, still the Langevin thermostat is not the most suited choice for simulations in the nonlinear regime. The Langevin dynamics will damp all velocities, including a bulk flow component, which will cost for the Galilean invariance to break. The Galilean invariance is essential for hydrodynamic simulations in the microscopic limit, but is irrelevant for systems at rest. Moreover, it can be shown that it prevents the built-up of the hydrodynamic correlations, and of physically occurred, hydrodynamic instabilities [4]. Finding a method that could simulate complex system, but the same time restoring Galilean invariance and maintaining nice stabilization properties, led to the modification of the Langevin thermostat to the DPD algorithm.

3.3 The Original Dissipative Particle Dynamics model

As we seen before, computer simulation study a vast variety of complex systems, as soft matter systems, which offer consists of a liquid environment in which the objects are dissolved. Soft matter systems, also called complex fluids, are very interesting cases to study, since their behavior are affective to both microscopic and macroscopic scale. They are fluids, and their evolution is described by the Navier-Stokes equation, their microscopic structure affect the system fundamentally, and it cannot be easily ignored. That is, because the observable phenomena on the microscopic scale are caused by the constituents that exist on the microscopic scale. Disparate scales that are caused by this distinctiveness poses a problem for computer simulations, since most of the Navier-Stokes equation solvers are insufficient because the microscopic behavior of the complex fluid cannot be inappropriately correctly. Respectively, MD simulations are insufficient to simulate the system for long times, as a macroscopic model requires. To bridge these scales, we focus on techniques that simulate in mesoscopic scale. The Langevin dynamics are a mesoscopic technique, but the drawbacks that we discussed before led to the development of an alternative simulation technique, the Dissipative Particle Dynamics.

Dissipative particle dynamics is a stochastic, particle based, mesoscopic simulation method, firstly introduced by Hoogerbrugge and Koelman [5]. It is based on the simulation of soft spheres, whose motion is governed by certain collision rules. More specifically, the collisions are determined by pairwise additive forces between the particles which are considered to be soft and finite. Despite being a particle based method, a dissipative particle is not identified with a physical particle of the fluid, but represents the center of mass of a mesoscopic portion of the fluid.

By the formulation introduced by Español and Warren [6], all particles interact by three forces: a conservative \mathbf{F}^C , a dissipative force \mathbf{F}^D , and a random force \mathbf{F}^R , similar to the Langevin dynamics forces. The dissipative and the random force have to satisfy a certain relations in order that the system had a statistical mechanics corresponding to the canonical ensemble with a temperature related to the relative amplitudes of the random and dissipative interactions.

The basis of constructing the DPD model is the specification of coarse-grained force field governing the motion of the dissipative particles. The most common approach is to use empirical expressions for the coarse-grained potential with adjustable coefficients, which are parameterized and optimized to generate desired properties. More complicated approaches, use relative entropy rate based methodology and Bayesian inference to optimize the force field. Correcting methods are usually used to opti-

mize potentials for equilibrium properties, but they are not efficient for reproducing dynamical properties. Moreover, an empirical model can not easily be transferred to other systems, nor to the same system under other thermodynamics conditions.

The original DPD model is a stochastic particle model, which combines off-lattice version of Lattice gas, molecular dynamics and Langevin dynamics. Beginning with a system consisted of a set of particles with continuous positions \mathbf{r}_i and velocities \mathbf{v}_i , i denotes the particles with mass m_i , whose time evolution is described by Newton's equations of motion:

$$\dot{\mathbf{r}}_i = \mathbf{v}_i \quad (3.3.1)$$

$$\dot{\mathbf{v}}_i = \frac{\mathbf{F}_i}{m_i}, \quad i = 1, \dots, N. \quad (3.3.2)$$

By definition, there are three forces acting on the dissipative particle:

$$\mathbf{F}_i = \sum_{j \neq i} (\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R), \quad (3.3.3)$$

where each force contribution is:

- a conservative force:

$$\mathbf{F}_{ij}^C = \alpha \cdot w_C(\mathbf{r}_{ij}) \mathbf{e}_{ij},$$

- a dissipative force:

$$\mathbf{F}_{ij}^D = -\gamma w_D(\mathbf{r}_{ij}) (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{e}_{ij},$$

- a random force:

$$\mathbf{F}_{ij}^R = \sigma w_R(\mathbf{r}_{ij}) \mathbf{e}_{ij} d\mathbf{W}_{ij},$$

where $\mathbf{e}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/\mathbf{r}_{ij}$, with $\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ the velocity difference. By α we denote the repulsive force coefficient, γ and σ is the dissipative coefficient and noise strength coefficient in the direction parallel to \mathbf{e}_{ij} , respectively. The term dW_{ij} is symmetric Gaussian white noise, which are independent for different pairs of particles and different times. More specifically, dW_{ij} should satisfy the properties:

$$\begin{aligned} \langle dW_{ij}(t) \rangle &= 0, \\ \langle dW_{ij}(t) dW_{i'j'}(t') \rangle &= (\delta_{ii'} \delta_{jj'} + \delta_{ij'} \delta_{i'j}) \delta(t - t'). \end{aligned} \quad (3.3.4)$$

$w_C(R)$, $w_D(R)$, $w_R(R)$ are weight functions that describe the range of the dissipative and random forces and vanish for $R > R_C$. The dissipation and thermal noise

coefficients are connected through the Fluctuation-Dissipation theorem, so the following relationship is required: $\sigma^2 = 2\gamma k_B T$ and $w_D(R) = [w_R(R)]^2$. A common choice for the weighting functions w_D and w_R should be as so the force is a soft repulsion: $w_C(R) = 1 - R/R_C$ and $w_D(R) = (1 - R/R_C)^s$ for $R \leq R_C$, where R_C is the cutoff radius. Only one of the weighting functions can be chosen arbitrarily. The soft conservative interaction makes it possible to use a large time step in a discrete algorithm for integrating the equation of motion. Moreover, the conservative force is responsible for the determination of the thermodynamics of the system, i.e. the equation of state. According to Español and Warren, 1995, the weighting functions must satisfy the detailed balance condition, which ensures that a well-defined equilibrium state exists, is given by:

$$w_D(R) = [w_R(R)]^2 \equiv w(R). \quad (3.3.5)$$

The dissipative force is a friction force that acts on the relative velocities of particles. Generally, this force is not parallel to the radial direction \mathbf{e}_{ij} , but, on the case of conventional DPD, we consider only the the parallel coefficient. The term $(\mathbf{e}_{ij} \cdot \mathbf{v}_{ij})$ is the projection of the relative velocity on the distance unit vector. When the particles are departing, the relative velocity projection is positive, meaning that the dissipative force drags them together in the direction of \mathbf{e}_{ij} , and if it is negative, the particles approaching and the dissipative force repels them. If there were no other forces, in some point the particles would have stopped their relative motion.

To compensate the loss of kinetic energy due to the dissipative force, we need a random movement in the radial direction \mathbf{e}_{ij} that will keep the particles in thermal motion. The random force is build in such a way to do exactly that: is symmetric in ij , so when it is ‘applied’, it satisfied the Newton’s third law and conserve total momentum. If there were no other forces, but the random one, the kinetic energy would gradually increase. The isothermal process is ensured by the use of the dissipative and random force.

Note that the dissipative and random forces are similar of those of Langevin dynamics, but despite the appearance similarities, is quite different form the ones used in Brownian dynamics simulations. The main difference is that on the DPD model they depend only on the relative quantities \mathbf{R}_{ij} and \mathbf{V}_{ij} , such as the Galilean invariance is satisfied. Most importantly, the DPD equations, manage to conserve the total momentum, $d(\sum_i \mathbf{p}_i)/dt = 0$, because the three types of forces satisfy Newton’s Third Law.

Therefore, DPD model captures the essentials of mass and momentum conservation which are responsible for the hydrodynamic behavior of a fluid at large scales. In contrast, in the Langevin model, total momentum of the particles is not conserved

Model Parameters		
m	mass of DPD particles	
\mathbf{r}_c	cutoff radius, i.e. range of DPD interactions	
γ	friction coefficient	
σ	noise amplitude	
L	size of simulation box	$V = L^d$
N	number of particles	
Derived Parameters		
T_0	equilibrium temperature	$T_0 = m\sigma^2/2\gamma$
ρ	number of density	$\rho = N/L^d$

Table 3.1: DPD parameters model.

and only mass diffusion can be studied. Although DPD is an ad-hoc construction, there is a great interest for methods that derive the forces for the underlying microscopic dynamics.

The DPD equations of motion can be written as stochastic differential equations

$$\begin{aligned}
d\mathbf{r}_i &= \mathbf{v}_i dt \\
m_i d\mathbf{v}_i &= \sum_{j \neq i} \mathbf{F}_{ij}^C(\mathbf{r}_{ij}) dt - \gamma \sum_{j \neq i} w(\mathbf{r}_{ij}) (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{e}_{ij} dt \\
&= \sigma \sum_{j \neq i} w^{1/2}(r_{ij}) \mathbf{e}_{ij} d\mathbf{W}_{ij}.
\end{aligned} \tag{3.3.6}$$

The above stochastic differential equation (SDE) is mathematically equivalent to a Fokker-Planck equation, where the differential df , that we can find in an arbitrary function of phase space, is expanded to second order in $d\mathbf{r}_i$ and $d\mathbf{v}_i$. The Fokker-Planck equation obtain from the SDE:

$$\partial_t \rho(\Gamma; t) = \mathcal{L} \rho(\Gamma; t) = (\mathcal{L}_C + \mathcal{L}_D + \mathcal{L}_R) \rho(\Gamma; t), \tag{3.3.7}$$

where the Fokker-Planck operator is split into three parts corresponding to each of the three forces between dissipative particles:

$$\mathcal{L}_C = -\sum_i \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} - \sum_{j \neq i} \frac{\mathbf{F}_{ij}^C}{m_i} \frac{\partial}{\partial \mathbf{v}_i}, \quad (3.3.8)$$

$$\mathcal{L}_D = \frac{\gamma}{m_i} \sum_{i \neq j} w_D(\mathbf{r}_{ij}) \left(\mathbf{e}_{ij} \cdot \frac{\partial}{\partial \mathbf{v}_i} \right) (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij}), \quad (3.3.9)$$

$$\mathcal{L}_R = \frac{\sigma^2}{2m_i^2} \sum_{j \neq i} w_R^2(\mathbf{r}_{ij}) \left(\mathbf{e}_{ij} \cdot \frac{\partial}{\partial \mathbf{v}_i} \right) \left[\mathbf{e}_{ij} \cdot \left(\frac{\partial}{\partial \mathbf{v}_i} - \frac{\partial}{\partial \mathbf{v}_j} \right) \right] \quad (3.3.10)$$

The conservative operator is the classical Liouville operator corresponding to the Hamiltonian. The sum of the operators \mathcal{L}_D and \mathcal{L}_R can be written as follows

$$\mathcal{T}_D \equiv \mathcal{L}_D + \mathcal{L}_R = \frac{\gamma}{2m_i} \sum_{j \neq i} w(r_{ij}) \mathbf{e}_{ij} \mathbf{e}_{ij} : \left[\partial_{ij} \mathbf{v}_{ij} + \frac{\mathbf{k}_B \mathbf{T}}{\mathbf{m}_i} \partial_{ij} \partial_{ij} \right], \quad (3.3.11)$$

where $\partial_{ij} = \frac{\partial}{\partial \mathbf{v}_i} - \frac{\partial}{\partial \mathbf{v}_j}$, and the colon denotes a double tensor contraction and products of vectors are tensors. Considering that the noise amplitude and the friction coefficient are related by the fluctuation-dissipation relation, the equilibrium distribution

$$\rho^{eq}(r, v) = \frac{1}{Z} e^{-\frac{1}{k_B T} \left(\sum_i \frac{m_i v_i^2}{2} + V(r) \right)}, \quad (3.3.12)$$

where V is the potential function that gives rise to the conservative forces \mathbf{F}^C , k_B is Boltzmann's constant, T is the equilibrium temperature and Z is the normalizing partition function.

Chapter 4

Generalized Langevin Equation

The Generalized Langevin Equation (GLE) is a method used to simulate the time evolution of molecular and other systems when considering general non-equilibrium processes. The theory of GLE has been around for a while, but only recently started to be considered as a method for simulating non-equilibrium systems. The GLE approach, studies an open system, which interacts and exchanges energy with its dissipative environment. The GLE is derived by projecting the harmonic environment, which leads to a realistic coupling, while the equations of motion are non-Markovian. This technique has many promising applications, especially as a thermostat for equilibrium in molecular dynamics simulations, but the weakness of this method is that the algorithms to solve the GLE for realistic memory effects is difficult to implement. A common approach to overcome this caveat is to use Markovian approximations to reduce the GLE to a stochastic differential equation. However, this approach is not clearly justified mathematically, and often fails

Here, we review a more recent procedure, introduced by Hijòn et al., which basically alter underlying microscopic dynamics by including an artificial parameter which controls the ratio between time-scales. The resulting equations has the form of dissipative particle dynamics motion equations. Contrary to the empirical methods, this method promises to provides a forward path of modeling directly from the microscopic dynamics.

This chapter is organized as follows: the first section presents the derivation of the GLE for the simple case of a harmonic Hamiltonian bath. Then we use the Mori-Zwanzig formalism to derive the Generalized Langevin equation (GLE) and discuss the caveats of the method. In the third section, we present the standard Markovian approximation used to transform the GLE into a stochastic differential equation, and we discuss the caveats of this method. Finally, we review a method

suggested by [7], in order to overcome these caveats. Their method leads to a model in the framework of the dissipative particle dynamics.

4.1 Derivation of the Generalized Langevin Equation for Harmonic Hamiltonian bath

Consider a system consisted by a small number of degrees of freedom, that can be used to describe a reaction. We are interested in the variable that describes the distance between the two atoms of the molecule, which is basically the variable whose detailed dynamics we want to exams. A model that has maintained a certain level of both popularity and success is the **harmonic bath** model, in which the environment to which the special degrees of freedom couple is replaced by a effective set of harmonic oscillators. We will examine this model for the case of a single variable, designate as q .

Using a classical treatment of this Hamiltonian we will derive an equation for the detailed dynamics of q . This equation is known as the generalized Langevin equation.

We denote the generalized coordinates q_1, \dots, q_{3N} . Consider $q_1 \equiv q$ to be the system's coordinate and $q_2, \dots, q_{3N} \equiv y_1, \dots, y_n$ to be the coordinates of the bath, with $n = 3N - 1$. The Hamiltonian for the system coordinate q , coupled to a harmonic bath is:

$$\begin{aligned} \mathcal{H} &= \frac{p^2}{2\mu} + V(q) \\ &= \sum_{\alpha=1}^n \left[\frac{p_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} \sum_{\alpha=1}^m m_{\alpha} \omega_{\alpha}^2 x_{\alpha}^2 \right] + q \sum_{\alpha=1}^n g_{\alpha} x_{\alpha} \end{aligned}$$

where: $y_a = \sum_{\beta=1}^n R_{\alpha\beta} x_{\beta}$, $g_{\alpha} = \sum_{\beta} c_{\beta} R_{\alpha\beta}$, index α runs over all the bath degrees of freedom, m_{α} are the harmonic bath masses is an orthogonal and $R_{\alpha\beta}$ is an orthogonal matrix that triagonalizes the original Hamiltonian. Our goal is to find an evolution equation for the phase variable $\mathcal{A} = \{A\}_{i=1}^m$, $m < n$.

Starting from the Hamiltonian's equation for this system, we have the following equations of motion:

$$\begin{aligned}
\dot{q} &= \frac{\partial H}{\partial p} = \frac{p}{\mu} \Rightarrow \mu \dot{q} = p \\
\dot{p} &= -\frac{\partial H}{\partial q} = -\frac{dV}{dq} - \sum_{\alpha} g_{\alpha} x_{\alpha} \\
\dot{x}_{\alpha} &= \frac{\partial H}{\partial p_{\alpha}} = \frac{p_{\alpha}}{m_{\alpha}} \Rightarrow m_{\alpha} \dot{x}_{\alpha} = p_{\alpha} \\
\dot{p}_{\alpha} &= -\frac{\partial H}{\partial x_{\alpha}} = -m_{\alpha} w_{\alpha}^2 x_{\alpha} - g_{\alpha} q
\end{aligned}$$

We can write this set of equations as second order differential equation:

$$\mu \ddot{q} = -\frac{dV}{dq} - \sum_{\alpha} g_{\alpha} x_{\alpha} \quad (4.1.1)$$

$$m_{\alpha} \ddot{x}_{\alpha} = -m_{\alpha} w_{\alpha}^2 x_{\alpha} - g_{\alpha} q, \quad \text{subject to } q(0), \dot{q}(0), x_1(0), \dots, \dot{x}_n(0) \quad (4.1.2)$$

In order to derive an equation for q , we solve explicitly for the dynamics of the bath variables and substitute into the equation for q . The equation for x_{α} is a second order inhomogeneous differential equation, which can be solved by Laplace transforms. We take the Laplace transform of both sides. The Laplace transform and its properties can be found on the appendix [A]. The Laplace transforms of q and x_{α} as:

$$\tilde{q}(s) = \int_0^{\infty} dt e^{-st} q(t) \quad (4.1.3)$$

$$\tilde{x}_{\alpha} = \int_0^{\infty} dt e^{-st} x_{\alpha}(t) \quad (4.1.4)$$

and by using the Laplace properties we obtain the following for $\tilde{x}_{\alpha}(s)$:

$$\begin{aligned}
s^2 \tilde{x}_{\alpha}(s) - \dot{x}_{\alpha}(0) - s x_{\alpha}(0) + w_{\alpha}^2 \tilde{x}_{\alpha}(s) &= -\frac{g_{\alpha}}{m_{\alpha}} \tilde{q}(s) \Rightarrow \\
\tilde{x}_{\alpha}(s) &= \frac{s}{s^2 + w_{\alpha}^2} \dot{x}_{\alpha}(0) - \frac{g_{\alpha}}{m_{\alpha}} \frac{\tilde{q}(s)}{s^2 + w_{\alpha}^2}
\end{aligned}$$

The variable $x_{\alpha}(t)$ can be obtain by inverse Laplace transformation, which is equivalent to the Bromwich contour (*see Appendix*). The inverse Laplace transform

$$\frac{1}{2\pi i} \oint ds \frac{se^{st}}{s^2 + w_\alpha^2} = \frac{1}{2\pi i} \oint ds \frac{se^{st}}{(s + iw_\alpha)(s - iw_\alpha)}. \quad (4.1.5)$$

The integrand has two poles on the imaginary s -axis at $\pm iw_\alpha$. Integration over the contour that encloses these poles picks up both residues from these poles. Since the poles are simple, from the residues theorem:

$$\frac{1}{2\pi i} \oint ds \frac{se^{st}}{(s + iw_\alpha)(s - iw_\alpha)} = \frac{1}{2\pi i} \left[\left(\frac{iw_\alpha e^{iw_\alpha t}}{2iw_\alpha} + \frac{-iw_\alpha e^{-iw_\alpha t}}{-2iw_\alpha} \right) \right] = \cos w_\alpha t. \quad (4.1.6)$$

This is the Laplace transform of a product of $\tilde{q}(s)$ and $1/(s^2 + w_\alpha^2)$. From the convolution theorem of Laplace transforms, the Laplace transform of a convolution gives the product of Laplace transforms, thus the last term will be the convolution of $q(t)$ with $(\sin w_\alpha t)/w_\alpha$. Gathering these results, and by expressing the convolution term in terms of \dot{q} , rather than in terms of q and be integrating it by parts:

$$\frac{g_\alpha}{m_\alpha w_\alpha} \int_0^t d\tau q(\tau) \sin(w_\alpha(t-\tau)) = \frac{g_\alpha}{m_\alpha w_\alpha^2} [q(t) - q(0) \cos w_\alpha t] - \frac{g_\alpha}{m_\alpha w_\alpha^2} \int_0^t d\tau \cdot q(\tau) \cos w_\alpha(t-\tau), \quad (4.1.7)$$

we get the solution for $x_\alpha(t)$:

$$\begin{aligned} x_\alpha(t) &= x_\alpha(0) \cos(w_\alpha t) + \frac{1}{w_\alpha} \dot{x}_\alpha(0) \sin(w_\alpha t) - \frac{g_\alpha}{m_\alpha w_\alpha} \int_0^t d\tau \sin[w_\alpha(t-\tau)] q(\tau) \quad (4.1.8) \\ &= x_\alpha(0) \cos(w_\alpha t) + \frac{1}{w_\alpha} \dot{x}_\alpha(0) \sin(w_\alpha t) \\ &\quad - \frac{g_\alpha}{m_\alpha w_\alpha} \left[\frac{1}{w_\alpha} (q(t) - q(0) \cos(w_\alpha t)) - \frac{1}{w_\alpha} \int_0^t d\tau \cos(w_\alpha(t-\tau)) q(\tau) \right] \quad (4.1.9) \end{aligned}$$

Substituting $x_\alpha(t)$ in equation of motion for q :

$$\begin{aligned} \mu \dot{q} &= -\frac{dV}{dq} - \sum_\alpha g_\alpha x_\alpha(t) \\ &= -\frac{dV}{dq} - \sum_\alpha g_\alpha \left[x_\alpha(0) \cos(w_\alpha t) + \frac{p_\alpha(0)}{w_\alpha m_\alpha} \sin(w_\alpha t) \right. \\ &\quad \left. + \frac{g_\alpha}{m_\alpha w_\alpha^2} q(0) \cos(w_\alpha t) \right] \\ &\quad - \sum_\alpha \frac{g_\alpha^2}{m_\alpha w_\alpha^2} \int_t^0 d\tau q(\tau) \cos[w_\alpha(t-\tau)] + \sum_\alpha \frac{g_\alpha^2}{m_\alpha w_\alpha^2} q(t) \quad (4.1.10) \end{aligned}$$

We define the following:

$$W(q) = V(q) - \sum_{\alpha} \frac{1}{2} \frac{g_{\alpha}^2}{m_{\alpha} w_{\alpha}^2} q^2 : \text{ Potential of mean force}$$

$$\zeta(t) = \sum_{\alpha} \frac{g_{\alpha}^2}{m_{\alpha} w_{\alpha}^2} \cos(w_{\alpha} t) : \text{ Dynamic friction kernel}$$

$$R(t) = - \sum_{\alpha} g_{\alpha} \left[(x_{\alpha}(0) + \frac{g_{\alpha}}{m_{\alpha} w_{\alpha}} q(0)) \cos(w_{\alpha} t) + \frac{p_{\alpha}(0)}{m_{\alpha} w_{\alpha}} \sin(w_{\alpha} t) \right] : \text{ Random force.}$$

Substituting the above equations in eq. (1.3) we have the **generalized Langevin equation**:

$$\mu \ddot{q} = \frac{dW}{dq} - \int_0^t \dot{q}(\tau) \zeta(t - \tau) d\tau + R(t)$$

Notes:

- In the case of the GLE, we assume that the potential of mean force has been generated by some other means (*see Appendix*) and attempts to model the dynamics of the system on this surface using the friction kernel and the random force to represent the influence of the bath.
- In the context of harmonic bath, the term random force is not quite accurate, since $R(t)$ is completely deterministic. It does not depend on the dynamics of the system coordinate q . In this sense, it is orthogonal to q within the phase space picture. From the explicit form of $R(t)$, it is straightforward that the correlation function

$$\langle \dot{q}(0) R(t) \rangle = 0$$

i.e. the velocity correlation \dot{q} with the random force is 0. The term $R(t)$ is uncorrelated and is determined by the detailed dynamics of the bath. However, it is almost impossible to follow the detailed dynamics of a larger system. Thus, we usually model the $R(t)$ by a completely random process, which we make sure that it satisfies certain desirable features that are characteristic of a more general bath. These random processes are defined by a particular time sequence of random numbers, and a set of related time correlation functions. There is a big variety for someone to choose, always depending on the bath, e.g. for a low density bath, one might try modeling $R(t)$ as a Poisson process of very strong collisions or a Gaussian process for a high density bath. Wherever

the model is chosen for $R(t)$, if it a random process that can only act at discrete points in time, then the GLE takes the form of a stochastic integro-differential equation.

- The convolution integral term $\int_0^t d\tau \dot{q}(\tau) \zeta(t - \tau)$ is called memory integral because it depends, in general, on the entire history of the evolution of q . It expresses the fact that the bath requires a finite time to respond to any fluctuation in the motion of the system. Thus, the force that the bath exerts to the system depends on what the system coordinate q did in the past. However, we expect that what the system did very far in the past will no longer affect the force in the present, i.e. that the lower limit of the memory integral (which is rigorously 0) could be replaced by $t - \bar{t}$, where \bar{t} is the maximum time over which the system coordinate's past behavior affect the system. The correlation time of the random force will determinate the decay time of the memory kernel.

Consider the case that the bath is capable of responding infinitely quickly to changes in the system coordinate q . Then, the bath retains no memory of what the system did in the past, and we could take $\zeta(t) = 2\zeta_0\delta(t)$. Then:

$$\int_0^t d\tau \dot{q}(\tau) \zeta(t - \tau) = \int_0^t d\tau \dot{q}(t - \tau) \zeta(\tau) = 2\zeta_0 \int_0^t d\tau \delta(\tau) \dot{q}(t - \tau) = \zeta_0 \dot{q}(t), \quad (4.1.11)$$

the GLE becomes

$$\mu \ddot{q} = -\frac{dW}{dq} - \zeta_0 \dot{q}(t) + R(t), \quad (4.1.12)$$

which is the Langevin equation. As we can see the Langevin equation we discussed before in section [3.2] is a special case of the more generalized equation of motion.

In the other extreme, where the bath responds extremely slowly to changes in the system coordinate, we may take the the friction kernel to be constant $\zeta \equiv \zeta(0)$, at least for short times compared to the response time of the bath. Then the integral becomes:

$$\int_0^t d\tau \dot{q}(\tau) \zeta(t - \tau) \approx \zeta(q(t) - q(0)), \quad (4.1.13)$$

and the GLE:

$$\mu \ddot{q} = \frac{\partial}{\partial q} \left(\phi(q) + \frac{1}{2} \zeta (q - q_0)^2 \right) + R(t). \quad (4.1.14)$$

Now the friction term manifests itself as an extra harmonic term added to the potential. A term like that has the effect of trapping the system in certain regions of configuration space, an effect known as **dynamic caging**.

- The relation between $R(t)$ and $\zeta(t)$ for a harmonic bath model is

$$\langle R(0)R(t) \rangle = kT\zeta(t), \quad (4.1.15)$$

which is also known as the second fluctuation dissipation theorem.

4.2 Mori-Zwanzig formalism for the derivation of GLE

The Mori-Zwanzig formalism is an effective tool to derive differential equations describing the evolution of a small number of resolved variables. We will use this tool to derive an generalized Langevin equation that can be used to describe any system. We are going to show, that for an arbitrary phase variable, evolving under equations of motion which preserve the equilibrium distribution function, one can always write down a Langevin equation. Our approach will be to work directly with the equation of motion for the relevant variables rather than the one for the probability density function of these variables. Lastly, the derivation presented here, is using the Zwanzig's projection operator, instead of Mori's operator. Using Mori's operator, the derived equation is a linearized generalized Langevin equation for arbitrary systems close to thermal equilibrium. In the other had, Zwanzig's operator, leads to an equation that describes the Brownian motion in nonlinear systems.

For the derivation, we will work within the framework of conventional Hamiltonian dynamics, but we use generalized dynamics, without explicitly distinguish between coordinates and momenta.

We focus on a system determined by a set of system N variables, denoted as $(\mathbf{q}_i, \mathbf{p}_i)$, for $i = 1, \dots, N$. We also denote the vector $\mathbf{u}(t) = (\mathbf{u}_1, \dots, \mathbf{u}_{6N})$, which each component is a set of $(\mathbf{q}_i, \mathbf{p}_i)$. Consider that the Hamiltonian dynamics of the system can be written as:

$$\frac{d\mathbf{u}(t)}{dt} = J \frac{\partial H(\mathbf{u}(t))}{\partial \mathbf{u}}, \quad \mathbf{u}(0) = \mathbf{u}, \quad (4.2.1)$$

where \mathbf{u} denote the initial condition, H is the Hamiltonian of $\mathbf{u}(t)$ and J is a symplectic matrix: $J = (\{0, -1\}, \{1, 0\})$.

We are interested in the evolution of a specific phase variable, denoted by $\mathbf{A}(\mathbf{u}(t))$, where $\mathbf{A}(\mathbf{u}) = (A_1(\mathbf{u}), \dots, A_M(\mathbf{u}))$ is specific observable, i.e. any set of M variables defined on the phase space. Our goal is to calculate the statistical properties of $\mathbf{A}(\mathbf{u}(t))$, for the ensemble of initial conditions $\mathbf{u}(0) = \mathbf{u}$, satisfying $\mathbf{A}(\mathbf{u}) = \alpha$, for some fixed α and with \mathbf{u} distributed according to the equilibrium density $\rho^{eq}\mathbf{u}$ conditional to $\mathbf{A}(\mathbf{u}) = \alpha$.

We first define a time evolution operator $A(\mathbf{u}(t)) \equiv \alpha(t, \mathbf{u})$, such as:

$$\alpha(t, \mathbf{u}) = e^{t\mathcal{L}}\mathbf{A}(\mathbf{u}), \quad (4.2.2)$$

where the exponential operator is defined through its Taylor series expansion and the Liouville operator \mathcal{L} such as

$$\mathcal{L} = -\frac{\partial H}{\partial \mathbf{u}} J \frac{\partial}{\partial \mathbf{u}} \quad (4.2.3)$$

$\alpha(t, \mathbf{u})$ will be a solution of the equation

$$\begin{aligned} \frac{\partial}{\partial t}(\alpha(t, \mathbf{u})) &= \mathcal{L}\alpha(t, \mathbf{u}) \\ \mathbf{A}(0, \mathbf{u}) &= \mathbf{A}(\mathbf{u}). \end{aligned} \quad (4.2.4)$$

Let P be a conditional expectation operator that applies to any function $F(\mathbf{u})$ of phase space

$$PF = \frac{1}{\Omega(\alpha)} \int F(\mathbf{u}) \rho^{eq}(\mathbf{u}) \delta(\mathbf{A}(\mathbf{u}) - \alpha) d\mathbf{u}, \quad (4.2.5)$$

where ρ^{eq} is the equilibrium probability density and $\Omega(\alpha)$ is the probability density of $\mathbf{A}(\mathbf{u})$ defined:

$$\Omega(\alpha) = \int \rho^{eq}(\mathbf{u}) \delta(\mathbf{A}(\mathbf{u}) - \alpha) dz. \quad (4.2.6)$$

The effect of the operator P on an arbitrary function of phase space is to transform it into a function of the relevant variables $A(\mathbf{u})$. We introduce its complementary projection operator $Q = I - P$. The operators satisfy the following properties:

- They are Hermitian and they satisfy:

$$\begin{aligned} P^2 &= P \\ Q^2 &= Q, \end{aligned}$$

- and also, for arbitrary functions $A(\mathbf{u})$, $B(\mathbf{u})$

$$\int dz \rho_N^0 A(\mathbf{u}) P B(\mathbf{u}) = \int dz \rho_N^0 B(\mathbf{u}) P A(\mathbf{u}),$$

Combining $\mathcal{L}\alpha(t, \mathbf{u}) = \mathcal{L}e^{t\mathcal{L}}\mathbf{A} = e^{t\mathcal{L}}\mathcal{L}\mathbf{A}$ with $I = P + Q$, we get the transformed eq.(4.2.4):

$$\partial_t \alpha(t, \mathbf{u}) = e^{t\mathcal{L}} P \mathcal{L} \mathbf{A} + e^{t\mathcal{L}} Q \mathcal{L} \mathbf{A} \quad (4.2.7)$$

Using the Dyson identity (see Appendix) for $e^{t\mathcal{L}}$:

$$e^{t\mathcal{L}} = e^{tQ\mathcal{L}} + \int_0^t d\tau e^{\mathcal{L}(t-\tau)} P \mathcal{L} e^{Q\mathcal{L}\tau}.$$

We apply this identity to the left hand side of 4.2.7:

$$\begin{aligned} \partial_t \alpha(t, \mathbf{u}) &= e^{t\mathcal{L}} P \mathcal{L} \mathbf{A} \\ &+ \int_0^t ds e^{(t-s)\mathcal{L}} P \mathcal{L} \tilde{\mathcal{R}}(s, \cdot) \\ &+ \tilde{\mathcal{R}}(t, \mathbf{u}), \end{aligned} \quad (4.2.8)$$

where $\tilde{\mathcal{R}}(t) = e^{tQ\mathcal{L}} Q \mathcal{L} \mathbf{A}$. The term $\tilde{\mathcal{R}}(s, \cdot)$ depends on the \mathbf{u} only through $\mathbf{A}(\mathbf{u})$. We will simplify the second term of eq.(4.2.8), starting with $P \mathcal{L} \tilde{\mathcal{R}}(s, \cdot)$, which we write component-wise using the indices $\mu, \nu = 1, \dots, M$ to denote the components of \mathbf{A} and α and Einstein sum convention over repeated indices:

$$\begin{aligned}
P\mathcal{L}\tilde{\mathcal{R}}_\mu(s, \cdot) &= \frac{1}{\Omega(\alpha)} \int d\mathbf{u} \rho^{eq}(\mathbf{u}) \delta(\mathbf{A}(\mathbf{u}) - \alpha) \\
&\times \mathcal{L}e^{sQ\mathcal{L}} Q\mathcal{L}\mathbf{A}_{\mu} \\
&= \frac{1}{\Omega(\alpha)} \int d\mathbf{u} \rho^{eq}(\mathbf{u}) [e^{sQ\mathcal{L}} Q\mathcal{L}\mathbf{A}_\mu] \\
&\times \mathcal{L}\delta(\mathbf{A}(\mathbf{u}) - \alpha) \\
&= \frac{1}{\Omega(\alpha)} \int d\mathbf{u} \rho^{eq}(\mathbf{u}) [e^{sQ\mathcal{L}} Q\mathcal{L}\mathbf{A}_\mu] \\
&\times [\mathcal{L}\mathbf{A}_\nu(\mathbf{u})] \frac{\partial}{\partial \alpha_\nu} \delta(\mathbf{A}(\mathbf{u}) - \alpha) \\
&= \frac{1}{\Omega(\alpha)} \frac{\partial}{\partial \alpha_\nu} \int d\mathbf{u} \rho^{eq}(\mathbf{u}) \delta(\mathbf{A}(\mathbf{u}) - \alpha) [\mathcal{L}\mathbf{A}_\nu(\mathbf{u})] \\
&\times [e^{sQ\mathcal{L}} Q\mathcal{L}\mathbf{A}_\mu] [\mathcal{L}\mathbf{A}_\nu(\mathbf{u})] \\
&= \frac{1}{\Omega(\alpha)} \frac{\partial}{\partial \alpha_\nu} \left(\Omega(\alpha) P([e^{sQ\mathcal{L}} Q\mathcal{L}\mathbf{A}_\mu] [\mathcal{L}\mathbf{A}_\nu]) \right) \\
&= M_{\mu\nu} \frac{\partial S(\alpha)}{\partial \alpha_{\mu\nu}} + k_B \frac{\partial M_{\mu\nu}(\alpha, s)}{\partial \alpha_\nu}, \tag{4.2.9}
\end{aligned}$$

where as $S(\alpha) = k_B \ln \Omega(\alpha)$ we denote the entropy and as $M_{\mu\nu}(\alpha, t)$ we denote the memory matrix, whose components are given by the following conditional expectation:

$$M_{\mu\nu}(\alpha, t) = \frac{1}{k_B} P([\mathcal{L}\mathbf{A}_\nu] [e^{tQ\mathcal{L}} Q\mathcal{L}\mathbf{A}_\mu]) \tag{4.2.10}$$

$$= \frac{1}{k_B} P(\tilde{\mathcal{R}}_\mu(t, \cdot) \tilde{\mathcal{R}}_\nu(0, \cdot)) \tag{4.2.11}$$

We substitute the eq. (4.2.9) in eq(4.2.8) and we use the property $e^{t\mathcal{L}} f(\mathbf{A}(\mathbf{u})) = f(\alpha(t, \mathbf{u}))$, to get the following simplified equations for the terms that form eq. (4.2.8):

$$\begin{aligned}
e^{t\mathcal{L}} P\mathcal{L}\mathbf{A}(\mathbf{u}) &= P\mathcal{L}\mathbf{A}(\mathbf{u}), \\
e^{(t-s)\mathcal{L}} M(\mathbf{A}(\mathbf{u}), s) \frac{\partial S(\mathbf{A}(\mathbf{u}))}{\partial \alpha} &= M(\alpha(t-s, \mathbf{u}), s) \frac{\partial S(\alpha(t-s, \mathbf{u}))}{\partial \alpha}, \\
e^{(t-s)\mathcal{L}} k_B \frac{\partial M(\mathbf{A}(\mathbf{u}), s)}{\partial \alpha} &= k_B \frac{\partial M(\alpha(t-s, \mathbf{u}), s)}{\partial \alpha},
\end{aligned}$$

and so we have a more simplified version of eq.4.2.8:

$$\begin{aligned} \partial_t \alpha(t, \mathbf{u}) &= \mathbf{v}(\alpha(t, \mathbf{u})) + \int_0^t ds M(\mathbf{A}(t-s, \mathbf{u}), s) \frac{\partial S}{\partial \alpha}(A(t-s, \mathbf{u})) \\ &+ k_B \int_0^t ds \frac{\partial M}{\partial \alpha}(\alpha(t-s, \mathbf{u}), s) + \tilde{\mathcal{R}}(t, \mathbf{u}), \end{aligned} \quad (4.2.12)$$

where $\mathbf{v}(\alpha)$ is defined as the conditional expectation $\mathbf{v}(\alpha) = P\mathcal{L}\mathbf{A}$.

We are not interested on solving the equation 4.2.12 for a specific initial condition, but rather for an ensemble of initial conditions \mathbf{u} satisfying $\alpha(0, \mathbf{u}) = \mathbf{A}(\mathbf{u}) = \alpha(0)$ for some fixed $\alpha(0)$ and \mathbf{u} distributed according to the equilibrium density $\rho^{eq}(\mathbf{u})$ conditional on $\mathbf{A}(\mathbf{u}) = \alpha(0)$. The only term of eq.(4.2.12) that does not involves the function $\alpha(t, \mathbf{u})$ is $\tilde{\mathcal{R}}(t, \mathbf{u})$, and so this term is interpreted as noise term, whose statistics must be consistent with the equation of the memory matrix. With that in mind, let $\alpha(t, \mathbf{u}) = \alpha(t)$, and rewrite the eq.(4.2.12) as an integro-differential equation, which contain a random term:

$$\begin{aligned} \frac{d\alpha(t)}{dt} &= \mathbf{v}(\alpha(t)) + \int_0^t ds M(\alpha(t-s), s) \frac{\partial S}{\partial \alpha}(\alpha(t-s)) \\ &+ k_b \int_0^t ds \frac{\partial M}{\partial \alpha}(\alpha(t-s), s) + \mathbf{R}(t), \end{aligned} \quad (4.2.13)$$

where $\mathbf{R}(t)$ is a zero-mean random process, which follows the statistics that we specified previously for $\tilde{\mathcal{R}}$, i.e. we want \mathbf{u} to be distributed according to the equilibrium density $\rho^{eq}(\mathbf{u})$ conditional on $\mathbf{A}(\mathbf{u}) = \alpha(0)$.

The eq.(4.2.13) is the generalized Langevin equation. This equation has been derived without placing restriction on the properties of the systems, in particular, its equation of motion may be arbitrarily nonlinear. It is been made to describe the motion of a system interacting with a heat bath, which is basically a collection of harmonic oscillators.

4.3 Markovian approximation and the Fokker-Planck Equation

The GLE (4.2.13) derived in the previous section, is an exact and rigorous closed equation. No approximations needed to be made for its derivation and, essentially,

it is another way of rewriting the Liouville equation. Unfortunately, the GLE is rather useless as practical computational tool. Although, the terms $\mathbf{v}(\alpha)$ and the gradient $\partial S/\partial\alpha$ are conditional expectations that could be calculated using constrained dynamics, the memory term $M(\alpha, t)$ and the noise term $\mathbf{R}(t)$ is impossible to compute efficiently as they are, since they involve the projected dynamics associated with $Q\mathcal{L}$, which is not possible to generate. Moreover, the process $\mathbf{R}(t)$ is non-Gaussian in general, i.e. it is not specified completely by its correlation function. But even if we knew how to calculate $M(\alpha, t)$ and the full statistics of $R(t)$, the GLE (4.2.13) would remain very challenging to integrate numerically, because of its non-Markovian character. One, widely used, approach to overcome the non-Markovian character of the GLE, is the so called *Markovian approximation* that transforms the integro-differential equation into a Fokker-Planck equation.

The Markovian approximation is about the separation of time scales between the time scale of evolution of the phase variable $\mathbf{A}(\mathbf{u})$ and the rest of the variables of the system. Assume that the time scale of variation of the relevant variables is larger than the time scale in which memory kernel $M(\alpha, t)$ decays. Then, we write the memory term (4.2.10) as:

$$M(\alpha, t) \approx \tilde{\mathcal{M}}(\alpha)\delta(t), \quad (4.3.1)$$

where the time-independent matrix $\tilde{\mathcal{M}}(\alpha)$ is defined as:

$$\tilde{\mathcal{M}}(\alpha) = \int_0^T dt M(\alpha, t) = \int_0^T P(\tilde{\mathcal{R}}(t, \cdot) \otimes \tilde{\mathcal{R}}(0, \cdot)) \quad (4.3.2)$$

This approximation, basically, extend the upper limit of the integration to a time T sufficiently large for the memory kernel $M(t)$ to have decayed. According to the (4.3.1), the random term $\mathbf{R}(t)$ in 4.2.13 could now be modeled as a white-noise, i.e. a Gaussian process with mean zero and whose correlation at $\alpha(t) = \alpha$:

$$\langle \mathbf{R}(t) \otimes \mathbf{R}(s) \rangle = k_B \tilde{\mathcal{M}}(\alpha) \delta(t - s). \quad (4.3.3)$$

Under these assumption, in can be shown that the GLE becomes the stochastic differential equation:

$$\frac{d\alpha(t)}{dt} = \mathbf{v}(\alpha(t)) + \tilde{\mathcal{M}}(\alpha(t)) \frac{\partial A}{\partial \alpha}(\alpha(t)) + k_B \frac{\partial \tilde{\mathcal{M}}}{\partial \alpha}(\alpha(t)) + R(t). \quad (4.3.4)$$

Finally, we have to show the how to calculate the memory matrix. Assume that the projected dynamics $e^{tQ\mathcal{L}}$ can be replaced by the real dynamics $e^{t\mathcal{L}}$, i.e.:

$$\begin{aligned}\tilde{\mathcal{R}}(t, \mathbf{u}) &\approx e^{t\mathcal{L}}Q\mathcal{L} \\ &= \mathcal{L}\mathbf{A}(\mathbf{u}(t)) - \mathbf{v}(\alpha(t)),\end{aligned}\tag{4.3.5}$$

where $\mathbf{v}(\alpha)$ is defined as previously, $\mathbf{u}(t)$ is the solution of the original Hamiltonian, and by the short hand notation, we write $\alpha(t) = \alpha(t, \mathbf{u})$. Equation (4.3.5) can be computed using a combination of standard MD simulations, in order to compute $\mathbf{u}(t)$, and constrained molecular simulation, to compute $\mathbf{v}(\alpha)$.

Equation 4.3.4 is the Fokker-Planck equation (FPE) for the mesoscopic coarse-grained level of description and it is mathematically equivalent to the GLE (4.2.13). All of the terms of this equation ($\mathbf{v}, \tilde{\mathcal{M}}, \mathbf{R}$), have a definite microscopic definition. The FPE is valid whenever there is a clear separation of time scales such that the Markovian approximation is valid. Specifically, it is efficient for short times, when the time integrals in eq. 4.2.8 can be neglected. There is no guarantee for the justification of the FPE in times that extend further than the integration limit T . In fact, if we extend T to infinity, then the integral vanishes. This is called the *plateau problem*, and it is usually treated by selecting a time T to be large compared to the correlation time of the orthogonal dynamics, but small enough compared to the time scale of evolution of the macroscopic variables. Although, in theory, this solution for the plateau problem seems easy, in practice, it is difficult to predict a value for T so that the T -depending results would be correct.

4.4 Modified dynamics approximation

Kinjo and Hyodo [8] and Hijón et al. [7], proposed an application for the Mori-Zwanzing operators that will transform the equations of motion for the dynamics of the mesoscopic variables, with an explicit relationship to the mesoscopic description, and that will make the GLE manageable. Here, we follow the method proposed by Hijón et al.

Consider a change of variables $s = \epsilon^2\tau$, where ϵ is a non-dimensional control parameter. By substituting into time integrals in the GLE (4.2.13), we get:

$$\begin{aligned}\frac{d\alpha(t)}{dt} &= \mathbf{v}(\alpha(t)) + \epsilon^2 \int_0^t d\tau M(\alpha(t - \epsilon^2\tau)) \frac{\partial S}{\partial \alpha(t - \epsilon^2\tau)} \\ &+ \epsilon^2 k_B \int_0^t d\tau \frac{\partial M}{\partial \alpha}(\alpha(t - \epsilon^2\tau), \epsilon^2\tau) + \mathbf{R}(t).\end{aligned}\tag{4.4.1}$$

If the following limit exists

$$\lim_{\epsilon \rightarrow 0} \epsilon^2 M(\alpha(t - \epsilon^2 \tau), \epsilon^2 \tau) \equiv m(\alpha(t), \tau), \quad (4.4.2)$$

and by taking the limit $\lim_{\epsilon \rightarrow 0}$ of eq. (4.4.1), we get the stochastic differential equation:

$$\begin{aligned} \frac{d\alpha(t)}{dt} &= \mathbf{v}(\alpha(t)) + \bar{M}(\alpha(t)) \frac{\partial S}{\partial \alpha}(\alpha(t)) \\ &+ k_B \frac{\partial \bar{M}}{\partial \alpha}(\alpha(t)) + \bar{\mathbf{R}}(t) \end{aligned} \quad (4.4.3)$$

with fiction matrix:

$$\bar{M}(\alpha) = \int_0^\infty m(\alpha, \tau) d\tau,$$

random term correlation at $\alpha(t) = \alpha$:

$$\langle \mathbf{R}(t) \mathbf{R}(s) \rangle = k_B \bar{M}(\alpha) \delta(t - s)$$

Note that the random term $\bar{\mathbf{R}}(t)$ is a Gaussian process with mean zero.

To justify the approximation, we have to specify under which conditions the limit in eq. 4.4.2 exists. To take an idea of how the operators must be so that the limit exists, we firstly substitute in the formalistic obtained equation of memory kernel (4.2.10), for $\alpha(t, \mathbf{u}) = \alpha(t - \epsilon^2 \tau, \mathbf{u})$, $t = \epsilon^2 \tau$, and we get the following:

$$\epsilon^2 M(\alpha(t - \epsilon^2 \tau, \mathbf{u}), \epsilon^2 \tau) = \frac{\epsilon^2}{k_B} P_{\alpha(t - \epsilon^2 \tau, \mathbf{u})} ([e^{\epsilon^2 \tau Q \mathcal{L} \mathbf{A}} Q \mathcal{L} \mathbf{A}] \otimes [Q \mathcal{L} \mathbf{A}]). \quad (4.4.4)$$

We can assume now, that the Liouville operator has the following form:

$$\mathcal{L} = \mathcal{L}_0 + \frac{1}{\epsilon} \mathcal{L}_1 + \frac{1}{\epsilon^2} \mathcal{L}_2, \quad (4.4.5)$$

We want the operators \mathcal{L}_1 and \mathcal{L}_2 must satisfy:

$$\begin{aligned} P \mathcal{L}_2 &= 0 \\ P \mathcal{L}_1 P &= 0, \end{aligned} \quad (4.4.6)$$

and indeed, the eq. 4.4.4 becomes:

$$\epsilon^2 M(\alpha(t - \epsilon^2 \tau, \mathbf{u}), \epsilon^2 \tau) = \frac{1}{k_B} P_{\alpha(t)}([e^{\tau \mathcal{L}_2} \mathcal{L}_1 \mathbf{A}] \otimes [\mathcal{L}_1 \mathbf{A}]) + \mathcal{O}(\epsilon). \quad (4.4.7)$$

Finally, the equation of the memory kernel, when $\epsilon \rightarrow 0$ is given by:

$$\bar{M}(\alpha) = \frac{1}{k_B} \int_0^\infty d\tau P_{\alpha(t)}([e^{\tau \mathcal{L}_2} \mathcal{L}_1 \mathbf{A}] \otimes [\mathcal{L}_1 \mathbf{A}]), \quad (4.4.8)$$

and the drift term is given by:

$$\mathbf{v}(\alpha) = P_\alpha(\mathcal{L}_0 \mathbf{A}). \quad (4.4.9)$$

Until this point, the derivation is quite heuristic. It can be shown that under a suitable ergodicity assumption of the dynamics associated with the operator \mathcal{L}_2 , eq.(4.4.3) captures exactly the dynamics $\mathbf{A}(\mathbf{u}(t))$ at the limit as $\epsilon \rightarrow 0$. This derivation also explains why the noise term $\bar{\mathbf{R}}(t)$ in eq.(4.4.3) is indeed a white-noise to be interpreted in Itô sense. Moreover, it proves that the integral in eq. (4.4.8) converges nicely to a value such as the dynamics associated with \mathcal{L}_2 is mixing sufficiently fast besides being ergodic. As a result of the converge, the matrix $\bar{M}(t)$ does not appear to have the plateau problem.

For a general selection of the relevant variables, it is not a priori clear how to derive eq. 4.4.3, mainly because the Liouville operators does not always have the form we saw above. Its is always possible to decompose the Liouville operator as $\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_1 + \mathcal{L}_2$ (see Appendix for details). We define

$$\begin{aligned} \mathcal{L}_0 &= P(\mathcal{L} - \mathcal{R}) \\ \mathcal{L}_1 &= Q(\mathcal{L} - \mathcal{R}) \\ \mathcal{L}_2 &= \mathcal{R}, \end{aligned} \quad (4.4.10)$$

where P is the expectation with respect to the equilibrium distribution associated with the operator \mathcal{R} . We expecting that the operator \mathcal{R} will leave the Hamiltonian and the relevant variables invariant

$$\begin{aligned} \mathcal{R}f(H(\mathbf{u})) &= 0 \\ \mathcal{R}g(\mathbf{A}(\mathbf{u})) &= 0 \end{aligned}$$

for arbitrary functions f, g . We have construct the operator $\mathcal{L}_0, \mathcal{L}_1, \mathcal{L}_2$ so they satisfy the properties in (4.4.6). Consider a modified dynamics operator \mathcal{L}^ϵ as in (4.4.5)

$$\mathcal{L}^\epsilon \equiv \mathcal{L}_0 + \frac{1}{\epsilon} \mathcal{L}_1 + \frac{1}{\epsilon^2} \mathcal{L}_2.$$

In case $\epsilon = 1$, the dynamics associated with \mathcal{L}^ϵ concurs with the real dynamics of the system. Inserting the operators defined at (4.4.10) into eq. (4.4.8), we get

$$\begin{aligned} \mathbf{v}(\alpha) &= P(\mathcal{L}\mathbf{A}), \\ \bar{M}(\alpha) &= \frac{1}{k_B} \int_0^\infty d\tau P([e^{\tau\mathcal{R}}\mathcal{L}\mathbf{A}] \otimes [\mathcal{L}\mathbf{A}]). \end{aligned} \quad (4.4.11)$$

The projected dynamics in the equation above are approximated by $e^{t\mathcal{L}_2} \equiv e^{t\mathcal{R}}$, instead of the $e^{tQ\mathcal{L}}$ projected dynamics we saw in previously. We can state, that eq. (4.4.11) is explicit and practical to use to compute constrained averages. In the next section, we will see how the operators \mathcal{R} can be specified, under the assumption that the $\mathbf{A}(\mathbf{u})$ is a linear function of the relevant variables.

Finally, we want to define the conditional expectations in eq. 4.4.11. Assume that the constrained dynamics are ergodic. The constrained trajectory with initial condition is denoted $\mathbf{u}_{\mathcal{R}}(t) = e^{t\mathcal{R}\mathbf{u}}$, with initial condition $\mathbf{u}_{\mathcal{R}}(0) = \mathbf{u}$, with \mathbf{u} such that $\mathbf{A}(\mathbf{u}) = \alpha$ and $H(\mathbf{u}) = E$. Under these assumptions, the conditional expectations are given by the expressions:

$$P\mathcal{L}\mathbf{A} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt \mathcal{L}\mathbf{A}(\mathbf{u}_{\mathcal{R}}(t)) \quad (4.4.12)$$

$$\begin{aligned} \bar{M}(\alpha) &= \lim_{T' \rightarrow \infty} \frac{1}{k_B} \int_0^{T'} dt' \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt \\ &\times [\mathcal{L}\mathbf{A}(\mathbf{u}_{\mathcal{R}}(t+t'))] \otimes [\mathcal{L}\mathbf{A}(\mathbf{u}_{\mathcal{R}}(t))]. \end{aligned} \quad (4.4.13)$$

To approximate the limits in the expressions above, let T and T' grow big enough so the equations (4.4.12) and (4.4.13) do not suffer from the plateau problem.

To sum up the procedure described in this section, we derived an SDE equation (4.4.3) that reproduce the dynamics of relevant variables. Then we replace \mathcal{L} by \mathcal{L}^ϵ and let $\epsilon \rightarrow 0$, so the coefficients in eq. (4.4.3) are given explicitly by (4.4.12) and (4.4.13). The disadvantage of this method, is that we end up modeling the original system by a approximated equation,, whose dynamics are associated with \mathcal{L}^ϵ rather that with \mathcal{L} . For this approximation to be valid, the real dynamics \mathcal{L} and the projected dynamics \mathcal{R} must be similar, i.e. the relevant variables $\mathbf{A}(\mathbf{u})$ have to be comparatively slow.

Chapter 5

Coarse-graining of complex systems

To demonstrate the coarse-graining procedure we discussed so far, we consider a collection of big molecules, described only by the variables of their center of mass (CoM). The method can be applied to a large extent on any molecule, provided that they are made of many atoms and they are isotropic. For non-isotropic molecules, further orientation information may be required in addition to the CoM variables.

5.1 Derivation of Coarse-Grained equations of motion

Consider a fluid system, composed by M molecules and each molecule contains N_m atoms, whose coordinates and momenta are denoted as \mathbf{r}_{i_μ} and \mathbf{p}_{i_μ} respectively. Greek indexes denote the molecules and so $i_\mu \in 1, \dots, N_m$ while the index $\mu \in 1, \dots, M$.

We will start from an microscopic N_μ -particle particle system, the Hamiltonian of which is written as follows

$$\begin{aligned} H &= K + U \\ K &= \sum_{\mu=1}^M \sum_{i_\mu=1}^{N_m} \frac{\mathbf{p}_{i_\mu}^2}{2m_{i_\mu}} \\ U &\equiv \phi(\mathbf{r}_{i_\mu}). \end{aligned}$$

We denote the phase-space coordinate of the system as $\hat{\Gamma} \equiv \{\hat{\mathbf{r}}_{i_\mu}(t), \hat{\mathbf{p}}_{i_\mu}(t)\}$ and Γ the corresponding field variables. Then the phase-space density for all atoms is given by

$$\Omega(\hat{\Gamma}(t); \Gamma) \equiv \delta(\hat{\Gamma}(t) - \Gamma) \equiv \prod_{\mu, i} \delta[\hat{\mathbf{r}}_{i_\mu}(t) - \mathbf{r}_{i_\mu}] \delta[\hat{\mathbf{p}}_{i_\mu}(t) - \mathbf{p}_{i_\mu}] \quad (5.1.1)$$

which is a generalization of the phase-space density appearing in the kinetic theory for dilute and moderately dense gases.

Consider a description of the system by coordinates and momenta of the CoM of the coarse-grained particles can be employed

$$\mathbf{R}_\mu(\mathbf{r}) \equiv \frac{1}{M_\mu} \sum_{i_\mu=1}^{N_m} m_{i_\mu} \hat{\mathbf{r}}_{i_\mu} \quad (5.1.2)$$

$$\mathbf{P}_\mu(\mathbf{p}) \equiv \sum_{i_\mu=1}^{N_m} \hat{\mathbf{p}}_{i_\mu}, \quad (5.1.3)$$

where $\mathbf{M}_\mu = \sum_{i_\mu=1}^{N_m} \mathbf{m}_{i_\mu}$ is the total mass of the molecule μ . For the description by $\hat{\Gamma}_s(t) \equiv \{\mathbf{R}_\mu, \mathbf{P}_\mu\}$, we also define the phase-space density for the CoMs,

$$\begin{aligned} \Omega_s(\hat{\Gamma}_s(t); \Gamma_s) &\equiv \delta(\hat{\Gamma}_s(t) - \Gamma_s) \\ &\equiv \prod_{\mu} \delta(\hat{\mathbf{R}}_\mu(t) - \mathbf{R}_\mu) \delta(\hat{\mathbf{P}}_\mu(t) - \mathbf{P}_\mu). \end{aligned} \quad (5.1.4)$$

The phase-space of the atomistic coordinates and the CoM coordinates are referred to as Γ space and Γ_s space, respectively. The phase-space density $\Omega(\hat{\Gamma}_s(t); \Gamma_s)$ depend on t via the phase point $\{\hat{\mathbf{r}}_{i_\mu}(t), \hat{\mathbf{p}}_{i_\mu}(t)\}$. The motion of them is determined by Hamilton's equation. Hence, the time evolution of Ω along the trajectory in the Γ space is written as:

$$\begin{aligned} \left(\frac{d}{dt}\right)_\Gamma \Omega_s &= - \sum_{\mu} \sum_{i_\mu} \left\{ \frac{\partial H}{\partial \hat{\mathbf{r}}_{i_\mu}} \cdot \frac{\partial}{\partial \hat{\mathbf{p}}_{i_\mu}} - \frac{\partial H}{\partial \hat{\mathbf{p}}_{i_\mu}} \right\} \Omega_s \\ &= \sum_{\mu} \left\{ \hat{F}_\mu \cdot \frac{\partial}{\partial \hat{\mathbf{P}}_\mu} + \frac{\hat{\mathbf{P}}_\mu}{\mathbf{M}_\mu} \cdot \frac{\partial}{\partial \hat{\mathbf{R}}_\mu} \right\} \Omega_s \\ &= - \sum_{\mu} \left\{ \hat{F}_\mu \cdot \frac{\partial}{\partial \mathbf{P}_{\mu u}} + \frac{\hat{\mathbf{P}}_\mu}{\mathbf{M}_\mu} \cdot \frac{\partial}{\partial \mathbf{R}_\mu} \right\} \Omega \equiv \mathcal{L}_s \Omega_s, \end{aligned}$$

where

$$\hat{\mathbf{F}}_{i_\mu} \equiv -\frac{\partial\phi}{\partial\mathbf{r}_{i_\mu}}. \quad (5.1.5)$$

is the sum of the force acting on atoms belonging to a coarse-grained particle μ . The Liouville operator in the Γ_s space is defined as

$$\mathcal{L}_s = -\sum_{\mu} \left\{ \hat{\mathbf{F}}_{\mu} \cdot \frac{\partial}{\partial\mathbf{P}_{\mu}} + \frac{\hat{\mathbf{P}}_{\mu}}{\mathbf{M}_{\mu}} \cdot \frac{\partial}{\partial\mathbf{R}_{\mu}} \right\}$$

The equilibrium distribution function is define as $\rho(\Gamma_s) = e^{-\beta H}$, where H is the Hamiltonian.

We have already define the projection operator P in eq.(4.2.5). In a similar way, we can an expression for the projection opetor P for an arbitrary phase function $G(\hat{\Gamma}(t))$ onto the Γ_s space.

We want to introduce a Hilbert space representation, with scalar point defined as:

$$(A, B) \equiv \langle A(\hat{\Gamma})B(\hat{\Gamma}) \rangle = \int d\hat{\Gamma} A(\hat{\Gamma})B(\hat{\Gamma})\rho^{eq}(\hat{\Gamma}), \quad (5.1.6)$$

where $\rho(\hat{\Gamma}) = e^{\beta H/Z}$ is the equilibrium function. Consider the arbitrary phase function $G(\hat{\Gamma}(t))$, which we devide in two parts, such as

$$G(\hat{\Gamma}(t)) = G_P(\hat{\Gamma}(t)) + G_Q(\hat{\Gamma}(t)). \quad (5.1.7)$$

Assume that $G_P(\hat{\Gamma})$ can be expanded by a "basis set" $\{\Omega_s(\hat{\Gamma}_s(t_0); \hat{\Gamma}_s)\}$ as follows:

$$G(\hat{\Gamma}(t)) = \int d\Gamma'_s C(\Gamma'_s)\Omega_s(\hat{\Gamma}_s(t_0); \Gamma'_s), \quad (5.1.8)$$

where $C(\Gamma'_s)$ is the expansion coefficient. By taking the scalar product of both sides of the above equation with $\Omega_s(\hat{\Gamma}_s(t_0); \Gamma'_s)$, we obtain the coefficient in the form

$$\begin{aligned} C(\Gamma'_s) &= \int d\Gamma_s \langle \Omega_s(\hat{\Gamma}_s(t_0); \Gamma_s) g_P(\Omega_s(\hat{\Gamma}(t))) \rangle \\ &\times \langle \Omega_s(\hat{\Gamma}_s(t_0); \Gamma_s) \Omega_s(\hat{\Gamma}_s(t_0); \Gamma_s)^{-1} \rangle. \end{aligned} \quad (5.1.9)$$

Substituting the expansion coeeficient and using the assumption

$$\langle \Omega_s(\hat{\Gamma}_s(t_0); \Gamma_s) = 0 \rangle,$$

yields the desired operator P :

$$\begin{aligned}
PG(\hat{\Gamma}(t)) \equiv G_P(\hat{\Gamma}(t)) &= \int d\Gamma'_s \int d\Gamma''_s \Omega_s(\hat{\Gamma}(t_0); \Gamma'_s) \\
&\times \langle \Omega_s(\hat{\Gamma}_s(t_0); \Gamma'_s) \Omega_s(\hat{\Gamma}_s(t_0); \Gamma''_s) \rangle^{-1} \\
&\times \langle \Omega_s(\hat{\Gamma}_s(t_0); \Gamma''_s) G(\hat{\Gamma}(t)) \rangle. \tag{5.1.10}
\end{aligned}$$

The resultant operator $PG(\hat{\Gamma}(t))$ depends only on the $\hat{\Gamma}(t)$ explicitly. Following now the same procedure as in *Section 4.1*, we now can find the SDE for the CoM.

So, the entropy of the system expressed using the CG relevant variables, is given by:

$$\begin{aligned}
S(\Gamma_s) &\equiv S(\mathbf{R}, \mathbf{P}) = k_B \ln \Omega_s(\hat{\Gamma}_s(t); \Gamma_s) \\
S(\mathbf{R}, \mathbf{P}) &= k_B \ln \int d\Gamma_s \frac{1}{Z} e^{-\beta H} \\
&\times \prod_{\mu} \delta(\hat{\mathbf{R}}_{\mu}(t) - \mathbf{R}_{\mu}) \delta(\hat{\mathbf{P}}_{\mu}(t) - \mathbf{P}_{\mu}). \tag{5.1.11}
\end{aligned}$$

The momentum integrals involved in the entropy function can be performed explicitly with the result

$$S(\mathbf{R}, \mathbf{P}) = S_0 - \frac{1}{T} V \mathbf{R}_{\mu} - \frac{1}{T} \sum_{\mu} \frac{|\mathbf{P}_{\mu}|^2}{2M_{\mu}}.$$

where S_0 is a constant, and $V(\mathbf{R})$ an effective potential defined as

$$\begin{aligned}
V(\mathbf{R}) &\equiv -k_B \ln \left[\int d\Gamma_s \frac{1}{Z} e^{\beta \phi(\mathbf{u})} \right. \\
&\quad \left. \prod_{\mu} \delta(\mathbf{R}_{\mu}(\mathbf{u}) - \mathbf{R}_{\mu}) \right], \tag{5.1.12}
\end{aligned}$$

which satisfies: $-\frac{\partial V}{\partial \mathbf{R}_{\mu}} = \langle \mathbf{F}_{\mu} \rangle$. Eq. (4.4.3) can be written:

$$\begin{aligned}
\frac{d\mathbf{R}_{\mu}}{dt} &= \frac{\mathbf{P}_{\mu}}{M_{\mu}} \\
\frac{d\mathbf{P}_{\mu}}{dt} &= \langle \mathbf{F}_{\mu} \rangle + T \gamma_{\mu\nu} \frac{\partial S}{\partial \mathbf{P}_{\nu}} + k_B T \frac{\partial \gamma_{\mu\nu}}{\partial \mathbf{P}_{\nu}} + \tilde{\mathbf{F}}_i. \tag{5.1.13}
\end{aligned}$$

The friction tensor is defined as

$$\gamma_{\mu\nu}(\mathbf{R}, \mathbf{P}) = \frac{1}{k_B T} \int_0^\infty dt \langle \delta \mathbf{F}_\mu e^{t\mathcal{R}} \delta \mathbf{F}_\nu \rangle, \quad (5.1.14)$$

where $\delta \mathbf{F}_\mu = \mathbf{F}_\mu - \langle \mathbf{F}_\mu \rangle$ and \mathbf{F}_μ is the total force acting on the molecule μ , such as

$$\mathbf{F}_\mu = \sum_\nu \mathbf{F}_{\mu\nu} \equiv \sum_\nu \sum_{i_\mu j_\nu} \mathbf{F}_{i_\mu j_\nu}. \quad (5.1.15)$$

$\mathbf{F}_{i_\mu j_\nu}$ is the force that the atom j_ν exerts on the atom i_μ and $\mathbf{F}_{\mu\nu}$ is the total force that molecule ν exerts on molecule μ .

Now using the latter equation for the entropy, the equations for the evolution of the relevant variables (5.1.13), and Newton's third law stating $\sum_\nu \mathbf{F}_\nu = 0$, we get

$$\frac{d\mathbf{R}_\mu}{dt} = \frac{\mathbf{P}_\mu}{m_\mu} \quad (5.1.16)$$

$$\frac{d\mathbf{P}_\mu}{dt} = \langle \mathbf{F}_\mu \rangle - \gamma_{\mu\nu} \frac{\mathbf{P}_\nu}{M_\nu} + k_B T \frac{\partial \gamma_{\mu\nu}}{\partial \mathbf{P}_\nu} + \tilde{\mathbf{F}}_\mu. \quad (5.1.17)$$

Using equations (5.1.14), (5.1.15) and (5.1.17) we get the following SDE for the CoM provided by Zwanzig projection theory

$$\frac{d\mathbf{R}_\mu}{dt} = \frac{\mathbf{P}_\mu}{m_\mu} \quad (5.1.18)$$

$$\begin{aligned} \frac{d\mathbf{P}_\mu}{dt} &= \langle \mathbf{F}_\mu \rangle + \sum_\nu \gamma_{\mu\nu} (\mathbf{P}_\mu / M_\mu - \mathbf{P}_\nu / M_\nu) \\ &+ k_B T \sum_\nu \frac{\partial \gamma_{\mu\nu}}{\partial \mathbf{P}_\nu} + \tilde{\mathbf{F}}_\mu, \end{aligned} \quad (5.1.19)$$

where $\tilde{\mathbf{F}}_\mu$ is the stochastic force expressed as the sum of independent Wiener processes:

$$\tilde{\mathbf{F}}_\mu dt = \sum_\nu B_{\mu\nu} dW_\nu, \quad (5.1.20)$$

combined with the relation

$$B_{\mu\lambda} B_{\nu\lambda} = 2k_B T \gamma_{\mu\nu}, \quad (5.1.21)$$

this equations form the Fluctuation-Dissipation theorem for this problem. The eq. (5.1.18) resemble the standard DPD equations. The difference between the equations

we derived from the Mori-Zwanzig theory (MZ-DPD) and the standard DPD, which we talked in previous section, is that the effective potential $\langle \mathbf{F}_{\mu\nu} \rangle$ and the friction tensor $\gamma_{\mu\nu}(\mathbf{R}, \mathbf{P})$ depend, on principle, on the CoM variables of all the molecules in the system, and not only in the $\mathbf{R}_\mu - \mathbf{R}_\nu$ as in the standard DPD model.

The constrained dynamics \mathcal{R} can not be written simply by:

$$\begin{aligned} \frac{\partial \mathbf{r}_{i_\mu}}{\partial t} &= \mathbf{v}_{i_\mu} - \mathbf{V}_\mu \\ \frac{\partial \mathbf{p}_{i_\mu}}{\partial t} &= \mathbf{F}_{i_\mu} - \frac{m_{i_\mu}}{M_\mu} \mathbf{F}_\mu, \end{aligned}$$

that satisfies $\frac{\partial \mathbf{R}_{i_\mu}}{\partial t} = 0$ and $\frac{\partial \mathbf{P}_{i_\mu}}{\partial t} = 0$. It is important to note that for the derivation, we have to make two approximations:

- the Markovian approximation, i.e. forces between molecules will decorrelate much faster than the molecules velocities ($\tau_f \ll \tau_v$),
- the pairwise additive approximation, i.e. we construct a model of pair-wise interactions of atoms, in which the many-atomic interactions are effectively taken into account.

5.2 Application of the Mori-Zwanzig DPD model on complex systems

As an application, we consider a system of star polymers that form a polymer melt. The molecule of a star polymer consists of discrete monomers, so we can assume that the total force \mathbf{F}_{ij} between two clusters i and j is generally not parallel to the radial vector \mathbf{e}_{ij} , which is directed along center-to-center from j to i .

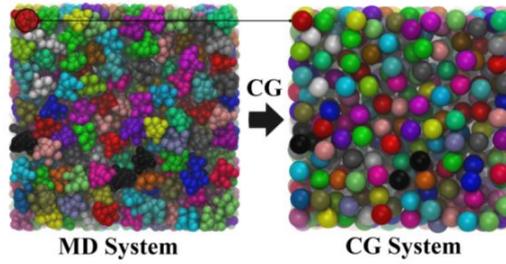


Figure 5.1: A MD system of star polymers melts projected into a corresponding coarse-grained system, in which the entire molecule of a star polymer in the MD system is coarsened into a single coarse-grained particle. [9]

The MZ-DPD system includes the dissipative and random forces in the direction along the perpendicular velocity component. The equation of motion governing the MZ-DPD system is given by:

$$\begin{aligned}
 \sum_{i \neq j} F_{\mu\nu} &= \langle \mathbf{F}_{\mu\nu} \cdot \mathbf{e}_{\mu\nu} \rangle \mathbf{e}_{\mu\nu} \\
 &- \sum_{i \neq j} \gamma_{\parallel}(R_{\mu\nu}) (\mathbf{e}_{\mu\nu} \cdot \mathbf{V}_{\mu\nu}) \mathbf{e}_{\mu\nu} \\
 &- \sum_{i \neq j} \gamma_{\perp}(R_{\mu\nu}) [\mathbf{V}_{\mu\nu} - (\mathbf{e}_{\mu\nu} \cdot \mathbf{V}_{\mu\nu}) \mathbf{e}_{\mu\nu}] \\
 &- (2k_B T)^{1/2} \left(\alpha(R_{\mu\nu}) d\bar{W}_{\mu\nu}^S + b(R_{\mu\nu}) \frac{\text{tr}[d\bar{W}_{\mu\nu}^S]}{3} \right), \quad (5.2.1)
 \end{aligned}$$

where:

$$\gamma_{\parallel} = -\frac{1}{k_B T} \int_0^{\infty} dt \langle (\delta \mathbf{F}_i(t) \cdot \mathbf{e}_{\mu\nu}^{\parallel}) (\delta \mathbf{F}_\nu(0) \cdot \mathbf{e}_{\mu\nu}^{\parallel}) \rangle \quad (5.2.2)$$

$$\gamma_{\perp} = -\frac{1}{k_B T} \int_0^{\infty} dt \langle (\delta \mathbf{F}_i(t) \cdot \mathbf{e}_{\mu\nu}^{\perp}) (\delta \mathbf{F}_\nu(0) \cdot \mathbf{e}_{\mu\nu}^{\perp}) \rangle \quad (5.2.3)$$

$$\alpha(R) = (2\gamma^\perp(R))^{1/2} \quad (5.2.4)$$

$$b(R) = \left(3\gamma^\parallel(R) - 4\gamma^\perp(R)\right)^{1/2}. \quad (5.2.5)$$

Here, $d\bar{W}_{\mu\nu}^S$ is a symmetric matrix of independent increments of the Wiener process. The values of $\gamma^\perp(R)$, $\gamma^\parallel(R)$ and $\langle \mathbf{F}_{\mu\nu} \cdot \mathbf{e}_{\mu\nu} \rangle$ are given by the center of mass MD simulations, rather than empirical formulas, as is usually been done in conventional DPD simulations.

Chapter 6

Simulation of complex systems

We perform MD simulations on star polymers melts in an cubic computational box with periodic boundary conditions. Star polymers are represented as chains of beads connected by linear springs, i.e. $\mathbf{F}_{ij}(\mathbf{r}_{ij}) = -k\delta\mathbf{r}_{ij}$, where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $e_{ij} = \mathbf{r}_{ij}/|\mathbf{r}_{ij}|$ the unit vector along \mathbf{r}_{ij} , and $\delta\mathbf{r}_{ij} \equiv \mathbf{r}_{ij} - \mathbf{r}_{ij}^{eq}$, where \mathbf{r}_{ij}^{eq} is the equilibrium distance and k is the spring constant. Each molecule of the star polymer has M arms and N_m monomers per arm and the total number of monomers in the system is given by $N = M \times N_m$. The volume fraction of the polymer is $\Phi = N(\pi/6)\sigma^3/L^3$, where L is the length of the computational box. All the results presented here, are given in Lennard-Jones units: energy, mass, length and time units being $\epsilon = 1$, $m = 1$, $\sigma = 2.415$, $\tau = (\sigma/\epsilon)^{1/2}$ respectively, and the parameters of the spring: $k = 20\epsilon/\sigma^2$ and the equilibrium distance

$$\mathbf{r}_{ij}^{eq} = \begin{cases} 1.147\sigma, & \text{for } i, j \text{ non-center monomers} \\ 1.615\sigma, & \text{for } i = 0, \text{ the center monomer.} \end{cases}$$

All simulations are carried out in the microcanonical ensemble NVE, with average temperature $k_bT = 3.965$. We run a long enough MD simulation and saved one configuration per each diffusion time, typically about $(R_g^2/D)\tau$, which will ensure that the producing set has independent initial configurations.

To produce independent initial configuration, we ran a long MD simulation and we save one configuration per each diffusion time. Starting for each of these configurations we ran simulations to collect the CoM molecular dynamics data. This set of runs are carried using constraint dynamics. The constraint dynamics that we use in order to compute the mean force $\langle \mathbf{F}_{\mu\nu} \rangle$ and the friction coefficient $\gamma_{\mu\nu}(\mathbf{R}, \mathbf{P})$ are:

$$\frac{d\mathbf{r}_{i_\mu}}{dt} = \frac{\mathbf{p}_{i_\mu}}{m_{i_\mu}} - \frac{\mathbf{P}_\mu}{M_\mu} \quad (6.0.1)$$

$$\frac{d\mathbf{p}_{i_\mu}}{dt} = \mathbf{F}_{i_\mu} - \frac{\mathbf{m}_{i_\mu}}{\mathbf{M}_\mu} \mathbf{F}_\mu \quad (6.0.2)$$

where:

- i_μ runs from $1, \dots, N_m$, where N_m is the number of atoms which compose the molecule.
- μ, ν labels molecules and they run from $1, \dots, M$, where M is the number of molecules in the system.
- \mathbf{P}_μ is the CoM momentum of molecule μ ,
- \mathbf{F}_{i_μ} is the total force on monomer i_μ ,
- \mathbf{F}_μ is the total force of molecule μ .

The equations above conserves the total energy, meaning that the positions and the momentum of the CoM are invariant. Also, they conserve the phase space volume. We compute $\langle \mathbf{F}_{\mu\nu} \rangle$ by taking the time averaging of the force $\mathbf{F}_{\mu\nu}$ that the molecule ν exerts on molecule μ . This force depends only on the CoM positions \mathbf{R}_μ and \mathbf{R}_ν of these two molecules. The average force will be:

$$\langle \mathbf{F}_{\mu\nu} \rangle \approx F(R_{\mu\nu}) \mathbf{e}_{\mu\nu} \quad (6.0.3)$$

where:

- $F(R_{\mu\nu}) = \langle \mathbf{F}_{\mu\nu} \cdot \mathbf{e}_{\mu\nu} \rangle$,
- $\mathbf{e}_{\mu\nu} = (\mathbf{R}_\mu - \mathbf{R}_\nu) / R_{\mu\nu}$,
- $R_{\mu\nu} = |\mathbf{R}_\mu - \mathbf{R}_\nu|$.

To calculate the friction coefficients $\gamma_{\mu\nu}(\mathbf{R}, \mathbf{P})$, we use the assumption that the correlation between the forces on molecule μ and ν depends only on the positions of these two molecules, thus we can introduce the following:

$$\gamma_{\mu\nu}(\mathbf{R}, \mathbf{P}) \approx -\gamma_\perp(R_{\mu\nu})(\mathbf{1} - \mathbf{e}_{\mu\nu} \mathbf{e}_{\mu\nu}^T) - \gamma_\parallel \mathbf{e}_{\mu\nu} \mathbf{e}_{\mu\nu}^T \quad (6.0.4)$$

where:

$$\gamma_\parallel(R_{\mu\nu}) = \frac{1}{k_b T} \int_0^\infty dt \langle (\delta \mathbf{F}_\mu(t) \cdot \mathbf{e}_{\mu\nu}) (\delta \mathbf{F}_\nu(0) \cdot \mathbf{e}_{\mu\nu}) \rangle, \quad (6.0.5)$$

$$\gamma_{\perp}(R_{\mu\nu}) = \frac{1}{k_b T} \int_0^{\infty} dt \langle (\delta \mathbf{F}_{\mu}(t) \cdot \mathbf{e}_{\mu\nu}^{\perp}) (\delta \mathbf{F}_{\nu}(0) \cdot \mathbf{e}_{\mu\nu}^{\perp}) \rangle. \quad (6.0.6)$$

We assume that the right-hand side of the equations above is the same for all the pairs that are at the same distance $R_{\mu\nu}$.

6.1 Simulation results for star polymers

The results concern the two different case of star polymers, polymer with 12 arms and 3 monomers per arm and one with 6 arms and 6 monomers per arm. They are tested for two different boxes, while keeping the volume concentration constant. Each of the star polymer are composed by “arms” and monomers attached to each arm. Each arm is connected to a central monomer so that the total number of monomers per polymer is $N_m = f \times m + 1$.

6.1.1 Microscopic Description

We test the effect of the size of the box on the systems, by considering two different geometries for each star. So, for the case of star polymer 12-3, we have results for a periodic box of size $L = 72\sigma$ and $L = 144\sigma$. The melts contained $M = 120$ polymer molecules (4440 monomers) in the case of $L = 72\sigma$ and $M = 970$ polymer molecules in the case of $L = 144\sigma$. We run simulations for $\Phi = 0.199$. The average temperature was $k_B T = 4\epsilon$. The diffusion coefficient is $D \approx 0.15\sigma^2/\tau$ and the gyration radius is $R_g^2 \approx 46\sigma$.

For the case of star polymers 6-6, we run simulations for periodic boxes of size $L = 78\sigma$ and $L = 39\sigma$, for polymer volume fraction $\Phi = 0.199$. Boxes contains $M = 336$ molecules, $N_{\mu} = 12432$ monomers and $M = 42$ molecules, $N_{\mu} = 1554$ monomers, respectively. The average temperature was $k_B T = 4\epsilon$. As before, simulations are carried out in the microcanonical NVE ensemble. The diffusion coefficient is $D \approx 0.15\sigma^2/\tau$ and the gyration radius is $R_g^2 \approx 47\sigma$.

We measuring the autocorrelation function of the force on the molecules, which gives an estimation for the decay of the friction coefficient we have seen in the memory kernel. Also we are interesting on the velocity autocorrelation function, which gives the time scale of the CoM velocity, i.e. one of the relevant variables.

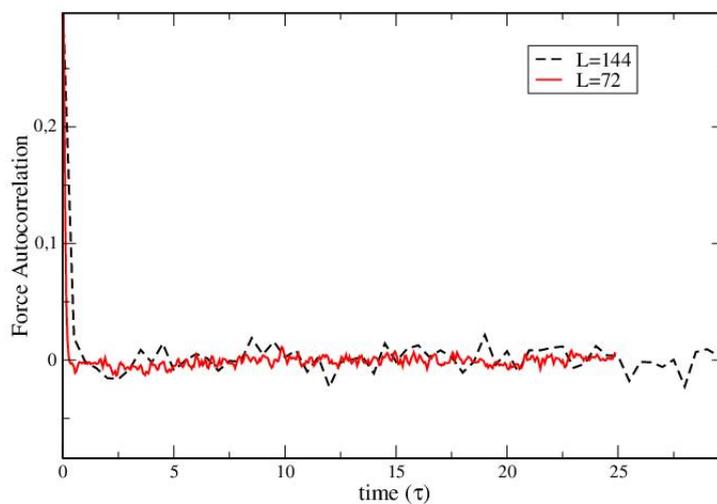


Figure 6.1: The autocorrelation function of the force $\langle \mathbf{F}_\mu \cdot \mathbf{F}_\mu(t) \rangle$, computed by MD simulations, for the case of star-polymer with 12 arms and 3 monomers per arm. The graph shows the same system in two different-size boxes.

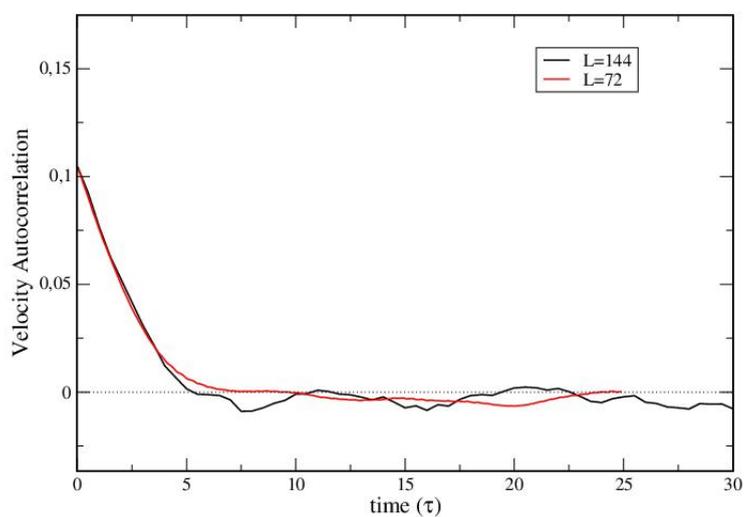


Figure 6.2: The velocity autocorrelation function of the CoM, computed by MD simulations, for the case of star-polymer with 12 arms and 3 monomers per arms. The graph shows the same system in two different-size boxes.

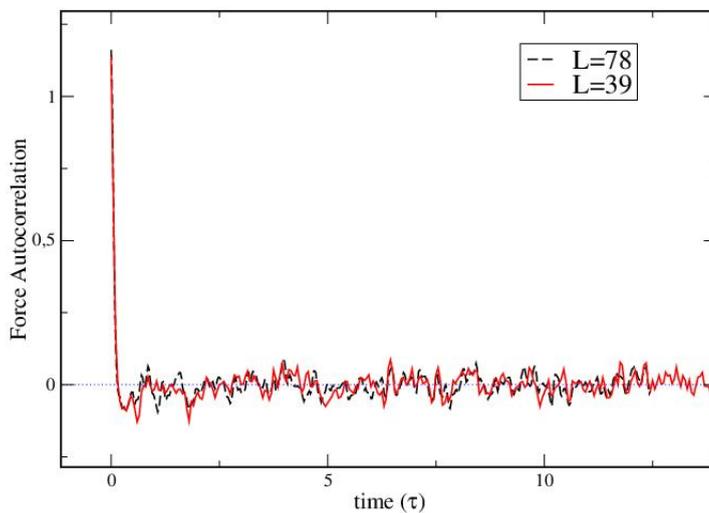


Figure 6.3: The autocorrelation function of the force $\langle \mathbf{F}_\mu \cdot \mathbf{F}_\mu(t) \rangle$, computed by MD simulations, for the case of star-polymer with 6 arms and 6 monomers per arm. The graph shows the same system in two different-size boxes.

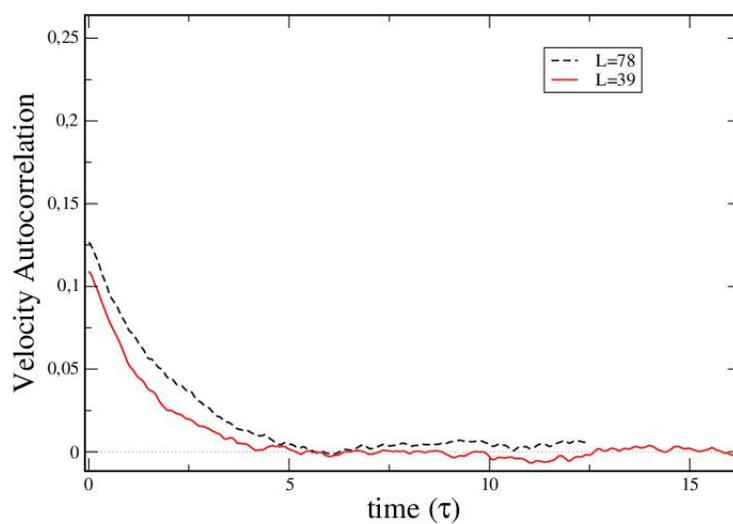


Figure 6.4: The velocity autocorrelation function of the CoM, computed by MD simulations, for the case of star-polymer with 12 arms and 3 monomers per arms. The graph shows the same system in two different-size boxes.

We observe a difference between the correlation times of the force autocorrelation and the velocity autocorrelation, in both cases. As mention in [7], this is caused by the CoM variables being slow variables, and also indicates that that the modified dynamics proposed in Section 4.4 will have a small impact on their dynamics. Moreover, one can notice a negative part on the force autocorrelation figures, which is responsible for the *plateau problem* discussed in Section 4.3. The plateau problem does not occur when we use constrained dynamics. Finally, we can conclude that the size of the box does not have any significant affect on the final results.

For the construction of coarse-graining models, it is important to specify the interactions between coarse-grained variables. One of the properties of great interest in such models is the radial distribution functions (RDF) for the CoM of each molecule in the MD simulation. There is many studies, that use the RDF, obtain for MD simulations, to calculate an effective coarse-grained potential by solving an inverse problem via optimization, i.e. the inverse Boltzmann method [10], inverse Monte Carlo [11], or the force matching method [12]. More on the RDF and the mean square displacement (MSD) can be found in the *Appendix A*. The next figures show the radial distribution functions for the CoM obtain from the MD simulations:

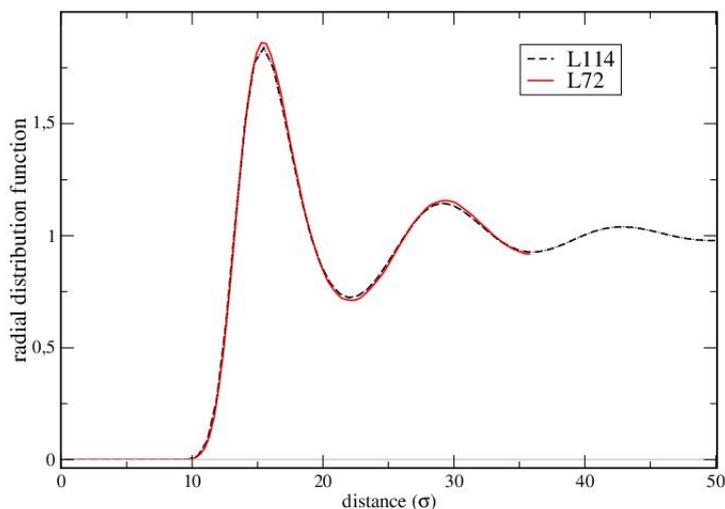


Figure 6.5: Results for the radial distribution function of the CoM, taken from the MD simulations. Case of study: star-polymer 12 arms, 3 monomer per arm.

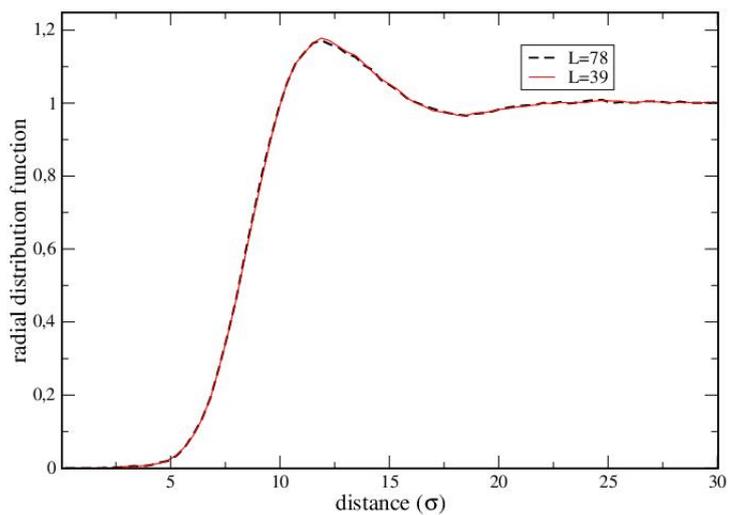


Figure 6.6: Results for the radial distribution function of the CoM, taken from the MD simulations. Case of study: star-polymer 6 arms, 6 monomer per arm.

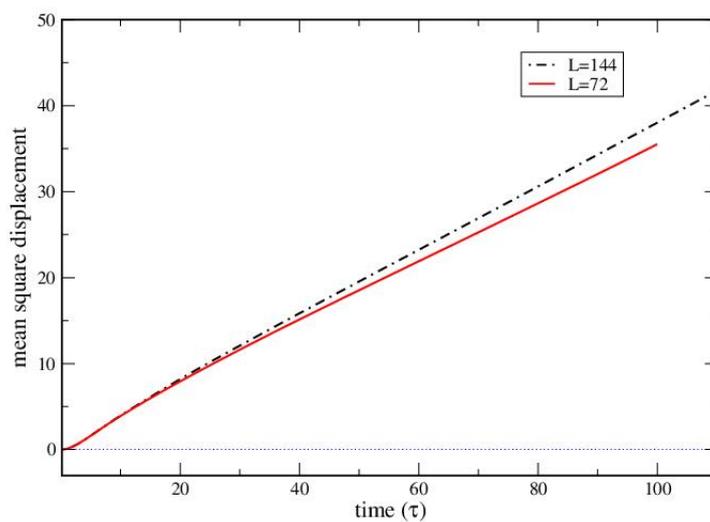


Figure 6.7: Mean square displacement for the study case of star-polymer with 12 arms and 3 monomers per arm, given by MD simulations

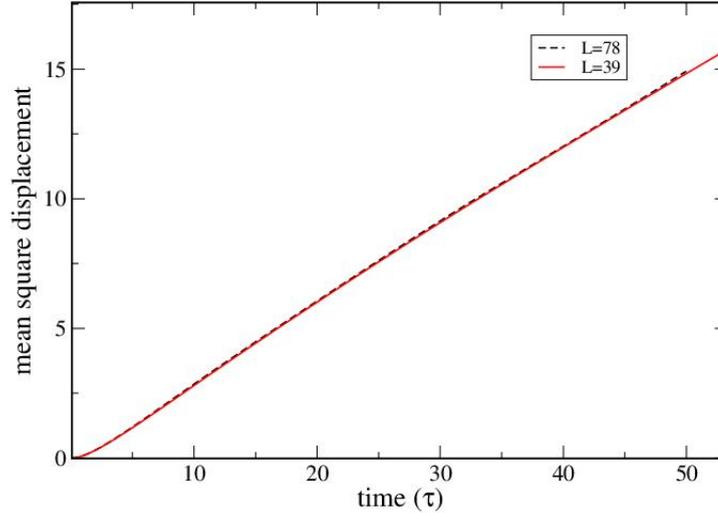


Figure 6.8: Mean square displacement for the study case of star-polymer with 6 arms and 6 monomers per arm, given by MD simulations

The perpendicular and the normal components of the computed friction coefficients $\gamma_{\perp\mu\nu}(R_{\mu\nu})$ and $\gamma_{\parallel\mu\nu}(R_{\mu\nu})$ versus the distance $R_{\mu\nu}$ are presented in figures 6.9 and 6.10. Their values obtained by integrating the correlated forces of the constrained dynamics simulations.

We note that the perpendicular becomes slightly negative for some values. This is probably a consequence of a dynamic aspect of depletion forces. We refer as depletion force, when in a suspension of large and small particles, the pressure of the latter produces an attractive force between the former. When the depletion forces tend to join back two neighbor molecules as soon as they move further away the mean molecular separation. The negative values of γ_{\perp} will not compromise that the full friction matrix $\gamma_{\mu\nu}$, which is a $3M \times 3M$ matrix, is positive definite. Another thing one can notice, is that we do not have data at short distances. This is because short distances are hardly visited by the CoM in the molecular dynamics simulations.

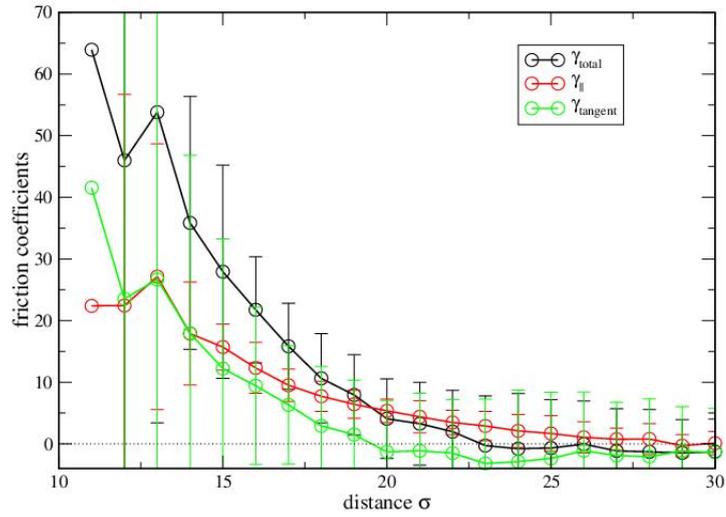


Figure 6.9: The friction coefficients γ_{\perp} and γ_{\parallel} , for the case of star-polymer 12-3, obtained from averaging over 81 MD constraint runs, over $T_r un = 1500\tau$ each.

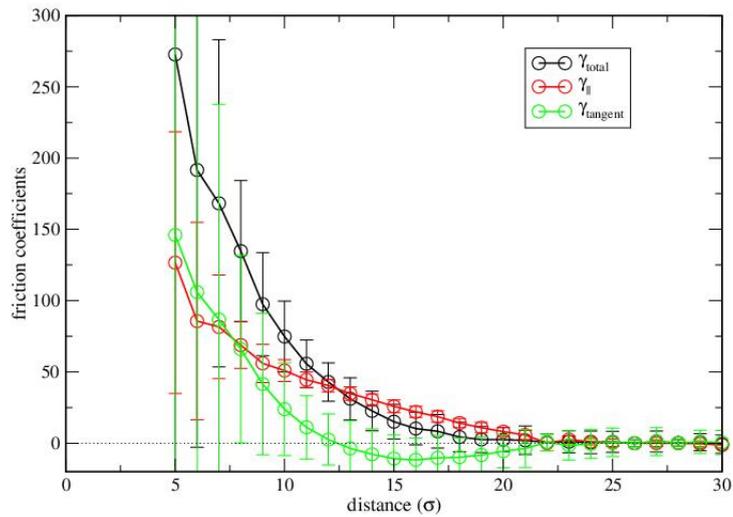


Figure 6.10: The friction coefficients γ_{\perp} and γ_{\parallel} , for the case of star-polymer 6-6, obtained from averaging over 81 MD constraint runs, over $T_r un = 1500\tau$ each.

Chapter 7

Conclusions-Future work

Theoretical background

In this work, we review some of the basic concepts of multiscale simulations, with a focus in the mesoscopic scale. We start by reviewing some basic concepts, such as what we define as a complex system, and basic concepts of Statistical Mechanics, that are used throughout this work. Then we discuss some well-known computer simulations techniques, such as the Molecular Dynamics, the Langevin dynamics and the Dissipative Particles Dynamics. The MD method is used mostly to simulate systems in the microscopic scale, where Langevin dynamics and DPD are methods used to describe systems in the mesoscopic scale.

Our main objective was the derivation of a set of equations that we are both mathematically explicit and computationally treatable. We start by studying the Generalized Langevin equations, which is an equation for the evolution of reduced variables. The GLE is a complicated integro-differential equation with random coefficients. It is not fully explicit, and so it is very difficult to use in computer simulations. However, if one assume that the Markovian approximation applies, i.e. the relevant variables are slow, then the dynamics should can be captured by an SDE. But, the derivation of this SDE is no obvious. The standard Markovian approximation used in this work suffers from the plateau problem, because it used the original dynamics instead of the unknown, projected dynamics to compute the coefficients in the SDE.

Based on the paper of [7], we study a different procedure, which permits to alleviate these difficulties. The procedure is based on a modification of of the original dynamics. The procedure amounts to make all the remaining variables to evolve infinitely fast compared to the relevant ones. In this limit, one can derive unambiguously

what the projected dynamics is, justify the Markovian approximation, and give a precise estimates for the coefficients in the SDE.

The importance of this method is that it provides an understanding of the dynamics of the system and it facilitates the simulation of the system. One of the most significant aspects of this method is that the coefficients appearing in the SDE, i.e. the effective forces and the frictions, depend, in general, on the whole set of relevant variables in a nontrivial way. In a theoretical point of view, this shows that the approach does not rely on extra assumptions on how the coefficients depend on the relevant variables, but this may be a disadvantage, when it comes on computer simulations. In practice, this means that for every configuration of the M molecules, we should have a different set of effective forces and frictions. A way around this multidimensionality, is to make the pair-wise additivity.

Future work

To apply the theory, we run simulations on star polymers melts. We perform MD simulations and we extract results for the center of mass of the molecule. Currently, we are working on the DPD part, which will help on verification of the theory.

We believe that this procedure is of great computational value, and there are many concepts that we will be interested to further investigate. We expect that by using a better method to extract the conservative force field, the DPD method will have much better results, and so it is in our future plans to perform such simulations. Another point of interest might be to start out analysis from a more detailed scale, e.g. atomistic, instead of the microscopic.

Appendices

Appendix A

Complementary theories and concepts

This chapter will serve as a complementary to the rest of the thesis. Here, we will mention briefly some of the theoretical concepts that are used throughout this work.

A.1 Introduction to Brownian motion

The random motion of a small particle immersed in a fluid with the same density as the particle is called Brownian motion. It is a simple approximate method to describe the dynamics of non-equilibrium systems.

Albert Einstein was the one who obtained a relation between the macroscopic diffusion constant D and the atomic properties of the matter. The relation that he came up with is:

$$D = \frac{RT}{N_A 6\pi\eta\alpha} = \frac{k_B T}{6\pi\eta\alpha} \quad (\text{A.1.1})$$

where R is the gas constant, N_A is the Avogadro's number, T is the temperature, η is the viscosity of the liquid and α is the radius of the Brownian particle and $k_B = R/N_A$ is Boltzmann's constant. But Einstein's theory of Brownian motion is not a dynamical theory in the Newton's sense since it does not involve the concept of velocity or acceleration. A model that takes account of the inertial effects of the Brownian particles was introduced by P. Langevin (1908). Following Newton's second law for a mesoscopic particle in a fluid of microscopic particles we have:

$$m \frac{d\vec{v}}{dt} = \vec{F}_E + \vec{F}_T \quad (\text{A.1.2})$$

where F_E is the sum of the external forces and F_T is the sum of the forces that each molecule of the fluid exerts on the mesoscopic particle: $\vec{F}_T = \sum_i \vec{f}_i$.

Mathematically, the definition of the Brownian motion is given by the following equation: **Brownian Motion:** Brownian motion is a stochastic process $w(\omega, t)$, $\omega \in \Omega$, $0 < t < 1$, that satisfies the following four axioms:

1. $w(\omega, 0) = 0$, for all ω
2. For each ω , $w(\omega, t)$ is a continuous function of t
3. For each $0 \leq s \leq t$, $w(\omega, t) - w(\omega, s)$ is a Gaussian variable with mean zero and variance $t - s$
4. $w(\omega, t)$ has increments; i.e. $0 \leq t_1 < t_2 < \dots < t_n$ then $w(\omega, t_i) - w(\omega, t_{i-1})$ for $i = 1, 2, \dots, n$ are independent.

Where the definition of Stochastic process is given below:

Stochastic Process: A stochastic process is a function $v(\omega, t)$ of two arguments where (Ω, \mathcal{B}, P) is a probability space, $\omega \in \Omega$, $t \in \mathbb{R}$, such that for each ω , $v(\omega, t)$ is a function of t and for each t , $v(\omega, t)$ is a random variable.

Some important consequences of the definition of Brownian motion (BM) are:

1. The correlation function of BM is:

$$E[w(t_1)w(t_2)] = \min t_1, t_2$$

2. Consider the variable:

$$\frac{w(\omega, t + \Delta t) - w(\omega, t)}{\Delta t}$$

It is a Gaussian with mean 0 and variance $(\Delta t)^{-1}$, which tends to infinity as Δt tends to zero. Therefore, the derivative of $w(\omega, t)$ for any fixed ω exists nowhere with probability 1.

Non-differentiable functions may have derivatives in the sense of distributions. The derivative in the sense of distributions $v(\omega, s)$ of a BM $w(\omega, s)$ is called **white noise** and is defined by the property:

$$\int_{t_1}^{t_2} v(\omega, s) ds = w(\omega, t_2) - w(\omega, t_1) \quad (\text{A.1.3})$$

A.2 Laplace transform and its properties

The Laplace transform of a function $f(t)$ is just one of the integral transforms of the form

$$\tilde{f}(s) = \int_0^{\infty} K(st)f(t)dt,$$

where $K(x)$ is a kernel that is typically a smooth and rapidly decaying function of x . The Laplace transform corresponds to the choice $K(x) = e^{-x}$. A Laplace transform $\tilde{f}(s)$ exists, if there is a positive constant s_0 such that $|e^{-s_0 t} f(t)| \leq M$ for M finite, for $s > s_0$. It can be shown that the Laplace transform has the following properties:

$$\begin{aligned} \int_0^{\infty} e^{-st} \frac{df}{dt} dt &= s\tilde{f}(s) - f(0) \\ \int_0^{\infty} e^{-st} \frac{d^2 f}{dt^2} dt &= s^2 \tilde{f}(s) - f'(0) - sf(0) \\ \int_0^{\infty} \int_0^{\infty} e^{-st} f(\tau)g(t-\tau)d\tau dt &= \tilde{f}(s)\tilde{g}(s). \end{aligned}$$

Laplace transforms are useful for simplifying linear differential equation and integro-differential equations. So, an ordinary differential equation for a function $f(t)$ can be converted into a simple algebraic equation for $\tilde{f}(s)$. This conversion is accomplished by expressing derivatives as simple algebraic expressions via Laplace transformation. Once an expression for $\tilde{f}(s)$ is found, obtaining $f(t)$ requires performing an inverse Laplace transform, and the inversion of Laplace transforms is not as easy as the forward Laplace transform.

We will see how the inverse Laplace transform arises. Let $f(t)$ exhibits an exponential divergence $e^{\gamma t}$, and define a function $g(t)$ by $f(t) = e^{\gamma t}g(t)$. Since the Laplace transform restricts t to the interval $[0, \infty)$, we can assume $g(t) = 0$ for $t < 0$. The function $g(t)$ is a well-behaved function, and therefore it can be defined via Fourier transform

$$g(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega t} \hat{g}(\omega). \quad (\text{A.2.1})$$

The Fourier transform $\hat{g}(\omega)$ can be also be expressed in terms of $g(t)$ as

$$\hat{g}(\omega) = \int_0^{\infty} dt g(t) e^{i\omega t}. \quad (\text{A.2.2})$$

Substituting (A.2.2) to (A.2.1), yields:

$$g(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega t} \int_0^{\infty} du g(u) e^{i\omega u}. \quad (\text{A.2.3})$$

Since $g(t) = e^{\gamma t} f(t)$, the eq. (A.2.3):

$$f(t) = \frac{e^{\gamma t}}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega t} \int_0^{\infty} du f(u) e^{i\omega u} e^{-\gamma u}, \quad (\text{A.2.4})$$

and if we let $s = \gamma + i\omega$, then

$$\begin{aligned} f(t) &= \frac{1}{2\pi} \int_{\gamma+i\infty}^{\gamma-i\infty} ds e^{st} \int_0^{\infty} du f(u) e^{-us} \\ &= \frac{1}{2\pi i} \int_{\gamma+i\infty}^{\gamma-i\infty} ds e^{st} \tilde{f}(s) \end{aligned} \quad (\text{A.2.5})$$

Equation (A.2.5) defines the Laplace inversion problem as an integral over a complex variables s , which can be performed using techniques of complex integration and the calculus of residues. For $t > 0$, eq. (A.2.5) specifies the use of a contour, known as *Bromwich contour*, whose leading edge is parallel to the imaginary s axis and is chosen far enough to the right to enclose all of the poles of $\tilde{f}(s)$. The contour is then closed in the left half of the complex plane.

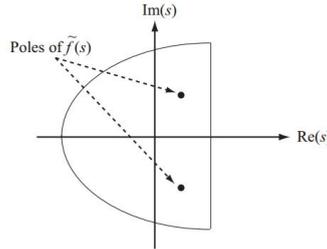


Figure A.1: *Bromwich contour*. Contains all of the poles of $\tilde{f}(s)$ [13]

If the Bromwich contour is denoted B , the inverse Laplace (A.2.5) becomes:

$$f(t) = \frac{1}{2\pi i} \oint_B ds e^{st} \tilde{f}(s). \quad (\text{A.2.6})$$

A.3 Dyson identity

For the derivation of the GLE, by the use of Mori-Zwanzig operator, we used the semigroup notation, according to which the solution of (4.2.1) is denoted by $e^{t\mathcal{L}}\phi(\mathbf{u})$. We also make use of a identity for operator.

Consider the Laplace transform of the exponential of an operator $-Rt$:

$$\begin{aligned}
 \int_0^\infty dt e^{-st} e^{-Rt} &= \int_0^\infty dt e^{-st} \sum_{n=0}^\infty \frac{(-1)^n}{n!} R^n t^n \\
 &= \sum_{n=0}^\infty \frac{(-1)^n}{n!} R^n t^n R^n \int_0^\infty e^{-st} t^n dt \\
 &= \sum_{n=0}^\infty (-1)^n \frac{R^n}{s^{n+1}} \\
 &= \frac{1}{s} \left(I + \frac{R}{s} \right)^{-1} \\
 &= (s + R)^{-1}
 \end{aligned} \tag{A.3.1}$$

It can be shown that:

$$(U + V)^{-1} = U^{-1} - U^{-1}V(U + V)^{-1},$$

from which it follows that:

$$(s + R + S)^{-1} = (s + R)^{-1} - (s + R)^{-1}S(s + R + S)^{-1}.$$

Using eq. (A.3.1), we can take the inverse Laplace transform products:

$$e^{-(R+S)t} = e^{-Rt} - \int_0^t d\tau e^{-R\tau} S e^{-(R+S)(t-\tau)}$$

which is the *Dyson operator identity*.

A.4 Distribution functions in classical liquids and gases

One of the most important quantities that one want to evaluate in order to the structure of a complex system is the pair distribution function $g(r)$. This function

gives the probability of finding a pair of atoms a distance r apart, relative to the probability expected for a completely random distribution at the same density. To define $g(r)$, we integrate the configuration distribution function over the positions of all atoms except two, incorporating the appropriate normalization factors.

Consider the general case of N -particle system with Hamiltonian

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (\text{A.4.1})$$

where all the particles are of the same type. Since all the thermodynamical ensembles are equivalent in the thermodynamic limit, we are free to choose the ensemble that is respectively more convenient. We will work on the canonical ensemble (NVT) for this analysis. The partition function for the canonical ensemble is

$$\begin{aligned} Q(N, V, T) &= \frac{1}{N! h^{3N}} \int d^{3N} p d^{3N} r e^{-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}} e^{\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)} \\ &= \frac{Z_N}{N! \lambda^{3N}}, \end{aligned} \quad (\text{A.4.2})$$

where $\lambda = \sqrt{\beta h^2 / 2\pi m}$ is the thermal wavelength, the quantity Z_N is known as the configuration partition function $Z_N = \int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)}$, and finally

$$\frac{e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)}}{Z_N} d\mathbf{r}_1 \dots d\mathbf{r}_N \equiv P^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_1, \dots, d\mathbf{r}_N, \quad (\text{A.4.3})$$

represents that the probability that the particle with the coordinate $N = 1$ will be found in a volume element $d\mathbf{r}_1$ at the point \mathbf{r}_1 , particle $N = 2$ will be found in a volume element $d\mathbf{r}_2$ at the point \mathbf{r}_2 and so on. To obtain the probability associated with some number $n < N$ of the particles, irrespective of the locations of the remaining $n + 1, \dots, N$ particles, we simply integrate this expression over the particles with indices $n + 1, \dots, N$:

$$P^n(\mathbf{r}_1, \dots, \mathbf{r}_n) d\mathbf{r}_1 \dots d\mathbf{r}_n = \frac{1}{Z_N} \left[\int d\mathbf{r}_{n+1} \dots d\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)} \right] d\mathbf{r}_1 \dots d\mathbf{r}_n. \quad (\text{A.4.4})$$

The probability that any particle will be found in the volume element $d\mathbf{r}_1$ at the point \mathbf{r}_1 and any particle will be found in the volume element $d\mathbf{r}_2$ at the point \mathbf{r}_2 , and so on, is defined as

$$\rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) d\mathbf{r}_1 \cdots d\mathbf{r}_n = \frac{N!}{(N-n)!} P^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) d\mathbf{r}_1 \cdots d\mathbf{r}_n \quad (\text{A.4.5})$$

which comes about since the first particle can be chosen in N ways, the second chosen in $N-1$ ways etc.

A general correlation function can be defined in terms of the probability distribution function $\rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)$ according to

$$\begin{aligned} g^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) &= \frac{1}{\rho^n} \rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) \\ &= \frac{V^n N!}{Z_N N^n (N-n)!} \int d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)}. \end{aligned} \quad (\text{A.4.6})$$

Also, in many cases, it is useful to write the correlation function in the following form

$$\begin{aligned} g^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) &= \frac{V^n N!}{Z_N N^n (N-n)!} \int d\mathbf{r}'_1 \cdots d\mathbf{r}'_N e^{-\beta U(\mathbf{r}'_1, \dots, \mathbf{r}'_N)} \delta(\mathbf{r}_1 - \mathbf{r}'_1) \\ &= \frac{V^n N!}{Z_N N^n (N-n)!} \left\langle \prod_{i=1}^n \delta(\mathbf{r}_i - \mathbf{r}'_i) \right\rangle_{\mathbf{r}'_1, \dots, \mathbf{r}'_N}, \end{aligned} \quad (\text{A.4.7})$$

i.e. the general n -particle correlation function can be expressed as an ensemble average of the product of δ -functions, with the integration being taken over the variables $\mathbf{r}'_1, \dots, \mathbf{r}'_N$.

Of particular importance is the of the pair correlation function, i.e. when $n=2$, or the correlation function $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$. The explicit expression for $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is

$$\begin{aligned} g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{V^2 N!}{N^2 (N-2)!} \langle \delta(\mathbf{r}_1 - \mathbf{r}'_1) \delta(\mathbf{r}_2 - \mathbf{r}'_2) \rangle \\ &= \frac{V^2 (N-1)}{N Z_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)} \\ &= \frac{N(N-1)}{\rho^2} \langle \delta(\mathbf{r}_1 - \mathbf{r}'_1) \delta(\mathbf{r}_2 - \mathbf{r}'_2) \rangle_{\mathbf{r}'_1, \dots, \mathbf{r}'_N}. \end{aligned}$$

In the general, for homogeneous systems in equilibrium, there are no special points in space so that $g^{(2)}$ should depend only on the relative position of the particles or the difference $\mathbf{r}_1 - \mathbf{r}_2$. In this case, it proves useful to introduce the change of variables:

$$\begin{aligned}
\mathbf{r} &= \mathbf{r}_1 - \mathbf{r}_2 \\
\mathbf{R} &= \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \\
\mathbf{r}_1 &= \mathbf{R} + \frac{1}{2}\mathbf{r} \\
\mathbf{r}_2 &= \mathbf{R} - \frac{1}{2}\mathbf{r}.
\end{aligned}$$

Then, we obtain a new function $\tilde{g}^{(2)}$, a function of \mathbf{r} and \mathbf{R} :

$$\begin{aligned}
\tilde{g}^{(2)}(\mathbf{r}, \mathbf{R}) &= \frac{V^2(N-1)}{NZ_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U(\mathbf{R} + \frac{1}{2}\mathbf{r}, \mathbf{R} - \frac{1}{2}\mathbf{r}, \mathbf{r}_3, \dots, \mathbf{r}_N)} \\
&= \frac{N(N-1)}{\rho^2} \left\langle \delta\left(\mathbf{R} + \frac{1}{2}\mathbf{r} - \mathbf{r}'_1\right) \delta\left(\mathbf{R} - \frac{1}{2}\mathbf{r} - \mathbf{r}'_2\right) \right\rangle_{\mathbf{r}'_1, \dots, \mathbf{r}'_N}. \quad (\text{A.4.8})
\end{aligned}$$

In the canonical ensemble, the average energy is given by

$$\begin{aligned}
E &= -\frac{\partial}{\partial \beta} \ln Q(N, V, \beta) \\
\ln Q(N, V, \beta) &= \ln Z_N - 3N \ln \lambda(\beta) - \ln N!.
\end{aligned}$$

Therefore,

$$E = \frac{3N}{\lambda} \frac{\partial \lambda}{\partial \beta} - \frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta},$$

and since

$$\lambda = \left[\frac{\beta h^2}{2\pi m} \right]^{1/2} \quad (\text{A.4.9})$$

$$\frac{\partial \lambda}{\partial \beta} = \frac{1}{2\beta} \lambda, \quad (\text{A.4.10})$$

thus,

$$\begin{aligned}
E &= \frac{3}{2}NkT + \frac{1}{Z_N} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N U(\mathbf{r}_1, \cdots, \mathbf{r}_N) E^{\beta U(\mathbf{r}_1, \cdots, \mathbf{r}_N)} \\
&= \frac{3}{2}NkT + \langle U \rangle.
\end{aligned}$$

In order to compute the average energy, therefore, one needs to be able to compute the average of the potential $\langle U \rangle$. In general, this is nontrivial task. Given the assumption of **pairwise additivity** of the interparticle forces, the potential can be given by

$$U(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \frac{1}{2} \sum_{i,j \neq j} u(|\mathbf{r}_i - \mathbf{r}_j|) \equiv U_{pair}(\mathbf{r}_1, \cdots, \mathbf{r}_N), \quad (\text{A.4.11})$$

i.e. U is a sum of terms that depend only on the distance between two particles at a time. This form turns out to be an excellent approximation in many cases. The potential U contains $N(N-1)$ total terms, and $\langle U \rangle$ becomes

$$\begin{aligned}
\langle U \rangle &= \frac{1}{2Z_N} \sum_{i,j \neq j} \int d\mathbf{r}_1, \cdots, d\mathbf{r}_N u(|\mathbf{r}_i - \mathbf{r}_j|) e^{-\beta U_{pair}(\mathbf{r}_1, \cdots, \mathbf{r}_N)} \\
&= \frac{N(N-1)}{2Z_N} \int d\mathbf{r}_1, \cdots, d\mathbf{r}_N u(|\mathbf{r}_i - \mathbf{r}_j|) e^{-\beta U_{pair}(\mathbf{r}_1, \cdots, \mathbf{r}_N)}.
\end{aligned}$$

The second line formed by the fact that all terms in the first line are the exact same integral, just with the labels changed. Thus,

$$\begin{aligned}
\langle U \rangle &= \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 u(|\mathbf{r}_1 - \mathbf{r}_2|) \left[\frac{N(N-1)}{Z_N} \int d\mathbf{r}_3, \cdots, d\mathbf{r}_N e^{-\beta U_{pair}(\mathbf{r}_1, \cdots, \mathbf{r}_N)} \right] \\
&= \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 u(|\mathbf{r}_1 - \mathbf{r}_2|) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\
&= \frac{N^2}{2V^2} \int d\mathbf{r}_1 d\mathbf{r}_2 u(|\mathbf{r}_1 - \mathbf{r}_2|) g^{(2)}(\mathbf{r}_1, \mathbf{r}_2).
\end{aligned}$$

Once again, we change variables to $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$. Thus, we find that

$$\begin{aligned}
\langle U \rangle &= \frac{N^2}{2V^2} \int d\mathbf{r} d\mathbf{R} u(r) \tilde{g}^{(2)}(\mathbf{r}, \mathbf{R}) \\
&= \frac{N^2}{2V^2} \int d\mathbf{r} u(r) \int d\mathbf{R} \tilde{g}^{(2)}(\mathbf{r}, \mathbf{R}) \\
&= \frac{N^2}{2V} \int d\mathbf{r} u(r) \tilde{g}(\mathbf{r}) \\
&= \frac{N^2}{2V} \int_0^\infty dr 4\pi r^2 u(r) g(r),
\end{aligned}$$

and therefore, the average energy becomes

$$E = \frac{3}{2} NkT + \frac{N}{2} 4\pi\rho \int_0^\infty dr r^2 u(r) g(r). \quad (\text{A.4.12})$$

So, we have an expression for E in terms of a simple integral over the pair potential form and the radial distribution function.

A.5 Diffusion coefficient and its mean square displacement

Einstein related the self-diffusion coefficient to the mean square displacement of a particle as a function of the observation time. The mean square displacement is proportional to the observation time in the limit that the observation time goes to infinity. The proportionality constant that relates the MSD to the observation time is called self-diffusivity. By convention, we write

$$D \equiv \frac{1}{2D} \lim_{t \rightarrow \infty} \frac{\langle [\mathbf{r}(t_0 + t) - \mathbf{r}(t_0)]^2 \rangle}{t}, \quad (\text{A.5.1})$$

where D is the self-diffusion coefficient, and d is the dimensionality of the system. The term $\langle [\mathbf{r}(t_0 + t) - \mathbf{r}(t_0)]^2 \rangle$ is the *mean square displacement*. The ensemble average is an average over all molecules in the simulation and all origins. By origins we mean that any time step can be considered the time zero in the eq.A.5.1, because it is only looking at observation times rather than some absolute time.

We can see that by having the positions as a function of time, we can calculate the MSD and obtain the self-diffusion coefficient.

A.6 Potential of Mean Force

Consider a Brownian system, where we are interested in the study of the microscopic system. A **potential mean force** (PMF) describes how the free energy changes as a particular coordinate (e.g. the CoM distance separation) is varied. The free energy change described by the PMF force includes the averaged effects of the solvent.

There are various methods for the calculation of PMF. The simplest type of PMF is the free energy change as the separation (\mathbf{r}) between two particles is changed. In this method, we calculate the PMF from the **radial distribution function** using the expression for the Helmholtz free energy:

$$A(\mathbf{r}) = -k_B T \ln g(\mathbf{r}) + \text{constant}, \quad (\text{A.6.1})$$

The constant is often chosen so that the most probable distribution corresponds to a free energy of zero.

The PMF may vary by several $k_B T$ over the range of parameter r . The logarithmic relationship between the potential of mean force and the radial distribution function means that a relatively small change in the free energy may correspond to $g(\mathbf{r})$ changing by an order of magnitude from its most value. Neither molecular dynamics, nor Monte Carlo simulation techniques can sufficiently model regions where the radial distribution function differs drastically from the most likely value, leading to inaccurate values for the potential of mean force.

A.7 Lattice Gas Model

The idea behind the lattice gas model is that the volume available to the fluid is divided into cells of molecular size. In most cases, we arrange these cells in a regular lattice with coordination number z , e.g. for $z = 6$ we have a simple cubic lattice, for $z = 8$ a body-centered cubic lattice, and for $z = 12$ a face-centered cubic. Each of these cells are occupied by one molecule at most, representing repulsion, and only nearest-neighbor cell attractive interactions are considered.

Appendix B

Simulation parameters

B.1 Lennard-Jones potential

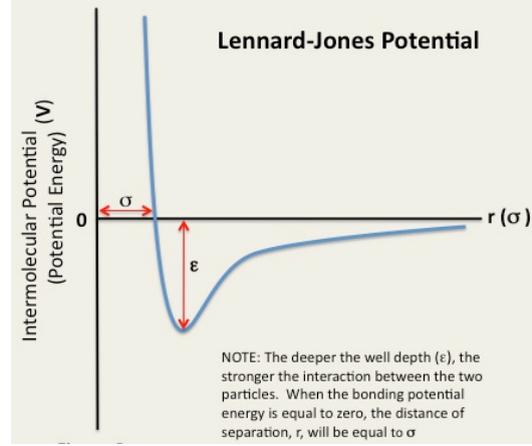
Consider a system of N identical particles interacting via a pair-wise additive potential of the form

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N \sum_{j=i+1}^N 4\epsilon \left[\left(\frac{\sigma}{|\mathbf{r}_i - \mathbf{r}_j|} \right)^{12} - \left(\frac{\sigma}{|\mathbf{r}_i - \mathbf{r}_j|} \right)^6 \right]. \quad (\text{B.1.1})$$

This potential is also known as the Van der Waals forces between simple rare gas atoms systems, as well as in more complex systems. It describes the weak interactions between neutral atoms and molecules. The parameter ϵ governs the strength of the interaction and σ defines a length scale. The Lennard-Jones potential is strongly repulsive at short distances and passes through 0 at $\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = \sigma$, $U(\sigma) = 0$. It reaches the minimum at $U(\mathbf{r}_m) = -\epsilon$ at $\mathbf{r}_m = 2^{1/6}\sigma \approx 1.1225\sigma$, and it exhibits an attractive behavior at large \mathbf{r}_{ij} . The parameters ϵ and σ are chosen to fit certain properties of the system.

The term proportional to \mathbf{r}_{ij}^{-6} dominates at large distances and it models the Van der Waals dispersion forces caused by the dipole-dipole interactions due to fluctuating dipoles. The inter-particle forces arising from the Lennard-Jones potential have the form:

$$\mathbf{f}_{ij} = \frac{48\epsilon}{|\mathbf{r}_i - \mathbf{r}_j|} \left[\left(\frac{\sigma}{|\mathbf{r}_i - \mathbf{r}_j|} \right)^{12} - \frac{1}{2} \left(\frac{\sigma}{|\mathbf{r}_i - \mathbf{r}_j|} \right)^6 \right] |\mathbf{r}_i - \mathbf{r}_j| \quad (\text{B.1.2})$$



It is common to work in dimensionless or reduced units when modeling fluids. Some of the advantages of using such units are:

- the possibility to work with numerical values of the order of unity, instead of the typically very small values associated with the atomic scale,
- the simplification of the equations of motion, due to the absorption of the parameters defining the model into the units,
- the possibility of scaling the results for a whole class of systems described by the same model.

When using the Lennard-Jones potential in simulations, the most appropriate system of units adopts σ , m and ϵ as units of length, mass and energy, respectively, and implies making the replacements:

$$\begin{aligned} \mathbf{r} &\rightarrow \mathbf{r}\sigma \\ E &\rightarrow E\epsilon \\ t &\rightarrow t\sigma(m/\epsilon)^{1/2}, \end{aligned}$$

and so, the equation of motion in MD units are:

$$\ddot{\mathbf{r}}_i = \sum_{j \neq i}^N \mathbf{f}_{ij}, \quad i = 1, 2, \dots, N,$$

where $\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and the interaction forces take the form:

$$\mathbf{f}_{ij} = 48 \left(\mathbf{r}_{ij}^{-14} - \frac{1}{2} \mathbf{r}_{ij}^{-8} \right) \mathbf{r}_{ij}.$$

The kinetic and the potential energies are given by:

$$E_{kin} = \frac{1}{2} \sum_{i=1}^N \mathbf{v}_i^2,$$

$$E_{pot} = 4 \sum_{i<j}^N (\mathbf{r}_{ij}^{-12} - r_{ij}^{-6}).$$

Since each translational degree of freedom contributes to the total kinetic energy by $k_B T/2$, the temperature of the system is defined by:

$$T = \frac{2k_B E_{kin}}{3N} \quad (\text{B.1.3})$$

In the table below, we list the definitions of the MD nits for various physical quantities of interest in simulations.

Physical Quantity	LJ unit
length	σ
mass	m
time	$\sigma(m/\epsilon)^{1/2}$
velocity	$(\epsilon/m)^{1/2}$
force	ϵ/σ
pressure	ϵ/σ^3
temperature	$F\epsilon/k_B$

This can be achieved by utilizing the harmonic spring potentials to reflect mechanical response, so:

$$\phi_i(\psi) = \frac{1}{2} k_i (\psi - \psi_0)^2, \quad (\text{B.1.4})$$

where k_i represent the harmonic spring stiffness, while ψ refers to either an interatomic distance or an angle, for stretching and bending deformations, respectively.

B.2 Tables of parameter

Tables containing the parameters of the star-polymer systems.

STAR POLYMER 12-3			
Box	L72	L144	L72-CONST
Number of monomers N_μ	4440	35520	4440
Number of molecules M	120	960	120
Sampling time \mathbf{dt}	0.005	0.005	0.005
Maximum sampling time \mathbf{tmax}	1000	10000	1500
\mathbf{nsave}	1000	1000	1000
Time between configurations $\mathbf{dt*nsave}$	5	5	5
Number of samples \mathbf{nsamp}	10	100	5
Spring constant	20	20	20
Temperature input	4.0	4.0	4.0

STAR POLYMER 6-6			
Box	L78	L39	L72-CONST
Number of monomers N_μ	12432	1554	12432
Number of molecules M	336	42	336
Sampling time \mathbf{dt}	0.005	0.005	0.005
Maximum sampling time \mathbf{tmax}	500	1000	1500
\mathbf{nsave}	1000	1000	1000
Time between configurations $\mathbf{dt*nsave}$	5	5	5
Number of samples \mathbf{nsamp} (<i>pair forces sampled each $\mathbf{nsamp*dt}$</i>)	5	10	5
Spring constant	20	20	20
Temperature input	4.0	4.0	4.0

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