Approximate Mori-Zwanzig dynamics for star polymers

Stavropoulou Eleftheria

University of Crete, Department of Mathematics and Applied Mathematics

MSc DIPLOMA THESIS

Committee
Associate Prof. Vagelis Harmandaris, (DMAM UOC)
Dr. Evangelia Kalligiannaki, (IACM/FORTH)
Dr. Ioannis Pantazis, (Researcher C, IACM/FORTH)

Abstract

Molecular dynamics (MD) simulations study the physical movement of atoms, providing valuable insight for a variety of physical systems. In order to study the motion of molecules inside these physical systems we use either classical mechanics, if we want to know the exact location of the particle in the space (determinism) or statistical mechanics, if we want to find the probability of the particle being in a particular position. The difficulties due to the temporal and spatial limitations of simulations, lead us to average out the details of atomistic, at the molecular level simulations. This can be achieved by dimensionality reduction. In the current work we adopt coarse graining as a dimensionality reduction approach. Having defined the new coarse grained system, the purpose is to specify structural and dynamical properties of the system. We focus on the equations of motion for the new coarse grained particles. These equations are the known Generalized Langevin Equations (GLE). In this work, we present the derivation of the GLE using the Mori-Zwanzig formalism. Then, we present a Markovian approximation of the GLE based on the constrained dynamics of the microscopic system with respect to the coarsening. This approximation leads to a closed system where the conservative and friction forces can be estimated from data provided by all-atom molecular dynamics simulations.

We present the application of the methodology for a high-dimensional system of a star polymer, an 8-arm polystyrene. The coarse-variables are the center of mass of each polystyrene molecule. We perform molecular dynamics simulations for a united-atom system firstly to ensure the system is at thermodynamic equilibrium. Then, we perform molecular dynamics simulations with constrained center of mass in order calculate the average pair force.

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Contents

Chapter 1

Introduction

Nowadays more and more researchers are interested in the structural and dynamical properties of polymers, especially of polymer stars. This happens because of their general use in everyday life, since polymer stars are used wisely for plastics. Polymer stars are the simplest class of branched polymers with a general structure consisting of several (at least three) linear chains connected to a central core. But most of these systems contain a large number of atoms (this can be 10^{23}) so is essential to reduce the degrees of freedom of the system. Additionally, with this reduction we can make our system less numerically expensive. This reduction is achieved through the coarse-graining methodology. However, there is effort to study these polymers though all-atom representation [3]. In order to study the behavior of physical systems we use molecular dynamics simulations.

Molecular dynamics (MD) simulations are a powerful tool for understanding molecules structures and functions with full atomistic detail. It is often used for studying the conformational rearrangements of molecules and their interactions with other molecular species in a range of environments. The method provides a dynamic description of the temporal behavior of atoms and molecules by using finite difference methods to numerically solve Newton's equations of motion. MD simulations treat the molecule as a collection of interacting classical particles and integrate the classical (Newtonian) equations of motion to simulate the atomistic position of macromolecules, [16, 1, 10]. The result of the simulation is a trajectory of the system over a certain period of time, usually tens to hundreds of nanoseconds. Various structural and dynamic properties of the system can then be calculated from the trajectory to gain a kinetic and thermodynamic understanding of the system. Simulations are performed using empirically parameterized force fields that include explicit solvent. But the main problem is that the computational modeling of realistic complex molecular systems at the molecular level requires long molecular simulations for an enormous distribution of length and time scales.

To solve this problem we need to apply dimensionality reduction, that is reductions of degrees of freedom by averaging out the details of atomistic, at the molecular level simulations. This is achieved with coarse-graining. More specifically coarse-graining means that you trace over a finite number of (microscopic) degrees of freedom in the problem. In this way one can reach longer time or length scales. Coarse-grained (CG) models have been proven very efficient means in order to increase the length and time scales accessible by simulations, [10, 11, 9, 14]. The challenge is thus to describe efficiently the *structural* and the *dynamical* behavior of the coarse grained system. To describe the structural behavior approximation to the many body potential of mean force (PMF) are employed, directly related to the *equilibrium* distribution of CG particles observed in simulations of atomically detailed models. To achieve effective PMF approximations, several numerical approaches have been introduced in recent years which correspond to fit a model for different observables. There exist various numerical methods that construct reduced CG models which approximate the properties of reference (microscopic) molecular systems and are based on statistical mechanics principles, [13, 20, 4, 22, 18, 12, 15]. The evolution of the coarse-grained variables corresponding to Hamiltonian microscopic dynamics can be described exactly with the Mori-Zwanzing formalism leading to a stochastic integro-differential system with strong memory terms, known as the generalized Langevin equation (GLE)[19, 25]. The GLE is in principle computationally intractable. Thus, approximate dynamical models are considered in recent studies, [5, 24, 6, 7, 17]. In this study we follow the approximation introduced in [24] where using the Mori-Zwanzig formalism and a Markovian approximation one constructs a CG model for big molecules. This approach uses constrained dynamics to calculate the terms of the GLE.

The purpose of the thesis is to apply the approach described in the work [24] to a high-dimensional polystyrene molecular system. In this work, using coarse graining as tool we describe the equation of motion of the new coarse grained particles. This equation is the generalized Langevin equation (GLE). We describe the derivation of generalized Langevin equation using the Mori-Zwanzig formalism. The Mori–Zwanzig formalism is a projection operator technique that produces the GLE, which describes the non equilibrium evolution of any set of functions defined on the phase-space of the microscopic system. But, the GLE is difficult to use as computational tool because of the so called "projected dynamics", which is included in the equation, is not the real dynamics that we can calculate using molecular dynamics (MD) simulations and it is difficult to write down explicitly in general. This means that the GLE is not explicit in general. Moreover, even if it were explicit, the GLE is an integro-differential equation with random coefficients and the numerical integration of such an equation is very difficult. To overcome these problems, it is usually assumed that both the projected and the real dynamics are equivalent, and that the relevant variables (the coarse particles) are such that they evolve on a time scale much larger that the correlation time of the memory kernel. In this case, the GLE can be rendered Markovian and turned into a standard stochastic differential equation (SDE). Then, we present the alternative approach followed in [24] where the projected dynamics are approximated by constrained to the CG variable dynamics instead of the real dynamics.

We follow the later analysis and perform molecular dynamics simulations to calculate the average force and the thermodymanic properties of our system with the new coarse grained particles. Our application is for a system of polystyrene star-polymer, with 8 arms and 38715 atoms. The coarse grained particles are the center of mass (CoM) of each polystyrene molecule. To collect the (all-atom) data that we need we firstly perform unconstrained simulations in order to achieved the equilibrium. Then, we conducted 10 independent constrained runs of 1 nanosecond respectively. The computational cost for one of these simulations is low, for example is approximately three hours. All simulations were performed in LAMMPS [21]. From these simulations we manage to evaluate the effective pair force and the thermodymanic properties of our system.

The structure of the thesis is as follows. In chapter 2 we introduce the thory of the mechanics(classical and statistical). In chapter 3 we describe the structure which the molecular systems have such the dynamics that we use for these systems. In chapter 4 we present the coarse grain methology while in 5 we analyse in detail its dynamics. Lastly in chapter 6 we describe our system, the procedure that we follow and the results of our work.

Chapter 2

Mechanics

2.1 Classical Mechanics

2.1.1 Introduction

Classical mechanics describes the motion of macroscopic objects, from projectiles to parts of machinery, and astronomical objects, such as spacecraft, planets, stars and galaxies. If the present state of an object is known it is possible to predict by the laws of classical mechanics how it will move in the future (determinism) and how it has moved in the past (reversibility). Classical mechanics provides extremely accurate results when studying large objects that are not extremely massive and speeds not approaching the speed of light. The earliest development of classical mechanics is often referred to as Newtonian mechanics. It consists of the physical concepts employed by and the mathematical methods invented by Isaac Newton and Gottfried Wilhelm Leibniz to describe the motion of bodies under the influence of a system of forces. Later, more abstract methods were developed, leading to the reformulations of classical mechanics known as Lagrangian mechanics and Hamiltonian mechanics. The latter will be analyzed in this chapter.

2.1.2 Lagrange equations of motion

We begin our analysis by a quick review of classical mechanics. Consider N particles whose position coordinates are given by a set of scalar quantities $\boldsymbol{r} = (r_1, ..., r_n)$. In a d-dimensional space, one needs d numbers to specify a location, so that $n = Nd$. The rate of change of the position is $\frac{d}{dt} r_i = \dot{r}_i$. We can write down the laws of motion by specifying the Lagrangian $L = L(\boldsymbol{r}, \dot{\boldsymbol{r}}, t)$ with the following steps. For any path $\boldsymbol{r}(s)$,

$t_0 \leq s \leq t$ that could take the particles from their locations at time t_0 to their locations at time t , we define an "action" by

$$A = \int_{t_0}^{t} L(\boldsymbol{r}(s), \dot{\boldsymbol{r}}(s), t) ds$$

and we require that the motion (according to the mechanics embodied in the Lagrangian) that takes us from $\boldsymbol{r}(t_0)$ to $\boldsymbol{r}(t)$ is along a path which is an extremal of the action. To simplify, we assume that $L = L(\boldsymbol{r}, \dot{\boldsymbol{r}})$ does not explicitly depend on t. We conclude thus in the Lagrange equations of motion :

$$\frac{\partial L}{\partial r_i} - \frac{d}{dt}\frac{\partial L}{\partial \dot{r}_i} = 0 \tag{2.1}$$

for all $i = 1, .., n$. Let us demonstrate with a simple example.

Example

Define the Lagrangian corresponding to a particle $\boldsymbol{r} = (r_1, r_2, r_3)$ in $\mathbb{R}^3$ of mass m with potential energy $U(\boldsymbol{r})$,

$$L = \frac{1}{2} m \dot{\boldsymbol{r}}^2 - U(\boldsymbol{r}). \tag{2.2}$$

Then, eqn. (2.1) gives the equations of motion

$$\begin{gathered} -\tfrac{\partial U}{\partial r_i} - \tfrac{\mathrm{d}}{\mathrm{d}t}(m\dot{r_i}) = 0,\ i = 1, 2, 3\,, \\ \boldsymbol{F} = -\nabla U(\boldsymbol{r}) = m\ddot{\boldsymbol{r}}\,, \end{gathered}$$

which are the known Newton's second law.

2.1.3 Hamiltonian equations of motion

Define now a momentum p_i conjugate to r_i by $p_i = \frac{\partial L}{\partial \dot{r}_i}$. The Hamiltonian function is

$$H = \sum p_i \dot{r}_i - L$$

By differentiating H with respect to $\dot{r}_i$ and using the definition of the p_i and the Lagrange equations of motion, one sees that H is not a function of $\dot{r}_i$, and therefore it is a function of only the r_i, p_i. By differentiating H with respect to the r_i and then the p_i one can see that the equations of motion can be written as:

$$\dot{r}_i = \frac{\partial H}{\partial p_i}, \dot{p}_i = -\frac{\partial H}{\partial r_i}$$

which are the Hamiltonian equations of motion. If the Hamiltonian does not depend explicitly on time, then it is a constant during the motion and

$$\frac{dH}{dt} = 0.$$

The constant value of the Hamiltonian is the energy E of the system. The Hamiltonian is the sum of the kinetic energy and the potential energy, while the Lagrangian L is the kinetic energy minus the potential energy. The particle trades kinetic energy for potential energy and back again, without loss. From now on, we will denote the vector of positions by $\boldsymbol{r}$ and the vector of momenta by $\boldsymbol{p}$ so that $H = H(\boldsymbol{r}, \boldsymbol{p})$.

Example
The Hamiltonian corresponding to the the example Lagrangian (2.2), is given by

$$H = \mathbf{p} \cdot \dot{\boldsymbol{r}} - L = \frac{1}{2} m \dot{\boldsymbol{r}}^2 + U(\boldsymbol{r}). \tag{2.3}$$

The Hamiltonian equation of motion are

$$\dot{r}_i = \frac{\partial H}{\partial p_i} = \frac{p_i}{m}, \; i = 1, 2, 3 \tag{2.4}$$

$$\dot{p}_i = -\frac{\partial H}{\partial r_i} = -\frac{\partial U}{\partial r_i} = \boldsymbol{F}_i. \tag{2.5}$$

2.2 Statistical Mechanics

2.2.1 Introduction

Consider the Hamiltonian system that we described above with n degrees of freedom $(r_1, p_1), ..., (r_n, p_n)$, and H does not depend explicitly on the time t. A *microscopic* state of the system (a "microstate" for short) is a set of values of the $r_1, ...r_n, p_1, ..., p_n$. The system evolves in a $2n$-dimensional space, which is denoted by Γ and is often called the *phase space*. The sequence of points in Γ that the system visits as it evolves from an initial condition is called a trajectory, [23]. If the system has many degrees of freedom, then it is impossible to follow its exact evolution in time, since specification of all the initial conditions is impossible and the numerical solution of the very large systems that arise in practice is also out of reach. One often assumes that the equations of motion are known with certainty, and deal with the uncertainty in the initial data by assuming that the initial data $\boldsymbol{r}(0)$ and $\boldsymbol{p}(0)$ are drawn from a initial probability density $W = W(\boldsymbol{r}, \boldsymbol{p}, t = 0)$. Then, instead of considering single trajectories, we look at the collection, or "ensemble," of trajectories that are initially distributed according to W. We note that standard theorems about the existence and uniqueness of solutions of ordinary differential equations guarantee that trajectories cannot intersect or stop, provided H is a smooth enough function of the $\mathbf{r}$ and $\boldsymbol{p}$. As the trajectories evolve individually, the probability density naturally changes; let the density of microstates at time t be $W(t)$, where each microstate is the location of a trajectory at that time. $W(t)$ describes the ensemble at time t; it is the "macrostate" of the ensemble. Thus, the microstate is a list of numbers, or a vector in Γ, and the macrostate is a probability density in Γ. The set of all macrostates corresponds to Ω.

2.2.2 Liouville equation

Consider a volume V in Γ-space that we described above and a probability density of system W. The number of microstates in V at a given time t is, on average,

$$\int_V W dV$$

where dV is the element of volume in Γ; when the position variables $\boldsymbol{r}$ are cartesian coordinates $dV = \boldsymbol{dr}\boldsymbol{dp}$ (where $\boldsymbol{dr} = dmr_1, ..., dmr_n$ and similarly for $\boldsymbol{dp}$). If microstates neither appear nor disappear, then the only change in the density W of systems in V can come from the inflow/outflow of systems across the boundary of V. Therefore, as in fluid mechanics,

$$\frac{d}{dt}\int_V W\boldsymbol{dr}\boldsymbol{dp} = -\int_{\partial V} W\boldsymbol{u}\cdot n dS = -\int_V \mathrm{div}(W\boldsymbol{u})dV$$

where n is normal to the boundary ∂V of V and dS is an element of area on ∂V. If we assume that the density is smooth, we can deduce from the above that

$$\frac{\partial W}{\partial t} + \mathrm{div}(W\boldsymbol{u}) = 0 \tag{2.6}$$

and, using the incompressibility of $\boldsymbol{u}$

$$\frac{\partial W}{\partial t} + \boldsymbol{u}\cdot \mathrm{grad}W = 0 \tag{2.7}$$

where

$$\mathrm{div}(\boldsymbol{v}) = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$$

and

$$\mathrm{grad}(f) = i\frac{\partial f}{\partial x} + j\frac{\partial f}{\partial y} + k\frac{\partial f}{\partial z}$$

This last equation is known as the Liouville equation. One can define a linear differential operator (the Liouville operator)

$$L = \sum_{i=1}^{n} \frac{\partial H}{\partial p_i}\frac{\partial}{\partial r_i} - \frac{\partial H}{\partial r_i}\frac{\partial}{\partial p_i}$$

and then (2.7) becomes

$$\frac{\partial W}{\partial t} = -LW$$

This equation is linear even when the original system is not. By finding an equation for W, we have traded in a problem in mechanics, where the unknowns were locations and momenta for a mechanical system with particular initial data, for a problem where the unknown is a probability density for an ensemble of systems, i.e., we have gone from mechanics to statistical mechanics. The Liouville equation is the linear partial differential equations whose characteristics are the Hamilton equations we started from. The big difference between the latter and the Liouville equation is that the solution of the Liouville equation is well defined for all $\mathbf{r}, \mathbf{p}$ in Γ, not only for those that lie on a trajectory that issues from a specific initial datum. Once we have the density $W(t)$, we can define physical observables for the ensemble, which are averages of physical quantities over the ensemble. The energy of each microstate is the value of the Hamiltonian H for that microstate; the energy of the ensemble is

$$E(t) = E[H(t)] = \int_{\Gamma} H(\boldsymbol{r}, \boldsymbol{p}) W(\boldsymbol{r}, \boldsymbol{p}, t) dV$$

where dV is an element of volume in the phase space Γ. Similarly, if $\Phi = \Phi(\boldsymbol{r}, \boldsymbol{p})$ is a property of a microstate, its macroscopic version is

$$E[\Phi] = \int_{\Gamma} \Phi(\boldsymbol{r}, \boldsymbol{p}) W(\boldsymbol{r}, \boldsymbol{p}, t) dV$$

A probability density W is invariant in time if it is a stationary solution of (2.6); that is, if we draw the initial data from W, solve the equations for each initial datum, and look at the density of solutions at some later time t, it is still the same W. Therefore, from (2.7) ,

$$\frac{\partial W}{\partial t} = 0.$$

In particular, one can choose as an invariant density $W(\boldsymbol{r}, \boldsymbol{p}) = Z^{-1} \exp(-\beta H(\boldsymbol{r}, \boldsymbol{p}))$ where $\beta > 0$ in a constant and $Z = \int_{\Gamma} \exp(-\beta H) d\boldsymbol{r} d\boldsymbol{p}$. A property of the Liouville operator is the following: Let $E[\cdot]$ is the expectation with respect to a canonical density; we have seen that if u, v are two functions defined on the relevant probability space, then $E[uv]$ defines an inner product, $(u, v) = E[uv]$,and then

$$(Lu, v) = E[(Lu)v] = -E[u(Lv)] = -(u, Lv)$$

(i.e., L is skew-symmetric).

2.2.3 Ensembles

Let us now introduce the ensemble theory which establishes the link between the microscopic and macroscopic realms. The principal conceptual breakthrough on which statistical mechanics is based is that of an ensemble, which refers to a collection of systems that share common macroscopic properties. Averages performed over an ensemble yield the thermodynamic quantities of a system as well as other equilibrium and dynamic properties. The idea that the macroscopic observables of a system are not sensitive to precise microscopic details is the basis of the ensemble concept. More formally, an ensemble is a collection of systems described by the same set of microscopic interactions and sharing a common set of macroscopic properties(e.g. the same total energy, volume, and number of moles). Each system evolves under the microscopic laws of motion from a different initial condition so that at any point in time, every system has a unique microscopic state. Once an ensemble is defined, macroscopic observables are calculated by performing averages over the systems in the ensemble. The fact that the systems in the ensemble evolve in time does not affect properties of this type, and we may freeze the ensemble at any instant and perform the average over the ensemble at that instant. These ensembles are known as equilibrium ensembles. Below we will further analyse three different types of ensembles.

The microcanonical ensemble

The microcanonical ensemble provides a starting point from which all other equilibrium ensembles are derived. It requires an isolated system of N particles in a container of volume V and a total energy E corresponding to a Hamiltonian $H(\boldsymbol{r})$. The variables N, V and E are all macroscopic thermodynamic quantities referred to as control variables. Control variables are simply quantities that characterize the ensemble and that determine other thermodynamic properties of the system. Different choices of these variables lead to different system properties. The state function of this ensemble is the entropy of the system, $S = S(N, V, E)$, since the change in S is related directly to the change in the three control variables of the ensemble. The entropy is a quantity that can be related to the number of microscopic states of the system. "Boltzmann relation" connects the entropy(S) with the number of microscopic states available to a system(Ω) with the following way

$$S(N, V, E) = k \ln \Omega(N, V, E) \tag{2.8}$$

where k is the Boltzmann's constant and its value is $1.3806505(24) \times 10^{-23} J \cdot K^{-1}$ This equation is a probability equation which relates the entropy S to the quantity Ω. Assuming we can determine $\Omega(N, V, E)$ from a microscopic description of the system, equation (2.8) then provides a connection between this microscopic description and a macroscopic thermodynamic observable. The microcanonical ensemble is not used very often because it is very hard to analyze it in practice, since it is very difficult to perform experiments under constant energy.

The canonical ensemble

Its thermodynamic control variables are constant particle number N, constant volume V and constant temperature T , which characterize a system in thermal contact with an infinite heat source. A canonical ensemble can be built from a microcanonical ensemble, by dividing it into many parts and regarding one of them as the system and the others as the thermal bath. The energy between them can be transferred (figure 2.1). Between the thermal bath and the remaining parts, we observe an exchange of heat, which makes the temperature to remain constant. The heat bath is taken to be much larger than the system so that $E_B \gg E_\nu$ where E_B is the total energy of the the heat bath and E_ν denotes the energy state of the system. Thus, the sum $E = E_B + E_\nu$ is constant.

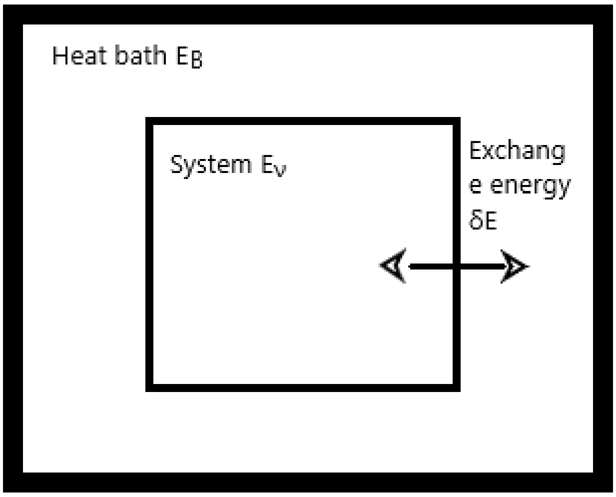

Figure 2.1: Molecular system in contact with a heat bath

At this point, we are interested in finding the microscopic quantity which we will use as a tool to observe a macroscopic property of the system. So, first we aim to find the probability ρ_{E_ν} which corresponds to an energy state E_ν. If the system is at energy state E_ν the number of states accessible to the system plus the bath is $\Omega(E_B) = \Omega(E - E_\nu)$. Thus, the equilibrium probability for observing the system in energy state E_ν obeys

$$\rho_{E_\nu} \propto \Omega(E - E_\nu) \propto e^{(ln(\Omega(E-E_\nu)))}$$

and taking the Taylor expansion of $ln(\Omega(E - E_\nu))$ around E_ν, we get

$$ln(\Omega(E - E_\nu)) \approx ln\Omega(E) - E_\nu \frac{\partial ln\Omega}{\partial E} + \cdots$$

We set $C = ln\Omega(E)$ as a constant due to the fact that the $ln\Omega(E)$ does not depend on E_ν and $E \gg E_\nu$; so from the relation $\rho_{E_\nu} \propto e^{(ln(\Omega(E-E_\nu)))}$ we have

$$\rho_{E_\nu} \propto e^C e^{-E_\nu} \frac{\partial ln\Omega}{\partial E}$$

Noting $\frac{\partial ln\Omega}{\partial E} = \beta$ we now have

$$\rho_{E_\nu} \propto C_0 e^{-\beta E_\nu} \tag{2.9}$$

where $e^C = C_0$ The relation (2.9) is called "Boltzmann distribution function". Using the fact that $\sum_\nu \rho E_\nu = 1$ we obtain

$$\frac{1}{C_0} = \sum_\nu e^{-\beta E_\nu}$$

and the final form of the "Boltzmann distribution function" is

$$\rho_{E_\nu} = \frac{1}{Z(N,V,T)} e^{-\beta E_\nu} \tag{2.10}$$

where $Z(N,V,T) = \sum_\nu e^{-\beta E_\nu}$ which is called "canonical partition function", and β is the thermodynamic beta. Each partition function relates to thermodynamic potentials. So at this point we aim to show the thermodynamic quantity which is related with the canonical partition function. The average energy in the canonical ensemble is

$$\langle E \rangle = \langle E_\nu \rangle = \sum_\nu \rho_{E_\nu} E_\nu = \sum_\nu \frac{1}{Z} e^{\beta E_\nu} E_\nu$$

since $-\frac{\partial Z}{\partial \beta} = \sum_\nu e^{-\beta E_\nu} E_\nu$ we obtain

$$\langle E_\nu \rangle = -\frac{\partial Z}{\partial \beta}\bigg|_{N,V} \frac{1}{Z} = -\frac{\partial \ln Z}{\partial \beta}\bigg|_{N,V} = k_B T^2 \frac{\partial \ln Z}{\partial T}\bigg|_{N,V}$$

where $\beta = \frac{1}{k_B T}$. Since the internal energy $E(\beta, N, V)$ is equal to $\langle E \rangle$ in the canonical distribution, using the famous relation for Helmholtz free energy $A(N,V,T) = E - TS$ and $S = -\frac{\partial A}{\partial T}$ we obtain

$$A = E + T\frac{\partial A}{\partial T}$$

where S denotes the entropy. Using the relations $\langle E_\nu \rangle = -\frac{\partial \ln Z}{\partial \beta}\big|_{N,V}$ and

$$T\frac{\partial A}{\partial T} = T\frac{\partial A}{\partial \beta}\frac{\partial \beta}{\partial T} = -T\frac{\partial A}{\partial \beta}\frac{1}{k_B T^2} = -\beta\frac{\partial A}{\partial \beta}$$

we obtain the relation

$$A + \frac{\partial \ln Z}{\partial \beta}\bigg|_{N,V} + \beta\frac{\partial A}{\partial \beta} = 0$$

The solution of the last equation is

$$A(N,V,T) = -k_B T \ln Z$$

Consequently, if we can compute the canonical partition function Z, then we can obtain the Helmholtz free energy A, which is a fundamental thermodynamic potential of the system. From that, we can obtain other thermodynamic properties.

Grand Canonical Ensemble

The Grand Canonical Ensemble represents the possible states of a mechanical system of particles that is being maintained in thermodynamic thermal and chemical equilibrium. We assume that the system can exchange energy and particles with a reservoir, while the system's volume, shape and other external coordinates are kept the same(figure 2.1). Thus, the various possible states of the system can differ in both their total energy and total number of particles. So while the absolute temperature T, the volume V , and the chemical potential μ are the control variables, the number of atoms is allowed to fluctuate. Now, we can define a grand canonical partition function for the grand canonical ensemble as the sum over all micro-states,

$$Z = \sum_{\nu} e^{\frac{-E_{\nu}+\mu N_{\nu}}{k_B T}}$$

where ν is the micro-state with total number of atoms N_{ν} and total energy E_{ν}. This partition function is closely related to the Grand Potential Φ_G by the relation,

$$\Phi_G = \langle E \rangle - TS - \mu \langle N \rangle = -k_B T$$

Thus, the Grand partition function is a bridge between microscopic features of the system and thermodynamically macroscopic functions.

Chapter 3

Molecular systems

At this chapter we will discuss the idea of multiscale molecular dynamics(MD) simulations and we present the meaning and the features of coarse graining. At first we will describe the interactions between particles in atomistic level. Then we will define coarse graining of the atomistic system.

3.1 Atomistic Description

We will start our analysis by studying how the atoms react in the atomistic level. In molecular systems, we have two types of interactions between atoms the bonded and the non-bonded interactions. As for the non-bonded interactions can be divided into intermolecular and intramolecular interactions between atoms of the same macromolecule. To define bonded interactions, we consider the fact that the position of each atom in time is determined by the distance d between bonds, the angle θ between two sequential bonds and the torsional φ angle (see pictures 3.1,3.2,3.3). To be more specific. a) In order to end up to the final form of the bond stretching potential, we do the following assuming. Supposing that the bond is at a particular reference length d_0 , its energy has the lowest value. If the bond is compressed, the atoms will overlap. If the bond is stretched, the bond will disassociate,i.e both cases, the energy increases . So, for small deviations from the equilibrium bond length, taking a Taylor expansion of energy in $d - d_0$, we obtain the following relation of bond stretching potential

$$U_{bond}(d) = \frac{1}{2}k_d(d - d_0)^2 \tag{3.1}$$

where k_d is the harmonic force constant $k_d = \frac{d^2U}{dd^2}$ for $d = d_0$ and d_0 is the equilibrium bond length.

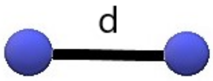

Figure 3.1: Bond between atoms

b)The bending angle potential is a function of angular displacement. It describes the oscillation of the angle between two consecutive bonds around the equilibrium position of angle θ_0. The potential function that can model this interaction is:

$$U_{bend}(\theta) = \frac{1}{2}k_\theta(\theta - \theta_0)^2 \tag{3.2}$$

where k_θ is the angle bending force constant. The energy which needs to distort an angle away from equilibrium is much lower than that which needs to distort a bond, so consequently bond angle bending force constants tend to be proportionally smaller than those for bond stretching.

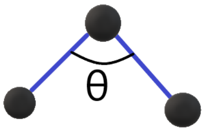

Figure 3.2: Bending angle between two consecutive bonds

c) The torsional angle potential describes the change in energy due to the rotation around a bond. Torsional energies are usually important only for single bonds because double and triple bonds are too rigid to permit rotation. These interactions are different to stretching and bending interactions due to the fact that internal rotation barriers are low compared to other interactions, meaning that changes in dihedral angles can be large. While the torsional potential is periodic through a 360° rotation, it is inappropriate to approximate it by a Taylor series. Thus it is most common to model it using a Fourier series:

$$U_{tor}(\varphi) = \sum_a \frac{1}{2} v_a cos(a\varphi) \tag{3.3}$$

where φ is the current torsional angle and v_a are the torsional rotation force constants while $a \in \{0, N_{atoms}\}$.

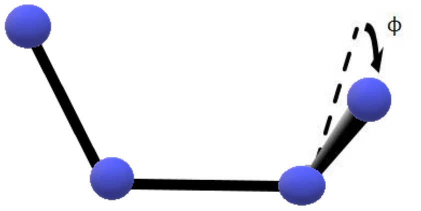

Figure 3.3: Tortional angle

Force fields also contain non-bonded interactions. These interactions appear both between atoms in the same molecule and between atoms in other molecules. They are divided into electrostatic and Van der Walls interactions. a) The electrostatic interactions arise due to the unequal distribution of charge in a molecule. This uneven distribution of charge can be modeled by placing point charges at each of the atomistic sites. While the electrostatic energy reduces slowly, it can affect atoms quite far apart. For a neutral molecule these interactions sum to zero. The form of these interactions can be modeled by Coulomb potential :

$$U_E(e, d) = \frac{1}{4\pi\varepsilon_0} \frac{e_1 e_2}{d} \tag{3.4}$$

with e_1, e_2 is the charge of two atoms, d is the distance between them, and ε_0 is the electric constant $\varepsilon_0 = 8.8510^{-12} Fm^{-1}$.
b) The most popular intermolecular interaction potential is the Lennard-Jones potential which approximates the interaction between a pair of neutral atoms due to temporarily dipoles. The most common expression is:

$$U_{LJ}(d_{ij}) = 4\varepsilon_{i,j}[(\frac{\sigma_{i,j}}{d_{ij}})^{12} - (\frac{\sigma_{i,j}}{d_{ij}})^6] \tag{3.5}$$

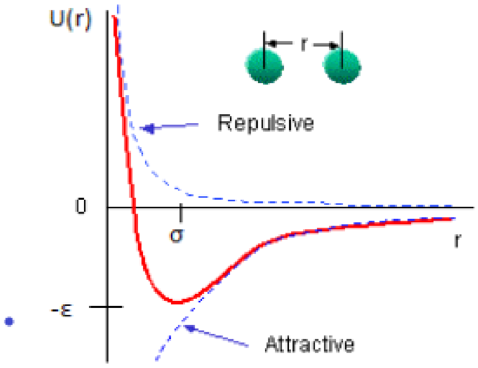

Figure 3.4: Lennard Jones potential

The $\varepsilon_{i,j}$ is the well depth, i.e., the region between i and j particles, surrounding a local minimum of U_{LJ}, $\sigma_{i,j}$ is a measure of how strongly the two particles attract each other and d_{ij} is the distance between the particles i and j. The $\sigma_{i,j}$ is the distance at which the intermolecular potential between the two particles is zero. Is referred to as the Van der Waals radius and using this we can measure how close two non-bonded particles can be. Obviously the parameters $\varepsilon_{i,j}, \sigma_{i,j}$ depend on the type of atoms. The first term in equation describes the repulsive forces between atoms while the latter one denotes the attraction. As we studied above, the value of the energy is calculated as a sum of bonded terms, (which describe the bonds, angles and bond rotations in a molecule), and a sum non-bonded terms, (which account for interactions between non-bonded atoms in the same or in different molecules). The final form of the total energy is given by :

$$U(\boldsymbol{r}) = \sum_{i,j} U_{bond}(d_{ij}) + U_E(d_{ij}, e_{ij}) + U_{LJ}(d_{ij}) + \sum_{i,j,k} U_{bend}(\theta_{ijk}) + \sum_{i,j,k,l} U_{tor}(\varphi_{ijkl}) \quad (3.6)$$

3.1.1 Configurational distribution function

The pair distribution function is very important quantity since will be used in comparison between atomistic and coarse grained systems. This function $g(\boldsymbol{r})$,(correlation function) in a system of particles (atoms, molecules etc.), describes how density varies as a function of distance d from a reference particle. If a given particle is taken to be at the origin O, and if $\rho = \frac{N}{V}$ is the average number density of particles, then the local time-averaged density at a distance r from O is $\rho g(\boldsymbol{r})$. Consider a system of N particles in a volume V and temperature T with an average number density $\rho = \frac{N}{V}$. The particle coordinates are given by the position vector $\boldsymbol{r} \in \mathbb{R}^{3N}, \boldsymbol{r} = [\boldsymbol{r}_1, ..., \boldsymbol{r}_N]$. The potential energy due to the interaction between particles is $U(\boldsymbol{r})$. The probability of an elementary configuration, namely finding particle 1 in $d\boldsymbol{r}_1$, particle 2 in $d\boldsymbol{r}_2$, etc. is given by

$$W(\boldsymbol{r})d\boldsymbol{r}_1...d\boldsymbol{r}_N = \frac{e^{-\beta U(\boldsymbol{r})}}{Z(\boldsymbol{r})}d\boldsymbol{r}_1...d\boldsymbol{r}_N \tag{3.7}$$

Where $Z(\boldsymbol{r}) = \int ... \int e^{-\beta U(\boldsymbol{r})}d\boldsymbol{r}_1...d\boldsymbol{r}_N$ is the configurational integral, taken over all possible combinations of particle positions. The total number of particles is huge, so that $W(\boldsymbol{r})$ in itself is not very useful. However, one can also obtain the probability of a reduced configuration, where the positions of only $m < N$ particles are fixed, in $d\boldsymbol{r}_1, ..., d\boldsymbol{r}_m$ with no constraints on the remaining $N - m$ particles. To this end, one has to integrate the above relation over the remaining coordinates $\boldsymbol{r}_{n+1}, ..., \boldsymbol{r}_N$:

$$W(\boldsymbol{r}_1, ..., \boldsymbol{r}_m) = \frac{1}{Z(\boldsymbol{r})}\int ... \int e^{-\beta U(\boldsymbol{r})}d\boldsymbol{r}_{m+1}...d\boldsymbol{r}_N \tag{3.8}$$

The particles are identical and so without loss of generality we can assume that any of them occupies positions $d\boldsymbol{r}_1...d\boldsymbol{r}_n$ in any permutation, so the density probability function of these n particles will be

$$\rho(\boldsymbol{r}_1, ..., \boldsymbol{r}_m) = \frac{N!}{(N-n)!}W(\boldsymbol{r}_1, ..., \boldsymbol{r}_m) \tag{3.9}$$

It is now time to introduce a correlation function $g(\boldsymbol{r}_1, ..., \boldsymbol{r}_m)$ by:

$$g(\boldsymbol{r}_1, ..., \boldsymbol{r}_n) = \frac{\rho(\boldsymbol{r}_1, ..., \boldsymbol{r}_n)}{\rho^n}. \tag{3.10}$$

From (3.9),(3.10) it follows that

$$g(\boldsymbol{r}) = \frac{V^n N!}{N^n(N-n)!}\frac{1}{Z(\mathbf{r})}\int ... \int e^{-\beta U(\boldsymbol{r})}d\boldsymbol{r}_{m+1}...d\boldsymbol{r}_N \tag{3.11}$$

which is the general form of distribution function. While this distribution describes how, on average, the atoms in a system are radially packed around each other, is a very useful tool for describing the structure of the system as long as is found in many methods for approximating the potential of mean force.

3.2 Molecular dynamics

Molecular Dynamics (MD) is a computer simulation method that can be used to investigate the evolution of a molecular system. Loosely speaking, it is a way to imitate a real life's system, knowing in every step the positions and velocities of all the bodies it is composed of, its energy, density and a variety of other quantities. Using this method we have the possibility repeat the simulations as many times as we need -with the same or different initial conditions- or stop it and restart it again with a much lower cost than in real experiments. Furthermore, we can control some quantities during this process such as the temperature and the material composition better than we have during a real-life experiment in a laboratory. The simulated system consists of N atoms and/or molecules that interact with each other by the terms of a force field, or so-called interatomic potential. The problem of finding the positions and velocities of each one of them is called N-body problem. In order to estimate the quantities of interest in a simulation, we need to know the trajectory of the atoms in the system. The trajectory is determined by the positions and velocities (or momenta) in every step of the simulation. This information can be obtained by solving numerically the classical equations of motion of every molecule or atom in the system concerning all the interactions between them.

3.2.1 Numerical solution of equations of motion

In order to solve numerically the equations of motion in every step of the previous algorithm there are some well-known integration methods. An integration method has to be,so as to be chosen, relatively accurate, fast and not computationally expensive, which means not to use a large amount of memory space. Moreover, it is highly important to use an algorithm that respects the energy conservation of the Hamiltonian system and which is time reversible as Newton's equation of motion is. We will mention one numerical integrator: Velocity Verlet , variant of general Verlet integrator.

Verlet integrator is a numerical method used to solve Newton's equations of motion. Although, as it is shown below, it is a "position-only" scheme and this is why it is not very applicable when velocities or momenta are requested. To generate its formula we determine as $\Delta t > 0$ the time step of the algorithm and we write Taylor expansion for $\boldsymbol{r}(t)$ at $(t+\Delta t)$ and $(t-\Delta t)$,where $\dot{\boldsymbol{r}}(t), \ddot{\boldsymbol{r}}(t), \dddot{\boldsymbol{r}}(t)$ denote, correspondingly, the first, second and third time derivative:

$$\begin{aligned}\boldsymbol{r}(t+\Delta t) = \boldsymbol{r}(t) + \dot{\boldsymbol{r}}(t)(t+\Delta t-t)+ \\ \frac{\ddot{\boldsymbol{r}}(t)(t+\Delta t-t)^2}{2!} + \frac{\dddot{\boldsymbol{r}}(t)(t+\Delta t-t)^3}{3!} + O(\Delta t^4)\end{aligned} \tag{3.12}$$

$$\begin{aligned}\boldsymbol{r}(t-\Delta t) = \boldsymbol{r}(t) + \dot{\boldsymbol{r}}(t)(t-\Delta t-t)+ \\ \frac{\ddot{\boldsymbol{r}}(t)(t-\Delta t-t)^2}{2!} + \frac{\dddot{\boldsymbol{r}}(t)(t-\Delta t-t)^3}{3!} + O(\Delta t^4)\end{aligned} \tag{3.13}$$

Consequently:

$$\boldsymbol{r}(t+\Delta t) = \boldsymbol{r}(t) + \boldsymbol{v}(t)(\Delta t) + \frac{\boldsymbol{a}(t)(\Delta t)^2}{2} + \frac{\boldsymbol{b}(t)(\Delta t)^3}{6} + O(\Delta t^4) \tag{3.14}$$

$$\boldsymbol{r}(t-\Delta t) = \boldsymbol{r}(t) - \boldsymbol{v}(t)(\Delta t) + \frac{\boldsymbol{a}(t)(\Delta t)^2}{2} - \frac{\boldsymbol{b}(t)(\Delta t)^3}{6} + O(\Delta t^4) \tag{3.15}$$

By the summation of equations 3.14 and 3.15:

$$\boldsymbol{r}(t+\Delta t) + \boldsymbol{r}(t-\Delta t) = 2\boldsymbol{r}(t) + \boldsymbol{a}(t)(\Delta t)^2 + O(\Delta t^4) \tag{3.16}$$

we get the final scheme of general Verlet integrator:

$$\boldsymbol{r}(t+\Delta t) = 2\boldsymbol{r}(t) - \boldsymbol{r}(t-\Delta t) + \boldsymbol{a}(t)(\Delta t)^2 + O(\Delta t^4) \tag{3.17}$$

where $\boldsymbol{r}(t)$ is the position in time t, $\boldsymbol{v}(t)$ the velocity in time t,$\boldsymbol{a}(t)$ the acceleration in time t, $\boldsymbol{b}(t)$ is a notation for the third derivative of $\boldsymbol{r}(t)$ with respect to the time and $O(\Delta t^4)$ is the order of the error of the approximation. Verlet algorithm does not require the velocity to compute the new position. However, one can derive the velocity from the difference of equations 3.14-3.15:

$$\boldsymbol{r}(t+\Delta t) - \boldsymbol{r}(t-\Delta t) = 2\boldsymbol{v}(t)\Delta t + O(\Delta t^3) \tag{3.18}$$

or

$$\boldsymbol{v}(t) = \frac{\boldsymbol{r}(t+\Delta t) - \boldsymbol{r}(t-\Delta t)}{2\Delta t} + O(\Delta t^3) \tag{3.19}$$

Therefore, for calculating the velocity using equation 3.19 we should know the position at next time which means that we cannot calculate both position and velocity in the same time step. In order to avoid this problem we present a derivative of the Verlet integrator.

Velocity Verlet

Velocity Verlet integrator is one of the most widespread methods. The advantage over classical Verlet is that this one incorporates velocity in the same time step as position. The formula goes as follows:

$$\boldsymbol{r}(t+\Delta t) = \boldsymbol{r}(t) + \boldsymbol{v}(t)\Delta t + \frac{F(t)\Delta t^2}{2m} \tag{3.20}$$

$$\boldsymbol{v}(t+\Delta t) = \boldsymbol{v}(t) + \frac{F(t) + F(t+\Delta t)}{2m}\Delta t \tag{3.21}$$

We have to make clear that instead of acceleration $\boldsymbol{a}(t)$ we write $\frac{F}{m}$ just to mention that $\boldsymbol{a}(t)$ is calculated from the interaction potential using $\boldsymbol{r}(t)$ and not from $\boldsymbol{v}(t)$, so $\boldsymbol{v}(t+\Delta t)$ can be calculated independently without the calculation of $\boldsymbol{a}(t+\Delta t)$.

3.2.2 Thermostats and Barostats

Sometimes it's necessary to see the evolution of a molecular system under specific conditions of temperature T (isotherm) and/or pressure P (isobaric conditions). In order to maintain T and P constant we use the appropriate thermostats and barostats, respectively. Below, we present two types of thermostats and one of barostat.

Nose-Hoover thermostat

Nose introduced a new parameter (degree of freedom) s which plays the role of a heat bath aiming to damp out temperature deviations from the desirable level and actually being an additional degree of freedom in the Lagrangian of the system. This new parameter results in one more term in potential energy (noted as U_s) and another one in the total kinetic energy (noted as K_s) giving the following Hamiltonian:

$$H_{Nose-Hoover}(\dot{\boldsymbol{r}}, \boldsymbol{r}) = H(\dot{\boldsymbol{r}}, \boldsymbol{r}) + K_s + V_s \tag{3.22}$$

where

$$K_s = \frac{p_s^2}{2Q} \tag{3.23}$$

for

$$p_s = Q\frac{\dot{s}}{s} \tag{3.24}$$

being the momentum associated with s as well as Q represents the "effective mass" associated with s. The potential energy with respect to s equals to:

$$U_s = gk_BTlns \tag{3.25}$$

with g equals to the total number of degrees of freedom and k_B being the Boltzmann constant.

Berendsen thermostat and barostat

Another way for performing isothermal and/or isobaric MD simulations is to use an extended Lagrangian, by coupling the system into a temperature and/or pressure bath. This is achieved by the following equations:

$$\frac{dT}{dt} = \frac{1}{\tau_T}(T - T_{ext}) \tag{3.26}$$

$$\frac{dP}{dt} = \frac{1}{\tau_P}(P - P_{ext}) \tag{3.27}$$

where T_{ext} and P_{ext} are the desired temperature and pressure values and τ_T and τ_P are the time constants characterizing the frequency of the system coupling to temperature and pressure baths. The solution of these equations forces velocities and positions to be scaled at every time step by factors x_T and x_P , respectively,with:

$$x_T = \left(1 + \frac{dt}{\tau_T}\left(\frac{T}{T_{ext}} - 1\right)\right)^{\frac{1}{2}} \tag{3.28}$$

$$x_P = 1 - \beta_T\frac{dt}{\tau_P}(P - P_{ext}) \tag{3.29}$$

Chapter 4

Coarse grained models

4.1 Coarse Graining Mapping

Coarse-grained models have long been used to understand and prove the properties of complex, many-body molecular systems. This method is considered from a mathematical point of view as a dimensionality reduction problem while the coarse-grained systems have fewer degrees of freedom than the corresponding atomistic systems. These models provide a reduced, low-resolution description of a given system in which for example molecules are described by sites. Thus, are expected to be highly computationally efficient providing also a powerful tool to understand many complex molecular phenomena with long time and length scale processes. The main purpose of this field is to develop a coarse-grained model that is significantly easier to simulate and also reproduces the same physical behavior as a reference all-atom one with possibly more site coordinates and known interactions. In other words, we target a cheaper and easier-to-estimate coarse grained model which maintains correct physical behavior. At this point it must be specified how the coarse-grained model is designed, i.e., we have to define a method for mapping any atomistic configuration to a corresponding coarse one. This mapping function takes as input a set of atomistic coordinates of chemical connected atoms in detailed system, which are sampled by a canonical ensemble. This canonical ensemble is a statistical ensemble used to represent the possible states of a system in thermal equilibrium with fixed temperature, volume and number of atoms, and maps it uniquely to a super-atom configuration in the coarse grained system. The reference coarse-grained description is presented by $\boldsymbol{R} = [R_1, .., R_M]$, $\boldsymbol{R} \in \mathbb{R}^{3M}$. From now on, the interacting particles in the atomistic model will be referred as “atoms” and the interacting particles in the coarse grained model as “coarse grained sites”. The mapping function is given by the form: $\xi : \boldsymbol{r} \rightarrow \boldsymbol{R}$. There are several mapping functions that can be used in coarse graining. For example, one coarse-grained site may correspond to the center of mass of a specific set of atoms on a molecule (see picture 4.1). Another function might map a coarse-grained site to the center of mass of a specific CG site, while another one might map it to the position of a single atom. The first mapping function is described by the following equation:

$$R_I = \frac{\sum_{i \in I} m_i r_i}{\sum_{i \in I} m_i} \tag{4.1}$$

where m_i describes the mass of each atom that corresponds to I CG site.

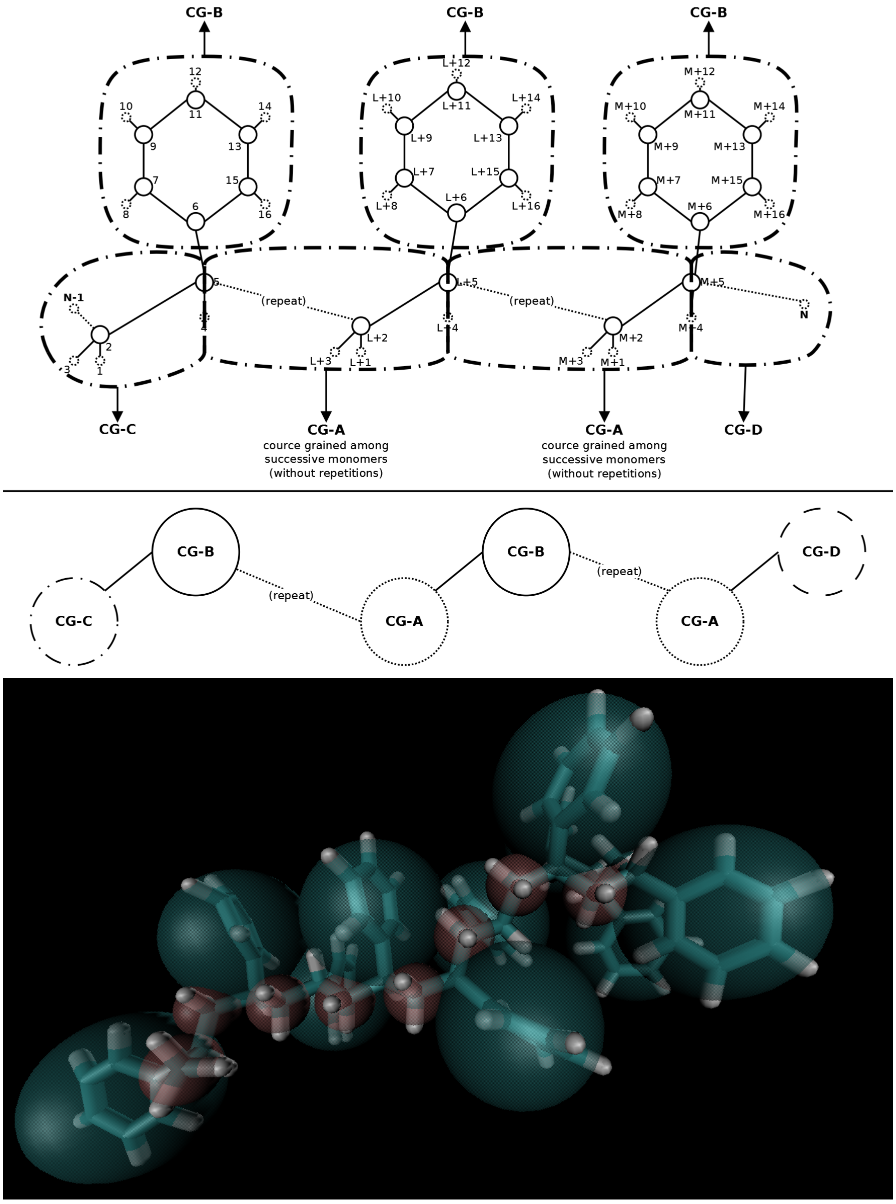

Figure 4.1: Coarse grained all-atom Polysterene

4.2 Coarse grained equilibrium distribution function

The task here is to provide that coarse model whose equilibrium distribution of CG sites is the same as in atomistic system. Having defined the mapping scheme, the second step is to define the interactions between the coarse-grained sites. The equilibrium probability density of states of atomistic model in canonical ensemble is given by

$$W^{AA}(\boldsymbol{r}) \propto \exp(-\frac{U(\boldsymbol{r})}{k_b T}) \tag{4.2}$$

where $\frac{1}{k_b T}$ the inverse temperature scaled by the Boltzmann constant k_b. Similarly, the probability of coarse-grained system is given by

$$W^{CG}(\boldsymbol{R}) \propto \exp(-\frac{U^{AA}(\boldsymbol{r})}{k_b T}) \tag{4.3}$$

We would like the configurational probabilities for coarse grained positions in the CG ensemble

$$W^{AA}(\boldsymbol{R}) = W^{CG}(\boldsymbol{R}) = W(\boldsymbol{r})\delta(\xi(\boldsymbol{r}) - \boldsymbol{R}) \tag{4.4}$$

Taking into consideration the fact that the probability of a coarse-grained configuration is the sum of the probabilities of all of the atomistic configurations that map to it via the mapping function, we get:

$$W^{CG}(\boldsymbol{R}) = \int W^{AA}(\boldsymbol{r})\delta[\xi(\boldsymbol{r}) - \boldsymbol{R}]d\boldsymbol{r}, \tag{4.5}$$

where δ denotes the Dirac delta function. The above relation describes a conditional probability function. Substituting the relations of probability in the above relation we get:

$$\exp(-\frac{W^{CG}(\boldsymbol{R})}{k_b T}) = \int \exp(-\frac{U(\boldsymbol{r})}{k_b T})\delta[\xi(\boldsymbol{r}) - \boldsymbol{R}]d\boldsymbol{r}. \tag{4.6}$$

While the solution of the last relation has been long appreciated, is not practical useful due to the highly multidimensional nature of this potential of mean force. It worth mentioning that the CG potential is a free energy of a particular configuration, described by $\boldsymbol{R}_{CG}$ which contains entropic effects. This potential energy is in fact the many-body potential of mean force (PMF) governing the equilibrium distribution of sites in the atomistic model and describing the mean force which is acting between sites. It is completely determined by the atomistic potential $U(\boldsymbol{r})$ and ξ.

4.3 Coarse Grained Potential of Mean Force

The coarse graining starts by assuming that the total coarse grained potential energy, can be separated into two parts, a bonded part and a non-bonded part:

$$U^{CG} = \sum U^{CG}_{bonded} + \sum U^{CG}_{non-bonded} \tag{4.7}$$

First, we are going to examine the potential which corresponds to the non-bonded interactions. We can define an effective potential, whose gradients determine the force field of the coarse grained model, as:

$$\exp(-\frac{U^{CG}(\boldsymbol{R})}{k_b T}) \cong \int \exp(-\frac{U(\boldsymbol{r})}{k_b T})\delta[\xi(\boldsymbol{r}) - \boldsymbol{R}]d\boldsymbol{r} \tag{4.8}$$

The left side of the above equation is the Boltzmann factor of a system with U^{CG} potential, while the right side is the sum of the Boltzmann factors of all microstates consistent with specified values of the coarse grained degrees of freedom. If we could sample from coarse grained system according to U^{CG} , all properties that depend only on the coarse grained degrees of freedom, could be calculated exactly. Keep in mind, however, that there is no guarantee that will have a particular functional form, i.e., there is no a priori reason that it should be a pairwise additive sum of interactions between the CG sites. This is due to the fact that the degrees of freedom that are coarse grained away have now been included in the effective remaining interactions. On the other hand, when we develop CG model energy functions we typically specify pairwise terms. This is an approximation to keep our simulations computationally efficient, but in fact this causes the deviation of the final potential from the initial estimate determined from the atomistic function. We will further analyse this method in section 5.5.

4.4 Methods of approximating the potential of mean force

In order to construct reduced CG models, which approximate the properties of reference (microscopic) molecular systems and are based on statistical mechanics principles, we use numerical parameterizing methods. Such methods consider the optimization of a proposed parametric model under different minimization principles. Specifically, they consist of the pre-selected observable φ and the minimization of (average) quantities over a parameter set Θ

$$\underset{\theta \in \Theta}{min} \mathcal{L}_{cost}(\phi; \theta)$$

where $\mathcal{L}_{cost}$ is a cost function. At below we will mention four of these methods.

Iterative Boltzmann Inversion

This method aims to construct a tabulated potential able to reproduce a target distribution from atomistic simulation, [2]. The distribution function can be bonded or non-bonded, but most of the time the IBI method is used in order to calculate an optimal potential for the non-bonded interactions.

Force Matching method

Force matching is an alternative to the Inverse Monte Carlo method to extract classical potentials from ab initio calculations. Like the Inverse Monte Carlo approach one performs a reference all-atom simulation and then is looking for an optimal CG model that "matches" it in some optimal sense. Its aim is not to reproduce various distribution functions but instead try to match forces on CG sites as closely as possible. Since is a non-iterative method for evaluating CG potential, is less computationally demanding. It represents a rigorous way of building up CG parameters bottom-up from atomistic simulations and requires only a trajectory for a reference system.

Relative Entropy

The relative entropy approach is based on minimizing an objective function, the relative entropy. This quantity has a direct relation with finding a CG potential that reproduces the multidimensional potential of mean force. Is a method which quantifies the extent of the configurational phase-space overlap between two molecular ensembles. In simple terms, it measures the information lost when moving from the all-atom configurational space to the CG configurational space. Since is based on the likelihood that random sampling of the CG system can correctly reconstruct the atomistic distribution, it can be used as a measure of the discrepancies between various properties of the CG system's and the reference all-atom system.

Inverse Monte Carlo

The inverse Monte Carlo method solves the inverse problem of the statistical mechanics, i.e., reconstructs the interaction potential between molecules if the distribution function is known. It is another iterative procedure that refines the CG potentials until the CG model reproduces a set of reference distribution functions. If we know from some source the distribution function between CG particles, we can calculate the corresponding pair interaction potential. By applying the Inverse Monte Carlo approach, any sampling method can be used as long as it provides a canonical sampling.

Chapter 5

Dynamics of the coarse grained model

After we define the new coarse grained system our goal is to define the new dynamics and the new equation of motion for the coarse grained particles. This equation is the generalized Langevin equation. To find this equation in a general form we will use Mori-Zwanzig procedure which use the pojection operator method.

5.1 Mori-Zwanzig theory

In this section we review the Mori–Zwanzig theory. We shall focus on systems whose microscopic state is characterized by the instantaneous positions and momenta of the N atoms of the system, $\{\boldsymbol{r}_i(t), \boldsymbol{p}_i(t)\}$ with $i = 1, \cdots, N$. We denote the collection of these variables by $\boldsymbol{Z}(t) = (Z_1(t), \cdots, Z_{6N}(t))$, which is a vector of $6N$ components. In terms of $\boldsymbol{Z}(t)$, the Hamiltonian dynamics of the system can be written as by

$$\frac{d\boldsymbol{Z}(t)}{dt} = J\frac{\partial H(\boldsymbol{Z}(t))}{\partial z}, \boldsymbol{Z}(0) = z \tag{5.1}$$

where z represent the initial condition, H is the Hamiltonian and J is the symplectic matrix with a block diagonal structure with the blocks given by

$$J = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \tag{5.2}$$

Assume that we are not interested in the evolution of $\boldsymbol{Z}(t)$, but of $\boldsymbol{A}(\boldsymbol{Z}(t))$ where $\boldsymbol{A}(z) = (A_1(z), ., A_M(z))$ is a specific observable, i.e. any set of M functions defined on phase-space. More specifically we want to calculate the statistical properties of $\boldsymbol{A}(\boldsymbol{Z}(t))$ for $t \geq 0$ for the ensemble of initial conditions $\boldsymbol{Z}(0) = z$ satisfying $\boldsymbol{A}(z) = \boldsymbol{\alpha}$ for some fixed α and with z distributed according to the equilibrium density $\rho^{eq}(z)$ conditional on $\boldsymbol{A}(z) = \boldsymbol{\alpha}$. Zwanzig's approach is a way to write an integro-differential equation with random coefficients whose solutions in different realizations generate the desired ensemble of $\boldsymbol{A}(\boldsymbol{Z}(t))$.

To see how this equation is derived, let us first make explicit the dependency in the initial condition z in $\boldsymbol{A}(\boldsymbol{Z}(t))$ by denoting $\boldsymbol{A}(\boldsymbol{Z}(t)) \equiv \boldsymbol{\alpha}(t,z)$. This function can be formally expressed as

$$\boldsymbol{\alpha}(t,z) = \exp\{tL\}\boldsymbol{A}(z) \tag{5.3}$$

in which the exponential operator is defined through its Taylor series expansion and L is the Liouville operator

$$L = -\frac{\partial H}{\partial z} J \frac{\partial}{\partial z} \tag{5.4}$$

Eqn(5.3) indicates that $\boldsymbol{\alpha}(t,z)$ satisfies the following equation

$$\partial_t \boldsymbol{\alpha}(t,z) = L\boldsymbol{\alpha}(t,z), \boldsymbol{\alpha}(0,z) = \boldsymbol{A}(z) \tag{5.5}$$

Next introduce the conditional expectation operator P_α whose action to an arbitrary phase function $F(z)$ gives the conditional equilibrium expectation of $F(z)$ at $\boldsymbol{A}(z) = \boldsymbol{\alpha}$ fixed, i.e. the function of $\boldsymbol{\alpha}$ defined as

$$P_\alpha F = \frac{1}{\Omega(\boldsymbol{\alpha})} \int F(z) \rho^{eq}(z) \delta(\boldsymbol{A}(z) - \boldsymbol{\alpha}) dz \tag{5.6}$$

Here $\rho^{eq}(z)$ is the equilibrium probability density (e.g. the microcanonical density $\rho^{eq}(z) = \Omega_0^{-1}\delta(H(z) - E)$ where E is the energy and Ω_0 is the normalization factor, assuming that $H(z)$ is the only invariant of motion), and we defined

$$\Omega(\boldsymbol{\alpha}) = \int \rho^{eq}(z) \delta(\boldsymbol{A}(z) - \boldsymbol{\alpha}) dz \tag{5.7}$$

$\Omega(\boldsymbol{\alpha})$ is the probability density of $\boldsymbol{A(z)}$ or, loosely speaking, "the number of microstates compatible with the macrostate $\boldsymbol{A(z)} = \boldsymbol{\alpha}$". Let $Q_\alpha = 1 - P_\alpha$, and in eqn (5.5) use $L\boldsymbol{\alpha}(t,z) = L\exp\{tL\}\boldsymbol{A(z)} = \exp\{tL\}L\boldsymbol{A(z)}$ and insert $1 = P_{\boldsymbol{A(z)}} + Q_{\boldsymbol{A(z)}}$ to transform this equation into

$$\partial_t \boldsymbol{\alpha}(t,z) = \exp\{tL\} P_{\boldsymbol{A(z)}} L\boldsymbol{A} + \exp\{tL\} Q_{\boldsymbol{A(z)}} L\boldsymbol{A} \tag{5.8}$$

Using the Duhamel–Dyson identity

$$\exp\{tL\} = \exp\{tQ_{\boldsymbol{A(z)}}L\} + \int_0^t ds \exp\{(t-s)L\} P_{\boldsymbol{A(z)}} L \exp\{sQ_{\boldsymbol{A(z)}}L\} \tag{5.9}$$

the second term at the right-hand side of eqn (5.8) can be written as

$$\partial_t \boldsymbol{\alpha}(t,z) = \exp\{tL\} P_{\boldsymbol{A(z)}} L\boldsymbol{A} + \int_0^t ds \exp\{(t-s)L\} P_{\boldsymbol{A(z)}} L\tilde{\boldsymbol{R}}(s,\cdot) + \tilde{\boldsymbol{R}}(t,z) \tag{5.10}$$

where we defined

$$\begin{aligned}\tilde{\boldsymbol{R}}(t,z) &= \exp\{tQ_{\boldsymbol{A(z)}}L\}Q_{\boldsymbol{A(z)}}L\boldsymbol{A}\\ &= Q_{\boldsymbol{A(z)}}\exp\{tQ_{\boldsymbol{A(z)}}L\}L\boldsymbol{A}\end{aligned} \tag{5.11}$$

and we used a dot instead of a z as second argument for $\tilde{\boldsymbol{R}}$ in $P_{\boldsymbol{A(z)}}L\tilde{\boldsymbol{R}}(s,\cdot)$ to emphasize that this term depends on z only through $\boldsymbol{A(z)}$ (the same is true for $P_{\boldsymbol{A(z)}}L\boldsymbol{A}$ but not for $\tilde{\boldsymbol{R}}(t,z)$ which is a general function of z). The second term at the right-hand side of eqn (5.10) can be simplified by means of the following identity which, for clarity, we write component-wise using the indices $\mu,\nu = 1,\cdots,M$ to denote the components of $\boldsymbol{A}$ and $\boldsymbol{\alpha}$ and Einstein sum convention over repeated indices which is defined for a random function as $\sum_{i=1}^{N} c_i x^i = c_i x^i$

$$\begin{aligned}P_\alpha L\tilde{R}_\mu(s,\cdot) &= \frac{1}{\Omega(\boldsymbol{\alpha})}\int dz\rho^{eq}(z)\delta(\boldsymbol{A(z)}-\boldsymbol{\alpha})L\exp\{sQ_{\boldsymbol{A(z)}}L\}Q_{\boldsymbol{A(z)}}LA_\mu\\ &= -\frac{1}{\Omega(\boldsymbol{\alpha})}\int dz\rho^{eq}(z)[\exp\{sQ_{\boldsymbol{A(z)}}L\}Q_{\boldsymbol{A(z)}}LA_\mu]L\delta(\boldsymbol{A(z)}-\boldsymbol{\alpha})\\ &= \frac{1}{\Omega(\boldsymbol{\alpha})}\int dz\rho^{eq}(z)[\exp\{sQ_{\boldsymbol{A(z)}}L\}Q_{\boldsymbol{A(z)}}LA_\mu][LA_\nu(z)]\frac{\partial}{\partial\alpha_\nu}\delta(\boldsymbol{A}(z)-\boldsymbol{\alpha})\\ &= \frac{1}{\Omega(\boldsymbol{\alpha})}\frac{\partial}{\partial\alpha_\nu}\int dz\rho^{eq}(z)\delta(\boldsymbol{A(z)}-\boldsymbol{\alpha})[LA_\nu(z)][\exp\{sQ_{\boldsymbol{A(z)}}L\}Q_{\boldsymbol{A(z)}}LA_\mu][LA_\nu(z)]\\ &= \frac{1}{\Omega(\boldsymbol{\alpha})}\frac{\partial}{\partial\alpha_\nu}(\Omega(\boldsymbol{\alpha})P_\alpha([\exp\{sQ_{\boldsymbol{A}}L\}Q_{\boldsymbol{A}}LA_\mu][LA_\nu]))\\ &= M_{\mu\nu}(\boldsymbol{\alpha},s)\frac{\partial S(\boldsymbol{\alpha})}{\partial\alpha_\nu}+k_B\frac{\partial M_{\mu\nu}(\boldsymbol{\alpha},s)}{\partial\alpha_\nu}\end{aligned} \tag{5.12}$$

Here and below the operators inside the brackets $[\cdot]$ only act on the terms at their right in these brackets and we have introduced the entropy

$$S(\boldsymbol{\alpha}) = k_B \ln\Omega(\boldsymbol{\alpha}) \tag{5.13}$$

as well as the memory matrix $M(\boldsymbol{\alpha},t) = M^T(\boldsymbol{\alpha},-t)$ whose components are given by the following conditional expectation

$$M_{\mu\nu}(\boldsymbol{\alpha},t) = \frac{1}{k_B}P_\alpha\left([LA_\nu][\exp\{tQ_AL\}Q_ALA_\mu]\right) = \frac{1}{k_B}P_\alpha\left(\tilde{R}_\mu(t,\cdot)\tilde{R}_\nu(0,\cdot)\right) \tag{5.14}$$

Inserting eqn (5.12) in eqn (5.10) and using the property that for any $f(\boldsymbol{A}(z))$, we have $\exp\{Lt\}f(\boldsymbol{A}(z)) = f(\boldsymbol{\alpha}(t,z))$ and so

$$\exp\{tL\}P_{A(z)}L\boldsymbol{A}(z) = P_{\alpha(t,z)}L\boldsymbol{A}(z), \exp\{(t-s)L\}M(\boldsymbol{A}(z),s)\frac{\partial S(\boldsymbol{A}(z))}{\partial\boldsymbol{\alpha}}$$

$$= M(\boldsymbol{\alpha}(t-s,z),s)\frac{\partial S(\boldsymbol{\alpha}(t-s,z))}{\partial \boldsymbol{\alpha}}, \exp\{(t-s)L\}k_B\frac{\partial M(\boldsymbol{A}(z),s)}{\partial \boldsymbol{\alpha}}$$
$$= k_B\frac{\partial M(\boldsymbol{\alpha}(t-s,z),s)}{\partial \boldsymbol{\alpha}}$$

we arrive at the following equation for $\boldsymbol{\alpha}(t,z)$

$$\begin{aligned}\partial_t\boldsymbol{\alpha}(t,z) &= \boldsymbol{\nu}(\boldsymbol{\alpha}(t,z)) \\ &+ \int_0^t dsM(\boldsymbol{\alpha}(t-s,z),s)\frac{\partial S}{\partial \boldsymbol{\alpha}}(\boldsymbol{\alpha}(t-s,z)) + k_B\int_0^t ds\frac{\partial M}{\partial \boldsymbol{\alpha}}(\boldsymbol{\alpha}(t-s,z),s) + \tilde{\boldsymbol{R}}(t,z)\end{aligned} \tag{5.15}$$

where $\boldsymbol{\nu(\alpha)}$ is the following conditional expectation

$$\boldsymbol{\nu(\alpha)} = P_\alpha L\boldsymbol{A} \tag{5.16}$$

Eqn (5.15) is a formally exact rewriting of eqn (5.5). Recall however that we are not interested in solving this equation for a specific initial condition $\boldsymbol{\alpha}(0,z) = \boldsymbol{A}(z)$ but rather for an ensemble of initial conditions z satisfying $\boldsymbol{\alpha}(0,z) = \boldsymbol{A}(z) = \boldsymbol{\alpha}(0)$ for some fixed $\boldsymbol{\alpha}(0)$ and with z distributed according to the equilibrium density $\rho^{eq}(z)$ conditional on $\boldsymbol{A}(z) = \boldsymbol{\alpha}(0)$. In this case, $\tilde{\boldsymbol{R}}(t,z)$, which is the only term in eqn (5.15) which is not a function of $\boldsymbol{\alpha}(s,z)$ for $0 \le s \le t$, can be interpreted as a noise term whose statistics must be consistent with eqn (5.14). With this in mind, we can introduce the shorthand notation $\boldsymbol{\alpha}(t,z) = \boldsymbol{\alpha}(t)$, and rewrite eqn (5.15) as an integro-differential equation with a random-source term which is usually referred to as the generalized Langevin equation(GLE):

$$\begin{aligned}\frac{d\boldsymbol{\alpha}(t)}{dt} &= \boldsymbol{\nu}(\boldsymbol{\alpha}(t)) \\ &+ \int_0^t dsM(\boldsymbol{\alpha}(t-s),s)\frac{\partial S}{\partial \boldsymbol{\alpha}}(\boldsymbol{\alpha}(t-s)) + k_B\int_0^t ds\frac{\partial M}{\partial \boldsymbol{\alpha}}(\boldsymbol{\alpha}(t-s),s) + \boldsymbol{R}(t)\end{aligned} \tag{5.17}$$

where $\boldsymbol{R}(t)$ is now viewed as a zero-mean random process whose statistical properties are specified by eqn (5.11) in which z is random and distributed according to the equilibrium density $\rho^{eq}(z)$ conditional on $\boldsymbol{A}(z) = \boldsymbol{\alpha}(0)$. By solving eqn (5.17) with the initial condition $\boldsymbol{\alpha}(0)$ in different realizations of $\boldsymbol{R}(t)$ we can then generate the exact statistics of $\boldsymbol{A}(Z(t))$ for $t \ge 0$ along an ensemble of trajectories consistent with $\boldsymbol{A}(Z(0)) = \boldsymbol{\alpha}(0)$.

While formally exact within the statistical interpretation above, the GLE (eqn (5.17)) is unfortunately rather useless in practice. Indeed, while $\boldsymbol{\nu(a)}$ and the gradient $\frac{\partial S}{\partial \boldsymbol{\alpha}}$ are conditional expectations which can in principle be computed using constrained molecular dynamics, we cannot calculate $M(\boldsymbol{\alpha},t)$ and $\boldsymbol{R}(t)$ since they involve the projected dynamics associated with $Q_{A(z)}L$ which we do not know how to generate. (Note also that the process $\boldsymbol{R}(t)$ is non-Gaussian in general, i.e. it is not specified completely by its correlation function in eqn (5.14).) On top of this, even if we knew how to compute $M(\boldsymbol{\alpha},t)$ and the full statistics of $\boldsymbol{R}(t)$, eqn (5.17) would remain very challenging to integrate numerically because of its non-Markovian character.

5.2 The standard Markovian approximation and its caveats

In order to made the GLE (eqn (5.17)) practical we use the "Markovian approximation".This approximation starts by assuming that the time scale of variation of the relevant variables is much larger than the time scale of decay of the memory matrix $M(\boldsymbol{\alpha}, t)$ defined in eqn(5.14), which can be approximated by

$$M(\boldsymbol{\alpha}, t) \approx M_T(\boldsymbol{\alpha})\delta(t) \tag{5.18}$$

where the time-independent friction matrix $M_T(\alpha)$ is defined as

$$M_T(\boldsymbol{\alpha}) = \int_0^T dt M_T(\boldsymbol{\alpha}, t) = \int_0^T dt P_\alpha(\tilde{R}(t, \cdot) \otimes \tilde{R}(0, \cdot)) \tag{5.19}$$

Note that the integral is capped at a finite time T rather than extended to infinity. Consistent with the approximation in 5.18, we can assume that the random term R(t) in (5.17) can be modelled as a white-noise, i.e. a Gaussian process with mean zero and whose correlation at $\boldsymbol{\alpha(t)} = \boldsymbol{\alpha}$ fixed is given by

$$\langle \boldsymbol{R}_T(t) \otimes \boldsymbol{R}_T(s) \rangle = k_B M_T(\boldsymbol{\alpha})\delta(t - s) \tag{5.20}$$

Under these assumptions, the GLE (eqn (5.17)) becomes the stochastic differential equation (SDE)

$$\frac{d\boldsymbol{\alpha}(t)}{dt} = \boldsymbol{v}(\boldsymbol{\alpha}(t)) + M_T(\boldsymbol{\alpha}(t))\frac{\partial S}{\partial \boldsymbol{\alpha}}(\boldsymbol{\alpha}(t)) + k_B \frac{\partial M_T}{\partial \boldsymbol{\alpha}}(\boldsymbol{\alpha}(t)) + \boldsymbol{R}_T(t) \tag{5.21}$$

The Fokker–Planck equation which is mathematically equivalent to 5.21 was derived by Zwanzig. The last thing left so as 5.21 be fully explicit is how to compute the friction matrix in 5.19. This is achieved by assuming that the projected dynamics $\exp\left\{t\mathcal{Q}_{A(z)}L\right\}$ can be replaced by the real dynamics $\exp\{tL\}$ in eqn (5.11), i.e.

$$\tilde{\boldsymbol{R}}(t, z) \approx \exp\{Lt\}\mathcal{Q}_{A(z)}L\boldsymbol{A} = L\boldsymbol{A}(\boldsymbol{Z}(t)) - \boldsymbol{\nu}(\boldsymbol{\alpha}(t)) \tag{5.22}$$

where $\boldsymbol{\nu}(\alpha)$ is defined in eqn (5.16), $\boldsymbol{Z}(t)$ is the solution of the original Hamilton eqn (5.1) and we used again the notation $\boldsymbol{\alpha}(t) = \boldsymbol{\alpha}(t, \boldsymbol{z})$. The right-hand side of eqn (5.22) can be computed using a combination of standard MD simulations (to compute $\boldsymbol{Z}(t)$) and constrained molecular simulation (to compute $\boldsymbol{v(\alpha)}$). Eqn (5.22) is valid for short times when the time integrals in eqn (5.15) can be neglected: indeed, using $\partial_t \boldsymbol{\alpha}(t, \boldsymbol{z}) = L\boldsymbol{A}(\boldsymbol{Z}(t))$ in eqn (5.15) and solving this equation with the integrals set to zero for $\tilde{\boldsymbol{R}}(t, \boldsymbol{z})$ gives eqn(5.22). Unfortunately, eqn (5.22) is harder to justify at later times. In particular, this approximation is the reason why the integral in eqn (5.19) must be capped at a finite T: if one extends the limit of integration T in eqn (5.19) to infinity using the approximation (eqn (5.22)) for $\tilde{\boldsymbol{R}}(t, \boldsymbol{z})$, then the integral vanishes. This is the well-known plateau problem and the current practice is to select for the upper time of integration a time T which is large compared to the correlation time of the (unspecified) orthogonal dynamics, but small compared to the time scale of evolution of the macroscopic variables. This intermediate time scale is assumed to exists, at least in situations where there is a clear separation of time scales, but the specific value for T is not provided by the theory, and it is difficult to predict how the results depend on T. In summary, both approximations eqn (5.18) and eqn (5.22) are uncontrolled and this clearly diminishes the confidence that one can have in eqn (5.21). Another procedure to derive an equation similar to eqn (5.21) but whose validity is easier to assess and which does not suffer from the plateau problem is using modified dynamics and Markovian limiting equation.

5.3 Modified dynamics and Markovian limiting equation

In order to replace eqn (5.18) and (5.22) by more controlled approximations, consider the time integrals appearing in the GLE (eqn (5.17)) and perform the change of variables $s = \varepsilon^2\tau$, where ϵ is a non-dimensional control parameter. This leads to

$$\begin{aligned}\frac{d\boldsymbol{\alpha}(t)}{dt} &= \boldsymbol{\nu}(\boldsymbol{\alpha}(t)) \\ &+ \varepsilon^2 \int_0^{\frac{t}{\varepsilon^2}} d\tau M(\boldsymbol{\alpha}(t-\varepsilon^2\tau), \varepsilon^2\tau) \frac{\partial S}{\partial \boldsymbol{\alpha}}(\boldsymbol{\alpha}(t-\varepsilon^2\tau)) \\ &+ \varepsilon^2 k_B \int_0^{\frac{t}{\varepsilon^2}} d\tau \frac{\partial M}{\partial \boldsymbol{\alpha}}(\boldsymbol{\alpha}(t-\varepsilon^2\tau), \varepsilon^2\tau) + \boldsymbol{R}(t)\end{aligned} \tag{5.23}$$

Now observe that if the following limit exists

$$\lim_{\varepsilon\to 0} \varepsilon^2 M(\boldsymbol{\alpha}(t-\varepsilon^2\tau), \varepsilon^2\tau) \equiv m(\boldsymbol{\alpha}(t), \tau) \tag{5.24}$$

then, in the limit as $\varepsilon \to 0$, eqn (5.23) reduces to the SDE

$$\frac{d\boldsymbol{\alpha}(t)}{dt} = \boldsymbol{\nu}(\boldsymbol{\alpha}(t)) + \bar{M}(\boldsymbol{\alpha}(t)) \frac{\partial S}{\partial \boldsymbol{\alpha}}(\boldsymbol{\alpha}(t)) + k_B \frac{\partial \bar{M}}{\partial \boldsymbol{\alpha}}(\boldsymbol{\alpha}(t)) + \bar{\boldsymbol{R}}(t) \tag{5.25}$$

Here the friction matrix $\bar{M}(\boldsymbol{\alpha})$ has the Green–Kubo form

$$\bar{M}(\boldsymbol{\alpha}) = \int_0^\infty m(\boldsymbol{\alpha}, \tau) d\tau \tag{5.26}$$

and the random term $\bar{\boldsymbol{R}}(t)$ is an *Itô* white-noise, i.e. a Gaussian process with mean zero and whose correlation at $\boldsymbol{\alpha}(t) = \boldsymbol{\alpha}$ is given by

$$\langle \boldsymbol{R}(t)\boldsymbol{R}(s)\rangle = k_B \bar{M}(\boldsymbol{\alpha})\delta(t-s) \tag{5.27}$$

We want to find out under what conditions the limit in eqn (5.24) exists. By using the definition in eqn (5.14) we can write

$$\varepsilon^2 M(\boldsymbol{\alpha}(t-\varepsilon^2\tau, z), \varepsilon^2\tau) = \frac{\varepsilon^2}{k_B} P_{\boldsymbol{\alpha}(t-\varepsilon^2\tau, z)} \left(\left[\exp\left\{\varepsilon^2\tau Q_A L\right\} Q_A L\boldsymbol{A}\right] \otimes \left[Q_A L\boldsymbol{A}\right]\right) \tag{5.28}$$

From this expression, it can be checked by direct calculation that one way to ensure that the limit eqn (5.24) exists is by assuming that the Liouville operator has the following form

$$L = L_0 + \frac{1}{\varepsilon}L_1 + \frac{1}{\varepsilon^2}L_2 \tag{5.29}$$

with the operators L_1, L_2 satisfying

$$\begin{aligned} P_{A(z)}L_2 &= 0 \\ P_{A(z)}L_1P_{A(z)} &= 0 \end{aligned} \tag{5.30}$$

So in this case, eqn(5.28) becomes

$$\varepsilon^2 M(\boldsymbol{\alpha}(t-\varepsilon^2\tau, z), \varepsilon^2\tau) = \frac{1}{k_B}P_{\boldsymbol{\alpha}(t)}([exp\{\tau L_2\}L_1\boldsymbol{A}] \otimes [L_1\boldsymbol{A}]) + O(\varepsilon) \tag{5.31}$$

and the limiting dynamic equation obtained from eqn (5.17) when $\varepsilon \to 0$ precisely is eqn (5.25) with the Green–Kubo friction matrix $\bar{M}(\boldsymbol{\alpha})$ now given explicitly by

$$\bar{M}(\boldsymbol{\alpha}) = \frac{1}{k_B}\int_0^\infty d\tau P_{\boldsymbol{\alpha}}([exp\{\tau L_2\}L_1\boldsymbol{A}] \otimes [L_1\boldsymbol{A}]) \tag{5.32}$$

and the drift term is given by

$$\boldsymbol{\nu(\alpha)} = P_\alpha L_0\boldsymbol{A} \tag{5.33}$$

Now we want to make clear in which situations eqn(5.25) is useful. To start our analysis we use the fact that Liouville operator can be decomposed as $L = L_0 + L_1 + L_2$ by defining

$$\begin{aligned} L_0 &= P_{A(z)}(L - \mathcal{R}) \\ L_1 &= Q_{A(z)}(L - \mathcal{R}) \\ L_2 &= \mathcal{R} \end{aligned} \tag{5.34}$$

and letting $P_{A(z)}$ be the expectation with respect to the equilibrium distribution associated with the operator $\mathcal{R}$. This operator, to be specified more fully later, should be similar to L, except that it leaves both the Hamiltonian and the relevant variables invariant, that is

$$\begin{aligned} \mathcal{R}f(H(z)) &= 0 \\ \mathcal{R}g(A(z)) &= 0 \end{aligned} \tag{5.35}$$

for any functions f and g. By construction, the operators L_0, L_1, L_2 in eqn (5.34) satisfy the properties in eqn (5.30). This suggests the introduction of a modified dynamic operator L^ε as in eqn (5.29)

$$L^\varepsilon \equiv L_0 + \frac{1}{\varepsilon}L_1 + \frac{1}{\varepsilon^2}L_2 \tag{5.36}$$

The dynamics associated with L^ε coincides with the real dynamics when $\varepsilon = 1$ and produces a dynamics of the relevant variables which is governed by the SDE (eqn (5.25)) when $\varepsilon \to 0$. By inserting the operators eqn (5.34) into eqn (5.32), (5.33) we obtain

$$\begin{aligned} \boldsymbol{\nu(\alpha)} &= P_\alpha(L\boldsymbol{A}) \\ \bar{M}(\boldsymbol{\alpha}) &= \frac{1}{k_B}\int_0^\infty d\tau P_{\boldsymbol{\alpha}}([exp\{\tau\mathcal{R}\}L\boldsymbol{A}] \otimes [L\boldsymbol{A}]) \end{aligned} \tag{5.37}$$

The advantage of the above procedure, which differs from the usual prescription in that the projected dynamics $exp\{tQ_{A(z)}L\}$ is approximated by $exp\{tL_2\} \equiv exp\{t\mathcal{R}\}$ rather than $exp\{tL\}$, is that we have now an explicit and practical method to compute the constrained averages once we specify the operator $\mathcal{R}$. If we assume that this constrained dynamics is ergodic and denote compactly by $Z_\mathcal{R}(t) = exp\{t\mathcal{R}\}z$ the constrained trajectory with initial condition $Z_\mathcal{R}(0) = z$ with z such that $\boldsymbol{A(z) = \alpha}$ and $H(z) = E$ then the conditional expectations in eqn(5.37) can be expressed as time averages

$$P_\alpha L\boldsymbol{A} = \lim_{T\to\infty}\frac{1}{T}\int_0^T dtL\boldsymbol{A}(\boldsymbol{Z}_\mathcal{R}(t)) \tag{5.38}$$

and

$$\bar{M}(\boldsymbol{\alpha}) = \lim_{T'\to\infty}\frac{1}{k_B}\int_0^{T'} dt' \lim_{T\to\infty}\frac{1}{T}\int_0^T dt[L\boldsymbol{A}(\boldsymbol{Z}_\mathcal{R}(t+t'))] \otimes [L\boldsymbol{A}(\boldsymbol{Z}_\mathcal{R}(t))] \tag{5.39}$$

5.4 An Approximate Solution of the Mori-Zwanzig Equations

5.4.1 Approximation 1: Simplified orthogonal dynamics.

Let us now introduce a general (not necessarily Hamiltonian) system described by a set of ordinary differential equations:

$$\frac{d}{dt}\phi(t) = M(\phi(t)) \tag{5.40}$$

where ϕ is an an n-dimensional vector with components $\phi_i, i = 1, \cdots, n$ with n may be infinite, M is an n-dimensional vector function of ϕ with components $M_i(\phi)$, and the initial values $\phi(0) = x$ are given. We are interested in only the first m components of the solution, where m is much smaller than n, $m \ll n$. Let $\hat{\phi}$ be the vector $\hat{\phi} = (\phi_1, \phi_2, \cdots, \phi_m)$ made up of these first m components. Also we define the initial data as $\hat{x} = (x_1, \cdots, x_m)$. Now consider as example a two-particle system in one space dimension with Hamiltonian $H = \frac{1}{2}(r_1^2 + r_2^2 + r_1^2 r_2^2 + p_1^2 + p_1^2)$ where the $r_i, p_i, i = 1, 2$, are positions and momenta. This is a system of two non-interacting harmonic oscillators coupled by a quartic interaction term. The harmonic oscillators, once set in motion, oscillate forever.

The equations of motion are:

$$\begin{aligned}\dot{r}_1 &= p_1\\ \dot{p}_1 &= -r_1(1+r_2^2)\\ \dot{r}_2 &= p_2\\ \dot{p}_2 &= -r_2(1+r_1^2)\end{aligned} \tag{5.41}$$

The Liouville operator is:

$$L = p_1\frac{\partial}{\partial r_1} - r_1(1+r_2^2)\frac{\partial}{\partial p_1} + p_2\frac{\partial}{\partial r_2} - r_2(1+r_1^2)\frac{\partial}{\partial p_2} \tag{5.42}$$

We assume that the initial values $r_1(0), p_1(0)$ of r_1, p_1 are given, while r_2, p_2 are sampled from the pdf $W(x) = \frac{e^{-H(r_1,p_1,r_2,p_2)}}{Z}$ (a canonical density with temperature T = 1). Our aim is to compute r_1, p_1 from the MZ equations. First we assume that e^{tQL} is e^{tL} in the memory term. Specifically we want to make clear that as for the evolution of the noise , the orthogonal dynamics are roughly the same as the correct dynamics; the orthogonal dynamics are not sensitive to the resolved variables. By definition,

$$PLe^{sQL} = Le^{sQL} - QLe^{sQL}$$

An operator commutes with any function of itself, so that

$$QLe^{sQL} = e^{sQL}QL$$

Using this last identity and then substituting $e^{sQL} \to e^{sL}$ on the right hand side of the equality, we have

$$PLe^{sQL} \approx Le^{sL} - e^{sL}QL$$

Then

$$e^{(t-s)L}PLe^{sQL} \approx e^{(t-s)L}Le^{sL} - e^{(t-s)L}e^{sL}QL = e^{tL}PL$$

making the integrand in the integral term of the MZ becomes independent of s, so that

$$\int_0^t e^{tL}PLQLx_j ds = te^{tL}PLQLx_j$$

where $\hat{x}$ is the vector with components $x_1 = r_1$ and $x_2 = p_1$. The memory term has been reduced to a differential operator multiplied by the time t; the time starts at $t = 0$ when the initial value of $r_1(t)$, $p_1(t)$ is assigned and when there is no uncertainty. The equations with the simplified integral term constitute the "t-model". Collecting terms, the t-model equations are:

$$\frac{d}{dt}e^{tL}\hat{x} = e^{tL}PL\hat{x} + te^{tL}PLQL\hat{x} + e^{tQL}QLx_j \tag{5.43}$$

In our case where the components x_j are r_1, p_1 we have:

$$\begin{aligned} Lr_1 &= p_1, \\ PLr_1 &= p_1, \\ QLr_1 &= 0, \\ LQLr_1 &= 0, \\ PLQLr_1 &= 0, \end{aligned} \tag{5.44}$$

and

$$\begin{aligned} Lp_1 &= -r_1(1+r_2^2) \\ PLp_1 &= -r_1(1+\frac{1}{1+r_1^2}) \\ QLp_1 &= -r_1(1+r_2^2)+r_1(1+\frac{1}{1+r_1^2}) \\ LQLp_1 &= p_1(-(1+r_2^2)+(1+\frac{1}{1+r_1^2})-\frac{2r_1^2}{(1+r_1^2)^2})-2r_1r_2p_2 \\ PLQLp_1 &= -\frac{2r_1^2p_1}{(1+r_1^2)^2} \end{aligned} \tag{5.45}$$

The approximate equations of motion for r_1, p_1 are:

$$\begin{aligned} &\frac{d}{dt}r_1 = p_1 \\ &\frac{d}{dt}p_1 = -r_1(1+\frac{1}{1+r_1^2})-2t\frac{r_1^2p_1}{(1+r_1^2)^2}+e^{tQL}QLp_1 \end{aligned} \tag{5.46}$$

where the noise term has not been made explicit.

Suppose all one wants to know are the quantities

$$E[r_1(t) \mid r_1(0), p_1(0)], E[p_1(t) \mid r_1(0), p_1(0)]$$

the conditional expectations of $r_1(t), p_1(t)$ given $r_1(0), p_1(0)$. An equation for these quantities can be obtained by premultiplying equations(5.46) by the constant operator P (remembering that by definition $Pr_1(t) = E[r_1(t) \mid r_1(0), p_1(0)]$ etc.). Now we have to deal with the difficulty: an average of a function of a variable does not generally equal the same function of the average; for example, it is not true in general that $E[r^2] = (E[r])^2$. An additional simplification is needed. This difficulty can be solved if we look for sample paths of the resolved variables, when it replaced by the need to solve the orthogonal dynamics equations for the noise.

5.4.2 Approximation 2: A "mean field" approximation.

Assume that for the functions on the right-hand-side of equations (5.46) averaging and function evaluation do commute, so that, for example, $E[(1+r_1^2)^{-1} \mid r_1(0), p_1(0)] \approx$

$(1+E[r_1(t) \mid \cdot]^2)^{-1}$. This mean field approximation is legitimate when the noise is small enough. If the noise is zero, the approximation is exact. In the specific problem under consideration it should be a good approximation if the initial data are sampled from a canonical density with low temperature. We use it here at the initial temperature $T=1$.

Define $R_1(t) = E[r_1(t) \mid r_1(0), p_1(0)], P_1(t) = E[p_1(t) \mid r_1(0), p_1(0)]$. The approximate equations of motion become:

$$\begin{aligned}
&\frac{d}{dt}R_1 = P_1 \\
&\frac{d}{dt}P_1 = -R_1(1+\frac{1}{1+R_1^2}) - t\frac{2R_1^2 P_1}{(1+R_1)^2}
\end{aligned} \tag{5.47}$$

These equations can be solved numerically. Notwithstanding the approximations, these graphs display the features one may expect in the solutions of the MZ equations in general: the amplitude of the noise grows in time (we have not calculated this amplitude explicitly, but it is reflected in the growing magnitude of the dissipation term), and the averages of the solutions decay to zero.

5.5 Coarsening big complex molecules

Let us now apply the previous methology in a collection of big molecules by using center of mass (CoM) variables as relevant variables. Later we will further analyse an application in a system of star polymers but now the framework is to a large extend independent of what kind of molecule we have, provided that they are made of many atoms and that they are isotropic. We assume that the fluid system is composed by M molecules and each molecule is made of N_m atoms whose positions and momenta are r_{i_μ}, p_{i_μ} where the index i_μ runs from $1,.,N_m$, while the index μ runs from $1,.,M$, i.e. Greek indices label molecules. The Hamiltonian of the system is

$$H(z) = \sum_{\mu=1}^{M}\sum_{i_\mu=1}^{N_m}\frac{p_{i_\mu}^2}{2m_{i_\mu}} + U \tag{5.48}$$

where m_{i_μ} is the mass of the atom i_μ and U is the potential energy The Liouville operator is given by

$$L = \sum_{\mu}\sum_{i_\mu}\frac{p_{i_\mu}}{m_{i_\mu}}\frac{\partial}{\partial r_{i_\mu}} + \sum_{\mu}\sum_{i_\mu}\boldsymbol{F}_{i_\mu}\frac{\partial}{\partial p_{i_\mu}} \tag{5.49}$$

where $\boldsymbol{F}_{i_\mu} = -\frac{\partial U}{\partial r_{i_\mu}}$ is the force on the atom i_μ. At a coarse-grained level, we will represent the complex molecule by just the position $\boldsymbol{R}_\mu$ and momentum $\boldsymbol{P}_\mu$ of its center of mass. These relevant variables are the following functions of the atomic variables

$$\begin{aligned}\boldsymbol{R}_\mu &= \frac{1}{M_\mu}\sum_{i_\mu=1}^{N_m} m_{i_\mu} r_{i_\mu}\\ \boldsymbol{P}_\mu &= \sum_{i_\mu=1}^{N_m} p_{i_\mu}\end{aligned} \tag{5.50}$$

where $M_\mu = \sum_{i_\mu=1}^{N_m} m_{i_\mu}$ is the total mass of the molecule μ.

Note that we have $L\boldsymbol{R}_\mu = \frac{\boldsymbol{P}_\mu}{M_\mu}$, this is, the Liouville operator applied to a relevant variable is (proportional to) a relevant variable itself. As a consequence, the conditional average of P_μ conditioned to $\boldsymbol{P}_\mu$ and $\boldsymbol{R}_\mu$ is just $\boldsymbol{P}_\mu$ itself. This means that there are no dissipative terms (nor noise terms) in the evolution of the positions, and eqn (5.25) reduces to

$$\begin{aligned}\frac{d\boldsymbol{R}_\mu}{dt} &= \frac{\boldsymbol{P}_\mu}{M_\mu}\\ \frac{d\boldsymbol{P}_\mu}{dt} &= \langle F_\mu\rangle + T\gamma_{\mu\nu}\frac{\partial S}{\partial \boldsymbol{P}_\nu} + k_B T\frac{\partial \gamma_{\mu\nu}}{\partial \boldsymbol{P}_\nu} + \tilde{\boldsymbol{F}}_\mu\end{aligned} \tag{5.51}$$

where we recall that the sum over repeated indices is implied. Here we use the shorthand notations $\boldsymbol{R} = (\boldsymbol{R}_1, ..., \boldsymbol{R}_M), \boldsymbol{P} = (\boldsymbol{P}_1, ..., \boldsymbol{P}_M)$ and we denote by $\langle\cdot\rangle$ the conditional expectation $P_{(\boldsymbol{R},\boldsymbol{P})}$ at $(\boldsymbol{R},\boldsymbol{P})$ fixed. The friction tensor is defined by

$$\gamma_{\mu\nu} = \frac{1}{k_B T}\int_0^\infty dt\,\langle\delta\boldsymbol{F}_\mu \exp\{t\mathcal{R}\}\delta\boldsymbol{F}_\nu\rangle \tag{5.52}$$

where $\delta\boldsymbol{F}_\mu = \boldsymbol{F}_\mu - \langle\boldsymbol{F}_\mu\rangle$ and $\boldsymbol{F}_\mu$ is the total force acting on the molecule μ:

$$\boldsymbol{F}_\mu = \sum_\nu \boldsymbol{F}_{\mu\nu} \equiv \sum_\nu\sum_{i_\mu j_\nu} \boldsymbol{F}_{i_\mu j_\nu} \tag{5.53}$$

Here $\boldsymbol{F}_{i_\mu j_\nu}$ is the force that atom j_ν exerts on atom i_ν, and $\boldsymbol{F}_{\mu\nu}$ is the total force that molecule ν exerts on molecule μ. The entropy has the form

$$S(\boldsymbol{R},\boldsymbol{P}) = k_B \ln\int dz\frac{1}{Z}\exp\{-\beta H(z)\}\prod_\mu \delta(\boldsymbol{R}_\mu(z) - \boldsymbol{R}_\mu)\delta(\boldsymbol{P}_\mu(z) - \boldsymbol{P}_\mu) \tag{5.54}$$

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

$$S(\boldsymbol{R},\boldsymbol{P}) = S_0 - \frac{1}{T}V(\boldsymbol{R}) - \frac{1}{T}\sum_\mu \frac{|\boldsymbol{P}_\mu|^2}{2M_\mu} \tag{5.55}$$

where S_0 is a constant and $V(\boldsymbol{R})$ is the so called effective potential defined by

$$V(\boldsymbol{R}) \equiv -k_B \ln\int dz\frac{1}{Q}\exp\{\beta\phi(z)\}\prod_\mu \delta(\boldsymbol{R}_\mu(z) - \boldsymbol{R}_\mu) \tag{5.56}$$

This effective potential satisfies

$$-\frac{\partial V}{\partial \boldsymbol{R}_\mu} = \langle \boldsymbol{F}_\mu \rangle \tag{5.57}$$

which justify its name. By using 5.55 in 5.51, this equation reduces to

$$\begin{aligned} \frac{d\boldsymbol{R}_\mu}{dt} &= \frac{\boldsymbol{P}_\mu}{M_\mu} \\ \frac{d\boldsymbol{P}_\mu}{dt} &= \langle \boldsymbol{F}_\mu \rangle - \gamma_{\mu\nu} \frac{\boldsymbol{P}_\nu}{M_\nu} + k_B T \frac{\partial \gamma_{\mu\nu}}{\partial \boldsymbol{P}_\nu} + \tilde{\boldsymbol{F}}_\mu \end{aligned} \tag{5.58}$$

Note that we have $\sum_\nu \boldsymbol{F}_\nu = 0$, because of Newton's Third Law. From 5.52 this implies that the friction coefficient defined in 5.52 satisfies $\sum_\mu \gamma_{\mu\nu} = 0$ and,therefore,

$$\gamma_{\mu\mu} = \sum_{\nu \neq \mu} \gamma_{\mu\nu} \tag{5.59}$$

While we expect that $\gamma_{\mu\mu}$ will be a positive quantity (because it is the time integral of an autocorrelation function), this equation shows that $\gamma_{\mu\nu}$ may be negative. Using 5.53 and 5.59, 5.58 can be written as

$$\begin{aligned} \frac{d\boldsymbol{R}_\mu}{dt} &= \frac{\boldsymbol{P}_\mu}{M_\mu} \\ \frac{d\boldsymbol{P}_\mu}{dt} &= \langle \boldsymbol{F}_\mu \rangle + \sum_\nu \gamma_{\mu\nu} (\frac{\boldsymbol{P}_\mu}{M_\mu} - \frac{\boldsymbol{P}_\nu}{M_\nu}) + k_B T \sum_\nu \frac{\partial \gamma_{\mu\nu}}{\partial \boldsymbol{P}_\nu} + \tilde{\boldsymbol{F}}_\mu \end{aligned} \tag{5.60}$$

where we wrote the sums explicitly to avoid confusions (not all repeated indices are summed in 5.60).

The stochastic force $\tilde{\boldsymbol{F}}_\mu$ can be expressed in terms of a linear combination of Wiener processes as, for example,$\boldsymbol{F}_\mu = \sum_\alpha B_{\mu\nu} \frac{d\boldsymbol{W}_\nu(t)}{dt}$ with

$$\sum_\alpha B_{\mu\alpha} B_{\nu\alpha} = 2k_B T \gamma_{\mu\nu} \tag{5.61}$$

This is the Fluctuation–Dissipation theorem for this problem. Note that 5.60 has the structure of dissipative particle dynamics (DPD). However, an important difference with the usual DPD equations is that the effective force $\langle \boldsymbol{F}_{\mu\nu} \rangle$ and the friction tensor $\gamma_{\mu\nu}(\boldsymbol{R}, \boldsymbol{P})$ depend, in principle, on the CoM variables of all the molecules in the system and not only on $\boldsymbol{R}_\mu - \boldsymbol{R}_\nu$ as in DPD.

Chapter 6

Simulation results for a system of star polymers

As an application we now consider a system of star polymer that form in a polymer melt. The star-shaped polymers are the simplest class of branched polymers with a general structure consisting of several (at least three) linear chains connected to a central core. The core, or the center, of the polymer can be an atom, molecule, or macromolecule; the chains, or "arms", consist of variable-length organic chains. Star-shaped polymers in which the arms are all equivalent in length and structure are considered homogeneous, and ones with variable lengths and structures are considered heterogeneous.

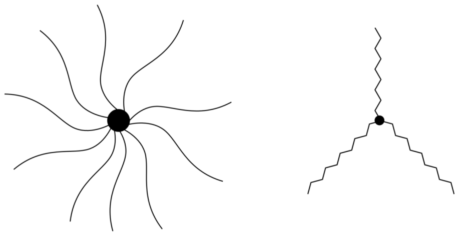

Figure 6.1: Shape of a polymer star

In our case the polymer is polysterene. Polystyrene(PS) is a synthetic aromatic hydrocarbon polymer made from the monomer known as styrene. Polystyrene can be solid or foamed. General-purpose polystyrene is clear, hard, and rather brittle. It is an inexpensive resin per unit weight. It is a rather poor barrier to oxygen and water vapour and has a relatively low melting point and it's one of the most widely used plastics. Polystyrene can be naturally transparent, but can be coloured with colourants. As a thermoplastic polymer, polystyrene is in a solid (glassy) state at room temperature but flows if heated above about 100^oC, its glass transition temperature. It becomes rigid again when cooled. This temperature behaviour is exploited for extrusion (as in Styrofoam) and also for molding and vacuum forming, since it can be cast into molds with fine detail. In chemical terms, polystyrene is a long chain hydrocarbon wherein alternating carbon centers are attached to phenyl groups (a derivative of benzene). Polystyrene's chemical formula is $(C_8H_8)_n$; it contains the chemical elements carbon and hydrogen. Some of it's uses include protective packaging (such as packing peanuts and in the jewel cases used for storage of optical discs such as CDs and occasionally DVDs), containers, lids, bottles, trays, tumblers, disposable cutlery and in the making of models.

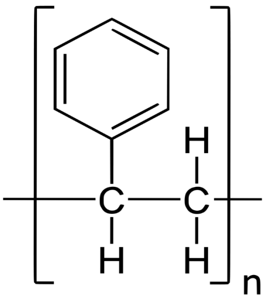

Figure 6.2: Chemical type of polysterene

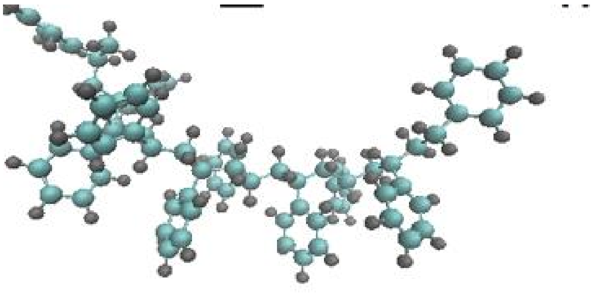

Figure 6.3: A snapshot of a model single polysterene chain

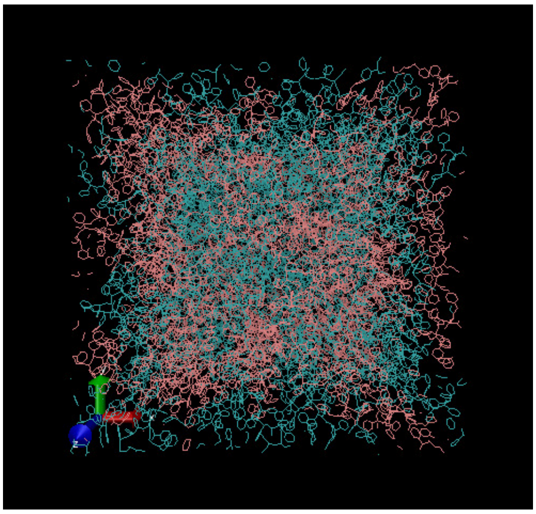

Figure 6.4: A snapshot of the polysterene star

In our system the star polymers have $f = 8$ arms and $m = 40$ monomers per arm. Each arm is connected to a central monomer so that the total number of monomers per polymer is $N_m = f \times m + 1$. The melt contained a collection of M polymer molecules, with $M = 15$ each on them has 2581 atoms so we have 38715 atoms in total. In order to simulate the system we use LAMMPS [21] simulation package where the interactions between all the atoms are defined through the united-atom model of TRAPPE force field [3]. LAMMPS is a molecular dynamic simulator with a focus on materials modeling. So as to run a simulation in this simulator we have to have two files, one which contains the definition of our system (the number of the atoms, the bonds, e.t.c.) and the other with the information about the ensemble, the time that we need e.t.c. (see A.1).

The procedure that we perform so as to take the data that we want is the following. Starting from the initial configuration [8] where our system has already reached the equilibrium we run an NPT simulation for 10 nanoseconds(ns) with unconstrained dynamics. Then, we do an energy minimization for 10,000 femtoseconds(fs). Using the data from the previous simulation we perform an NVT simulation for 10ns with unconstrained dynamics and we perform again the energy minimization with the same way that we did before. Then, we run an NVT simulation for 20ns with unconstrained dynamics so as to collect a set of 20 configurations, each one having an independent set of positions and momenta $(\boldsymbol{R}, \boldsymbol{P})$ of the CoM of the molecules. In this step we can see that our system is in equilibrium by ploting the thermodynamic properties of the system(see appendix A ,6.5, 6.6). Starting from each of these 20 configurations we run a short simulation (1ns) with NVT to collect the required CoM molecular dynamics raw data. These set of short runs were carried out using the constrained dynamics (eq.6.1). In all the above simulations we use Nose Hoover thermostat, Velocity-Verlet integrator and the temperature is 450 Kelvin.

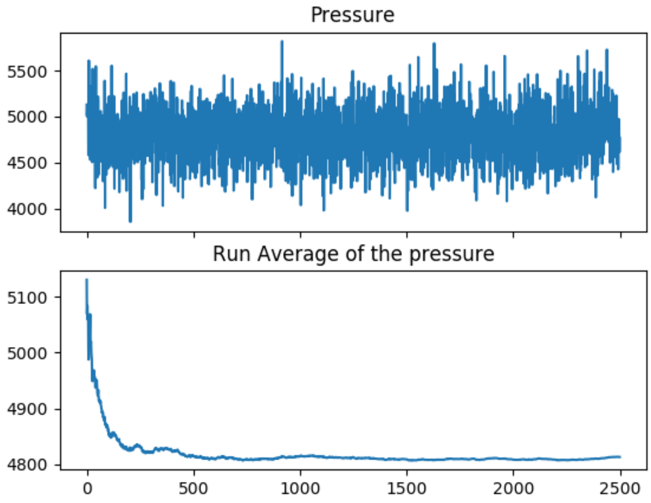

Figure 6.5: Pressure in atmospheres

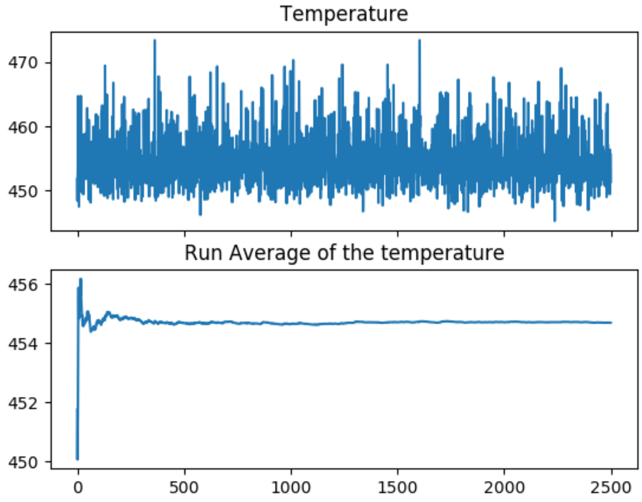

Figure 6.6: Temperature in Kelvin

In order to check that the system has reached equilibrium we calculate the systems thermodynamic quantities, e.g. the temperature and the pressure. The running average that we plot in figures 6.5 and 6.6, is a calculated by creating a series of averages of different subsets of the full data set. We calculate it as follows. Suppose that we have the equally weighted configurations $n_1, n_2, \cdots, n_N$ then the values that we use in order to find the average are calculated as $\bar{n}_i = \bar{n}_{i-1} + \frac{1}{\sum_{j=1}^{i} j}(n_i - \bar{n}_{i-1})$ for $i = 1, \cdots, N$.

Then, a procedure that we have to follow is to compute the autocorrelation function of the CoM and the force autocorrelation function on the molecules in order to compare them and find if we have a separation of time scales. The former gives the time scale of the CoM velocity, which is a relevant variable. The latter provides an estimate of the typical time scale at which the memory function in the definition of the friction coefficient decays.

The constrained dynamics $\mathcal{R}$ that we discuss before and we use in order to compute the mean force $\langle \boldsymbol{F}_{\mu\nu} \rangle$ and the friction coefficient $\gamma_{\mu\nu}(\boldsymbol{R}, \boldsymbol{P})$ is the following

$$\begin{aligned} \frac{d\boldsymbol{r}_{i_\mu}}{dt} &= \frac{\boldsymbol{p}_{i_\mu}}{m_{i_\mu}} - \frac{\boldsymbol{P}_\mu}{M_\mu} \\ \frac{d\boldsymbol{p}_{i_\mu}}{dt} &= \boldsymbol{F}_{i_\mu} - \frac{m_{i_\mu}}{M_\mu}\boldsymbol{F}_\mu \end{aligned} \tag{6.1}$$

where $\boldsymbol{P}_\mu$ is the CoM momentum of molecule μ, $\boldsymbol{F}_{i_\mu}$ is the total force on monomer i_μ and $\boldsymbol{F}_\mu$ is the total force on molecule μ. These equations conserve the total energy, they leave the positions and momentum of the CoM invariant, and they also conserve the volume in phase space. For these reasons, this dynamic samples the constrained ensemble that appears in the definition of $\langle \boldsymbol{F}_{\mu\nu} \rangle$ and $\gamma_{\mu\nu}(\boldsymbol{R}, \boldsymbol{P})$, and these averages may be computed as time averages.

Consistent with eqn(5.38), by running eqn (6.1), we can compute $\langle \boldsymbol{F}_{\mu\nu} \rangle$ as the time average of the force $\boldsymbol{F}_{\mu\nu}$ that molecule ν exerts on molecule μ. In principle $\langle \boldsymbol{F}_{\mu\nu} \rangle$ depends on all the CoM positions $\boldsymbol{R}$. If it happens, as we expect, that the force that molecule ν exerts on molecule μ depends only on the CoM positions $\boldsymbol{R}_\mu$ and $\boldsymbol{R}_\nu$ of these two molecules and does not depend much on where the rest of molecules are located, then a pair-wise approximation should be valid. By translational and rotational symmetry we expect that the average force will be of the form

$$\langle \boldsymbol{F}_{\mu\nu} \rangle \approx F(R_{\mu\nu}) e_{\mu\nu} \tag{6.2}$$

where $F(R_{\mu\nu}) = \langle \boldsymbol{F}_{\mu\nu} \cdot e_{\mu\nu} \rangle$, $e_{\mu\nu} = \frac{(\boldsymbol{R}_\mu - \boldsymbol{R}_\nu)}{R_{\mu\nu}}$ and $R_{\mu\nu} =\mid \boldsymbol{R}_\mu - \boldsymbol{R}_\nu \mid$. Consistent with this assumption, we computed the modulus of the average force $F(R_{\mu\nu})$ by averaging the result of $\langle \boldsymbol{F}_{\mu\nu} \cdot e_{\mu\nu} \rangle$ over all those pairs μ, ν that are at a certain distance $R_{\mu\nu}$. In practice, to perform these constrained dynamics we employed the LAMMPS[21] modulus 'recenter'. This modulus constrain the center-of-mass position of a group of atoms by adjusting the coordinates of the atoms every timestep. This is simply a small shift that does not alter the dynamics of the system or change the relative coordinates of any pair of atoms in the group.

The results are depicted in fig. 6.7 and fig. 6.8 for two sets of simulated data. The first set of data is composed of 50000 configurations while the second set is made by 5000 configurations.

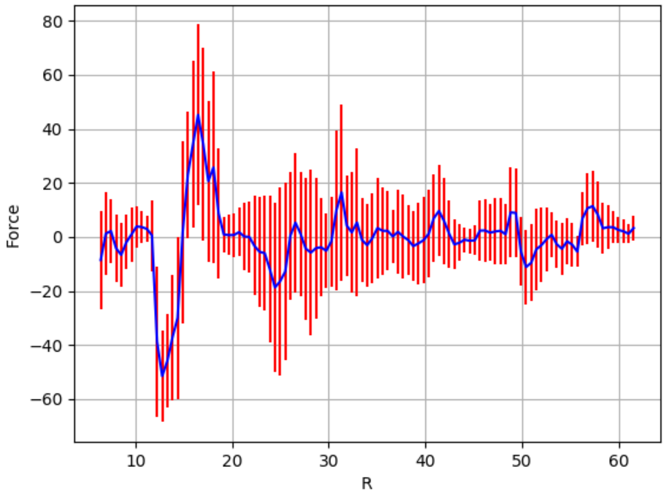

Figure 6.7: The conservative force used by the present pair-wise approximation $\langle \boldsymbol{F}_{\mu\nu} \cdot e_{\mu\nu} \rangle$ versus the distance $R_{\mu\nu}$ between center of masses of two interacting molecules.

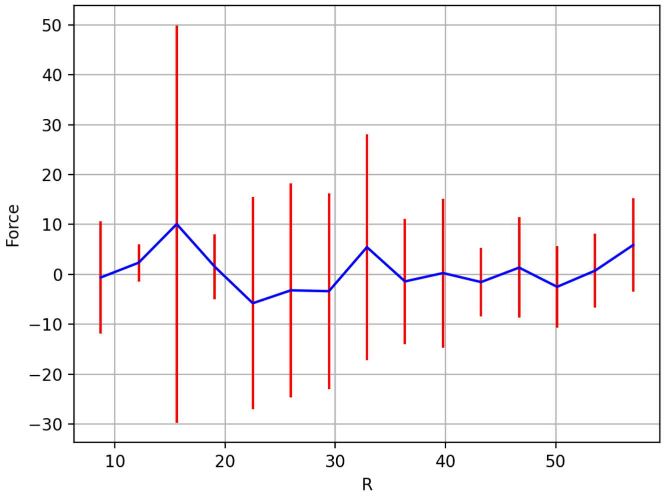

Figure 6.8: The conservative force used by the present pair-wise approximation $\langle \boldsymbol{F}_{\mu\nu} \cdot e_{\mu\nu} \rangle$ versus the distance $R_{\mu\nu}$ between center of masses of two interacting molecules.

Regarding the figures we observe that the pair force tends to zero as the distances grow up as we expected. For small values of distances we observe abnormal behavior. This abnormal behavior is a result of the poor statistics (i.e. we need more simulations) in combination to the fact that we need to verify the validity of the constrained dynamics we impose. The poor statistics may be a consequence of the temperature that we use, which is 450 Kelvin. We assume that the atoms can't move fast in this temperature, so longer simulation times are necessary to have a wider range of configurations.

Let us now define the friction coefficients $\gamma_{\mu\nu}(\boldsymbol{R}, \boldsymbol{P})$. Again, one has to deal with the problem of their many arguments. Here we do the assumption that the correlation between the forces on molecule μ and ν will depend on the positions of these two molecules but will not depend much on the positions and momenta of the rest of the molecules. Thus we have the following expression:

$$\gamma_{\mu\nu}(\boldsymbol{R}, \boldsymbol{P}) \approx -\gamma_{\perp}(R_{\mu\nu})(1 - e_{\mu\nu}e^{T}_{\mu\nu}) - \gamma_{\|}(R_{\mu\nu})e_{\mu\nu}e^{T}_{\mu\nu} \tag{6.3}$$

The right-hand side of this equation only depends on $\boldsymbol{R}_{\mu}$ and $\boldsymbol{R}_{\nu}$ and it is a general form for a tensor that is invariant by rotations along the axis joining the particles μ, ν. Compatibility of eqn(6.3) with eqn(5.52) then requires that

$$\begin{aligned} \gamma_{\|}(R_{\mu\nu}) &= -\frac{1}{k_B T}\int_0^{\infty} dt\, \langle(\delta\boldsymbol{F}_{\mu}(t)\cdot e_{\mu\nu})(\delta\boldsymbol{F}_{\nu}(0)\cdot e_{\mu\nu})\rangle \\ \gamma_{\perp}(R_{\mu\nu}) &= -\frac{1}{k_B T}\int_0^{\infty} dt\, \left\langle(\delta\boldsymbol{F}_{\mu}(t)\cdot e^{\perp}_{\mu\nu})(\delta\boldsymbol{F}_{\nu}(0)\cdot e^{\perp}_{\mu\nu})\right\rangle \end{aligned} \tag{6.4}$$

Assuming that the right-hand side of eqn(6.4) is the same for all the pairs that are at the same distance $R_{\mu\nu}$, we may average over all the pairs $\mu\nu$ that happen to be at the distance $R_{\mu\nu}$, this is

$$\boldsymbol{\gamma}_{\|}(R_{\mu\nu}) = \frac{1}{N_{\mu\nu}}\sum_{\mu\nu}{}^{'}\frac{1}{k_B T}\int_0^{\infty} dt\, \langle(\delta\boldsymbol{F}_{\mu}(t)\cdot\boldsymbol{e}_{\mu\nu})(\delta\boldsymbol{F}_{\nu}(0)\cdot\boldsymbol{e}_{\mu\nu})\rangle \tag{6.5}$$

where $\sum'_{\mu\nu}$ is a sum over all those pairs that are at a given distance $R_{\mu\nu}$ and $N_{\mu\nu}$ is the number of pairs at that distance.

Chapter 7

Conclusions and Discussion

To conclude our work, we summarize our approach, findings and future steps. Because the molecular systems we study are very complex, due to the large number of particles, they are difficult to simulate. Thus, we have to reduce the degrees of freedom. This is achieved with the coarse graining process. We present analytically the equation of motion of the coarse grained particles, the generalized Langevin equation. This equation is a result of the Mori-Zwanzig projection method. It is an integro-differential equation with memory terms, rendering the dynamics governing the coarse variables non-Markovian. Applying the Markovian approximation one reduces the memory term of the GLE equation to have explicit form. The common approach approximates the evolution operator of the integrated out degrees of freedom by the real dynamics. In the current work, this approximation is based on the the constrained (to the coarse variables) dynamics of the all-atom system.

We applied the later approach for the polystyrene system. That is, we simulated the polystyrene system and applied the coarse graining method with relevant variables the center of mass of each polystyrene star in order to compute the average force and the thermodynamic properties of the system. Since the system is high dimensional we faced serious problems in achieving adequate statistics for the estimation of the force field. We presented the resulted pair force estimated using observations of the united-atom evolution of the system with the constrained center of mass of the molecules. However, though we encountered difficulties in presented the pair force, due to poor statistics (i.e. we need more simulations) in combination to the fact that we need constrained dynamics we could not reach in a good representation of our system. A problem may be the temperature that we use, which is 450 Kelvin. We assume that the atoms can't move fast in this temperature, so longer simulation times are necessary to have a wider range of configurations.

The next goal is to calculate the velocity autocorrelation function of the center of mass and comparing the result with the force autocorrelation function on the molecules. Additionally we want to calculate the friction coefficients of the system so as to represent the total movement of the new coarse-grained particles.

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Appendix A

Thermodynamic properties of an NVT ensemble

We present the thermodymanic properties for a simulation with uncostrained dynamics in a system in equilibrium.

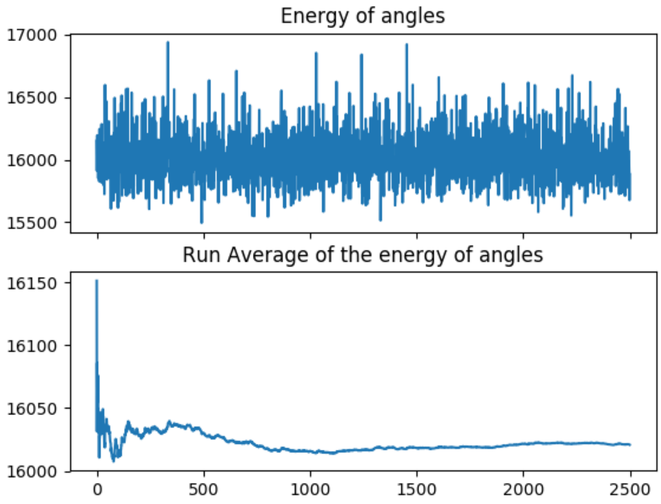

Figure A.1: Energy of angles in Kcal/mole

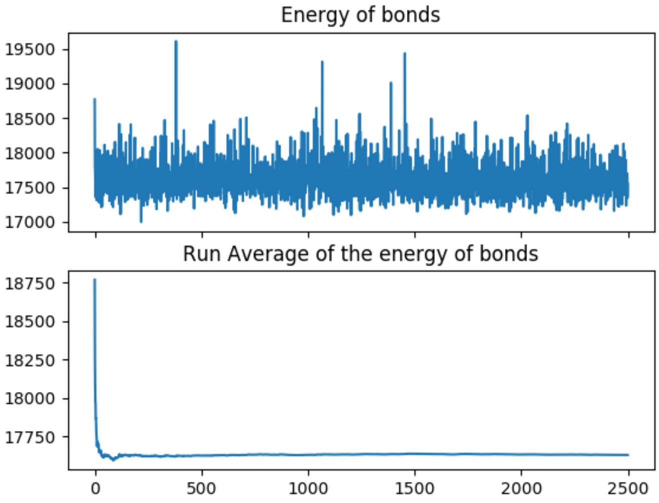

Figure A.2: Energy of bonds in Kcal/mole

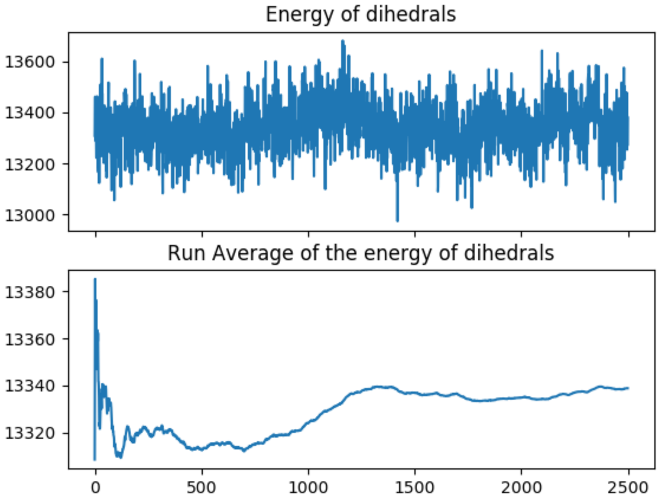

Figure A.3: Energy of dihedrals in Kcal/mole

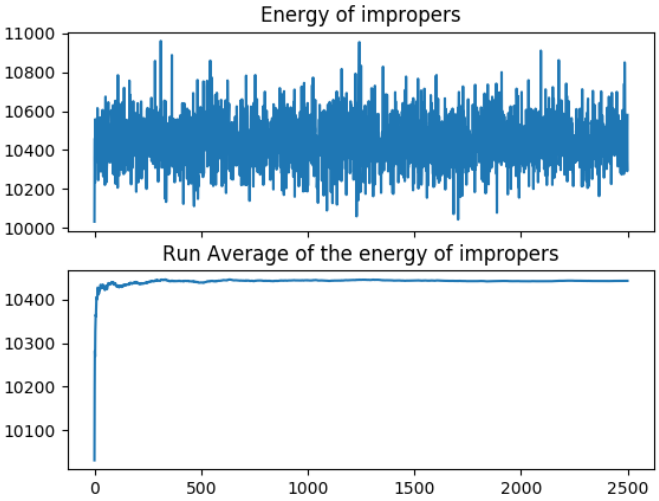

Figure A.4: Energy of impropers in Kcal/mole

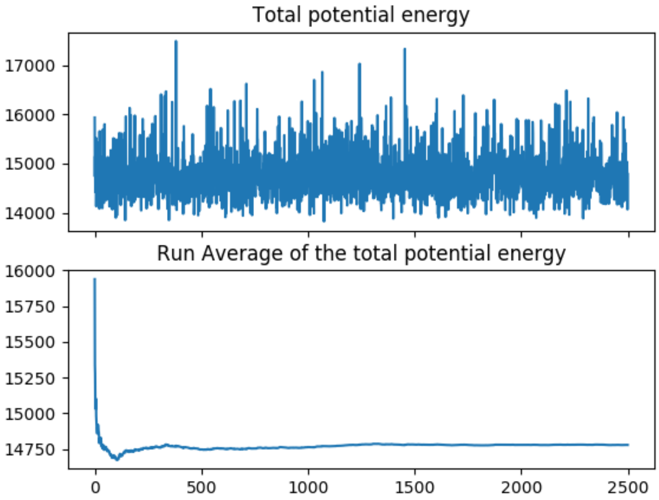

Figure A.5: Potential energy in Kcal/mole

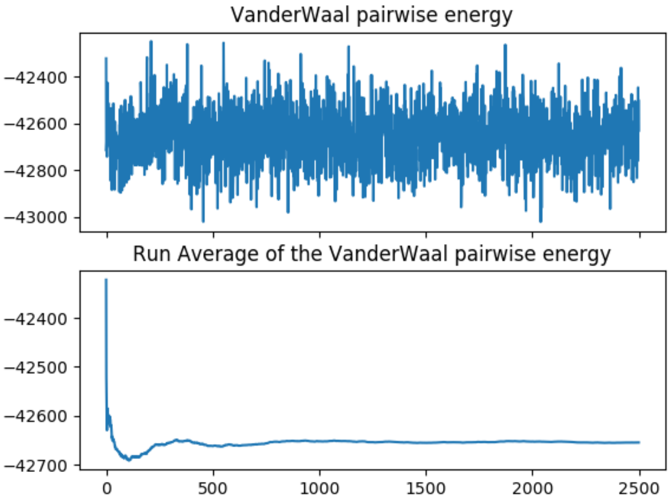

Figure A.6: VanderWaal energy in Kcal/mole

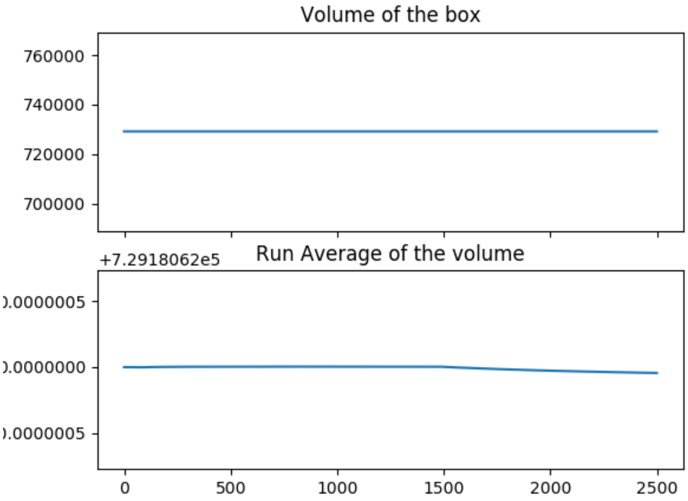

Figure A.7: Volume

A.1 Information of the system

In all the previous simulations that we performed we have the following information as input:

number of atoms	38715
σ of each type of atom	
1	6.4
2	4.65
3	3.95
4	3.7
5	3.695
6	3.75
ε of each type of atom	
1	0.0009935
2	0.0198614
3	0.0914914
4	0.0596080
5	0.1003107
6	0.1950048
initial size of the box	in xyz directions
lower value	0.0000000
higher value	100.0000000
Mass of each type of atom	
1	12.0110000
2	13.0190000
3	14.0270000
4	12.0110000
5	13.0190000
6	15.0350000
Units	Real
mass	grams/mole
distance	Angstroms
time	femtoseconds
energy	Kcal/mole
velocity	Angstroms/femtosecond
force	Kcal/mole-Angstrom
torque	Kcal/mole
temperature	Kelvin
pressure	atmospheres
dynamic viscosity	Poise
charge	multiple of electron charge (1.0 is a proton)
dipole	chargeAngstroms
electric field	volts/Angstrom
density	$\frac{gram}{cm^{d}im}$
bond style	hybrid harmonic
angle style	hybrid harmonic
dihedral style hybrid	charmm multi/harmonic
improper style	hybrid harmonic