Department of Physics, Chemistry and Biology

Master's Thesis

Molecular Dynamics of the Adsorption of Organic Molecules on Organic Substrates

Patrik Åkesson

Thesis conducted at Karl-Franzens-Universität Graz, Austria

 $\rm LiTH\text{-}IFM\text{-}A\text{-}EX\text{-}13/2850\text{-}SE$



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Linköping, 28 December 2013

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ALOPINGS UNIVERS	Avdeln Division	ing, Institution , Department		Datum Date
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Språk Language Svenska/Swedish Engelska/English Engelska/English D-uppsats Ovrig rapport URL för elektronisk version http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-XXXXX Titel Adsorption av organiska molekyler på org Title Molecular Dynamics of the Adcorption		ISBN ISRN LiTH-IFM-A-EX Serietitel och serier Title of series, number ganiska substrat studerat of Organic Molecules on	-13/2850–SE nummer ISSN ing t med molekyldynamik Organic Substrates	
Författare Patrik Åkesson Author				
Sammanfattning Abstract A great interest has been shown for self-assembled organic nano-structures that can be used in a variety of optoelectronic applications, from element detection to home electronics. It is known from experimental research that sexiphenyl (6P) grown on muscovite mica substrate form uniaxially self-assembled nanofibers which together with sexithiophene (6T) deposited on top gives the possibility to tune their polarized emission. A key to continue develop and explore the full potential of this technique is to understand the mechanisms behind the growth. This thesis investigate the initial growth of 6P and 6T on a 6P(111) nanofiber substrate through Molecular Dynamics (MD) simulations. The adsorption of the molecules has been simulated with Simulated Annealing (sA) where 6P align perfectly with the substrate for all coverage while 6T starts to align after a certain amount of coverage. Both molecules show a monotonic increase in the adsorption energy per molecule with an increasing coverage. The surface diffusion of the molecules has been studied and shows a higher movement for both in the direction of the long molecular axis.				
Nyckelord Keywords	Molecular D ence, Simula CHARMM	ynamics, Empirical Force ted Annealing, Organic Mo	Field, Computational lecules, Sexiphenyl, Sex	Physics, Material Sci- ithiophene, LAMMPS,

Abstract

A great interest has been shown for self-assembled organic nano-structures that can be used in a variety of optoelectronic applications, from element detection to home electronics. It is known from experimental research that sexiphenyl (6P) grown on muscovite mica substrate form uniaxially self-assembled nanofibers which together with sexithiophene (6T) deposited on top gives the possibility to tune their polarized emission. A key to continue develop and explore the full potential of this technique is to understand the mechanisms behind the growth. This thesis investigate the initial growth of 6P and 6T on a $6P(11\overline{1})$ nanofiber substrate through Molecular Dynamics (MD) simulations. The adsorption of the molecules has been simulated with Simulated Annealing (SA) where 6P align perfectly with the substrate for all coverage while 6T starts to align after a certain amount of coverage. Both molecules show a monotonic increase in the adsorption energy per molecule with an increasing coverage. The surface diffusion of the molecules has been studied and shows a higher movement for both in the direction of the long molecular axis.

Sammanfattning

Ett stort intresse har visats för självorganiserade organiska nanostrukturer som kan användas i ett stort antal optoelektroniska applikationer, från grundämnesdetektion till hemelektronik. Det är känt från experimentell forskning att sexifenyl (6P) som växes på substrat av muskovit glimmer bildar enaxiella självorganiserade nanofibrer, som med sexitiofen deponerad ovanpå ger möjligheten att justera dess polariserade emission. För att kunna fortsätta att utveckla och utforska denna tekniks fulla potential så är det av yttersta vikt att förstå mekanismerna som styr framväxten. I detta examensarbete undersöks den initiella framväxten av 6P och 6T på ett substrat av $6P(11\overline{1})$ nanofiber genom Molekyldynamik (MD) simulationer. Adsorptionen av molekyler har blivit simulerad genom Simulerad glödgning (SA) där 6P riktar sig perfekt efter substratet för all täckning medan 6T börjar rikta sig efter substratet först vid en viss grad av täckning. Båda molekylerna visar en monoton ökning i adsorptionsenergin per molekyl för ökande täckning. Molekylernas ytdiffusion har studerats och visar för bägge en högre rörlighet i riktningen för den långa molekylaxeln.

Acknowledgements

I would first of all like to thank Peter Puschnig for making it possible for me to write my thesis at Karl-Franzens-Universität in Graz, Austria. He has always been very helpful with advice and guidance and his experience in the field of computational physics has been indispensable. Furthermore my gratitudes goes to Clemens Simbrunner who is leading the project "Hetero-epitaxy of organic-organic nanofibers", funded by the Austrian Science Fund (FWF) as project P25154-N20, in which this thesis is a part of. I would also like to thank Valeriu Chirita and Björn Alling, who took me on as supervisor and examiner on short notice.

My gratitude goes to Otello Roscioni from Università di Bologna who supplied papers, tools and advice for simulations. My gratitude goes also to Elisabeth Verwüster at TU Graz who helped us calculating the charges in Gaussian. Thank you Christian Röthel and Iris Hehn also at TU Graz for helpful discussions and sharing of knowledge.

Ett stort tack till min familj Claes-Göran, Iréne, Niklas, Alexsandra och Filip som alltid har funnits där och stöttat mig, i goda tider och i mindre goda tider. Meine liebe Valentina, vielen Dank für alles was du mir gegeben hast, ohne dich wäre all dies nicht möglich.

Linköping, December 2013

Patrik Åkesson

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Glossary

6P Sexiphenyl
6T Sexithiophene
AFM Atomic Force Microscopy
CHARMM Chemistry at HARvard Macromolecular Mechanics
CGenFF CHARMM General Force Field
CMAP Correction MAP
CG Conjugate Gradient
DFT Density Functional Theory
EFF Empirical Force Field
FF Force Field
LAMMPS Large-scale Atomic/Molecular Massively Parallel Simulator
LJ Lennard-Jones
MD Molecular Dynamics
MIC Minimum Image Convention
MM Molecular Mechanics
MPI Message Passing Interface
MSD Mean Square Displacement
PBC Periodic Boundary Condition
QM Quantum Mechanics
SA Simulated Annealing
\mathbf{vdW} van der Waals
VMD Visual Molecular Dynamics
XRD X-Ray Diffraction

Chapter 1 Introduction

This master project is embedded into the project "Hetero-epitaxy of organic-organic nanofibers" which is funded as project P25154-N20 by the Austrian Science Fund (FWF). One of the main goals of this FWF project is to understand and control the structure of organic molecular thin films used in organic laser devices [1, 2]. The role of this master project has been to perform Molecular Dynamics (MD) simulations employing Empirical Force Fields (EFFs) as a complement to the experimental part with growth studies and structural investigations using X-Ray Diffraction (XRD) and Atomic Force Microscopy (AFM) measurements. The experimental part is performed at Johannes Kepler Universität Linz, Austria while the theoretical modelling is done at Karl-Franzens-Universität Graz, Austria.

1.1 Background

The semiconductor laser is of great importance for a increasing number of optoelectronic applications, which span from element detection at the nanoscale through telecommunications to home electronics like DVD-players at the macroscale. Materials research plays a crucial role in developing and improving novel laser structures. One category of the materials to investigate is that of the organic semiconductors which combine novel optoelectronic properties, simple fabrication and possibility to tune the chemical structure to give desired features. All together it makes them attractive to use as laser materials [3].

Rod-like molecules in well-ordered molecular crystals exhibit a parallel alignment of the molecules in the crystal unit cell. The resulting molecular order is advantageous not only for optical resonators but also for achieving high charge carrier mobilities. Two such rod-like molecules are *thiophenes* [4] and *phenylenes* [5] which combined with *muscovite mica* as substrate have become an extraordinary material combination. Perhaps the most interesting feature is that parallel-aligned self-assembled nano-fibers may be processed in several micrometer long entities and transferred to prefabricated device structures by drop-casting or roll-on transfer [6, 7]. It has been acknowledged as an unique *bottom-up* strategy for the fabrication of 1D nanostructures at low cost [8].

Two resourceful techniques for retrieving crystalline and highly ordered molecular heterostructures are self-assembly processes and organic-organic heteroepitaxy. By combining them it is possible to fabricate highly crystalline and uniaxially oriented self-assembled nanofibers whose polarized emission is possible to tune [9]. The process is depicted in Figure 1.1. In this article α -sexithiophene on a para-sexiphenyl fiber template on muscovite mica substrate was grown and through XRD a sexithiophene crystalline needle with $(11\overline{1})$ contact plane was identified.



Figure 1.1 First image show a nominal layer of 120 nm of 6P grown on a substrate of Muscovite Mica which gives highly aligned, blue-emitting nanofibers. Then if 6T is deposited on top through heteroepitaxy with a layer thickness of less than 1 nm, it results in green-emitting fibers as in the second image. If an increasing deposition to a layer thickness of 400 nm, this results in green-and red-emitting nano-fiber. (Figures from [9])

1.2 Outline of Thesis

Theoretical investigations will shed light on the initial stages of organic molecular growth for sexiphenyl and sexithiophene on a substrate(the needle) of sexithiophene with surface $(11\overline{1})$, as in Figure 1.2. This surface was chosen as a first step and is motivated by the fact that it appears in experiments. In our simulations we will investigate how the two molecules arrange on such a substrate and of particular interest is how they orient and at which sites they adsorb. The results can be readily compared to experimentally deduced data and will provide further insight of the adsorption process on a molecular level. The large simulation cell that the molecules introduce together with the need for long simulation times makes pure ab-initio methods unthinkable and makes the choice of MD with EFF natural. The central tool for the simulations is the freely distributed MD-code Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) together with the EFF from Chemistry at HARvard Macromolecular Mechanics (CHARMM). They are both powerful tools that provides many options for simulations.

In Chapter 2 the theory building up this thesis will be explained and may serve as a first introduction to the subject. Further reading is also presented. In Chapter 3 the



Figure 1.2 In this thesis the blue $6P(11\overline{1})$ needle serves as substrate, on which 6P and 6T are deposited. (Figure from [9])

methods, techniques and settings used in the project are presented. In Chapter 4 the results of the simulated scenarios together with discussions are presented. An Appendix, detailing lengthy files and scripts which have been used, has also been included.

Chapter 2

Fundamentals

In this chapter the theory behind this work is presented. It has been based on standard text books [10–12] in the field.

2.1 Molecular Modelling

How to simulate the movement of a molecule? The most accurate methods today come from the theory of Quantum Mechanics (QM) where the electrons are represented. This makes it possible to retrieve properties that depend on electron distributions. Some of the popular theories to model molecules through QM are *Ab-initio* methods including Density Functional Theory (DFT). So why does not everyone use these theories to model and simulate systems of molecules? The answer to this is the limitation of computers, the calculations are simply too time-consuming. Therefore when it comes to molecules or atom systems containing a large number of atoms, one has to go to other theories.

The natural step to improve the computational time is to avoid the calculations of electrons. Through the Born-Oppenheimer approximation the fast movements of the electrons and the slow nuclear movement can be separated. The energy of a molecule in its ground electronic state is then a function of the nuclear coordinates only. Force Field (FF) methods, also known as Molecular Mechanics (MM), do ignore the electron movements and calculate the energy of the system as a function of the nuclear coordinates only. But more than that, they also answer our first question - how molecules move and behave.

2.2 Empirical Force Fields

Empirical Force Fields (EFFs), usually just FF are fairly simple functional forms that model the interactions between atoms in molecules fitted to empirical data from experiments or QM calculations.

2.2.1 Force Fields

Common for most FFs is that they have five basic parts of intra- and intermolecular terms that are always included. These are bond stretching, angle bending, torsion around bond¹ and non-bonded interactions where the latter includes electrostatic interactions and van der Waals (vdW) interactions which are typically modelled by a Lennard-Jones (LJ) potential. In Figure 2.1 the different types are depicted.



Figure 2.1 The five basic parts in a Force Field are depicted. In the upper part are the bonded interactions; bond stretching, angle bending and torsion around bond. In the lower part are the non-bonded interactions; the electrostatic and the vdW interactions.

An example of the simplest functional form of a FF taken from [11, p. 166] is given in Equation (2.1),

$$E(\boldsymbol{r}^{N}) = \sum_{bonds} \frac{k_{i}}{2} (l_{i} - l_{i,0})^{2} + \sum_{angles} \frac{k_{i}}{2} (\theta_{i} - \theta_{i,0})^{2} + \sum_{torsion} \frac{V_{n}}{2} (1 + \cos(n\omega - \gamma)) + \sum_{i=1}^{N} \sum_{j=1}^{N} \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_{i}q_{j}}{4\pi\varepsilon_{0}r_{ij}} \right\}$$
(2.1)

where $E(\mathbf{r}^N)$ is the potential energy as a function of the positions of N particles. The fact that the parameters in the equation are connected directly to movements makes it easy to understand their physical behaviour and how to improve the parametrization. Other more advanced classes of FFs have additional terms that give extra complexity. A class I FF has the same functional form as Equation (2.1) and may also have additional terms modelled as harmonic potentials. A class II FF has cross terms that are dependent on mostly two internal coordinates but sometimes more, i.e. stretch-stretch or bend-bend-torsion as in Figure 2.2. Cross terms are often for more advanced and sensitive properties, for instance when vibrational spectra are of interest. When choosing a FF, there is always a tradeoff between complexity and computational time, which depends on the application.

Transferability is an important property in MD simulations and means that a certain system (set of atoms, a molecule, etc.) is tested to work for a number

¹The variable in this term is an angle named *Torsion Angle* or *Dihedral Angle*.



Figure 2.2 Example of cross terms, here stretch-stretch and bend-bend-torsion.

of cases. Then it may be used for other materials in the same category directly, without having to parametrize it again. But for FFs a parametrization is only made for one material and is usually not transferable.

2.2.2 CHARMM FF

CHARMM [13] is a molecular simulation and modelling program. It is mostly used for computational medicinal chemistry research (i.e. drug design) but is also found important for material science. The group behind the program provides optimized parametrizations of a large number of molecules in their own CHARMM FF that is a class I. CHARMM was developed for macromolecules like proteins and lipids but has in recent years also been extended with the CHARMM General Force Field (CGenFF) [14], that is made for smaller organic molecules. Important to know is that it is not transferable, which means that for every molecule to be investigated, a parametrization has to be made. CGenFF is the FF used for the molecules in this thesis and its potential energy function shown in Equation (2.2) is a sum of bonded and non-bonded interactions between the atoms in a certain molecule.

$$E(r) = E_{bonded} + E_{non-bonded} \tag{2.2}$$

Bonded Interactions

The bonded interactions are bonds, angles, dihedrals, impropers², Urey-Bradley and a 2D dihedral energy Correction MAP (CMAP). But neither the Urey-Bradley nor the improper terms have been used which both are thought to optimize the fit to the QM vibrational spectra and out-of-plane motion [13, p. 1551]. The CMAP is normally used only for modelling backbone peptides and has not been used in this thesis. This leaves the bonded energy to have three terms as in Equation (2.3)

 $^{^{2}}$ Four atoms are positioned in the same plane, three of these atoms are bonded to a central atom. If one of the three atoms that are bonded to the central atom leaves the plane, we have an improper torsion.

$$E_{bonded} = \sum_{bonds} K_b (b - b_0)^2 + \sum_{angles} K_\theta (\theta - \theta_0)^2 + \sum_{dihedrals} K_\phi (1 + \cos(n\phi - \delta)) \quad (2.3)$$

where $K_b, K_{\theta}, K_{\phi}$ consist of force constants and b_0 and θ_0 are reference values that also are optimized in the parametrization (Note that they are not equilibrium values taken from QM calculations). The dihedral term includes n and δ which are the dihedral multiplicity and phase shift respectively.

Nonbonded Interactions

The non-bonded interactions are Coulomb interactions and vdW forces. The Coulomb term is the electrostatic energy between point charges while the vdW forces are modelled by a LJ potential with a repulsive term, often called Pauli repulsion, and an attractive term which is the vdW dispersion interaction between two atom cores. The potential energy from these terms is presented in Equation (2.4),

$$E_{non-bonded} = \sum_{\substack{non-bonded \\ pairs}} \left\{ \varepsilon_{ij}^{min} \left[\left(\frac{R_{ij}^{min}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{ij}^{min}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon r_{ij}} \right\}$$
(2.4)

where r_{ij} is the distance between the interacting atoms, R_{ij}^{min} is the distance at which the LJ has its minimum energy, ε_{ij}^{min} represent the binding energy in the LJ, ε and ε_0 are the relative dielectric constant and permittivity of vacuum respectively and q_i, q_j are the partial atomic charges of atoms i and j. Potentials between two objects are often referred to as *pair potentials* and both nonbonded terms are of this type.

2.3 Molecular Dynamics

In this section some of the most central concepts of MD are presented. Naturally it does not cover all but is thought as an introduction. To reach a better understanding, the text books referenced in the beginning of this chapter are recommended for further reading.

MD is based on the laws of classical mechanics. This means that the nuclear motion is determined by solving Newton's equations of motion. To calculate the trajectory we solve the ordinary differential equation embodied in Newton's second law, Equation (2.5).

$$\frac{d^2 \boldsymbol{r}}{dt^2} = \frac{\boldsymbol{F}}{m} \tag{2.5}$$

By integrating the equations of motion we get consecutive configurations of the atoms in the system studied. The steps in short are:

- 1. Calculate the forces acting on each particle based on its position relative to all other atoms in the system.
- 2. Integrate the equations of motion to get the positions at time $t + \delta t$.
- 3. Update the positions.

Equation (2.5) can be separated in two problems for each dimension, as in Equation (2.6).

$$\frac{d\boldsymbol{r}_{i}}{dt} = \boldsymbol{v}_{i}$$

$$\frac{d\boldsymbol{v}_{i}}{dt} = \frac{\boldsymbol{F}}{m}$$

$$i = x, y, z$$
(2.6)

Then, if the system we study has N particles, at every step 6N first order differential equations must be solved. Rewritten, Equation (2.6) can be stated in Hamiltonian formalism, given in Equation (2.7). In this formalism we have a trajectory $\Gamma(t) = g(\mathbf{r}_1, ..., \mathbf{r}_N, \mathbf{p}_1, ..., \mathbf{p}_N)$ in 6N-dimensional phase-space. Changes in the system energy can thus be considered as movement on a multidimensional energy surface.

$$\frac{d\boldsymbol{r}_{i}}{dt} = \frac{\boldsymbol{p}_{i}}{m}$$

$$\frac{d\boldsymbol{p}_{i}}{dt} = \boldsymbol{F}$$

$$i = x, y, z$$
(2.7)

The first interaction potentials used in MD simulated totally elastic collisions with discrete values for certain distances. Such interaction potentials are very easy to implement in a computer but does not give a very realistic model. When we deal with physically more correct potentials, these must of course be continuous and so the motion of all particles in the system is coupled. This means that we have a many-body problem that can not be solved analytically. Therefore one use a *finite difference method* to integrate the equations of motion. The idea is to divide the integration in small parts all separated by a fix time δt , called *time step*. It is not hard to imagine that the smaller the time step, the better the integration and if not chosen properly it might make the simulation non-physical. An initial starting time step suitable for most systems is 1 fs.

2.3.1 Integration Method

Since there are so many equations to calculate at every step the demand on the integrator to be fast and efficient is high. The most common integrator algorithms today are variants of the *Verlet* algorithm which we will look at closer. Common

to all integrators using finite difference methods is that they make the assumption that properties like positions, velocities and accelerations of the atoms can be approximated by Taylor expansions as in Equation (2.8)

$$\boldsymbol{r}(t+\delta t) = \boldsymbol{r}(t) + \boldsymbol{v}(t)\delta t + \frac{1}{2}\boldsymbol{a}(t)\delta t^{2} + \dots$$
$$\boldsymbol{v}(t+\delta t) = \boldsymbol{v}(t) + \boldsymbol{a}(t)\delta t + \frac{1}{2}\boldsymbol{b}(t)\delta t^{2} + \dots$$
$$\boldsymbol{a}(t+\delta t) = \boldsymbol{a}(t) + \boldsymbol{b}(t)\delta t + \frac{1}{2}\boldsymbol{c}(t)\delta t^{2} + \dots$$
(2.8)

To retrieve the next position $\mathbf{r}(t + \delta t)$, the Verlet method uses the current position $\mathbf{r}(t)$, the current acceleration $\mathbf{a}(t)$ calculated from Equation (2.6) (Through calculating the forces acting on the atom at this time step during which the forces are considered constant) and the previous position $\mathbf{r}(t - \delta t)$, see Equation (2.9). From summation between $\mathbf{r}(t + \delta t)$ and $\mathbf{r}(t - \delta t)$ one gets this result. To achieve the velocities a similar approach is used.

$$\boldsymbol{r}(t+\delta t) = 2\boldsymbol{r}(t) - \boldsymbol{r}(t-\delta t) + \boldsymbol{a}(t)\delta t^2$$
(2.9)

There are some drawbacks with the Verlet method, like low precision and that the velocities will not be calculated until the next step. That is why many variants of it calculate the position, velocity and acceleration of the next time step all at the current time step and with a improved precision. One of these is the *velocity Verlet* algorithm, described in Equation (2.10), which is the almost universal choice.

$$\boldsymbol{r}(t+\delta t) = \boldsymbol{r}(t) + \boldsymbol{v}(t)\delta t + \frac{1}{2}\boldsymbol{a}(t)\delta t^{2}$$
$$\boldsymbol{v}(t+\delta t) = \boldsymbol{v}(t) + \frac{1}{2}[\boldsymbol{a}(t) - \boldsymbol{a}(t+\delta t)]\delta t \qquad (2.10)$$

2.3.2 Boundaries

If we would like to simulate some properties of a silver cube with volume 1 cm^3 the number of atoms to include would be approximately 5×10^{22} . Solving 6N differential equations at every time step would be impossible with the computer resources we have today. The trick to still be able to simulate bulk properties is to use Periodic Boundary Conditions (PBCs). We use a *simulation box*³ that has a finite number of atoms inside. When one atom exits the box at one end it will enter again on the opposite end of the box, as in Figure 2.3. That means that the system feels the forces as in a bulk and we might mimic the large infinite bulk with a small system of just a few hundred or thousand atoms. Another reason to use

 $^{^{3}}$ We will also use the name *Simulation Cell*, which is related to the unit cell of the molecules and mean the same thing.

PBCs is that the number of surface particles is much larger in a small system and might give unwanted effects. If we work in three dimensions, having all of them periodic means that we simulate a bulk. If we instead let one of the dimensions being fixed, we simulate a surface. The shape of the simulation box might be of any type if it fills up the entire space using translational operations of the center simulation cell.



Figure 2.3 The principle of Periodic Boundary Conditions (PBCs), showed in two dimensions. When one atom exits one end of the simulation box, it enters in the opposite end (blue atom) and in this manner it mimics an infinite bulk structure. The center square is our simulation cell while the rest are images of this.

The most time consuming part in a simulation are the non-bonded interactions. These must be calculated between every pair of atoms in the system but for some potentials this is excessive, e.g. the LJ potential at a distance of 2.5σ has only a value 1% of that at the distance σ . A way to get around this problem is to use a *non-bonded cutoff* r_c together with the Minimum Image Convention (MIC). The cutoff is a truncation in the potential which means that only atoms inside the cutoff radius will be considered. Atoms outside the cutoff do not interact. The MIC means that the simulation cell has to be big enough or the cutoff small enough so that a atom only interact with neighbour atoms once. Formulated differently, an atom should not be able to interact with itself. An example of this is shown in Figure 2.4. The same rule governs the molecules, they should not be able to interact with themselves.

Computationally, significant gain is achieved when we implement the cutoff and the MIC, which is done through so called *neighbour lists*. Not having to calcu-



Figure 2.4 The principle of a spherical cutoff (blue circle) for an atom (marked in red) and the Minimum Image Convention (MIC) showed in two dimensions. The center square is our simulation cell while the rest are images of this.

late the distances between every pair is a huge save of computational time. For each atom the neighbour lists keep track of the atoms that are inside the cutoff and they are referred to as the neighbours. Only these will contribute to the force acting on the atom. The list contains all atoms and the neighbours to each. The distance between two atoms is only saved once. Since the atoms move, new neighbours will enter and old neighbours will exit the limit to be just this neighbours. Thus it is of great importance to update the list every now and then. How often depends on the system and its current configuration. Some systems need to update the list at every time step while others need updates every 10, 50 or 100 time steps. Usually, a so called *skin* is used to add atoms that might become new neighbours. This means that all atoms inside the cutoff plus the skin distance are stored in the neighbour lists and the need to update the list is less often.

A drawback with the cutoff is that it creates a discontinuity in the potential energy and the forces near the cutoff. There are several ways to deal with this problem. One of the better ones and the one used with LAMMPS in combination with CHARMM, is a *switching function* that ramps the potential from one to zero between an inner and outer cutoff.

2.3.3 Long- and Short-Range Forces

Even though we use a cutoff, one problem is still remaining and this is due to the interactions that decay slower than r^{-n} where *n* denotes the dimension of the system. The problem that might arise is that the interactions are longer than half of the box length, which is the limit of the MIC. The Coulomb or electrostatic interaction is decaying with a rate of r^{-1} and therefore has this problem. For certain issues it is particularly important to solve this problem. These *long-range forces* can be treated by certain methods and in LAMMPS there are especially two of interest, the *Ewald summation method* [11] and the *particle-particle particle-mesh method* [15], usually called *PPPM*. The Ewald summation is basically summing the charge-charge contributions to the potential energy, as in Equation (2.11) for the simulation box but also for the images of the boxes.

$$E_p = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$
(2.11)

The smart thing with this method is that it separates the series of all pair interactions in a fast converging series and in a slow converging series. The former is solved in real space and is for the *short-range interactions*, while the latter is solved in reciprocal space and is for the *long-range interactions*. When we solve the slow converging series in reciprocal space it converges faster, so overall, we have two fast converging series.

2.4 Statistical Mechanics

The connection between the microscopical (atoms at nanometre scale) and the macroscopic level (material properties) goes through statistical mechanics.

2.4.1 Ergodic Hypothesis

Statistical mechanics gives us the expectation value of certain properties as the ensemble averages $\langle A \rangle$. This is the probability to have a certain configuration taken over all possible configurations and is what gives us the macroscopic properties. What we measure in MD is a time average of these properties $\langle A \rangle_{time}$ taken over the simulation time. The ergodic hypothesis states that the time-average is equal to the ensemble average when the time goes toward infinity, as in Equation (2.12). Note that not all systems are ergodic, which would mean that a system is dependent of its initial position. In our simulations this is not probable, one reason is the high temperatures, and we will assume the system to be ergodic.

$$\langle A \rangle = \lim_{t \to +\infty} \langle A \rangle_{time} \tag{2.12}$$

2.4.2 Equilibration

Another important aspect of MD simulations is the *equilibration*. It is necessary in order to lose the influence of the initial conditions and should be performed in order to fulfil the ergodic hypothesis. There are many criteria of when equilibrium is reached, which is when certain properties have reached a stationary value. What is stable enough, depends on systems and types of simulations. The first property to check is that the total energy is conserved. According to Allen and Tildesley [10, p.98], for a simple LJ-system fluctuations of 1 part in 10^4 are considered acceptable. To calculate this fluctuation we use a mean E_{mean} that is taken from the start of our test of equilibrium to the latest timestep (it is updated at every timestep) and a temporary mean E_{temp} over the latest *m* timesteps, where *m* is a fix number. A schematic of the means is shown in Figure 2.5.



Figure 2.5 An example of how to test the equilibrium by monitoring the property of interest, in this case the conservation of the total energy. Two means are calculated at each timestep and the difference gives the fluctuation of the property.

The acceptable level of fluctuation may then be calculated as in Equation (2.13), where the right hand side shows the level for the simple LJ-system mentioned.

$$\left|\frac{E_{mean} - E_{temp}}{E_{mean}}\right| \le 10^{-4} \tag{2.13}$$

Usually in simulations where we are interested in calculating thermodynamic variables, it starts with a first equilibration phase where we go from initial configuration to equilibrium. Then the next stage starts when we do the proper time averages to retrieve the desired variables. It is clear from the ergodic hypothesis that the second phase must be long enough to get good statistical results.

2.4.3 Ensembles

Of great importance in statistical mechanics are the ensembles and so naturally also in MD. There are many options and choosing ensemble is of course dependent on what you want to simulate. When phase transitions are studied the Gibbs Free Energy G is the interesting observable and one must therefore use the Isobaric and Isothermal NPT ensemble. This ensemble has constant temperature T, pressure P and number of particles N. The most common ensemble is the microcanonical (NVE) which has constant energy E, volume V and number of particles N. It is mostly used in combination with a thermostat in order to stabilise temperature.

2.5 Simulated Annealing

Simulated Annealing (SA) is a method that is used with the aim to find the global minimum of a cost function, in our case the global minimum of the potential energy function. The method was described by Kirkpatrick et al. [16] who suggested to

be used in several optimization problems. It has similarities with the Metropolis Algorithm [17] where a Markov Chain is simulated until it reaches equilibrium. The problem with this approach is that the simulations have to be performed at low temperature, consequently the time to reach equilibrium might be excessive. What SA does to overcome this limitation is to use a slowly decreasing cooling schedule [18].

2.6 Self-Diffusion Coefficient

Diffusion describes the movement or migration of atoms or molecules in different systems. Self-diffusion is defined by $IUPAC^4$ as

"Diffusion which takes place in the absence of a chemical potential gradient, describing the uncorrelated movement of a particle." [19]

In our simulations the self-diffusion describe the random motion of the molecules on top of a substrate, where no chemical gradient exist. To quantify the motion we will calculate the *self-diffusion coefficient* D as in Equation (2.14) which is defined by [10, p.60] as the Einstein relation, valid at long times calculated in the microcanonical ensemble.

$$2tD = \frac{1}{3} \left\langle \left| \boldsymbol{r}_i(t) - \boldsymbol{r}_i(0) \right|^2 \right\rangle$$
(2.14)

The right side represents the Mean Square Displacement (MSD) based on the particle positions. The 1/3 factor is related to the dimensionality of the system - here in three dimensions. It is also important to wait with the calculation of the MSD until equilibrium is reached. The self-diffusion coefficient is interesting to study in each dimension independently and can easily be done through changing the MSD to the wanted dimension and the 1/3 factor to a 1. From the self-diffusion coefficient D, the activation energy or energy barrier E, could also be calculated through Equation (2.15) [20, p.588].

$$D = D_0 \exp\left(\frac{-E}{k_B T}\right) \tag{2.15}$$

2.7 Organic Molecules

Organic molecules and substrates are based on carbon. The first molecule we treat is the para-sexiphenyl $C_{36}H_{26}$ (para-6P, p6P or just 6P - the latter will be used hereafter), also called para-hexaphenyl and is a molecule with 36 carbon and 26 hydrogen atoms. The 6P is an oligomer based on six monomer phenyl rings (C_6H_5), where the four rings in the middle are slightly changed (C_6H_4). The single phenyl ring has six carbon atoms connected by alternating single/double bonds and five of

⁴IUPAC - International Union of Pure and Applied Chemistry, www.iupac.org

them are connected to a hydrogen atom while the last is connected to a substituent. These types of bonds between the carbon atoms can be modelled as aromatic rings, which means that the bonds in the rings have an average, since in the same ring it does not matter between which carbons the double bonds are. The position at which the substituent is in the phenyl rings has different names and in the case of 6P these positions in the two rings are the para-positions. The outer rings are then connected to five hydrogen atoms and another ring, while the middle rings are connected to four hydrogen atoms and two other rings. Figure 2.6a illustrates the 6P molecule.

The second molecule is the α -sexithiophene $C_{24}H_{14}S_6$ (will be referred to as 6T), also called α -hexathiophene and is a organic molecule which contains 24 carbon, 14 hydrogen and six sulphur atoms. It is an oligomer based on six thiophene rings (C_4H_4S) . The two outer rings are C_4H_3S and the four middle rings are C_4H_2S . As for 6P, the 6T might be modelled with six aromatic rings. The outer rings are connected to three hydrogen atoms and one other ring while the inner rings are all connected to two hydrogen atoms and two other rings. The sulphur atoms are stable when connected with two extra electrons and do not connect with any other atoms. The 6T is shown in Figure 2.6b.



Figure 2.6 The organic molecules drawn with vdW spheres, in (a) sexiphenyl - 6P and in (b) sexithiophene - 6T.

Chapter 3 Methodology

In this chapter the methods used in this thesis are presented. This includes all the techniques, calculations and software with settings. How to reproduce the simulations performed in this thesis, should be clear after reading this part.

3.1 Experimental Setup

The central tool in this thesis is the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software [21] which is a freely distributed classical MD code. The parallel Message Passing Interface (MPI) version from February 3rd, 2013 has been acquired from the LAMMPS webpage[22]. The simulations have been done in a parallel environment on two clusters. The first is a local cluster with two nodes, and each node has 2×12 cores of type AMD Opteron 6176SE 2.3 GHz and the other is a central cluster of type IBM iDataPlex dx360 M3 which has 38 nodes, with 12 cores each, both at Karl-Franzens-Universität Graz. To be able to simulate atomic systems through LAMMPS and to analyse and present the results both preand post-processing are needed. This makes it necessary to use several different programmes to make the workflow efficient. An overview of how the files and the software used for preprocessing are connected, is given in Appendix A.1.

3.1.1 Preprocessing

As discussed in Section 2.2, a FF is utilized to model the movements of the molecules and in Section 2.2.2 we have presented the one we used, namely the CHARMM General Force Field (CGenFF), version 2b7 [14] which is made for small organic molecules. The topology file (top_all36_cgenff.rtf) and the parameter file (par_all36_cgenff.par) of the CGenFF are freely distributed from Professor Alexander Mackerrel's webpage [23]. In Table 3.1 the different file formats in the preprocessing are summarized.

General steps to run a simulation:

The **first step** to model the molecules is to create a geometry file in the PDBformat containing initial coordinates and bonds of the molecule based on some reference values, e.g. from DFT-calculations. The initial coordinates are not critical but may reduce equilibration time, and possible initial huge forces if chosen wisely. The **second step** is to create a topology file (RTF) including partial charges for the molecule. Note that the total charge of the molecule should be zero because it is neutral. The file has been based on the CGenFF topology file and the partial charges have been calculated within the framework of DFT utilizing the Gaussian 09, Revision C.01 [24]. The topology files that have been used for the molecules are found in Appendix B.1.

The **third step** is to create a structure file in the PSF-format that has information about atom types, numbering of atoms, masses, charges, bonds, angles and dihedrals. We have created the PSF-files with the molecular visualization program Visual Molecular Dynamics (VMD) version 1.9.1 [25, 26] and a plugin called *psfgen* version 1.6. The *psfgen* requires a PDB-file(s) and a RTF-file(s) as input and creates a PSF-file and a PDB-file with the same type of ordering of the atoms. It is recommended to use these to avoid problems later.

The **fourth step** is to convert from CHARMM input to LAMMPS input. This is done through a perl script (charmm2lammps.pl, version 1.8.1) included in the LAMMPS distribution. The script requires a PSF-file, a PDB-file, the topology file (RTF) and parameter file (PAR) from CGenFF. From this we then get a data file (DATA) containing all necessary information about the atoms and molecules to run a simulation. If new parameters are added or if one just want to have the parameters for the specific molecule by itself, the topology and parameter files from CGenFF can be changed but kept with the same name. If a simulation box is nonorthogonal, in our case monoclinic, it is easy to change. Either manually, loading the cell data from a CIF-file, or making the definition directly in LAMMPS. The parameter files that have been used for the molecules can be found in Appendix B.2.

The **fifth step** is now to write an input script with the settings one want to have for a certain simulation. An example of how an input script might look like is found in Appendix B.3.

Name	Fileformat	Filetype	Description
RTF	.rtf	Topology	From CGenFF
PAR	.par	Parameter	From CGenFF
PDB	.pdb	Structure/Geometry	Protein Data Bank
PSF	$.\mathrm{psf}$	Structure	Protein Structure File
DATA	.data	Data	Data for LAMMPS simulations
CIF	.cif	Crystal Data	Crystallographic Information File

 Table 3.1
 A summary of the types of files used in the preprocessing to a simulation.

3.1.2 Postprocessing

LAMMPS can produce several types of output in different ways. The standard output is a log file to which you can print thermodynamic data with the **thermo** keyword. Through so called **dump** commands one can produce different types of output data:

- 1. Trajectory file formats as .xyz or the binary .dcd. The latter has mostly been used in this thesis.
- 2. Averaged data over a interval specified by the user.
- 3. Calculated system, or user defined, variables at every time step.

The output data must afterwards be handled since there is no routines for this included in LAMMPS.

Some examples of postprocessing done on output data:

Test of Equilibrium - A python script has been written which takes as input the value of the variable of interest at every time step. Then it will produce two arithmetic means. The first is a long average being updated at every step with a new value and running over the whole timespan chosen for equilibration (for instance at step 102 it makes an average over the first 102 values, at step 103 it makes an average over the first 103 values, etc.). The second is a temporary average of an interval with a fix length m over the latest m timesteps, much smaller than the whole time interval (the mean is updated at every time step with a new value coming in and the oldest value getting "kicked out"). See the theory in Section 2.4.2 for a further description. The default time interval that we test equilibrium on is 10^6 steps with a time step of 1 fs that gives a total of 1 ns. The temporary average interval has been over 50 000 steps. The arithmetic means have been printed to a separate file and then plotted. The value to monitor is the left side in Equation (2.13) in order to decide if the system is stable enough.

Visualization of trajectories - Through VMD it is possible to follow the trajectories of the atoms and molecules, creating videos of their movements. This is very useful when searching for errors and not least to see if the molecules are behaving physically correct. In our case we have also found it very useful to see how molecules are moving on a substrate, how the diffusion is and where their end positions (Adsorption sites) are during SA.

Averages of angle data - VMD provides many powerful analysis tools, one is the possibility to mark a dihedral angle and see in which angle it ends up during an energy minimization. Another one is the possibility to make an average of the dihedral angle during a simulation. VMD simply uses the trajectory file and calculates the data wanted from the atom coordinates. Also included is a Tcl scripting interface which we have used extensively to calculate parameters and variables that are not standard in the VMD-programme. Among these are the herringbone angle and the molecule orientation relative to the substrate. **Rendering of images** - Most of the images in this thesis have been rendered with the program Tachyon version 0.99 that is built into VMD.

Other averaged data - All thermodynamic data has been equilibrated and then averages have been calculated with python scripts in the same manner as described in the Equilibration paragraph above.

3.1.3 General Settings in LAMMPS

Here we will present the settings that are common for all simulations that we have done. The settings that differ will be presented in connection with the specific simulation. An example of how an LAMMPS input script might look like and how settings are done can be found in Appendix B.3. It can be helpful for the explanations of the concepts below, presented in the order of appearance in the script. Some of the settings are default and will therefore not appear in the script. Commands are presented in **this typeface** and are found in the LAMMPS manual under *Commands* [27].

We have chosen real units with commando units real which measures distance in Å, temperature in K, pressure in atm and energy in kcal/mole. The integrator is a standard *Velocity Verlet* by default. A neighbour list with the default skin distance of 2 Å is used and it is updated at every time step through the commando neigh_modify delay 0 every 1. As default is several settings but one important to mention is the neigh_modify check yes which means that a new neighbour list should be built only if some atom has moved half the skin distance or more. In this project we have only done three-dimensional simulations but we will distinguish two different types, namely bulk simulations and surface simulations. The bulk simulation is chosen by the command boundary p p p, which means that the boundaries are periodic in all three dimensions. The surface simulations are chosen by the command boundary p p f which means that the z-direction is fix. This setting must be combined with an extra command when a long-range solver *ewald* or *PPPM* are used, namely the slab command, invoked by kspace_modify slab 3.0.

When choosing the CHARMM pair potential it is also necessary to specify the cutoffs. The CHARMM FF has a switching function that ramps the LJ part between an inner and outer cutoff specified by the user. The Coulomb part is set by default to the outer LJ cutoff if not specified by the user and has an additional damping factor applied to it. The inner cutoff has been set to a distance of $\sigma = 2.5$ with $\sigma = 4$ Å for the longer carbon - carbon and sulphur - sulphur bonds. The command used in the bulk simulations has been, pair_style lj/charmm/coul/long 10.0 12.0 which gives LJ cutoffs 10 Å and 12 Å and Coulomb cutoff 12 Å. The command used in all other simulations has been, pair_style lj/charmm/coul/long 10.0 12.0 11.0 which gives LJ cutoffs 10 Å and 12 Å and Coulomb cutoff 11 Å. A further description of choosing the CHARMM pair potential is found in the corresponding LAMMPS

manual [28]. The long-range parameters ε_{ij} and σ_{ij} must be mixed to give the right attraction between two atoms of different types. We have used the arithmetic option to match the CHARMM potential function, in which the parameters are calculated as in Equation (3.1).

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$
(3.1)

General settings used specifically by CHARMM FF in LAMMPS are atom_style full, bond_style harmonic, angle_style charmm, dihedral_style charmm and at last special_bonds charmm. As long-range solver we have used the *ewald dispersion* since this was the only one that worked with simulations of triclinic simulation cells. This is not perfectly consistent with the pair potential of the short-range interactions and is discussed in Section 4.4. It is invoked through the commando kspace_style ewald/disp 1.0e-4 where the last number is the accuracy in these force calculations. Initial random velocities of the atoms are initiated with the following command, velocity group create temperature number dist uniform which means that they are chosen from an uniform distribution at a certain temperature.

The time step used in all simulations is 1 fs. According to Leach [11, p.362],

"When simulating flexible molecules a useful guide is that the time step should be approximately one-tenth the time of the shortest period of motion."

For the molecules we simulate, the fastest motion is the C-H bond, which has a 10 fs period for its bond stretching. It is then implied that it needs at least a time step of 1 fs to be simulated correctly ¹. This motivates the time step chosen.

3.1.4 How the Parametrization of the Molecules was made

The idea of our parametrization of the molecules is to use existing parametrizations as far as possible. The topology and parameter files from CGenFF have been the starting point. As mentioned earlier the topology and parameter files that have been used for simulations can be found in Appendices B.1 and B.2.

Parametrization of 6P

In the CGenFF topology file, the FF parameters of a Biphenyl molecule (marked as residue BFL) can be found. This served as building block and the parameters of 6P was set up by simply extending it to six rings. There are two different carbons, one for interring carbon (CG2R67) and one for all other carbon (CG2R61). The carbons in the latter category are all connected to one hydrogen atom (HGR61) each. The partial charges in the topology file were calculated in Gaussian and

¹ Constraints that fix certain bond lengths to their equilibrium lengths could also be used but this might affect the conservation of energy and has therefore not been used.

averages of the results have been made on symmetry positions. The C16 and C19 are on the same distance from the molecules center of mass and should have the same value, produced by taking an arithmetic mean of the values. The same must be true for four carbon atoms like C14, C18, C21 and C23 or four hydrogen atoms like H10, H13, H15 and H16. Because there already are two rings in Biphenyl, the difficult torsion term around the interring bond does not have to be calculated. We have made an approximation that the torsion of all interrings are the same. This means that all parameters in the parameter file already exist, except for the dihedral CG2R67-CG2R61-CG2R61-CG2R67. But because this is a dihedral inside a ring, it must have the same parameters as another corresponding dihedral out of four carbons in the ring, i.e. from CG2R61-CG2R61-CG2R61-CG2R61-CG2R61. For 6P the CGenFF parameter file has been modified with the addition of this missing dihedral. The initial structure file (.pdb) for 6P has been taken from DFT-calculations [29].

Parametrization of 6T

In the case of 6T it was based on a Thiophene ring (marked as residue THIP in the CGenFF topology file) that worked as the base for the sexithiophene. The problematic part here is that there is only one ring and therefore no interring term parametrized. The interring was modelled after an article from Pizzirusso et al. [30]. In the paper they match the interring torsion to QM data, which results in a truncated Fourier series for the Amber FF, quite similar to the CHARMM FF. To implement the interring in the CHARMM FF we have let the Fourier series be represented in one of the four dihedrals involved in the interring and then set the remaining three to zero. This approach is not in accordance with the parametrization philosophy of the CGenFF and is discussed in Section 4.4. Several other terms have been necessary to add, mainly in connection to the interring. There are four types of atoms in the parametrization; the interring carbon atoms (CG2R54), the rest of the carbon atoms (CG2R51) that are all connected to one hydrogen atom (HGR51) each and at last the sulphur atoms (SG2R50). The initial structure file (.pdb) for 6T has been taken from DFT-calculations [31, 32].

3.1.5 Bulk Crystal Structures

The crystallographic data of the unit cell for 6P and 6T are presented in this section together with schematic views.

Bulk Crystal Structure of 6P

The crystallographic data for the unit cell of 6P is taken from the paper of Baker et al. [5], which has characterized a complete crystal structure based on X-ray diffraction experiments on 6P. The monoclinic unit cell including two molecules has at 295 K the lattice parameters a = 26.241 Å, b = 5.568 Å, c = 8.091 Å and the angle $\beta = 98.17^{\circ}$ as in Figure 3.1a. A crystal data file (.cif) for the unit cell was created from these values in the so called herringbone arrangement which is defined by the setting angle $\Theta = 55^{\circ}$ and the intersection angles $\omega = 26^{\circ}$ and $\phi =$
71°. The herringbone angle is calculated from these values to be $\tau = 61^{\circ}$ as shown in Figure 3.1b.



(a) Orthographic view of the 6P unit cell containing two molecules in the herringbone structure.

(b) The top image shows the unit cell in perspective and the bottom image the herringbone angle.

Figure 3.1 Structure of the 6P unit cell

Bulk Crystal Structure of 6T

The crystallographic data of the low-temperature polymorph of 6T has been taken from Horowitz et al. [4], which have characterized the molecule experimentally. The monoclinic unit cell at 292 K contains four 6T molecules and has the lattice parameters a = 44.708 Å, b = 7.851 Å, c = 6.029 Å and the angle $\beta = 90.76^{\circ}$ as in Figure 3.2a. A file with the crystal data was created from these values along with the tilt of the long molecular axis L with respect to a as $\phi = 23.5^{\circ}$ and the herringbone angle $\tau = 67^{\circ}$ shown in Figure 3.2b.

3.2 Bulk Simulations

Since only smaller molecules are parametrized in CGenFF one must construct larger molecules out of these and make a new parametrization. Then some kind of test



(a) Orthographic view of the 6T unit cell containing four molecules in the herringbone structure.

(b) The top image shows the unit cell in perspective and the bottom image the herringbone angle.

Figure 3.2 Structure of the 6T unit cell

must be made to confirm their validity. In order to validate the FF parametrizations we have performed MD simulations for bulk structures of 6P and 6T and compared crystallographic data to experiments and earlier made simulations. The bulk structure has been built out of unit cells with the free software GDIS version 0.90 [33]. A simulation of a free molecule has also been done for 6P and 6T and is meant to compare the torsion angle of these to the ones in the bulk simulations. The bulk for both molecules has been calculated in the NPT ensemble with the command fix id all npt temp t1 t1 100.0 tri 1.0 1.0 1000.0, where 100.0 and 1000.0 are damping factors for the temperature and pressure respectively, the 1.0 1.0 is the pressure in atm and the $t_1 t_1$ is the temperature in K². The *tri* keyword means that all lattice parameters and cell angles are controlled independently by the respective stress component as driving force.

3.2.1 Bulk Simulation of 6P

The 6P bulk structure was built with the unit cell from Section 3.1.5. We then constructed a super cell to be as close as possible to a cube, containing $2 \times 9 \times 6$ unit cells, thus giving a total of $2 \times 9 \times 6 \times 2 = 216$ molecules and super cell dimensions a = 52.482 Å, b = 50.112 Å, c = 48.546 Å and angle $\beta = 98.17^{\circ}$. The dimensions were chosen to be the smallest super cell as close as possible to a tilted cube and still fulfilling the MIC.

The simulation was started with four consecutive energy minimizations. A minimization is a algorithm that change the atom coordinates to minimize the energy and when suitable also the pressure of the system. The minimization method chosen was the Conjugate Gradient (CG) algorithm which in LAMMPS is the Polak-Ribiere version. The setting for this was a quadratic line search. Each round had an decreased stopping tolerance for the energy and the force, in order 10^{-8} , 10^{-12} , 10^{-18} and 10^{-25} . The external pressure was set to atmospheric pressure, 1 atm. Since we want to test how well the FF can reproduce the crystal data the simulation box dimensions and shape were allowed to vary by applying an external pressure to the simulation box. At the end of the minimization the system potential energy has reached a (local) minimum and the system pressure tensor should be close to the external pressure tensor.

Then an equilibration of the bulk was made during 2 ns followed by a production period of 1 ns, both in the NPT ensemble and at 295 K. The simulation was made with PBC in all three dimensions and the k-space solver chosen was the *ewald/disp* with a precision of 10^{-4} . In Figure 3.3 the simulation cell can be seen before the PBCs have started to act. The equilibrium was tested through the total energy fluctuation as described in Section 2.4.2 where we have chosen the fix interval of E_{temp} to be m = 50000 timesteps.

 $^{^2\}mathrm{The}$ reason for two values is when a ramping between two temperatures or two pressures is desired.



Figure 3.3 The left image shows the 6P simulation cell from the side with the bottom cell side closest to the viewer corresponding to lattice side a and the vertical to c. When the simulation starts the PBCs will kick in and make the atoms outside the simulation box enter the opposite side and fill up the simulation cell. The right image is the left image rotated counterclockwise around the normal to the ab-plane 90° and shows clearly the herringbone stacking with the bottom cell side closest to the viewer corresponding to lattice side b.

3.2.2 Bulk Simulation of 6T

The 6T bulk structure was built with the unit cell from Section 3.1.5. The super cell was created with $1 \times 5 \times 7$ unit cells giving $1 \times 5 \times 7 \times 4 = 140$ molecules to match the simulation by [30]. This gave the super cell dimensions a = 44.708 Å, b = 39.255 Å, c = 42.203 Å and angle $\beta = 90.76^{\circ}$. The simulation was started with the same minimization process as for the 6P bulk. Also here the external pressure was chosen as equal to the atmospheric pressure, 1 atm. After this, an equilibration of the bulk during 2 ns followed by a production period of 1 ns, both in the NPT ensemble and at 292 K, was started. The simulation was made with PBC in all three dimensions and the k-space solver chosen was the *ewald/disp* with a precision of 10^{-4} . In Figure 3.4 the simulation cell is seen before the PBCs have started to act.

3.2.3 Free Molecule at Room Temperature

In order to compare the angle data from bulk simulations, a free molecule has also been simulated. A simulation of one free 6P molecule at 295 K and a simulation of one free 6T molecule at 292 K were made in the same set ups as the 6P and 6T bulk simulations respectively, except for the ensemble which here was the NVE together with a Berendsen thermostat. This ensemble is invoked by two separate commands, the first is fix id1 all nve and the second is fix id2 all temp/berendsen t1 t1 100. For the free molecules no minimizations have been done since it would not make any sense to talk about pressure for a single molecule in a big simulation box. After having stabilized, the molecules are expected to spin around their center of mass at a relatively constant angular velocity. This angular velocity is calculated as the rest of the thermodynamic



Figure 3.4 The left image shows the 6T simulation cell from the side with the bottom cell side closest to the viewer corresponding to lattice side a and the vertical to c. When the simulation starts the PBCs will kick in and make the atoms outside the simulation box enter the opposite side and fill up the simulation cell. The right image is the left image rotated clockwise around the normal to the ab-plane 90° and shows clearly the herringbone stacking with the bottom cell side closest to the viewer corresponding to lattice side b.

properties through making an average over a larger period.

3.3 Simulated Annealing of 6P and 6T on Substrate

In this thesis we have used Simulated Annealing (SA), presented in Section 2.5, to find the preferred adsorption site of organic molecules on organic substrates. First we will present the substrate that we have used, the simulation cell chosen and then the settings of the different simulations done. The main purpose of the simulations presented in this section is to find the preferred adsorption sites of the molecules on top of the substrate and the adsorption energy as a function of the coverage. For 6P was also investigated how the starting position of the molecule affected the end position and for this reason three different initial positions have been tested.

A simulation with SA starts with a period where the molecule on top of the substrate shall be randomized and forget its initial configuration. This is called the *thermalization period* as it is produced at constant temperature. After thermalization, the *annealing period* or cooling can be started. It might then be divided in several cooling stages from the previous constant temperature to a temperature as close as possible to 0 K. For technical reasons LAMMPS can not reach 0 K.

3.3.1 Substrate - 6P needle with $(11\overline{1})$ Surface

The substrate in the simulation is constructed to be the 6P needle with $(11\overline{1})$ surface grown on a muscovite mica substrate from the article by Simbrunner et al.

[9]. The substrate is based on the 6P unit cell with two molecules from Section 3.1.5 and was constructed in GDIS as $2 \times 5 \times 2$ unit cells, giving a total of 40 molecules in the substrate. The dimensions are a=49.1088 Å, b=52.6767 Å and c=9.1324 Å with the angle $\beta = 98.17^{\circ}$. The size of the substrate was chosen to be as small as possible for reasonable simulation times and large enough to fulfil the MIC in the xand y-dimensions. The substrate is *frozen in* which means that each atom is fixed and will not move during the whole simulation. There are different ways to realize this and we used the perhaps simplest one - to not integrate the atoms in the substrate. The x-, y- and z-axis are presented with the substrate in Figure 3.5a.

To define a molecules orientation, a set of axis are defined as in Figure 3.5b. Rotation is counted as positive in the counterclockwise direction around the short molecular axis ϕ_x , the long molecular axis ϕ_y and the normal molecular axis ϕ_z . We also introduce an orthogonal reference system in Figure 3.6b based on the flat molecule in the substrate whose long side is parallel with the coordinate axis a_2 , its short side parallel with coordinate axis a_1 and whose normal is the coordinate axis a_3 . The angle between a_1 and the x-axis rotated around the z-axis equals -12.45° , the angle between a_2 and the y-axis also rotated around the z-axis equals -14.36° and the last angle a_3 and the z-axis rotated around the y-axis equals 21.31°.

Rotation around ϕ_x is measured with respect to the \mathbf{a}_3 axis, rotation around ϕ_y is measured with respect to the \mathbf{a}_1 axis and rotation around ϕ_z is measured with respect to the \mathbf{a}_2 axis. We will hereafter refer to the geometries of all molecules according in this way. The two types of orientation in the substrate, the *flat* molecule f and the *edge on* molecule e marked in Figure 3.6b have in order the orientations $\phi_x = -90^\circ$, $\phi_y = 0^\circ$, $\phi_z = 0^\circ$ and $\phi_x = -90^\circ$, $\phi_y = 61^\circ$ (the herringbone angle), $\phi_z = 0^\circ$.



(a) The x-, y- and z-direction relative to the substrate.



(b) Definition of molecule axes. Rotation around an axis is measured as positive in the counterclockwise direction.



(a) The 6P substrate before it is put into a simulation cell.

(b) Definition of the orientation of a molecule in the substrate through an orthogonal coordinate system.

Figure 3.6 The 6P needle substrate.

3.3.2 Simulation Cell

Since the simulation cell is set with respect to the size of the substrate it will be the same for both molecules. The monoclinic simulation cell is periodic in the plane of the substrate (x- and y-direction) while the normal to the substrate (z-direction) is fixed and set by the user. The setting used in LAMMPS to realise this is the **slab** option, which actually is periodic in the z-direction but with additional extra forbidden space (effectively a vacuum), two times the z-value chosen. This extra space is inserted above the simulation box and makes the slab-slab interaction close to zero. This approximation works fine and is described in more detail at the LAMMPS-webpage[27] under the **kspace_modify** command. The theory behind the method is explained by Yeh and Berkowitz [34]. In our simulations three z-values have been chosen, with the aim to find a good compromise between accuracy (large vacuum spacing) and computational effort for the k-space part of the long range interactions. This gives three different simulation cells; x=49.1088 Å and y=52.6767 Å with z=30 Å, z=38 Å or z=45 Å.

3.3.3 Adsorption Energy of 6P and 6T

One parameter of interest is the binding energy of the adsorbed molecule to the substrate. We define this *adsorption energy* in the following way:

$$E_{ad} = E_{total \, system} - E_{substrate} - E_{molecule} \tag{3.2}$$

where $E_{total system}$ is the potential energy of the system in the end of a simulation of SA reaching a temperature of 0.1 K, $E_{substrate}$ is the potential energy from a static calculation of the substrate and $E_{molecule}$ is the potential energy from one molecule cooled down from 1 K to 0.1 K over 100 000 steps. All three have been made in simulation cells with identical dimensions. In the case of adsorption energy for two or more molecules the calculation is similar but $E_{molecule} = n \cdot E_{one molecule}$ where n is the number of molecules calculated. Also the E_{ad} is divided by the number of molecules to give the value per molecule. The calculations have been made for several different cases, including different simulation cells and different accuracies in the k-space solver.

3.3.4 Setup of 6P

For 6P, three different initial positions were tested and each one of them had a different simulation box. The three initial positions have been run with the same settings. The use of the the k-space solver ewald/disp 1e-4 should be mentioned here. One simulation has also been conducted at 800 K with k-space solver ewald/disp 1e-5. Simulations with accuracies as high as ewald/disp 1e-8 have been started but cancelled because of extremely long simulation time.

All three simulations have been made in the NVE ensemble with a 2 ns thermalization period at a constant temperature of 600 K. Then all of them have been cooled in 1 ns-intervals; From 600 K to 400 K, then from 400 K to 200 K and at last

from 200 K to 1 K. A final cooling has been made from 1 K to 0.1 K over 0.1 ns. The potential energy of the system for the calculation of adsorption energy is taken from the last step of the cooling, at 0.1 K. The total runtime for all the simulations of one molecule is 5.1 ns.

Perpendicular to molecules in Substrate

This simulation had a simulation box with z = 30 Å and the initial position of the molecule was approximately 1.9 Å above the surface. The long molecular axis of the molecule is almost perpendicular to the long molecular axis of the molecules in the substrate. The initial position is depicted in Figure 4.9a.

Aligned with molecules in Substrate

This simulation had a simulation box with z = 38 Å and the initial position the molecule was approximately 1.9 Å above the surface. The long molecular axis of the molecule is close to parallel with the long molecular axis of the molecules in the substrate. The initial position is shown in Figure 4.9b.

Standing position 45 degrees inclination to Substrate

This simulation had a simulation box with z = 45 Å and the initial position the molecule was approximately 1.4 Å above the surface. The long molecular axis of the molecule is rotated 45° around the surface normal and then rotated 45° up and away from the surface. The initial position can be seen Figure 4.9c.



(a) 6P in perpendicular position (b) 6P in aligned position and (c) 6P in standing position and and z = 30 Å. z = 38 Å. z = 45 Å.

Figure 3.7 The three initial positions of a single 6P molecule on top of a 6P substrate.

3.3.5 Setup of 6T

For 6T, in the case of one molecule only one case has been simulated, but an initial study of also 6T would be interesting to investigate. The simulation was made in the NVE ensemble and with k-space solver setting ewald/disp 1e-4. The simulation

scheme is identical to the one for 6P in the case of one molecule on top of the substrate.

Perpendicular to molecules in Substrate

This simulation had a simulation box with z = 38 Å and the initial position of the molecule was approximately 2.2 Å above the surface. The long molecular axis of the molecule is almost perpendicular to the long molecular axis of the molecules in the substrate. The initial position is depicted in Figure 3.8.



Figure 3.8 6T in perpendicular position and z = 38 Å.

3.3.6 Growth of Monolayer

More and more molecules are added for each simulation with SA until we have reached a full layer of 20 molecules. This layer, which is one molecule thick is called a *monolayer*. The number of molecules that we have simulated for both molecules are 1, 2, 3, 4, 5, 6, 10, 11, 15, 20 and 21 on top of the substrate. The last simulation of 21 molecules is therefore one monolayer plus one molecule. The setup is exactly the same as for one molecule, explained in Sections 3.3.4 to 3.3.5 with the only difference that we have added 1 ns of thermalization, which gives 3 ns thermalization period and a total simulation time of 6.1 ns. The simulation box for all is the one with z = 38 Å. Since the initial position theoretically should not be critical, none of the initial positions are shown here.

3.4 Diffusion of 6P and 6T on Substrate

The aim with these simulations is to find the self-diffusion coefficients in each dimension as described in Section 2.6. The x- and y-directions defined and showed in Figure 3.5a are the dimensions for which we calculate the diffusion. What is needed is the MSD for the molecule and in LAMMPS the command compute ID group-ID msd/molecule does this. This command calculates the MSD for the center-of-mass of the molecule and also includes all effects due to atoms passing through periodic boundaries. The simulations are equilibrated for

3 ns and then we start to calculate the MSD. The first 0.1 ns are left out to avoid strange values and then we simulate 3 ns of data. In practice, a good way to get the self-diffusion coefficient is to slightly change Equation (2.14) so it looks like Equation (3.3).

$$\left\langle \left| \boldsymbol{r}_{i}(t) - \boldsymbol{r}_{i}(0) \right|^{2} \right\rangle = b + (2dD)t \tag{3.3}$$

If we plot left side versus time, we see that 2dD acts as the slope of the line that is expected to be linear. The constant d is the dimensionality and the constant b is just to get the linear fit of the slope right.

The trajectory of the molecule is assumed to be a random walk³. This means that that there is no correlation between timesteps t_1 and t_2 and that at all timesteps there starts a new random walk. So instead of making 100 simulations of length 3 ns each, one can simply make 100 intervals of length T_i , with random starting times in the existing set, and the average will be the data point at time T_i . Important in order to get good statistics is to not use the whole dataset but only a part of it. If not, the last timesteps will sample the same data point and not average over several. We used time intervals from 10^3 fs to 10^6 fs corresponding to a third of the dataset to ensure good statistics. For each data point 100 intervals were calculated and averaged over.

The energy barrier in Equation (2.15) is practically easier to achieve if the natural logarithm is applied to both sides:

$$\ln(D) = \ln(D_0) - \frac{E}{k_B} \frac{1}{T}$$
(3.4)

We see here a linear relationship and by plotting $\ln(D)$ against 1/T the slope of the line will be E/k_B . The unknown constant D_0 will also become clear from the line. But in order to find the equation of the line, more than one simulation must be done and at different temperatures. We made four simulations at 300 K, 400 K, 500 K and 600 K.

³A random walk is a trajectory with a succession of random steps.

Chapter 4 Results and Discussion

Three types of simulations have been done for each molecule; bulk simulations to test the parametrization of each molecule, Simulated Annealing (SA) to retrieve adsorption energies and adsorption geometries and at last diffusion simulations to find the self-diffusion coefficients in each respective dimension. The results of them are presented in this chapter together with discussions.

4.1 Bulk Simulations

Bulk simulations of 6P and 6T have been made to test how well the parametrization can reproduce lattice parameters and angles of the unit cells. A comparison of the torsion angles in the bulk to the torsion angles in a free molecule, both at room temperature is also included.

4.1.1 Bulk of 6P

The 6P bulk was tested if in equilibrium in the interval 1-2 ns and is shown in Figure 4.1. The graphs in the figure shows the fluctuation of the total energy, which we consider to have stabilized sufficiently to be considered equilibrated as discussed in Section 2.4.2. Even if the data fluctuates a bit more than the acceptable level discussed in that section, marked with red horizontal lines, for a molecule system that has more complex interactions the result is still stable and fairly close to the limit. The production period started at 2 ns and lasted 1 ns over which an arithmetic mean of the crystallographic data was made. The results of the lattice parameters and the cell angles are found in Figures 4.2 to 4.3. The crystallographic data from the simulation are presented in Table 4.1. As can be seen, the FF parameters reproduce the unit cell very well and have therefore been considered good enough for use in simulations.

Angle Data at Room Temperature

Two dihedral angles per molecule have been calculated for two molecules in the bulk simulation and for the free molecule, displayed in Figure 4.4. The temperature of the simulations was 295 K and the data are taken from the period 2-3 ns. A



Figure 4.1 Test if the 6P bulk is equilibrated. The top figure shows the total energy and two means calculated from it. In the bottom figure the dimensionless fluctuation is calculated and the two red horizontal lines marks an acceptable level for a simple LJ-system.



Figure 4.2 Crystallographic data produced in a bulk simulation of 6P. The super cell is created by 2x9x6 unit cells and here are the lattice parameters shown. The numbers shown in the graphs are the mean values averaged over the whole dataset of 10^6 timesteps.



Figure 4.3 Crystallographic data produced in a bulk simulation of 6P. The super cell is created by $2 \times 9 \times 6$ unit cells and in the graph the super cell angles are shown. The numbers shown in the graphs are the mean values averaged over the whole dataset of 10^6 timesteps.

Table 4.1	Crystallographic	data of the $6\mathrm{P}$	Bulk simulation	compared to	o references
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6P	$a(\text{\AA})$	b(Å)	$c(\text{\AA})$	$\alpha(°)$	$\beta(\degree)$	$\gamma(°)$	$\operatorname{Temp}(K)$
$\mathrm{sim}^{\mathrm{a}}$	53.1985	49.414	51.2675	90.0422	98.2596	90.0292	295
sim^b	26.5993	5.4904	8.5512	90.0422	98.2596	90.0292	295
$\exp^{\rm c}$	26.241	5.568	8.091	90	98.17	90	295

^a From our simulation ^b From our simulation and normalized to unit cell ^c Experimental data from Reference [5]

comparison of the dihedral angles together with the herringbone angles is found in Table 4.2 and the graphs of the respective dihedral and herringbone angle are found in Appendix C.1. Interesting to notice is the herringbone angle which is a bit larger than the reference value 61°. After the equilibration period, the free 6P molecule has started to spin at a relatively constant angular velocity. A mean was calculated over the period and gave the angular velocity $\omega = 1.41$ rad/ps.



Figure 4.4 Two dihedral angles per molecule have been calculated for the molecules shown.

Table 4.2 Dihedral and herringbone angles from a 6P bulk simulation and dihedral angles from a free 6P simulation. The data comes from the production period 2-3 ns, after the respective system has been equilibrated.

$\mathbf{Resid}^{\mathrm{a}}$	$\mathbf{Dihedral}^{\mathrm{b}}$	Min(°)	Max(°)	Mean(°)	$A.Mean(°)^{c}$	$\mathbf{Median}(^{\circ})^{d}$
6P Bull	X					
181	C24	-35.57	36.53	2.02	18.67	19.70
	C20	-55.82	61.31	2.49	23.23	23.66
182	C24	-61.59	54.26	-2.10	22.94	23.26
	C20	-55.25	55.84	-2.02	23.32	23.38
6P mole	ecule					
1	C24	28.28	38.56	33.82	33.82	-
	C20	28.63	39.02	33.82	33.82	-

Herringbone Resid ^a	Min(°)	Max(°)	Mean(°)	$\mathbf{St.dev.}(^{\circ})$	Median(°)
6P Bulk 181-182	35.52	101.23	66.05	9.18	65.65

^a Resid is a molecule id ^b The dihedral of the four atoms C17-C16-C19-*

^c The absolute value of the angles is used to calculate the mean

^d The median is calculated from the set of absolute values of the angles

4.1.2 Bulk of 6T

As for 6P, the 6T bulk was tested if in equilibrium in the interval 1-2 ns and is shown in Figure 4.5. The fluctuations are a bit bigger than for the 6P bulk but still not extremely big and we consider it to be sufficient. Furthermore, after 1 ns of equilibration the result does not look as it will improve or worsen anymore and it is probably as good as it gets. The red lines are also here the limit discussed in the fundamentals chapter and the deviation from this limit should be seen in the light of a more complex potential function. The fact that the 6T bulk has bigger fluctuations than 6P could be explained by that the latter has a better parametrization and a much more symmetric geometry. The production period started at 2 ns and lasted 1 ns over which an arithmetic mean of the crystallographic data was made. The results of the lattice parameters and the cell angles are found in Figures 4.6 to 4.7. The crystallographic data from the simulation are presented in Table 4.3. As can be seen, the FF parameters reproduce the unit cell well, only the β -angle is off and should be possible to improve through a better parametrization. The results are all together good and we have continued with further simulations with the parameter set presented in Section 3.1.4.



Figure 4.5 Test if the 6T bulk is equilibrated. The top figure shows the total energy and two means calculated from it. In the bottom figure the dimensionless fluctuation is calculated and the two red horizontal lines marks an acceptable level for a simple LJ-system.

Angle Data at Room Temperature

Two dihedral angles per molecule have been calculated for two molecules in the bulk simulation and for the free molecule, displayed in Figure 4.8. The temperature



Figure 4.6 Crystallographic data produced in a bulk simulation of 6T. The super cell is created by $1 \times 5 \times 7$ unit cells and here are the lattice parameters shown. The numbers shown in the graphs are the mean values averaged over the whole dataset of 10^6 timesteps.

6P	a(A)	b(A)	c(A)	$\alpha(°)$	$\beta(\degree)$	$\gamma(\circ)$	$\operatorname{Temp}(K)$
sim^{a}	45.0142	40.5429	42.8940	89.9975	92.6834	90.0027	292
$\mathrm{sim}^{\mathrm{b}}$	45.0142	8.1086	6.1277	89.9975	92.6834	90.0027	292
$\mathrm{sim}^{\mathrm{c}}$	45.650	7.804	6.113	89.70	89.52	89.79	292
\exp^{d}	44.708	7.851	6.029	90	90.76	90	292
$\mathrm{sim}^{\mathrm{e}}$	45.001	7.682	6.023	90	89.97	90	292

Table 4.3 Crystallographic data of the 6T Bulk simulation compared to references

^a From our simulation ^b From our simulation and normalized to unit cell

^c Simulation data from Reference [30] ^d Experimental data from Reference [4]

 $^{\rm e}\,{\rm Simulation}$ data from Reference [35]



Figure 4.7 Crystallographic data produced in a bulk simulation of 6T. The super cell is created by $1 \times 5 \times 7$ unit cells and here are the super cell angles shown. The numbers shown in the graphs are the mean values averaged over the whole dataset of 10^6 timesteps.

of the simulations was 292 K and the data are taken from the period 2-3 ns. A comparison of the dihedral angles together with the herringbone angles is presented in Table 4.4 and the graphs of the respective dihedral are found in Appendix C.2. After the equilibration period, the free 6T molecule has started to spin at a relatively constant angular velocity. A mean was calculated over the period and gave the angular velocity $\omega = 1.20 \text{ rad/ps}$.



(a) 6T Bulk.

(b) Free 6T molecule.

Figure 4.8 Two dihedral angles per molecule have been calculated for the molecules shown in the graphs.

Table 4.4 Dihedral and herringbone angles from a 6T bulk simulation and dihedral angles from a free 6T simulation. The data comes from the production period 2-3 ns, after the respective system has been equilibrated.

$\mathbf{Resid}^{\mathrm{a}}$	${f Dihedral^b}$	Min(°)	Max(°)	Mean(°)	$A.Mean(°)^{c}$	$\mathbf{Median}(^{\circ})^{\mathrm{d}}$
6T Bull	X					
61	S3	-37.71	38.61	-1.67	8.99	7.63
	C11	-41.16	39.73	-1.40	10.22	8.72
62	S3	-37.25	32.99	-1.62	9.01	7.68
	C11	-58.36	39.87	-1.49	10.22	8.69
6T mole	ecule					
1	S3	-35.26	-19.02	-27.58	-27.58	-
	C11	-38.78	-20.77	-30.24	-30.24	_

Herringbone Resid ^a	Min(°)	Max(°)	Mean(°)	$\mathbf{St.dev.}(^{\circ})$	Median(°)
6T Bulk 61-62	30.27	85.52	57.50	7.18	57.55

^a Resid is a molecule id ^b The dihedral of the four atoms C14-C13-C12-*

^c The absolute value of the angles is used to calculate the mean

^d The median is calculated from the set of absolute values of the angles

4.2Adsorption on Substrate

We have investigated the adsorption of 6P and 6T on a substrate consisting of the (111) surface of the 6P crystal. In this section, we present the most favourable adsorption sites and the adsorption energy as a function of coverage, obtained with SA.

4.2.1Adsorption Geometry 6P

First of all we investigated how sensitive the final adsorption position is with respect to an arbitrarily chosen initial configuration. The initial positions are found in Figure 3.7 and the result is presented in Figure 4.9 with data in Table 4.5 from which it is clear that the initial position has no importance for the end position with the setup we have used. No matter which initial position, the single 6P molecule ends up in a position aligned with the molecules in the substrate. From the same simulations we made a convergence test that is presented in Section 4.2.2.



tial perpendicular position and tial aligned position and z = tial standing position and z = $z = 30 \, \text{A}.$

38 Å.

(a) End position of 6P with ini- (b) End position of 6P with ini- (c) End position of 6P with ini-45 Å.

Figure 4.9 The three end positions of three different initial positions of a single 6P molecule on top of a 6P substrate.

Further investigations focused on the final positions of 6P molecules as a function of the coverage. An overview of the resulting adsorption geometries is presented in Figure 4.10 together with a summary of characteristic geometrical properties in Table 4.6. The molecules are well aligned with the substrate which can be seen in the values of ϕ_x close to -90° and ϕ_z close to 0° . The herringbone stacking order is clearly seen in the ϕ_u values where the *edge on* molecule *e* range approximately 50° to 70° and the *flat* molecule f range approximately 3° to 7°. Another relation that clearly shows is that *edge on* molecules has 1° to 5° lower mean torsion angle than the *flat* molecules. This result is explained by the edge on position which only has atoms in the lower part of the rings close to the substrate while the flat position has all atoms in the rings close to the substrate that leads to a higher attraction of all atoms for the former and thus a smaller torsion angle.

In the table one can also see that the mean herringbone angle for configurations with high coverage is smaller than the optimal angle of 61° in the substrate (from 6P crystal at room temperature), ranging from 53° to 61° for configurations with five molecules or more. Furthermore the mean torsion angle is decreasing for a coverage greater than 10 molecules. One explanation could be that with an increased number of layers, the molecules will be pressed down and the mean herringbone angle gets closer to the value found in experiments, perhaps at the cost of an even smaller mean torsion angle.

Table 4.5 Orientation of a single 6P molecule that adsorbs on top of the 6P substrate and a monolayer of 6P molecules respectively. n stands for the number of molecules and the z indicates which simulation box was used and its initial position.

n	Resid ^a	ϕ_x (°)	$\phi_y(°)$	$\phi_z(°)$	Torsion(°) ^b
1	$z=30\text{\AA}$	-90.92	-79.98	-0.18	29.80
1	$z=38\text{\AA}$	-89.96	-71.77	0.03	29.42
1	$z=45\text{\AA}$	-94.31	-71.90	-1.21	25.66
21	$z=38\text{\AA}$	-101.90	-79.65	-2.19	35.48

^a Resid is a molecule id. ^b The torsion angle is an average of the five dihedral angles between the six rings.

Table 4.6 Data for the orientation of 6P molecules that adsorbs on top of the 6P substrate where n stands for the number of molecules. Twenty molecules constitute a full layer.

n	Resid 1	ϕ_x (°)	$\phi_y(°)$	$\phi_z(\circ)$	$\mathbf{Torsion}(^{\circ})^2$	$\mathbf{Herringbone}(^{\circ})^{3}$
1	41f	-89.96	-71.77	0.03	29.42	-
2	42e	-82.08	68.52	-3.33	22.30	
	41f	-88.79	7.62	-4.81	24.22	63.61
3	41e	-104.35	77.44	3.26	28.19	
	42f	-93.45	5.65	0.90	29.75	71.65
	43e	-82.17	61.46	-4.21	24.49	56.14
	mean	f: 5.65 e	: 69.45 d	liff: 63.79	27.48	63.89
4	41f	-91.96	7.98	-0.19	29.81	
	43e	-91.98	64.95	0.40	32.93	58.63
	42f	-91.55	5.30	0.22	31.29	61.74
	44e	-101.73	81.56	1.66	34.75	79.61
	mean	f: 6.64 e	: 73.26 d	liff: 66.62	32.19	64.29

Continued on next page

¹Resid is a molecule id represented by a number and the letters stand for f = flat position and e = edge on position. A schematic of these positions is found in Figure 3.6b.

²The torsion angle is an average of the five dihedral angles between the six rings.

³The herringbone angle is calculated between neighbour molecules, which for each number in the list (where it applies) are the resid from the present line and from the one above.

n	Resid	ϕ_x (°)	$\phi_y(°)$	$\phi_z(\circ)$	$\mathbf{Torsion}(^{\circ})$	Herringbone(°)
5	43f	-91.85	8.38	0.02	30.50	
	42e	-89.58	53.08	-0.42	23.94	44.94
	45f	-91.28	6.30	-0.49	18.58	49.16
	44e	-95.33	67.00	1.51	24.66	48.12
	41f	-91.54	6.09	-0.90	29.25	67.86
	mean	f: 6.92 e	: 60.04 c	liff: 53.12	25.39	53.28
6	43e	-89.72	68.63	-0.18	25.70	
	46f	-89.93	6.53	-0.03	18.65	62.10
	42e	-89.98	63.00	-0.13	21.83	56.47
	44f	-90.00	7.77	0.19	17.80	55.23
	41e	-90.97	53.09	0.40	18.03	45.32
	45f	-90.09	4.46	-0.12	22.08	48.63
	mean	f: 6.25 e	: 61.57 d	liff: 55.32	20.68	53.55
10	е	-89.06	67.06	-0.45	29.96	
	f	-91.30	5.63	-0.48	26.83	
	diff	2.24	61.43	0.03	3.13	
	mean	-90.90		-0.09	27.76	60.71
11	48	-92.54	-70.18	-0.87	28.66	
	е	-92.76	62.71	0.73	28.48	
	f	-90.68	4.99	0.21	24.32	
	diff	2.08	57.73	0.52	4.16	
	mean	-91.72		0.47	26.40	57.73
15	49e	-90.36	69.08	0.11	25.87	
	54f	-89.79	6.20	0.67	19.48	62.88
	44e	-91.00	55.74	0.48	19.73	49.54
	52f	-90.03	3.22	0.46	24.26	52.52
	41e	-100.26	76.40	2.51	32.73	73.18
	mean	f: 4.71 e	: 67.07 c	liff: 62.36	24.42	59.53
	е	-89.99	61.11	-0.15	25.60	
	f	-90.68	3.74	0.40	23.95	
	diff	0.67	57.37	0.55	1.66	
	mean	-90.34		0.12	25.60	57.38
20	е	-90.65	56.68	0.62	26.75	
	f	-90.20	3.74	0.81	21.12	
	diff	0.45	52.94	0.19	5.63	
	mean	-90.42		0.72	23.94	53.29
21	59	-101.90	-79.65	-2.19	35.48	
	е	-90.77	57.61	0.67	24.68	
	f	-90.21	3.66	0.85	20.16	
	diff	0.56	53.95	0.18	4.52	
	mean	-90.49		0.76	22.42	54.55

..continued from previous page



Figure 4.10 The images show the end positions of 6P molecules on top of the substrate in SA simulations. In order from left to right and from top to bottom, the coverage is 1, 2, 3, 4, 5, 6, 10, 11, 15, 20 and 21 6P molecules. Since a full layer corresponds to 20 6P molecules, 21 molecules equals one layer plus one molecule (coloured in blue).

4.2.2 Adsorption Energy 6P

In Table 4.7, the convergence of the calculated adsorption energy with respect to the size of the simulation box can be seen. For box heights z larger than 38 Å, the change in adsorption energy is converged to be approximately 0.01 eV. In Table 4.8 and Figure 4.11, the results of the adsorption energy as a function of coverage are presented. When a full layer of 20 6P molecules has been filled, the adsorption energy is with respect to the molecule on top. The relation of the adsorption energy per molecule in Figure 4.11 decrease monotonically. This is a logical result since with an increasing coverage, the molecules acquire adsorption sites which approach those of the perfect stacking sequence and are thus more favourable. The small jump upwards from 10 to 11 molecules is due to the fact that 10 molecules complete a row while the eleventh molecule is a single molecule in the other row with higher adsorption energy. The difference in adsorption energy between one molecule on top of the substrate and one molecule on top of a monolayer could be explained by the fact that the substrate is rigid while the monolayer is relaxed.

Table 4.7Adsorption energy of a single 6P molecule on the substrate. All simulations here aremade with the k-space solver Ewald and accuracy 1e-4.

Туре	Perpendicular z=30 Å	Aligned $z=38$ Å	Standing $z=45$ Å
$E_{ad}/molecule (eV)$	-1.977875	-2.026851	-2.038146

Table 4.8 Adsorption energy of n 6P molecules on the substrate. All simulations here are madewith the Ewald k-space solver and an accuracy 1e-4 in the simulation cell with z=38 Å

n	$E_{ad}/molecule (eV)$
1	-2.027
2	-2.127
3	-2.269
4	-2.349
5	-2.395
6	-2.422
10	-2.548
11	-2.524
15	-2.576
20	-2.664
21	-1.988

4.2.3 Adsorption Geometry 6T

The final positions of 6T molecules on the substrate as a function of coverage have been investigated. An overview of the resulting adsorption geometries is presented in Figure 4.12 together with a summary of characteristic geometrical properties in Table 4.9. There is a noticeable difference in the adsorption of the two molecules, in general the 6T molecules are more twisted and have therefore been harder to



Figure 4.11 Adsorption energy depending on coverage of 6P molecules in the simulation cell. All simulations are done with k-space solver Ewald 1e-4 and the simulation cell with z=38 Å.

categorize than the 6P.

Single 6T molecules seem to prefer the position next to the groove, but from a coverage of three molecules and higher they start to align with the substrate. Differently from 6P, the 6T with its shorter molecule length, overlaps the grooves and is not as perfectly aligned in the a_2 direction which can be seen in all configurations of 6T. Above a coverage of five molecules the well aligned behaviour can be seen in the values of ϕ_x close to -90° and ϕ_z close to 0° . The herringbone stacking order is clearly seen in the ϕ_{y} values where the *edge on* molecule *e* range approximately 50° to 54° and the *flat* molecule f range approximately 11° to 13°. That these ranges are smaller than for the 6P molecules is interesting and could possibly say something about the molecules. Also, for 6T, one can clearly observe a lower mean torsion angle for the *flat* molecule than for the *edge on* molecule, with the difference in the interval 11° to 22°, actually very large in comparison to 6P. The difference can be explained in the same manner as for 6P but the reason that it is greater in the 6T case is directly explained by a much smaller torsion angle in the flat position. This indicates either that the 6T rings have a larger attraction, maybe due to the sulphur atom, or that the parametrization of the molecule is affecting the result. The ring orientation has not been taken into account for the torsion angles, merely the smallest angle between two adjacent rings.

In the table one can also see that the mean herringbone angle for configura-

tions with high coverage is much smaller than the optimal angle of 67° in a 6T crystal at room temperature. With five molecules or more, the angles range from 38° to 42° and is much more narrow than in the case of 6P, which is very curious, especially since the 6T molecules are more twisted. The reason for the much smaller angle could simply be that the 6T adapts to the 6T substrate.

n	Resid 4	ϕ_x (°)	$\phi_y(\circ)$	$\phi_z(\circ)$	$\mathbf{Torsion}(^{\circ})^{5}$	$Herringbone(°)^6$
1	41	-102.15	-59.59	-68.82	31.51	-
2	41	-93.07	28.89	102.74	27.44	
	42	-102.27	-60.39	-68.84	31.67	-
3	42e	-80.06	62.58	-7.89	39.72	
	41f	-95.18	-8.54	-7.55	26.53	19.55
	43e	-84.88	45.63	-11.24	34.24	36.59
	mean	f: -8.54	e: 54.105	diff: 62.645	33.50	28.07
4	42	-98.64	-28.35	-7.27	30.40	
	44	-104.72	-77.18	11.64	45.64	11.71
	43	-92.05	54.23	8.73	25.53	48.25
	41	-100.31	-28.85	-9.74	30.15	12.55
	mean	-98.93	-20.03	0.85	32.93	24.17
5	44f	-89.86	16.55	-1.34	28.23	
	43e	-90.57	52.85	-0.00	23.98	36.31
	45f	-90.04	12.85	-0.73	6.23	40.01
	41e	-89.91	55.20	-0.24	12.38	42.35
	42f	-90.01	9.08	-0.51	7.71	46.12
	mean	f: 12.82	e: 54.03 c	liff: 41.20	15.71	41.20
6	44e	-89.17	45.59	-0.82	31.33	
	46f	-88.46	11.03	-0.38	16.05	34.55
	45e	-90.03	51.74	-0.30	12.24	40.73
	43f	-90.04	13.46	-0.49	6.28	38.28
	42e	-91.26	51.48	0.31	25.39	38.03
	41f	-89.65	8.80	-1.23	8.19	42.71
	mean	f: 11.10 e: 49.60 diff: 38.50		16.58	38.86	
10	41	-93.85	26.19	103.01	33.96	
	е	-92.52	53.06	0.84	22.14	
	f	-89.91	11.30	-0.71	10.88	
	diff	2.61	41.76	1.56	11.26	
	mean	-91.07	_	-0.02	15.88	41.40

Table 4.9 Data for the orientation of 6T molecules that adsorps on top of the 6P substrate where n stands for the number of molecules. Twenty molecules constitutes a full layer.

Continued on next page

⁴Resid is a molecule id represented by a number and the letters stand for f = flat position and e = edge on position. A schematic of these positions is found in Figure 3.6b.

⁵The torsion angle is an average of the five dihedral angles between the six rings.

⁶The herringbone angle is calculated between neighbour molecules, which for each number in the list (where it applies) are the resid from the present line and from the one above.

n	Resid	ϕ_x (°)	$\phi_y(°)$	$\phi_z(\circ)$	$\mathbf{Torsion}(^{\circ})$	Herringbone(°)
11	44	-91.77	68.68	79.30	47.83	
	е	-91.22	50.81	-0.21	26.19	
	f	-90.11	12.09	-0.91	4.77	
	diff	1.11	38.72	0.70	21.42	
	mean	-90.67		-0.56	15.48	38.77
15	55e	-89.42	59.44	-0.09	17.70	
	51f	-89.99	12.43	-0.38	8.72	47.01
	44e	-88.58	51.72	-0.97	21.66	39.29
	52f	-89.40	13.38	0.29	16.75	38.32
	49e	-91.97	49.26	0.90	22.51	35.92
	mean	f: 12.91	e: 53.47 c	liff: 40.57	17.47	40.1364
	е	-91.15	51.23	-0.25	21.92	
	f	-89.89	10.87	-0.53	6.47	
	diff	1.26	40.36	0.27	15.45	
	mean	-90.53		-0.39	14.20	40.43
20	е	-93.72	52.49	1.81	27.37	
	f	-91.13	12.27	-0.18	10.21	
	diff	2.59	40.22	2.00	17.17	
	mean	-92.43		0.81	18.79	40.22
21	54	-45.27	-100.09	79.91	-47.24	
	е	-88.08	52.55	-0.99	22.42	
	f	-89.31	12.45	-0.63	10.34	
	diff	1.23	40.10	0.37	12.08	
	mean	-88.69		-0.81	16.38	40.09

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4.2.4 Adsorption Energy 6T

In Table 4.10 and Figure 4.13 are the results of the calculations of adsorption energy with regard to the number of molecules simulated. When a full layer has been filled the adsorption energy is with respect to the molecule on top. The difference in adsorption energy between one molecule on top of the substrate and one molecule on top of a monolayer could be explained by the rigid substrate and the relaxed monolayer but also that the end position of the molecule on top is dipping down in the monolayer. What is meant with dipping down can be seen in the last image in Figure 4.12.

4.3 Diffusion on Substrate

Here we present the results from the simulations where we measure the diffusion of 6P and 6T on a substrate of 6P with surface $(11\overline{1})$.



Figure 4.12 The images show the end positions of 6T molecules on top of the substrate in SA simulations. In order from left to right and from top to bottom, the coverage is 1, 2, 3, 4, 5, 6, 10, 11, 15, 20 and 21 6T molecules. A full layer corresponds to 20 6P molecules, but as can be seen the 6T molecule is slightly smaller and does not fill up the layer with 20 molecules. Therefore for 21 molecules the top molecule (coloured in blue) is dipping down in the first layer.

n	$E_{ad}/molecule (eV)$
1	-1.899
2	-1.919
3	-2.092
4	-2.031
5	-2.215
6	-2.221
10	-2.266
11	-2.316
15	-2.335
20	-2.391
21	-1.723

Table 4.10Adsorption energy of n 6T molecules on the substrate. All simulations here aremade with the Ewald K-space solver and a accuracy 1e-4 in the simulation cell with z=38 Å



Figure 4.13 Adsorption energy depending on coverage of 6T molecules in the simulation cell. All simulations are done with K-space solver Ewald 1e-4 and the simulation cell with z=38 Å.

4.3.1 Diffusion of 6P

The diffusion of one 6P molecule on top of the substrate has been measured and analysed. The graphs that fit Equation (3.3) can be found in Appendix D.1 and the graph that fits Equation (3.4) is shown in Figure 4.14. The results of the diffusion of the 6P molecule are all found in Table 4.11. The results seem reasonable, especially the energy barrier of the molecule. The higher movement of the molecule in the y-direction than in the x-direction is reflected. In the z-direction the probability to move is approximately $\exp(-E_{ad}/k_BT) = \exp(-2eV/k_B \cdot 600K) \approx 1.5 \cdot 10^{-17}$. In other words it is highly unlikely for the molecule to leave the surface at the temperatures we simulate.

Table 4.11 Diffusion constants and barriers of a 6P molecule on top of a 6P $(11\overline{1})$ at four different temperature values.

	$D_x \ (\mathrm{nm}^2 \mathrm{ns}^{-1})$	$D_y \ (\mathrm{nm}^2 \mathrm{ns}^{-1})$	$D \ (\mathrm{nm}^2 \mathrm{ns}^{-1})$
600 K	2.67	16.43	4.84
$500\mathrm{K}$	0.93	3.97	0.96
$400\mathrm{K}$	0.02	3.12	1.04
$300\mathrm{K}$	$6.3 \cdot 10^{-5}$	0.01	$3.6 \cdot 10^{-3}$
$D_{0i} \ ({\rm nm}^2 {\rm ns}^{-1})^{\ a}$	281250	30822	6519
$E_i \text{ (meV)}^{a}$	571.5	368.2	355.6

^a From equation $\ln(D_i) = \ln(D_{0i}) - E_i/k_BT$ which can be found in Section 3.4.

4.3.2 Diffusion of 6T

The diffusion of a 6T molecule on top of the substrate has been measured and analysed. The graphs that fit Equation (3.3) can be found in Appendix D.2 and the graph that fits Equation (3.4) is shown in Figure 4.15. A summary of the results is found in Table 4.12. The diffusion coefficients in the x-direction and z-direction are quite similar to the ones for 6P while in the y-direction it is much less. Interpreting the movement of the 6T molecule by instead looking at the energy barriers, in the y-direction it is quite similar of the 6T molecule, even though it has lower diffusion coefficients. In the x-direction the energy barrier is much smaller and could be explained either by a more flexible geometry where the torsion of the rings is higher or by a bad fit. The z-direction has the same interpretation as for the 6P molecule.

4.4 Conclusions

The purpose of this thesis has been to give a better understanding of the initial growth stages of two organic molecules, 6P and 6T on top of an organic substrate constituted of 6P molecules with a $(11\overline{1})$ surface. This configuration has been investigated through FF studies with MD simulations in LAMMPS with additional data analysis. Three types of simulations have been done for each molecule; bulk simulations to test the parametrization of each molecule, Simulated Annealing (SA)





Figure 4.14 The graph shows an Arrhenius plot that gives the linear relationship of a 6P molecules diffusion on the substrate depending on the temperature. The slope is proportional to the energy barrier of the molecule.

Table 4.12 Diffusion constants and barriers of a 6T molecule on top of a 6P $(11\overline{1})$ at four different temperature values.

	$D_x \ (\mathrm{nm}^2 \mathrm{ns}^{-1})$	$D_y \ (\mathrm{nm^2ns^{-1}})$	$D \ (\mathrm{nm}^2 \mathrm{ns}^{-1})$
600 K	1.65	2.08	0.95
$500\mathrm{K}$	0.65	2.66	0.99
$400\mathrm{K}$	0.14	0.57	0.17
$300\mathrm{K}$	$3.56 \cdot 10^{-3}$	$1.82 \cdot 10^{-3}$	$4.1 \cdot 10^{-4}$
$D_{0i} \ ({\rm nm}^2 {\rm ns}^{-1})^{\ a}$	1010	10554	9170
$E_i \text{ (meV)}^{a}$	319.3	383.0	418.6

^a From equation $\ln(D_i) = \ln(D_{0i}) - E_i/k_BT$ which can be found in Section 3.4.

to retrieve adsorption energies and adsorption geometries and at last diffusion simulations to find the self-diffusion coefficients in each respective dimension.

The bulk simulations confirmed that the parametrization of each molecule reproduces lattice parameters and angles satisfactorily, and thus, are suitable to use in further simulations. The simulation of the 6T gave one value deviating slightly more, result indicating that the parametrization could be improved. The bulk

Diffusion Coefficient of 6T



Figure 4.15 The graph shows an Arrhenius plot that gives the linear relationship of a 6T molecules diffusion on the substrate depending on the temperature. The slope is proportional to the energy barrier of the molecule.

simulations also contributed to give a comparison of the dihedral angles between a bulk structure and a free molecule at room temperature and the herringbone angle in the bulk.

In order to investigate the adsorption of 6P and 6T molecules on the substrate a thermalization period of 3 ns and a cooling scheme of 3 ns have turned out successful to find the adsorption sites of the molecules. The 6P molecules align very well to the substrate in all simulations and the initial position has been found to not influence the final position. Single 6T molecules tend to end up in a perpendicular position along the groove. First at a coverage of three molecules or higher they align to the substrate, but only along the direction of the long molecular axis defined as a_2 , which means that they in some cases overlap the grooves. For both molecules the characteristic herringbone structure starts to reveal more clearly with a coverage of five molecules or higher. A clear monotonic increase of the adsorption energy per molecule has been revealed as the coverage increase and means that the molecules augment their binding to the surface.

From diffusion simulations at four different temperatures the self-diffusion coefficient and the energy barrier have been calculated. For both molecules the diffusion in the y-direction (which is closed to be aligned with the long molecular axis) is higher than in the x-direction.

At the time of the project, LAMMPS did not offer a fully integrated solution to simulate a surface in a monoclinic simulation cell with the CHARMM FF. The feature offered has therefore introduced an inconsistency in the electrostatic interactions. This drawback does not affect the results of the adsorption and diffusion, which are mainly affected by the vdW forces between molecules and substrate.

Future work should include an improvement of the parametrizations as they are not optimized according to parametrization philosophy of the CGenFF. Either by using the CHARMM programme to optimize or by using the VMD plugin called ffTK (Force Field Toolkit) together with Gaussian. Both these optimize all the parameters to QM reference data and in water. Another improvement to the simulations would be to include the new feature in LAMMPS launched in May 2013 that erase the inconsistency in the electrostatic interactions. The thermalization period and cooling schedule in SA in combination with the k-space solver have not been optimized but could also be the scope of an improvement, giving more effective simulations.

For future investigations, several possible scenarios would be interesting to investigate, such as the effect on the structure when growing several layers, especially regarding the herringbone and torsion angles. Introducing movement of the top layer in the substrate and a larger size of it in the x- and y-directions. To connect with the experimental project as this thesis is a part of, the growth of 6P and maybe also 6T on mica substrates would be of highest interest. The biggest challenge to do this lays in creating a FF parametrization of the mica substrate.

Appendix A

Workflow

Material describing how the process to prepare a simulation is done.

A.1 Preprocessing

An overview schematic of the file formats needed to run a MD simulation in LAMMPS is shown in Figure A.1



Figure A.1 Overview of the required files and connections in the preprocessing to LAMMPS.

Appendix B

Files and Scripts used in this Thesis

B.1 Topology Files (.rtf)

B.1.1 6P.rtf

This is the topology file of 6P with an example of the numbering. The right column of ATOM starting with number C32 should be placed after C31. This is only done to save space in this document.

```
! Masses chosen after Biphenyl found in top_all36_cgenff.rtf
! The interring carbons in para-positions has a different ID than the
! rest of carbon atoms
MASS
       302 CG2R61
                    12.01100 ! 6-mem aromatic C
MASS
       307 CG2R67
                     12.01100
                               ! 6-mem aromatic carbon of biphenyl
MASS
       277 HGR61
                      1.00800
                               ! aromatic H
!
     H5
           H4
                H6
                      H7
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RESIDUE P6P
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GROUP
ATOM C1
            CG2R61
                    -0.131480
                                     ATOM
                                            C32
                                                  CG2R61
                                                          -0.168906
                                            C33
ATOM
      C2
            CG2R61
                    -0.101476
                                     ATOM
                                                 CG2R61
                                                          -0.101476
ATOM
      СЗ
            CG2R61
                    -0.168906
                                     ATOM
                                            C34
                                                 CG2R61
                                                          -0.131480
ATOM C4
            CG2R67
                    0.097921
                                     ATOM
                                            C35
                                                 CG2R61
                                                          -0.101476
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ATOM	C5	CG2R61	-0.168906	ATOM	C36	CG2R61	-0.168906
ATOM	C6	CG2R61	-0.101476	ATOM	H1	HGR61	0.118571
ATOM	C7	CG2R67	0.043560	ATOM	H2	HGR61	0.114838
ATOM	C8	CG2R61	-0.146684	ATOM	HЗ	HGR61	0.119619
ATOM	C9	CG2R61	-0.161158	ATOM	H4	HGR61	0.119619
ATOM	C10	CG2R67	0.074256	ATOM	H5	HGR61	0.114838
ATOM	C11	CG2R61	-0.161158	ATOM	H6	HGR61	0.121465
ATOM	C12	CG2R61	-0.146684	ATOM	H7	HGR61	0.121999
ATOM	C13	CG2R67	0.064914	ATOM	H8	HGR61	0.121999
ATOM	C14	CG2R61	-0.155364	ATOM	H9	HGR61	0.121465
ATOM	C15	CG2R61	-0.157430	ATOM	H10	HGR61	0.122402
ATOM	C16	CG2R67	0.068954	ATOM	H11	HGR61	0.122347
ATOM	C17	CG2R61	-0.157430	ATOM	H12	HGR61	0.122347
ATOM	C18	CG2R61	-0.155364	ATOM	H13	HGR61	0.122402
ATOM	C19	CG2R67	0.068954	ATOM	H14	HGR61	0.122347
ATOM	C20	CG2R61	-0.157430	ATOM	H15	HGR61	0.122402
ATOM	C21	CG2R61	-0.155364	ATOM	H16	HGR61	0.122402
ATOM	C22	CG2R67	0.064914	ATOM	H17	HGR61	0.122347
ATOM	C23	CG2R61	-0.155364	ATOM	H18	HGR61	0.121999
ATOM	C24	CG2R61	-0.157430	ATOM	H19	HGR61	0.121465
ATOM	C25	CG2R67	0.074256	ATOM	H20	HGR61	0.121465
ATOM	C26	CG2R61	-0.161158	ATOM	H21	HGR61	0.121999
ATOM	C27	CG2R61	-0.146684	ATOM	H22	HGR61	0.119619
ATOM	C28	CG2R67	0.043560	ATOM	H23	HGR61	0.114838
ATOM	C29	CG2R61	-0.146684	ATOM	H24	HGR61	0.118571
ATOM	C30	CG2R61	-0.161158	ATOM	H25	HGR61	0.114838
ATOM	C31	CG2R67	0.097921	ATOM	H26	HGR61	0.119619
BOND	C1 H1	. C2 H2 C	3 H3 C5 H4 C6	Н5			
BOND	C1 C2	2 C2 C3 C	C3 C4 C4 C5 C5	C6 C6 C	1		
BOND	C4 C7	7					

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B.1.2 6T.rtf

This is the topology file of 6T with an example of the numbering. The right column of ATOM starting with number C21 should be placed after C22. This is only done to save space in this document.

! Masses chosen after Thiophene found in top_all36_cgenff.rtf ! All carbons are considered to be of the same type but carbons with ! dihedral chosen to have different name

MASS 275 HGR51 1.00800 ! Aldehyde H, formamide H (RCOH); nonpolar ! H,neutral 5-mem planar ring C adjacent to heteroatom or + charge MASS 299 CG2R51 12.01100 ! 5-mem ring, his CG, CD2(0), trp MASS 300 CG2R54 12.01100 ! Interring carbon MASS 377 SG2R50 32.06000 ! THIP, thiophene

!]	H4	H5			H8	Н9		H1	.2	H13
!			\	/			λ	/			\	/
!			C6	C7			C14	-C15			C22	-C23
!	S1		I	Ι	S3		Ι		S5		I	I
!	/	\	_C5	C8	/	\	_C13	C16	_ /	\	C21	C24-H14
! H	1-C1	C4	Ν.	/	C9	C12	\	/	C17	C20	Λ	/
!			S2		I		S4		I	Ι	S6	
!	C2	-C3			C10	-C11			C18	-C19		
!	/	\			/	\			/	\		
!	H2	HЗ		Н	6	H7		H1	LO	H11		

RESIDUE STH 0.00 GROUP

4110 01							
ATOM	C1	CG2R51	-0.103133	ATOM	C23	CG2R51	-0.277134
ATOM	C2	CG2R51	-0.277134	ATOM	C24	CG2R51	-0.103133
ATOM	C3	CG2R51	-0.014641	ATOM	H1	HGR51	0.183902
ATOM	C4	CG2R54	-0.042706	ATOM	H2	HGR51	0.171928
ATOM	C5	CG2R54	0.119595	ATOM	HЗ	HGR51	0.147582
ATOM	C6	CG2R51	-0.165728	ATOM	H4	HGR51	0.160320
ATOM	C7	CG2R51	-0.202657	ATOM	H5	HGR51	0.194308
ATOM	C8	CG2R54	0.078211	ATOM	H6	HGR51	0.191545
ATOM	C9	CG2R54	0.115567	ATOM	H7	HGR51	0.193203
ATOM	C10	CG2R51	-0.203821	ATOM	H8	HGR51	0.193203
ATOM	C11	CG2R51	-0.205867	ATOM	H9	HGR51	0.191545
ATOM	C12	CG2R54	0.102639	ATOM	H10	HGR51	0.194308
ATOM	C13	CG2R54	0.102639	ATOM	H11	HGR51	0.160320
ATOM	C14	CG2R51	-0.205867	ATOM	H12	HGR51	0.147582
ATOM	C15	CG2R51	-0.203821	ATOM	H13	HGR51	0.171928
ATOM	C16	CG2R54	0.115567	ATOM	H14	HGR51	0.183902
ATOM	C17	CG2R54	0.078211	ATOM	S1	SG2R50	-0.073063
ATOM	C18	CG2R51	-0.202657	ATOM	S2	SG2R50	-0.181239
ATOM	C19	CG2R51	-0.165728	ATOM	S3	SG2R50	-0.188811
ATOM	C20	CG2R54	0.119595	ATOM	S4	SG2R50	-0.188811

ATOM C21 CG2R54 -0.042706 ATOM S5 SG2R50 -0.181239 ATOM C22 CG2R51 -0.014641 ATOM S6 SG2R50 -0.073063 BOND C1 H1 C2 H2 C3 H3 BOND C1 C2 C2 C3 C3 C4 C4 S1 S1 C1 BOND C4 C5 BOND C6 H4 C7 H5 BOND C5 C6 C6 C7 C7 C8 C8 S2 S2 C5 BOND C8 C9 BOND C10 H6 C11 H7 BOND C9 C10 C10 C11 C11 C12 C12 S3 S3 C9 BOND C12 C13 BOND C14 H8 C15 H9 BOND C13 C14 C14 C15 C15 C16 C16 S4 S4 C13 BOND C16 C17 BOND C18 H10 C19 H11 BOND C17 C18 C18 C19 C19 C20 C20 S5 S5 C17 BOND C20 C21 BOND C22 H12 C23 H13 C24 H14 BOND C21 C22 C22 C23 C23 C24 C24 S6 S6 C21 END

Parameter Files (.par) **B.2**

1.00800

B.2.1 6P.par

Since there already exists one good parametrization of the biphenyl it is easy to extend it to sexiphenyl. The only line one has to add to the CGenFF parameter file (par_all36_cgenff.par) is:

CG2R67 CG2R61 CG2R61 CG2R67 3.1000 2 180.00 !Sexiphenyl term

6T.par **B.2.2**

ATOMS MASS 274 HGR51 MASS 299 CG2R51 12.01100 MASS 300 CG2R54 12.01100

MASS 377 SG2R50 32.06000 BONDS CG2R51 CG2R51 410.00 1.3600 С

CG2R51SG2R50300.001.7300CG2R54CG2R54410.001.3600CG2R54SG2R50300.001.7300CG2R51HGR51350.001.0800	CG2R51	CG2R54	410.00	1.3600
CG2R54CG2R54410.001.3600CG2R54SG2R50300.001.7300CG2R51HGR51350.001.0800	CG2R51	SG2R50	300.00	1.7300
CG2R54 SG2R50 300.00 1.7300 CG2R51 HGR51 350.00 1.0800	CG2R54	CG2R54	410.00	1.3600
CG2R51 HGR51 350.00 1.0800	CG2R54	SG2R50	300.00	1.7300
	CG2R51	HGR51	350.00	1.0800

ANGLES										
CG2R51	CG2R51	CG2R51	90.00	107.20						
CG2R51	CG2R51	CG2R54	90.00	107.20						
CG2R51	CG2R54	CG2R54	105.00	129.90						
CG2R54	CG2R54	SG2R50	105.00	120.10						
CG2R51	CG2R51	SG2R50	105.00	109.00						
CG2R51	CG2R54	SG2R50	105.00	109.00						
CG2R51	CG2R51	HGR51	32.00	126.40	2	5.00 2.17	300 ! INDO	/TRP		
CG2R54	CG2R51	HGR51	32.00	126.40	2	5.00 2.17	300 ! INDO,	/TRP		
SG2R50	CG2R51	HGR51	45.00	121.00						
CG2R51	SG2R50	CG2R54	105.00	95.00						
CG2R54	SG2R50	CG2R54	105.00	95.00						
DIHEDR	ALS									
!Ring										
CG2R51	CG2R51	CG2R51	CG2R51	15.0000	2	180.00				
CG2R54	CG2R51	CG2R51	CG2R54	15.0000	2	180.00				
CG2R51	CG2R51	CG2R51	CG2R54	15.0000	2	180.00				
CG2R51	CG2R51	CG2R51	SG2R50	8.5000	2	180.00				
CG2R51	CG2R51	CG2R54	SG2R50	8.5000	2	180.00				
CG2R51	CG2R51	SG2R50	CG2R51	8.5000	2	180.00				
CG2R51	CG2R51	SG2R50	CG2R54	8.5000	2	180.00				
CG2R51	CG2R54	SG2R50	CG2R51	8.5000	2	180.00				
CG2R51	CG2R54	SG2R50	CG2R54	8.5000	2	180.00				
!Intern	ring									
SG2R50	CG2R54	CG2R54	SG2R50	0.4650	1	0.00				
SG2R50	CG2R54	CG2R54	SG2R50	2.3333	2	180.00				
SG2R50	CG2R54	CG2R54	SG2R50	0.1310	3	0.00				
SG2R50	CG2R54	CG2R54	SG2R50	0.3870	4	0.00				
SG2R50	CG2R54	CG2R54	SG2R50	0.0010	5	180.00				
SG2R50	CG2R54	CG2R54	SG2R50	0.0480	6	180.00				
CG2R51	CG2R54	CG2R54	CG2R51	0.0000	2	180.00	!Interring	set	to	zero
SG2R50	CG2R54	CG2R54	CG2R51	0.0000	2	180.00	!Interring	set	to	zero
CG2R51	CG2R54	CG2R54	SG2R50	0.0000	2	180.00	!Interring	set	to	zero
!Inter	ring bo	nd in th	ne end							
CG2R54	CG2R54	CG2R51	CG2R51	15.0000	2	180.00				
CG2R54	CG2R54	SG2R50	CG2R51	8.5000	2	180.00				
CG2R54	CG2R54	SG2R50	CG2R54	8.5000	2	180.00				
CG2R51	CG2R51	CG2R51	HGR51	1.0000	2	180.00				
CG2R54	CG2R54	CG2R51	HGR51	1.0000	2	180.00				
!Hydrog	gens			4 0000	~					
CG2R51	CG2R51	CG2R51	HGR51	1.0000	2	180.00				
CG2R54	CG2R51	CG2R51	HGR51	1.0000	2	180.00				
HGR51	CG2R51	SG2R50	CG2R51	4.0000	2	180.00				
HGR51	CG2R51	SG2R50	CG2R54	4.0000	2	180.00				
SG2R50	CG2R51	CG2R51	HGR51	4.0000	2	180.00				

```
SG2R50 CG2R54 CG2R51 HGR51
                                4.0000 2
                                             180.00
HGR51 CG2R51 CG2R51 HGR51
                                1.0000 2
                                             180.00
NONBONDED nbxmod 5 atom cdiel fshift vatom vdistance vfswitch -
cutnb 14.0 ctofnb 12.0 ctonnb 10.0 eps 1.0 e14fac 1.0 wmin 1.5
HGR51
         0.0
                   -0.0300
                               1.3582
CG2R51
         0.0
                   -0.0500
                               2.1000
                               2.1000
CG2R54
         0.0
                   -0.0500
SG2R50
         0.0
                   -0.4500
                               2.0000
```

B.3 LAMMPS Input Script

Lines marked with a star '*' in the beginning of the line should be attached to the previous line. Since the text width in this thesis is not wide enough this was the solution. The script should serve as an example of how an input script might look like conceptually and has not been used for any simulations. It is really based on two types of input scripts, one for bulk simulations including minimization and NPT ensemble and the other a surface simulation showing how to group molecules and calculate properties based on these groups with running a simulation in the NVE ensemble and will therefore not work before modification.

```
#-----General Settings------General Settings------
units
               real
neigh_modify
                delay 0 every 1
boundary p p p
atom_style
                full
bond_style
                harmonic
angle_style
                charmm
dihedral_style
                charmm
pair_style
                lj/charmm/coul/long 10.0 12.0 11.0
pair_modify
                mix arithmetic
kspace_style
                ewald/disp 1.0e-4
read_data
                6P_system.data
special_bonds
                charmm
#-----Definition of variables-----
variable volume equal vol
variable a equal cella
variable b equal cellb
variable c equal cellc
variable alpha equal cellalpha
variable beta equal cellbeta
variable gamma equal cellgamma
#-----Minimization------
```

fix crysta all ave/time 1 1 1 v_volume v_a v_b v_c * v_alpha v_beta v_gamma file crystInit.data fix boxRelax all box/relax tri 1.0 vmax 0.001 min_style cg min_modify line quadratic minimize 1e-8 1e-8 50000 100000 #-----Settings-----group substrateMol molecule <> 1 40 group molec molecule 41 #System variable nSys equal atoms variable tempSys equal temp variable pressSys equal press variable keSys equal ke variable peSys equal pe variable teSys equal etotal #Molecule variable nMol equal count(molec) variable massMol equal mass(molec) compute temp6P molec temp compute press6P all pressure temp6P compute peAtom6P molec pe/atom compute pe6P molec reduce sum c_peAtom6P compute keAtom6P molec ke/atom compute ke6P molec reduce sum c_keAtom6P variable te6P equal c_pe6P+c_ke6P #Substrate variable Sub equal count(substrateMol) compute tempSub substrateMol temp compute pressSub all pressure tempSub variable peSub equal pe-c_pe6P variable keSub equal ke-c_ke6P variable teSub equal v_peSub+v_keSub thermo 10000 thermo_style custom step atoms vol temp c_temp6P c_tempSub *press c_press6P c_pressSub etotal v_te6P v_teSub & ke c_ke6P v_keSub pe c_pe6P v_peSub emol epair ebond eangle *edihed eimp evdwl ecoul elong etail & xy xz lx xlo xhi ly ylo yhi lz zlo zhi thermo_modify flush yes lost error line multi norm no thermo_modify format float %f

```
variable timeEq equal 1000000
variable tempMol equal 600.0
#-----Run-----Run------
timestep
             1.0
velocity
             all create ${tempMol} 428970848 dist uniform
restart 1000000 6Prestart*.rst
#-----NPT-----
dump
            tra6P all dcd 250 6P_thermalize.dcd
dump_modify tra6P flush yes first yes
fix ThermoBaro all npt temp ${tempMol} ${tempMol} 100.0
*tri 1.0 1.0 1000.0 nreset 1000 fixedpoint 0 0 0
run ${timeEq}
unfix ThermoBaro
undump tra6P
#-----NVE-----
fix 2 molec nve
fix 3 molec temp/berendsen ${tempMol} ${tempMol} 100
run ${timeEq}
unfix 2
unfix 3
dump rest all atom 1 6P_system2ns.dump
run O
undump rest
## SIMULATION DONE
print "All done!"
```

Appendix C Comparison of Angle Data

C.1 Angle Data of 6P Molecules

Here the graphs made for the comparison of the 6P bulk molecules, with a free 6P molecule, are presented.

C.1.1 Dihedral Angles of 6P Bulk

Graphs of the dihedral angles C17-C16-C19-C24 and C17-C16-C19-C24 for two molecules in the 6P bulk simulation are shown below, namely Figures C.1 to C.4.



Resid: 181 Dihedral C17-C16-C19-C24

Figure C.1 6P Bulk dihedral angle.









Resid: 182 Dihedral: C17-C16-C19-C24

Figure C.3 6P Bulk dihedral angle.





Figure C.4 6P Bulk dihedral angle.

C.1.2 Dihedral Angles of Free 6P Molecule

Two graphs of the dihedral angles C17-C16-C19-C24 and C17-C16-C19-C24 for the simulation of the free 6P molecule are shown below in Figure C.5 and Figure C.6. The data is shown over the whole simulation interval for the purpose of displaying the equilibration.

C.1.3 Herringbone Angles of 6P Bulk

In Figure C.7 the data for the herringbone angle simulated in the 6P bulk simulation is presented.

C.2 Angle Data of 6T Molecules

Here the graphs made for the comparison of the 6T bulk molecules, with a free 6T molecule, are presented.

C.2.1 Dihedral Angles of 6T Bulk

Graphs of the dihedral angles C14–C13–C12–S3 and C14–C13–C12–C11 for two molecules in the 6T bulk simulation are shown below, namely Figures C.8 to C.11.



Resid: 1 Dihedral: C17-C16-C19-C24

Figure C.5 Free 6P molecule dihedral angle.



Resid: 1 Dihedral: C17-C16-C19-C20

Figure C.6 Free 6P molecule dihedral angle.

Herringbone Angle of Resid: 181-182



Figure C.7 Herringbone angle from a 6P Bulk simulation.



Resid: 61 Dihedral: C14-C13-C12-S3

Figure C.8 6T Bulk dihedral angle









Resid: 62 Dihedral: C14-C13-C12-S3

Figure C.10 6T Bulk dihedral angle



Figure C.11 6T Bulk dihedral angle

C.2.2 Dihedral Angles of Free 6T Molecule

Graphs of the dihedral angles C14-C13-C12-S3 and C14-C13-C12-C11 for the simulation of the free 6T molecule are shown below in Figure C.12 and Figure C.13.

C.2.3 Herringbone Angles of 6T Bulk

In Figure C.14 the data for the herringbone angle simulated in the 6T bulk simulation is presented.



Resid: 1 Dihedral: C14-C13-C12-S3

Figure C.12 Free 6T molecule dihedral angle



Resid: 1 Dihedral: C14-C13-C12-C11

Figure C.13 Free 6T molecule dihedral angle



Figure C.14 Herringbone angle from a 6T Bulk simulation.

Appendix D

Diffusion

The graphs here shows the linear relation in Equation (3.3) by plotting MSD against the time for 6P and 6T.

D.1 Diffusion of 6P

Figures D.1 to D.4 plot the data and shows the linear relationship between MSD and time for 6P. The slope of the line equals 2dD and from this the self-diffusion coefficient is found.



Self-Diffusion Coefficient of 6P at 600K

Figure D.1 The linear relationship of the data between the MSD and time are shown.



Self-Diffusion Coefficient of 6P at 500K

Figure D.2 The linear relationship of the data between the MSD and time are shown.



Self-Diffusion Coefficient of 6P at 400K

Figure D.3 The linear relationship of the data between the MSD and time are shown.



Figure D.4 The linear relationship of the data between the MSD and time are shown.

D.2 Diffusion of 6T

Figures D.5 to D.8 plot the data and shows the linear relationship between MSD and time for 6T. The slope of the line equals 2dD and from this the self-diffusion coefficient is found.



Figure D.5 The linear relationship of the data between the MSD and time are shown.



Self-Diffusion Coefficient of 6T at 500K

Figure D.6 The linear relationship of the data between the MSD and time are shown.

Self-Diffusion Coefficient of 6T at 600K



Self-Diffusion Coefficient of 6T at 400K

Figure D.7 The linear relationship of the data between the MSD and time are shown.



Self-Diffusion Coefficient of 6T at 300K

Figure D.8 The linear relationship of the data between the MSD and time are shown.

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